STARCH AND CYCLODEXTRIN BASED ADSORBENTS FOR REMOVAL AND PRECONCENTRATION OF POLYCYCLIC AROMATIC HYDROCARBONS AND PHTHALATES IN WATER

BY

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ABSTRACT

The release of Polycyclic Aromatic Hydrocarbons (PAHs) and phthalates from anthropogenic sources into the aquatic environment is of public health concern. The C_{18} bonded silica and styrene-divinyl-benzene polymer adsorbents which are used for preconcentration and remediation of PAHs and phthalates polluted water are expensive and non-biodegradable. Hence, there is need to source for alternative adsorbents. Starch and cyclodextrin based polymers have been reported to be cheap and biodegradable, but have not been applied as adsorbents for PAHs and phthalates. In this study, starch and cyclodextrin based adsorbents were synthesised and employed for removal and preconcentration of PAHs and phthalates in water.

Starch (15.0 g), β-cyclodextrin (12.5 g), and γ-cyclodextrin (8.0 g) were cross-linked with epichlorohydrin (EPI) (34.0-340.1 mM), 1,6-hexamethylene diisocyanate, (HDI) (7.04-70.4 mM), and 4,4-methylene diphenyl diisocyanate, (MDI) (7.04-70.4 mM) to produce EPI, HDI, and MDI cross-linked adsorbents [EPI-starch, EPI-β-cyclodextrin, and EPI-γ-cyclodextrin; HDI-starch, HDI-β-cyclodextrin, and HDI-γ-cyclodextrin; and MDI-starch, MDI-β-cyclodextrin, and MDI-γ-cyclodextrin]. The adsorbents were characterised using infrared spectrophotometry, Brauner-Emmet-Teller surface analysis, Scanning Electron Microscopy (SEM) and elemental analysis. Effects of time, temperature, and initial adsorbate concentration on the adsorption of PAHs (acenaphthylene, phenanthrene, fluorene, benzo(a)anthracene) and phthalates (dimethyl and diethyl phthalates) were studied using standard methods. Data generated were used to study the adsorption kinetics and thermodynamics of the adsorption process, and also fitted to four isotherm models. The adsorbents' efficiencies were evaluated by their respective adsorption coefficients, K_d . The preconcentration studies applied off-line column Solid Phase Extraction (SPE) standard procedure using the adsorbents (250 mg) as the solid phase and the adsorbents were validated by recovery studies and detection limit.

The observed infra-red peaks of aromatic (3036, 1598, and 819 cm^{-1}), amine (1721 and 751 cm^{-1}), and carbonyl (1671 cm^{-1}) functional groups in the adsorbents indicated successful cross-linking process. Surface areas of adsorbents (3.3-40.4 m^2/g) were higher than those of native starch (1.0 m^2/g) and cyclodextrins (0.7 m^2/g). Increment in porosity was observed from SEM images, which confirmed the enhancement of surface area of adsorbents. The adsorbents had higher carbon content (42.7-59.9%) and lower hydrogen content (5.7-7.6%), an indication of increased hydrophobicity. The adsorption data for PAHs and phthalates were best described by pseudo-second order kinetics (r^2>0.996), which confirmed that surface adsorption was the rate-limiting step. The adsorption free energy values were negative, and thus confirmed the spontaneity of the adsorption process. Freundlich isotherm (r^2>0.746) best described PAHs adsorption, an indication of multilayer adsorption; while phthalate adsorption was best fitted by Langmuir isotherm (r^2>0.882), which was suggestive of monolayer adsorption. The log K_d values of the adsorbents (4.0-5.0 for PAHs and 2.7-3.0 for phthalates) indicated good sorption efficiency. The values of recoveries (71.7-126.0% for PAHs and 81.5-104.6% for phthalates) and detection limit (0.9–153.4 ng/L for PAHs and 78.1-117.3 ng/L for phthalates) indicated high analytical performance for SPE preconcentration method using the adsorbents.

Starch and cyclodextrin based adsorbents were effective in the removal and preconcentration of polycyclic aromatic hydrocarbons and phthalates in water; and hence are potential alternatives for the control of these chemical pollutants.

Keywords: Cross-linked starch, Cyclodextrin based adsorbents, Solid phase extraction, Polycyclic aromatic hydrocarbons, Phthalates

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CERTIFICATION

I certify that this work was carried out by Mr. P.C. Okoli in the Department of Chemistry, University of Ibadan.

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DEDICATION

This thesis is dedicated to God Almighty for His grace and unmerited favours that saw me through

and to

the loving memory of my late mother Mrs. Gladys Ejeaka Ugodiya Okoli-Uduogu

(nee Onyebuchi)

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CHAPTER ONE

Introduction

1.1 Water pollution and access to clean water

Water is the prime necessity of life and very essential for the survival of all living organisms. Indeed, it is a part of life itself, since the protoplasm of most living cells contains about 80% water. Hence, access to water of reliable and acceptable quality is one of the most important determinants of a healthy population. However, millions of people worldwide do not have access to water of acceptable quality. The United Nations recognized the health and economic burden of lack of access to clean water, and thus addressed the issue as one of the cardinal objectives of Millennium Development Goals (UNDESA, 2011).

One of the major factors that limit human access to clean water is pollution. Rapid pace of industrialization, population expansion, and unplanned urbanization have largely contributed to the severe pollution of not only water, but other environmental media. The main sources of freshwater pollution can be attributed to discharge of untreated sanitary and toxic industrial wastes, dumping of industrial effluents, and flood water from agricultural fields. According to the United Nations World Water Development Report (UN WWDR, 2003), about two million tons of waste per day are disposed off within receiving waters, including industrial wastes and chemicals, human waste, and agricultural wastes (fertilizers, pesticides, and pesticide residues). The severity of water pollution problem was summarized in the reports of the World Water Council and the World Health Organization, which opined that there is already more wastewater generated and dispersed today than at any other time in the history of our planet, and more than one out of six people lack access to safe drinking water (Gupta et al., 2009).

Chemical pollutants found in wastewater in dissolved states include heavy metals, dyes, phenols, detergents, pesticides, polychlorinated biphenyls (PCBs), polyclic aromatic hydrocarbon (PAHs), phthalate esters and a host of other inorganic and organic substances. Most of these chemicals are toxic above certain concentration levels, when present in water. The toxic effects of such pollutants are well documented in literature (Bhatnagar and Sillanpää, 2010).

Some of the pollutants are substantially degraded by some natural attenuation processes, whereas a whole lot of others are not, and therefore persist in the water environment, for a relatively long period of time. Even among the degradable pollutants, some of their bye-products or metabolites are considered more hazardous, thus natural attenuation is not considered to be an effective option in chemical water pollution control. Polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs), phthalate acid esters (PAEs), otherwise known as phthalates, and polybrominated diphenyl ethers (PBDEs) are major pollutants of organic origin which are found in water. Amongst these chemicals, PAHs and phthalates are of major health concern due to their deleterious health effects, environmental ubiquity and persistence in the environment (Zhu et al., 2004; Adewuyi, 2012).

The presence of PAHs in drinking, surface and waste water has been subject of many reports in literature (Sun *et al*, 2009; Wang *et al.*, 2009; Adedayo *et al.*, 2012). Aside being hydrophobic, PAHs exhibit mutagenic and carcinogenic toxicities even at ultra trace level (Diggs *et al*., 2011), and due to their persistence in the environment, they have been classified as priority pollutants with well established restrictive limits, by most environmental regulatory agencies such as United States Environmental Protection Agency (U.S. EPA) and European Union (Keith and Telliard, 1979; EESC, 2007). Phthalates are non-halogenated esters of phthalic acid that find widespread utilization in various industrial and consumer-orientated applications, where they have been widely used as an important additive to give improved flexibility, extensibility, and workability in plastic industrial processes for a long time. They are considered to be ubiquitous pollutant in aquatic environments because of their widespread presence in almost all water systems. Due to their endocrine disrupting, carcinogenic, or xenoestrogenic properties, some phthalates (for example, Di(2-ethylhexyl)phthalate (DEHP), Dimethyl phthalate (DMP), etc) have been listed among the priority pollutants in the environment especially in US and China (Blom et al., 1998; Foster, 2006; Wu et al., 2010).

Humans are exposed to PAHs and pthalates through several routes including air, water, food, skin contact, and occupational settings (Diggs *et al.*, 2011). However, one of the main routes of human exposure is via water, as these chemicals find their way into water bodies through effluent discharges, leaching from waste dumps, accidental discharges, atmospheric deposition, and through diffuse sources. In this vein, the potential health risk of exposure to these chemicals is higher in the developing countries due to the fact that water for domestic activities is collected directly from streams with little or no treatment in these areas (Bhatnagar and Sillanpää, 2010). The severity of the attendant health challenges associated with water pollution came to the fore when it was revealed that half of all patients occupying African hospital beds suffer from water-borne illnesses due to lack of access to clean water and sanitation (Noubactep, 2010; RSC-PACN, 2010).

1.2 Management of aqueous PAHs and phthalates pollution

Considering the fact that the major human activities that lead to chemical pollution like industrialization and agricultural activities cannot be completely avoided, it has become imperative for this problem to be managed to reduce the attendant impacts to human health and biota. The key aspects of management of environmental pollution are regulation, monitoring, enforcement and remediation. At every level (global, national, and municipal), these principal aspects of managing water pollution are developed, implemented and/or coordinated by environmental regulatory agencies like United Nations Environment Program (UNEP), United States Environmental Protection Agency (USEPA), Environment Canada, National Environmental Standards and Regulation Enforcement Agency (NESREA), Lagos State Environmental Protection Authority (LASEPA), etc. Hence, the roles of these regulatory agencies are predicated on these aforementioned principal aspects.

Among these principal aspects, monitoring studies (environmental analysis) plays a central and determinant role in chemical pollution management, since it confirms the presence or absence, as well as the level of pollutants of interest in the respective environmental media. It is the determinant for enforcement and remediation processes.

This is because of the fact that enforcement depends solely on whether the level of pollutant of interest is below or above the minimum allowable (permissible) limit that has been set by the regulatory body for a given environmental media. Also, remediation activities will only be necessary when the presence of pollutants of interest has been established to be above the permissible limit in a given environmental media. (Ladan, 2013). Hence, routine monitoring processes is necessary for effective management of water pollution by PAHs and phthalates. However, routine monitoring studies for PAHs, phthalates and other micro-pollutants in water is being hampered due mainly to complex nature of the samples, complex analytical procedures involved and the expensive nature of the entire process.

1.3 Preconcentration as a vital step in the environmental analysis of micro-organic pollutants

The analysis of organic micro-pollutants like PAHs and phthalates in water has some challenges owing to the following reasons. First, the levels of these pollutants in water media are below the detection limits of most instrumental methods, hence there is need for the enrichment of the levels of these analytes of interest. Secondly, some instrumental techniques like gas chromatography/mass spectrometry (GC/MS) are not amenable to detecting analytes in aqueous media, hence there is the need for change of phase from aqueous to organic solvent. Furthermore, since high levels of other toxic and non-toxic components are often found to be interfering with the analytes of concern. So, a clean-up step is often required. These and other problems encountered in the analyses of these pollutants are solved with preconcentration procedure.

Over the years, Liquid-Liquid Extraction (LLE) has been widely applied for the preconcnetration of micro-organic pollutants in water samples. LLE is a classical method for pre-concentrating pollutants and/or matrix removal, which is based on the principle of equilibrium partitioning of the pollutants between the aqueous and organic phases. Though LLE has proved effective in enrichment of the micro-pollutants, there are some observed drawbacks in certain areas. The obvious drawbacks are: (i) the method is slow, energy demanding, and time consuming, (ii) exposure of analysts to harmful organic solvents, (iii) poor selectivity since virtually all non-polar pollutants will partition themselves into the organic solvent while the polar ones will remain in aqueous media, (iv) consumption of high volume of organic solvent, (v) LLE cannot be automated, and (vi) it is cumbersome and easy to use. Hence, for a long time, environmental chemists have advocated for a more simplified and efficient preconcentration methods that will address the observed flaws of LLE, for routine monitoring exercise. Interestingly, these drawbacks associated with LLE technique could be circumvented by the usage of Solid Phase Extraction (SPE) procedure.

Solid-phase extraction and high performance liquid chromatography (HPLC) are both based on differential migration processes in which compounds are adsorbed and eluted as they are swept through a porous adsorbent medium by a mobile-phase flow, which is dependent on the differential affinities between the adsorbent material and the mobile phase. The basic approach involves passing the liquid sample through a column, a cartridge, a tube or a disk containing an adsorbent that retains the analytes. After the entire sample has been passed through the sorbent, the retained analytes are subsequently recovered upon elution with an appropriate solvent. Hence, retention is achieved with strong but reversible interactions between the analyte and the surface of the adsorbent. Apart from the main goal of extracting traces of the compounds of interest, SPE is also used to remove the interfering components of the matrix, change the solvent (e.g. aqueous to organic) and store and transport the analytes. However, the greatest advantage of SPE technique, which is its selectivity, is achieved owing to the array of many tunable SPE adsorbents (Huck and Bonn, 2000). In view of the obvious advantages, SPE has been included in some US EPA Methods which analyze pollutants in drinking water e.g. Methods 549.1 and 525.1 which use C_8 and C_{18} bonded silica sorbents, respectively, to analyze pesticides (Masque et al., 1998; Hennion, 1999).

To date, typical SPE adsorbents for PAHs and phthalates are bonded silica phases (C_8, C_{18}, cyano (CN) and other groups), Polystyrene-Divinyl Benzene copolymer (PS-DVB) based adsorbents, immunosorbents, and graphitized carbon blacks, etc. (Marce et al, 1998; Cai et al., 2003; Lopez-Jimenez et al., 2005). However, the application of these adsorbents for SPE pre-concentration of PAHs and phthalates has been limited due to certain chemical and physical properties of these adsorbents. For instance, the presence of residual surface silanol groups (even after an end-capping treatment) and a narrow pH stability range has posed great limitation to the continued application of bonded silica phases. Aside having biodegradation challenge, PS-DVB based SPE adsorbents have shown to be too hydrophobic, and hence, exhibit some level of irreversible interaction with PAHs/phthalates, while the use of other adsorbents like immunosorbents is limited on cost basis, since they are very expensive. This situation therefore elicited strong research interest from researchers, to search for adsorbents that are relatively cheap, biodegradable, and efficient for application as SPE phase for the pre-concentration/analysis of PAHs and phthalates in aqueous media.

1.4 Water treatment options and adsorption

As stated earlier, the outcome of monitoring study (in this case, water sample analysis) determines the next step to be taken. Water remediation becomes necessary if the level of target pollutant has been confirmed to have exceeded the permissible limit set by relevant regulatory agency. Advancement in the field of pollution control research has opened up innovations which are adapted for waste water treatment. These include coagulation, foam flotation, filtration, ion exchange, sedimentation, solvent extraction, adsorption, biodegradation, phytoremediation, electrolysis, chemical oxidation, disinfection, chemical precipitation, membrane process, etc.

However, these methods have their own shortcomings and limitations. For example, the methods based on chemical/biological oxidation, ion exchange and solvent extraction have shown low efficiency for the removal of trace levels of pollutants like PAHs and phthalates. Furthermore, coagulation requires pH control and causes further problems of sludge disposal, due to expected persistence of pollutants (especially POPs) in the sludge, whereas, ozonation though relatively efficient, does not minimize chemical oxygen demand (COD) (Aksu, 2005; Gupta et al., 2009)

Adsorption process is considered better when compared to other methods because of convenience, easy operation and simplicity of design. Also, this process can remove/minimize different type of pollutants and thus it has a wider applicability in water pollution control (Bhatnagar and Minochar, 2006).

Adsorption, which simply means the adhesion or accumulation of atoms, ions, or molecules from a gas, liquid, or dissolved solid on the surface of a solid (otherwise known as adsorbent or sorbent), is one of the most effective methods to remove organic pollutants from water, especially those pollutants present in low concentrations such as PAHs and phthalates. Since its first introduction for heavy metals removal, activated carbon has undoubtedly been the most popular and widely used adsorbent in waste-water treatment applications all over the world. Abundant information on the use of activated carbon for such adsoption of PAHs and phthalates abound in scientific literature (Venkata-Mohan et al. 2007; Valderrama, 2009). Due to their great capacity to adsorb pollutants, activated carbons are adjudged to be the most effective adsorbents. However, activated carbon presents several disadvantages. It is non-selective and quite expensive. The regeneration of saturated carbon by thermal and chemical procedure is also expensive, and results in loss of the adsorbent. Also, regeneration of activated carbon often requires a different facility, which is not always on the site of water treatment plants because of high cost, and thus requires the used adsorbents to be transported from the water treatment plant to the regeneration plant. All these conditions limit the full utilization of activated carbon adsorbent for water decontamination. The use of synthetic polymer is also being hampered by the fact that the spent adsorbent, after being used and regenerated severally, are not easily biodegraded, thus constitutes a waste management challenge. Overall, just like the case of SPE adsorbents, this situation led many workers to search for more economic and efficient adsorbents.

1.5 Polysaccharides: viable sources/precursors of low-cost adsorbents

In the continued search for alternative adsorbents to replace the costly activated carbon, attention has recently been focused on natural solid supports, which are able to remove pollutants from contaminated water at low cost, since cost is an important parameter for comparing the adsorbent materials. According to Bailey et al. (2005), a sorbent can be considered low-cost if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Therefore, starch and its derivative cyclodextrins, and lignocellulosic materials (materials containing lignin and cellulose as major components), have been identified to have potential as inexpensive, readily available materials and thus can be applied directly and/or serve as precursors for producing low-cost adsorbents for PAHs and phthalates.

Therefore, development of low-cost biodegradable adsorbents from readily available low-cost precursors like starch, cyclodextrin and waste lignocellulosic biomass will not only address the outlined challenges, thus making adsorption to be universally adopted as method of choice in remediation of polluted water, but will equally enhance environmental protection and waste management by valorization of waste materials that are being utilized as precursors.

Recently, numerous approaches have been studied for the development of cheaper and more effective adsorbents containing natural polymers. Among these, polysaccharides such as chitin and starch, and their derivatives (chitosan, cyclodextrin) have attracted increasing attention (Crini, 2005). These biopolymers represent an interesting and attractive alternative as adsorbents because of their particular structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards aromatic compounds and metals, resulting from the presence of chemical reactive groups (hydroxyl, acetamido or amino functional groups) in polymer chains. Moreover, it is well known that polysaccharides which are abundant, renewable and biodegradable resources, have a capacity to associate by physical and chemical interactions with a wide variety of molecules. Hence adsorption on polysaccharide derivatives can be a low-cost procedure of choice in water decontamination for extraction and separation of compounds, and a useful tool for protecting the environment. Besides, the increasing number of publications on adsorption of toxic compounds by these natural polymers shows that there is a recent interest in the synthesis of new adsorbent materials containing polysaccharides (Crini, 2005; Delval et al 2006; Farhat, 2006; Singh et al., 2007; Ozmen et al., 2008; Reddy, 2010; Kwak et al., 2011). Interestingly, much work has not been done on utilizing polysaccharide based adsorbents, for removal of polycyclic aromatic hydrocarbons and phthalates from aqueous media.

1.6 Aim and objectives of the study

The aim of this study was to develop low cost biodegradable adsorbents from starch and cyclodextrin for water remediation, and optimize a solid phase extraction pre-concentration method for PAHs and phthalates in water, using the developed adsorbents.

The specific objectives were:

i. To screen the cross-linking agents, and hence determine the feasibility of the new adsorbents in removing PAHs and phthalates from water, using Density Functional Theorem (DFT) molecular orbital simulation as a predictive theoretical approach.
ii. To prepare the cross-linked adsorbents using starch and cyclodextrin (β and γ forms) as precursors.
iii. To characterize the prepared adsorbents using Fourier Transform Infra-Red spectrophotometer (FTIR), elemental analyzer, Scanning Electron Microscope (SEM), Brauner Emmet Teller (BET) surface and porosity analyzer, and Thermogravimetric/ Differential Thermal analyzer (TGA/DTA).
iv. To carry out screening batch adsorption studies on all the synthesized adsorbents.
v. To carry out correlation studies between the DFT predictions and batch adsorption performance.
vi. To carry out detailed batch adsorption studies on the selected adsorbents
vii. To model the kinetic, isotherm, and thermodynamic adsorption data.
viii. To investigate the desorption characteristics of the selected adsorbents, and hence, assess the ease of regeneration of the adsorbents.
ix. To apply the developed adsorbents for adsorption of PAHs and phthalates from real environmental water samples using batch adsorption studies.
x. To optimize a Solid Phase Extraction/High Performance Liquid Chromatography (SPE-HPLC) analytical method for PAHs and phthalates, using the developed adsorbents.
xi. To assess and validate the analytical method performance of the developed SPE-HPLC method.
xii. To apply the SPE-HPLC method in real-time analysis of PAHs and phthalates in real environmental water samples.

1.7 Justification of the Study

Successful development of starch and cyclodextrin based adsorbents will boost widespread use of these easily accessible adsorbents for water remediation. Secondly, the cost limitation to successful application of adsorption in the control of PAHs and phthalates pollution will be substantially addressed since starch is the second most abundant natural polymer, after cellulose, and cyclodextrin is a derivative of starch. In a similar vein, since it has been proved that starch and cyclodextrin based polymer adsorbents are very much biodegradable, there would be no challenge of biodegradation and environmental friendliness from the utilization of these adsorbents. The kinetic, equilibrium, and thermodynamic data generated from this study will serve a meaningful guide in the engineering design of water treatment facilities that would utilize the adsorbents.

Also, successful utilization of the starch and cyclodextrin based adsorbents as solid phase, for preconcentration of PAHs and phthalates will promote the adoption of solid phase extraction as pre-concentration method of choice for routine analysis of PAHs and phthalates in aqueous media. Considering the inherent advantages of SPE over other preconcentration techniques like the possibility of automation, the challenge of complexity in analytical procedure will be substantially addressed. Cost limitation and availability will equally be addressed owing to the fact that analysts can easily synthesize these materials in their laboratory. Overall, water assay for the presence of these harmful compounds in water would be made simpler and cheaper.

CHAPTER TWO

Literature Review

2.1 Polycyclic aromatic hydrocarbons

2.1.1 Occurrence and chemistry

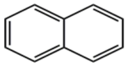
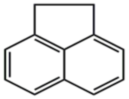
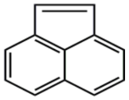
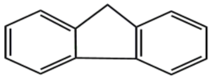
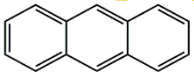
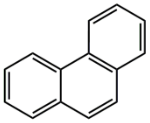
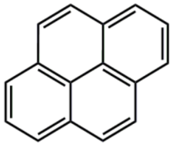
Polycyclic Aromatic Hydrocarbons (PAHs) are homologues of benzene in which two or more aromatic rings are joined in different configurations. They are an all-pervading group of hydrophobic organic compounds consisting of two or more combined benzene rings in linear, angular or cluster arrangements. In a particular sense, these compounds carry only carbon and hydrogen atoms with no substituent atoms or groups, whereas the general term, Polycyclic Aromatic Compounds (PACs) refer to those carrying substituent functional derivative. PAHs are formed during the thermal decomposition of organic molecules and their subsequent recombination. They are also formed by incomplete combustion of organic materials at high temperature (500–800°C) or subjection of organic material at lower temperature (100–300°C) for long periods. They occur as colorless, white/pale yellow solids with low solubilities in water, high melting and boiling points and low vapour pressure (Haritash and Kaushik, 2009)

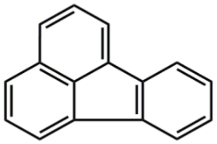
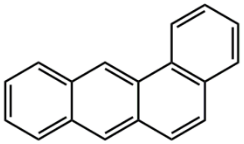
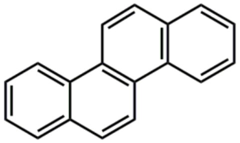
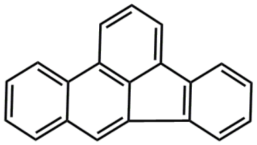
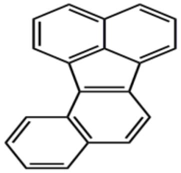
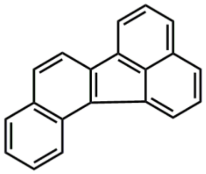
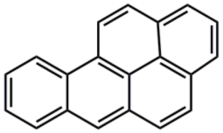
Table 2.1 shows some basic physicochemical data pertaining to the seventeen most studied PAHs. PAHs with high molecular weight/number of rings are more hydrophobic, and consequently more lipophilic. Also, molecular weight/number of rings exhibit negative correlation with the aqueous solubility values of PAHs, (with a few exceptions like anthracene and phenanthrene).

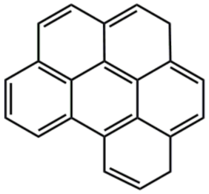
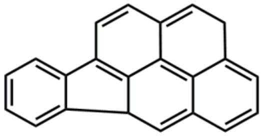
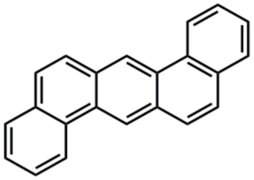
2.1.2 Sources of PAHs in the environment

Environmental pollution by PAHs occurs either from anthropogenic activities or by natural processes. However, emissions from anthropogenic sources accounted for the largest percentage in terms of annual global input (Awoyemi, 2011). Natural sources are forest and rangeland fires, oil seeps, volcanic eruptions and exudates from trees.

Table 2.1 Select Physicochemical properties of the 17(16+1) US EPA priority PAHs

PAH	Acronym	Molecular Structure	Molecular Formula	Molecular Mass (g/mol)	Aqueous Solubility (mg/L)	Log K_{ow}
Naphthalene	Naph		$C_{10}H_8$	128.0	31.7	3.3
Acenaphthalene	Ace		$C_{12}H_{10}$	154.2	1.93	3.92
Acenaphthylene	Acy		$C_{12}H_8$	152.2	3.93	3.94
Fluorene	Flu		$C_{13}H_{10}$	166.2	1.9	4.18
Anthracene	Ant		$C_{14}H_{10}$	178.2	0.043	4.45
Phenanthrene	Phe		$C_{14}H_{10}$	178.2	1.15	4.46
Pyrene	Pyr		$C_{16}H_{10}$	202.3	0.135	4.88

Fluoranthene	Flr		$C_{16}H_{10}$	202.3	0.26	5.16
Benzo[a]anthracene	BaA		$C_{18}H_{12}$	228.3	0.0094	5.76
Chrysene	Chry		$C_{18}H_{12}$	228.3	0.002	5.81
Benzo[b]fluoranthene	BbF		$C_{18}H_{12}$	252.3	0.0015	5.78
Benzo[j]fluoranthene	BjF		$C_{20}H_{12}$	252.3	0.0025	6.11
Benzo[k]fluoranthene	BkF		$C_{20}H_{12}$	252.3	0.0008	6.11
Benzo[a]pyrene	BaP		$C_{20}H_{12}$	252.3	0.00162	6.13

Benzo[g,h,i]perylene	BgP		$C_{22}H_{12}$	276.3	0.00026	6.63
Indeno[1,2,3-c,d]pyrene	IcP		$C_{22}H_{12}$	276.3	0.00019	6.7
Dibenzo[a,h]anthracene	DbA		$C_{22}H_{14}$	278.4	0.00249	6.75

Anthropogenic sources of PAH include burning of fossil fuel, coal tar, wood, garbage, refuse, used lubricating oil and oil filters, municipal solid waste incineration, petroleum spills and discharge, and tobacco smoking. As a result of these numerous and widespread sources, PAHs are ubiquitous and occur in all environmental matrices- air, water, soil and food, predominantly entering through the atmosphere. They enter surface water through wet and dry atmospheric deposition, hydrocarbon spillages, rainwater runoff into water bodies, and industrial effluent discharge, especially from hydrocarbon processing industries (for example coal gasification sites, coking plants, and bitumen and asphalt production plants). During any formation process, and subsequently in the matrices to which the population is exposed, PAHs are always present as a group and not as individual compounds (Menichini and Bocca, 2003).

2.1.3 Toxicological impacts of PAHs

PAHs have been categorized as priority pollutants by most environmental regulatory agencies all over the world due to their toxicity and persistence in the environment. There are more than a hundred known PAHs, of which seventeen are actively monitored by the US EPA. The seventeen were singled out because of the following reasons; (1) more information is available on these PAHs than on the others; (2) they are suspected to be more harmful than some of the others, and hence, they are believed to exhibit harmful effects that are representative of the PAHs; (3) there is a greater chance that one will be exposed to these PAHs than to their counterparts; and (4) amongst all the PAHs analyzed, these were the PAHs identified at the highest concentrations at hazardous waste sites (ATSDR, 1995a).

Human exposure to PAHs has been associated with an increased risk of developing cancer in a variety of tissues, such as the lung, bladder, stomach, and skin (including the scrotum), depending on the mode of exposure and the form of PAH (IARC, 2006). The potential mutagenic and carcinogenic effects of PAHs are the basic reasons of concern for the levels of these compounds in the environment. The Agency for Toxic Substances and Disease Registry's toxicological profile studies reported that individuals exposed by breathing or skin contact for long periods to mixtures that contain PAHs and other compounds can develop cancer (ATSDR, 1995a).

However, the profile report conceded the difficulty in conclusively evaluating the toxicity of the component PAHs in these mixtures in humans because of the potential interactions that could occur and the presence of other toxic substances in the mixtures. As such, most of the available information on the health effects of PAHs in humans are inferred from studies that reported the effects of exposure to complex mixtures that contain PAHs. In dealing with this, the U.S. EPA and other regulatory agencies developed a relative potency estimate approach for estimating the relative carcinogenic potency of PAHs relative to benzo[a]pyrene, a known carcinogen by reporting a value termed "toxicity equivalency factor" (Nisbet and Lagoy, 1992).

The widest spread on animal toxicity study of PAHs was the one conducted by the International Agency for Research on Cancer (IARC) which evaluated the carcinogenic evidence for 43 PAHs using the evidence in experimental animals (IARC, 1987). Based on an overall evaluation of available data, the IARC classified three PAHs (Benzo[a]anthracene, Benzo[a]Pyrene, and Dibenzo[a,h]anthracene) as "probably carcinogenic" to humans. However, recent review by Diggs et al. (2011) collating the latest reports on animal and human studies indicted polycyclic aromatic hydrocarbons to digestive tract cancer.

2.2 Phthalate esters

2.2.1 Background

Phthalate is the term commonly employed to refer to the dialkyl or alkyl aryl esters of 1,2-benzenedicarboxylic acid (phthalic acid). These are primarily synthesized using esterification of phthalic anhydride and the corresponding oxo alcohol in the presence of an acid catalyst such as sulphuric or p-toluene sulfonic acid. The general structure is a diester of 1,2-dicarboxy-benzene. The two alkyl groups may be similar or dissimilar; they may be branched or linear; and they may contain aromatic substitutes, e.g., butyl benzyl phthalate (BBP) or other functional groups. Although there are a high number of different phthalates, only about 60 have industrial applications (Llompart et al., 2006). Among them, only a small number, those with alkyl chains from 1 to13 carbons, are produced in large scale, with di(2-ethylhexyl) phthalate (DEHP) being the most widely produced phthalate.

2.2.2 Properties and uses

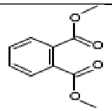
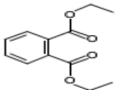
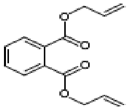
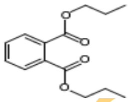
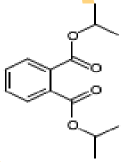
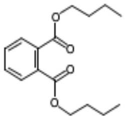
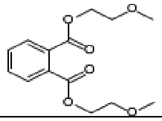
Phthalate esters have a wide range of physicochemical properties. Table 2.2 showed the summary of the properties for the common members of the phthalates family (Llompart et al., 2006). They are from colorless to faint yellow, oily liquids at room temperature with a slight aromatic odor, and molecular weights ranging from 194 (DMP: Dimethyl phthalate) to 530 g/mol (DTDP: Di-n-tridecyl phthalate). Phthalate esters have boiling points varying from approximately 230°C to 486°C (Staples, 1997). According to their water solubility, phthalates may be classified from moderately soluble (5.2 g/L for the DMP) to practically insoluble (0.1 ng/L for DTDP); being less soluble in saltwater than in freshwater, with the linear isomers being less soluble than the branched chain analogues. The Log K_{OW} values (ranging from 1.61 for DMP to 12.06 for DTCP) (Cousin and Mackay, 2000) indicate that phthalate esters are very hydrophobic, especially those with a higher number of carbons in their alcohol moiety.

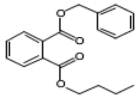
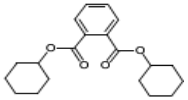
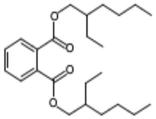
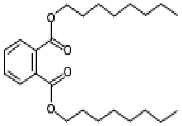
High molecular weight phthalate esters are widely employed in the manufacture of plastics, as nonreactive plasticizers, to make polymers softer, more flexible and workable, because of their high solubility in polymeric materials, its inertness, fluidity, low water solubilities and low volatilities. When used as plasticizers, phthalate esters can represent 5% to 60% of the total weight of the plastics and resins. Its main plasticizer application is the production of polyvinyl chloride (PVC), although they are employed in the manufacture of other polymeric material, such as epoxy and polystyrene resins, chlorinated, natural and synthetic rubbers, polysulfide, nitro-cellulose, ethyl cellulose, and polyurethane. Plastics and resins which contain phthalates, have a broad spectrum of applications including toys, rainwear, shower curtains, films for food packaging, carpets, wall coverings, shoes, cable and medical tubing, automobile, and furniture upholstery. Besides their main applications as plasticizers, phthalates are used as industrial solvents, as additives in the textile industries, as components of dielectric fluids, lubricants, fragrances, hairsprays, nail polish, deodorants, paints, glues, pesticide formulations, etc. (Llompart et al., 2006).

2.2.3 Toxicological impacts of phthalates

Toxicological studies have confirmed that phthalates and their metabolites produce reproductive and developmental toxicities in laboratory animals. These findings have

Table 2.2 Physicochemical properties of some selected phthalate esters

Phthalate	Acronym	Molecular Structure	Molecular Formula	Molecular Mass	Aqueous Solubility[a]	Log K_{ow}[a]
Dimethyl phthalate	DMP		$C_{10}H_{10}O_4$	194.2	1024	1.61
Diethyl phthalate	DEP		$C_{12}H_{14}O_4$	222.2	594	2.54
Diallyl phthalate	DAP		$C_{14}H_{14}O_4$	246.3	156	3.11
Di-n-propyl phthalate	DPP		$C_{14}H_{18}O_4$	250.3	1.3	5.12
Di-isopropyl phthalate	DiPP		$C_{14}H_{18}O_4$	250.3	NA	NA
Di-n-butyl phthalate	DBP		$C_{16}H_{22}O_4$	278.3	3.8	4.60[b]
Di(2-methoxy ethyl) phthalate	DMEP		$C_{14}H_{18}O_6$	282.3	NA	NA

Butyl benzyl phthalate	BBP		$C_{19}H_{20}O_4$	312.4	2.8×10^{-3}	4.70
Dicyclohexyl phthalate	DCHP		$C_{20}H_{26}O_4$	330.4	NA	NA
Di(2-ethyl hexyl) phthalate	DEHP		$C_{24}H_{38}O_4$	390.6	2.9×10^{-3}	7.73
Di-n-octyl phthalate	DnOP		$C_{24}H_{38}O_4$	390.6	5.0×10^{-4}	8.80[b]

[a] Llompart et al., 2006

[b] Memorandum of United States Consumer Product Safety, 2010

raised concern about the possibility of phthalates being contributors to reproductive and developmental adverse effects in humans. Some recent studies have suggested possible associations between environmental exposure to PAEs and adverse effects on human reproductive health. In view of this situation, the health impacts, especially the endocrine disruption potential of pthalate esters is regularly reviewed (Harris and Sumpter, 2001; Matsumoto et al., 2008).

The U.S. Agency for Toxic Substances and Disease Registry(ASTDR), (1995b, 1997, 2001, and 2002) the World Health Organization (IPCS, 1992; 1997; and 2003), the U.S. Department of Health and Human Services (DHHS), (NTP-CERHR, 2003) and the European Union (ECB, 2003) carried out comprehensive risk assessments regarding human health aspects for some phthalates. Based on rat and mice studies, the U.S. Environmental Protection Agency (EPA), concluded that DEHP and BBP are probable human carcinogens (group B2) and a possible human carcinogen (group C), respectively. EPA classified other phthalate esters, such as DBP and DEP, into group D (inadequate or no human and animal evidence of carcinogenicity). On the other hand, although initial evaluation stated DEHP as possibly carcinogenic to humans, later on, International Agency for Research on Cancer (IARC) evaluation, in 2000, (IARC, 2000) classified DEHP in group 3(not classifiable as to its carcinogenicity to humans) together with BBP. However, the latest study on phthalates toxicity by Lyche et al., (2009) indicated high toxicity potential for di(2-ethylhexyl) phthalate (DEHP), di-*n*-butyl phthalate (DBP), and butyl benzyl phthalate (BBP), but advocated for more studies to carried out in this regards in order to generate more widespread data.

2.3 Environmental fate, risk of human exposure and regulation of PAHs and phthalates water pollution

The global movement of PAHs showed that PAHs from anthropogenic sources are discharged into the atmosphere, either in the gaseous state or adsorbed onto particulates, and is subject to removal mechanisms such as oxidative and photolytic reactions, and wet and dries deposition (Gachanja, 2005). With relatively high Henry’s law constants, air currents and prevailing winds easily disperse and transport the PAHs over long distances and deposit them on soil, vegetation and in water. In addition to wet and dry deposition onto water bodies, PAHs on soil are also carried during storms by water runoff to rivers and seas. In the aquatic environment, the PAHs enter marine plants, fish, and sedentary organisms by bioaccumulation, owing to their low water solubility and hydrophobic nature.

On the part of phthalates, they enter the environment throughout their entire life cycle: during production, use, and disposal. This is owing to the fact that phthalate esters are not chemically bound to the polymeric matrix of the plastic products where they are used as plasticizers; hence, they can diffuse from these media into the environment. The main portion of phthalate esters released to the environment is due to evaporation from consumer products during their use, despite their relatively low vapor pressures. Their mobility to the surrounding media combined with their high volume production and large spectrum of applications, made phthalates ubiquitous in today's environment (Heise and Litz, 2004). Though diffusion into the air is the major route by which phthalate esters enter the environment, phthalates have relatively low vapor pressure and Henry's law constants, as well as relatively high K_{OW} and K_{OC}, hence, these compounds are found to only a limited extent in air. However, phthalate esters are present in air, in both the vapor phase and associated with particulates, at concentrations generally at the low ng/m^3 level. This implies that atmospheric fallout, via wet and dry deposition, is the dominant source of phthalate esters in water systems.

Route of exposure to these pollutants is dependent on many factors like physicochemical properties, uses and biodegradability of the compound in question. Humans are exposed to PAHs and phthalates through ingestion, inhalation, and dermal exposure (Menzie et al., 1992; Latini, 2005). For instance, dermal and inhalative exposures are considered to be the major route of exposure to diethyl phthalate that is found in hygiene products such as soap, shampoo, and conditioners. In contrast, for phthalates that are used mainly as plasticizers, such as DEHP, oral exposures predominate. Also, for certain subsets of the general population non-dietary ingestion (medical and occupational) or medical exposure constituted another reasonable way of exposure. Exposure of the general human population to DEHP has been studied more in depth than other phthalates. It has been estimated to be in the range of 3 to 30µg/kg of body weight/day (excluding occupational exposure, medical exposures, and non-dietary ingestions in children), the major source being from water and residues in food (Latini, 2005). These estimates already exceed chronic exposure levels believed to be tolerable for the general population. However, with the continuous ban on the use of phthalates plasticizers in the manufacture of food packaging devices, human exposure to phthalates through water dominates. Similarly, several studies have reported that human exposure to PAHs is mainly through inhalation and oral means, since PAHs do not have much known industrial applications. However, considering the fact that PAHs have low vapour pressure, oral exposure constituted the major route of exposure. In assessing the level of human exposure to PAHs, Menzie et al., (1992) reported that the potential dose of carcinogenic PAHs via drinking water ranges between 0.0002 pg/day and 0.12 pg/day, with median value of 0.006 pg/day, based on the assumption of an average drinking-water consumption rate of normal adult to be 2 litre/day.

Considering the risk posed by the level of human exposure to these harmful chemicals, there have been efforts at both the international level and national level to regulate the amount of PAHs and phthalates in water, in order to preserve both animal and human lives. Against this backdrop, the WHO set a 0.2µg/l standard for the total PAH concentration permitted in drinking water (WHO, 1971), while the following limits were set in the European Union for PAH in water intended for human consumption (European Union, 1998): 0.010 mg/l for Benzo[a]pyrene, and 0.10 mg/l for the sum of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, and indeno[1,2,3-c,d]pyrene. The Nigerian Industrial Standard also regulated the concentration of PAHs to be discharged in water bodies in order to preserve aquatic life as well as the maximum allowable limit of these harmful pollutants in drinking water (NIS, 2007). However, the effective regulation of PAHs and phthalates water pollution demands effective monitoring of water environment for these pollutants to enforce compliance, since it is the outcome of the monitoring exercise that determines the necessary steps to be taken.

2.4 Preconcentration techniques for analysis of PAHs and phthalates in aqueous samples

Considering the fact that micro-organic pollutants coexist with wide range of different compounds with similar characteristics in environmental water samples, these compounds are usually determined by a chromatographic technique. Also, the levels of these pollutants in water media are below the detection limits of most instrumental methods, hence there is need for the enrichment of the levels of these analytes of interest. Furthermore, some instrumental techniques like gas chromatography/mass spectrometry (GC/MS) are not amenable to detecting analytes in aqueous media, hence there is the need for change of phase from aqueous to organic solvent. Therefore, a sample pre-treatment is usually required for cleaning and/or preconcentrating the sample. Hence, the role of pre-concentration procedure in environmental analysis of micro-organic pollutants like PAHs and phthalates cannot be over-emphasized. The relevance of pre-concentration in the analysis of PAHs and phthalates in water samples is reflected on the volume of information available in literature. So far, the techniques employed for the extraction and preconcentration of PAHs and phthalates from aqueous samples include liquid–liquid extraction (Li et al., 2006; Cai et al., 2007; Brum et al., 2008; Tavakoli et al., 2008), liquid-phase microextraction (LPME) (Zhao et al., 2002; Psillakis and Kalogerakis, 2003; Liu et al., 2003), continuous-flow microextraction (Liu et al., 2007; Liang, 2008), membrane-assisted solvent extraction (Rodil et al., 2007), semi-permeable membrane device (SPMD) (Yusà et al., 2005), cloud-point extraction (CPE) (Delgado et al., 2004; Sikalos and Paleologos, 2005; Wang et al., 2007a) solid-phase extraction (SPE) (Marcé and Borrull, 2000; Li and Lee, 2001; Cai et al., 2003; Oliferova et al., 2005; Zhou et al., 2006; Wang et al, 2007b), solid-phase microextraction (SPME) (Luks-Betlej et al., 2001; Bruheim et al., 2003; Hsieh et al., 2006; Fernández-González et al., 2007), and stir bar sorptive extraction (SBSE) (Serôdio et al., 2004;Pérez-Carrera et al., 2007; Qin et al., 2008).

Among the listed techniques, literature data showed that LLE is the most widely reported technique for preconcentration of PAHs and phthalates, notwithstanding its drawbacks (Bruzzoniti et al., 2000). This observation is owing to the age of LLE technique, since it is the foremost extraction technique. However, recent environmental assays showed that LLE has continuously suffered waning acceptance in water assays due to emergence of better extraction options like SPE, SPME and SFE. Though SPME and SFE have been successfully applied for extraction of PAHs from environmental water samples, with acceptable recovery (Sargenti and McNair, 1998), widespread application is being limited on the basis of complex analytical technicalities involved.

Solid-phase extraction, having circumvented many drawbacks of liquid-liquid extraction (LLE) and created room for tuning the selectivity, affinity and/or capacity through development of new materials, has become the pre-concentration method of choice for PAHs and phthalates in recent times (Masque et al., 1998; Hennion, 1999; Bruzzoniti et al., 2000; Huck and Bonn, 2000; Żwir-Ferenc and Biziuk, 2006; Fontanals et al., 2011). For instance, Sargenti et al. (1998) compared four different extraction techniques (solid phase extraction, supercritical fluid extraction (SFE) solid-phase extraction followed by supercritical fluid extraction (SPE/SFE) and liquid–liquid extraction (LLE)) for the extraction of 16 PAHs from drinking water. The authors reported that the results showed that recoveries were good for SPE and for SPE/SFE for all compounds, recoveries for SFE were worse than SPE/SFE, and LLE had the worst recovery and reproducibility.

In view of these obvious advantages, SPE has been included in some US EPA Methods which analyze pollutants in drinking water (e.g. Methods 549.1 and 525.1 which use C_8 and C_{18} bonded silica sorbents, respectively, to analyze pesticides) (Masque et al., 1998; Hennion, 1999).

2.5 Principles and operation of solid phase extraction (SPE)

Solid phase extraction (SPE) is a powerful method for sample preparation that is being used by most chromatographers today. It has capabilities in a broad range of applications such as environmental analyses, pharmaceutical and biochemical analyses, organic chemistry and food analyses. The technique refers to the non-equilibrium, exhaustive removal of chemical constituents from a flowing liquid sample via retention on a contained solid sorbent, and subsequent recovery of selected constituents by elution from the sorbent. This affinity, which is strong enough to be analytically useful for sorbents that are inexpensive enough to be economically feasible, is useful in both pharmaceutical and environmental applications.

Retention is achieved with strong but reversible interactions between the analyte and the surface of the sorbent. Typical interactions are hydrophobic (van der Waals forces), polar (hydrogen bonding and dipole-dipole forces) or ion exchange interactions. Before selecting a sorbent for SPE, it is necessary to take into account some physicochemical considerations such as the functional groups of the analytes, the nature of the bonded phase, the energetic of the interactions, the secondary interactions between the analytes and the sorbent, the interactions between the sorbent and the components of the sample matrix, and the interactions between the analytes and the sample matrix (Marsque et al., 1998). Because the solute molecules interact more strongly with the stationary phase molecules than they do with the mobile phase molecules, solutes are retained in the stationary phase (regardless of its volume). For desorption processes, interaction between solute and solvent molecules results from three basic types of intermolecular force, all of which are electrical in nature. These types of interactive forces are dispersive, polar and ionic. Polar forces have been further divided into sub groups ranging from 'strong dipole-dipole interactions' (hydrogen bonding) to 'weak dipole-dipole interactions. Division into the two groups is appropriate, as it describes two physically different types of polar interaction that is very pertinent to chromatographic retention. Most molecular interactions that occur during desorption process consist of a mixture of at least two different types of interaction; the only type of interaction that can occur in isolation is dispersive (Scott, 2003). Hence, knowing the likely interactive force that will dominate in adsorption and recovery of analyte of interest is one of the fundamental guiding principles for selection or development of SPE adsorbents.

Sorbents in SPE can be divided into three classes, normal phase, reversed phase and ion-exchange sorbents. Normal phase sorbents have polar functional groups, e.g. cyano, amino and diol. These sorbents are characterized by their polar nature which is more likely that polar compounds, e.g. phenol, will be retained (Dean, 1998). Reversed phase types have non-polar functional groups, e.g. octadecyl (C_{18}), octyl (C_8) and methyl, and conversely are more likely to retain non-polar compounds, e.g. polycyclic aromatic hydrocarbons. Retention of organic analytes from polar solutions (e.g. water) onto the reversed phase sorbents which is the focus of this research, is due to the attractive forces between the carbon-hydrogen bonds in the analyte and the functional groups on the solid surface (Ball, 2009). Therefore, due consideration of these likely interactive forces, is necessary in the design of SPE sorbents for pre-concentration of phthalates and PAHs.

There are two main designs or formats in SPE namely: the cartridge and the disc formats. The most frequently used format or design in SPE is the cartridge. Many different types and amounts of sorbent are contained between two polyethylene or stainless steel frits in glass or polypropylene cartridges which have different column volumes. The second design which has become available in the last few years is the disk. Two different kinds of disk are now available: particle loaded membranes (PLMs) and particle-embedded glass fibre disks (PEGFDs). PLMs consist of a web of polytetrafluoroethylene (PTFE) micro-fibrils in which sorbent particles with a diameter of about 8 mm are suspended, and the membranes have a homogeneous flexible structure, while the PEGFDs contain particles embedded in a glass fibre supporting matrix. At present, cartridges are still the most frequently used, mainly because of the limited number of commercially available sorbents on disks, and cartridges normally use less solvent volume than disks (Masquè et al., 1998).

There are two main procedures commonly used for determination of organic or inorganic species in SPE technique; the off-line SPE and on-line SPE modes. Due to the comparative advantages of each of these procedures, both methods are in common use for the analysis of hydrophobic micro-pollutants like PAHs and phthalates, in aqueous systems. In the off-line SPE mode the sample preparation and the detection steps are carried out separately, whereas on-line mode achieves both sample preparation and detection in one single step. The advantages and limitations of both procedures have been reviewed by Poole *et al.*, (1990). Both procedures have been applied in the analysis of PAHs and phthalates. In this guise, literature has reported the off-line SPE technique for the analysis of PAHs (Kanchanamayoon and Tatrahun, 2008; Fladung, 1995;) and phthalates (Cai et al., 2003; Lopez-Jimenez et al., 2005; Del Carlo et al., 2008; Prapatpong and Kanchanamayoon, 2010; Wang et al., 2012). HPLC is the most used for determining PAHs and phthalates, and SPE-HPLC is the most straightforward coupling method. Hence, SPE has usually been coupled on-line with HPLC systems with UV-visible detectors (SPE-LC-UV). However, fluorescence detectors, electrochemical detectors, diode array detectors (SPE-LC-DAD) and mass spectrometers (SPE-LC-MS) have also been used (Berrueta, 1995). In this regards, C_{18} -bonded silica, Styrene Divyl Benzene (SDB), Boos silica, and Boos Glass have successfully been coupled to HPLC for the analysis of PAHs (Marce and Borrull, 2000). Also, immunosorbents (Ferrer and Barcelo, 1999; Bouzige et al., 1998), SFC, (Bernal et al., 1997) and Styrene Divyl Benzene (El Harrak et al., 1998) have been applied using on-line procedure for the analysis of PAHs. Similarly, online coupling of SPE with liquid chromatography has been reported for analysis of phthalates (Xu et al., 2010).

On-line methods are advantageous as compared with the off-line batch systems, because they are automated; make use of simpler apparatus with easier operation, much cheaper equipment and lower running costs. Moreover, procedures by batch using adsorption process are very efficient, but these involve tedious and delayed steps. On the other hand, flow injection procedures with solid phase extraction are preferred due to advantages obtained, such as: high sample throughput, high enrichment efficiencies, low sample and reagent consumption, high reproducibility and very limited laboratory bench space and utensils required. However, the major problem of the on-line systems is the peak broadening which can appear when the sorbent is much different than the stationary phase of the analytical column. This is more likely to occur when a surfactant is used as modifier because of the distribution of the analyte over the precolumn and the strong interaction of some analytes with the micelles (Brouwer, 1994). Considering the likelihood of peak broadening, off-line procedure (rather than on-line) is the preferred option when a new adsorbent is being developed for SPE application.

2.6 Method development for solid phase extraction

Development of an SPE method can be considered as a two-step procedure. First, the selection of appropriate sorbent, and secondly, the optimization of the most influential parameters. Obviously, optimization should initially be performed using spiked synthetic solutions, but it must be followed by the use of certified reference materials or spiked real samples, as matrix components (such as other organic molecules, ligands or other ions) may change the analyte retention on the sorbent, thereby decreasing expected recoveries of the target species.

2.6.1 Selection of solid sorbent

The most important attributes of an adsorbent for any application are: capacity, selectivity, regenerability, rate of adsorption/desorption process, compatibility, and cost. Rarely will a single adsorbent be optimal in all these respects. More often it will be possible to narrow the choice to one or two classes of adsorbents, but that still commonly leaves a vast array of possibilities.

Solid sorbents may be hydrophobic or polar. It is common to call reversed-phase sorbents the packing materials that are more hydrophobic than the sample, which are frequently used with aqueous samples. On the other hand, normal-phase sorbents refer to materials more polar than the sample and they are used when the sample is an organic solvent containing the target compounds.

The nature and properties of the sorbent are of prime importance for effective retention of target analytes. Careful choice of the sorbent is thus crucial to the development of SPE methodology. In practice, the main requirements for a solid sorbent are: (1) the possibility to extract a large number of target analytes over a wide pH range (along with selectivity towards major organic species); (2) the fast and quantitative sorption and elution; (3) a high capacity; (4) regenerability; and (5) accessibility. In particular, sorbents that allow fast reaction rates are preferred to achieve faster extraction as well as higher loading capacities. Hence, sorbents based on hydrophobic macro-porous polymers and cellulose or on fibrous materials provide excellent kinetic properties (Żwir-Ferenc and Biziuk, 2006). Considering the fact that sorbent selection and development is the core mandate of this study, a separate section is dedicated to the review of the various classes of SPE sorbents.

2.6.2 Optimization of the influential parameters

The main experimental variables that affect analyte recovery by SPE have been extensively reviewed by Poole et al. (2000). They are briefly discussed in this section and illustrated with reported applications. The operational steps for development and optimization of the influential parameters for a new SPE sorbent/method have been principally divided into three cagories viz: conditioning parameters, loading /sample parameters, and elution parameters.

The conditioning parameters are those steps taken to make the SPE adsorbent to be in the optimum condition towards achieving maximum retention capacity. The major procedure includes washing step and selection of the conditioning solvent. A washing step is highly recommended, especially when micro organic levels like PAHs and phthalates are to be determined. Even though some sorbents have been used without a conditioning step this is not recommended. This step will at least remove possible remaining contaminants and air from the sorbent bed. Additionally, in some cases, this step is crucial for successful retention of the analytes. The nature of the conditioning solvent must be appropriate to the nature of the solid sorbent to ensure good wettability of the functional groups. As an example with hydrophobic supports such as C_{18}-silica or PS-DVB, quite polar organic solvents such as methanol should be used. The sorbent should further be conditioned by a solvent whose nature is similar to that of the sample. This is the sole reason why most SPE procedure reported for analysis of PAHs and phthalates reported in literature, have adopted methanol and water as the conditioning solvent (Poole et al., 2000).

Loading parameters are those parameters that are considered to affect the retention of samples, which emanate from the way and manner the sample was loaded, while the elution parameters are those considered to affect the elution (desorption) of the retained analytes of interest from the SPE phase. The loading parameters include sample volume to be percolated, sample flow rate, sample pH, and sample modifier whereas the elution parameters include selection of the elution solvent, elution mode (whether in this manner with sample loading or reversed mode), solvent volume, and solvent flow rate. The details of the procedure for optimization, and justification behind these procedures have been extensively discussed in literature (Berrueta et al., 1995; Poole et al., 2000; Thurman and Snavely, 2000; Liška, 2000; He et al., 2007; Vidal et al, 2012).

2.6.3 Chromatographic techniques for PAHs and phthalates

PAHs and phthalates are often determined by high-performance liquid chromatography (HPLC) and gas chromatography (GC) (Wenzl et al., 2006; Poster et al., 2006).

Several PAH isomers are not resolved by gas chromatography. Although gas chromatography-mass spectrometry is a good technique, using surrogate standards to quantify and clean-up after extraction of both liquid (effluent or waste water) and solid samples has shown to be useful. However, the use of GC-MS has the major challenge of being relatively more expensive than HPLC, and not being amenable to directly determine analytes of interest in water, except after extraction.

Liquid chromatography with fluorescence detection is a very sensitive technique and more adapted to the analysis of several isomers. It is selective and requires much less clean up than GC-MS because it is easy to equip the analytical column with a guard precolumn. No clean-up is required for the analysis of surface water extracts. Hence, the continued application of HPLC in analysis of PAHs and phthalates is being driven by its analytical performance and cost efficiency as evidenced by the array of literature reports where HPLC has been used for determination of PAHs and phthalates (Marce and Borrull, 2000; Liang et al., 2008).

Also, because PAHs molecules display strong and characteristic UV absorption, are naturally and strongly fluorescent, and also give sensitized luminescence under peroxyoxalate chemiluminescence (PO-CL) conditions, (Gachanja, 2005), UV absorption and fluorescence detection are increasingly being used in the analysis of PAHs in studies where only single PAHs are being considered (Awoyemi, 2011).

2.7 Review of SPE sorbents

The broad variety of sorbents available explains one of the most powerful advantages of SPE, which is selectivity. Sorbents can be mainly categorized as organic based (natural polymers, as well as synthetic polymers), inorganic based ((silica gel (SiO_2), alumina ($A1_2O_{3)}$, magnesia (MgO) and other oxide species) and nanomaterials. Immobilization of organic compounds on the surface of the solid support is usually aimed at modifying the surface with certain target functional groups for a higher selectivity of the extraction. The selectivity of the modified solid phases towards certain target analytes is attributed to several well-known factors, such as the size of the organic compound used to modify the sorbent, the activity of the loaded surface groups, and the type of the interacting functional group. However, the selective extraction of a single organic species from other interfering components represents a direct challenge for finding a suitable phase capable of exhibiting a sufficient affinity to selectively bind that organic specie of interest. These interests and challenges formed the focus of the review of the SPE sorbents applied for the analysis of PAHs and phthalates in aqueous media. On this note, a review of the various classes of SPE adsorbents in common use for pre-concentration of PAHs and phthalates will bring out their high-points and draw-backs

2.7.1 Inorganic sorbents

2.7.1.1 Silica based SPE sorbents

Inorganic based sorbents are mainly made of silica gel even though other inorganic oxides may be used. Silica gel based sorbents present the advantages of mechanical, thermal and chemical stability under various conditions. Almost all organic compounds have a certain potential for non-polar interactions. Exceptions are compounds possessing a large number of polar or even ionic groups which shield the non-polar character of the carbon skeleton (e.g. carbohydrates). Silica gel, which is an unmodified form of silica, on the other hand shows no non-polar interactions. To overcome this challenge, non-polar chemical moieties are coupled to the silanol (Si-OH) groups of the silica to make them more hydrophobic. Two approaches are used for loading the surface with specific organic compounds, chemical immobilization and physical adsorption. In the first case, a chemical bond is formed between the silica gel surface groups and those of the organic compound (functionalized sorbent). In the second approach, the organic compound is directly adsorbed on the silanol groups of the silica gel surface (impregnated or loaded sorbent), either by passing the reagent solution through a column packed with the adsorbent, or by soaking the adsorbent in the reagent solution. Since the functional groups of most modified silicas are bonded to the silica surface via a hydrocarbon spacer, these modified silicas show a certain degree of non-polar interactions.

Typical silica based adsorbents with a pronounced non-polar character that are more widely applied for SPE extraction of PAHs and phthalates are the octadecyl bonded silica (C_{18}) and octyl bonded silica (C_8) hybrid adsorbents which are eighteen and eight carbon chain skeleton, respectively, coupled to silica base (Marce and Borrull, 2000). They frequently offer a high selectivity towards a given analyte of interest. In this regards, silica based SPE sorbents have been applied for extraction of PAHs and phthalates.

For PAHs, one of the earliest attempts on the application of silica based SPE which opened the flood gate of analytical optimizations, was carried out by Fladung (1995). The author who was commissioned by US EPA for the research, reported successful pre-concentration of PAHs using silica-based SPE method, and its subsequent HPLC analysis. It was after this report that other researchers followed. Due to the volume of research that followed, Marce and Borrull (2000) wrote a review on the flood gate of SPE and HPLC analysis of PAHs up to year 2000.

In one of the recent studies, Kanchanamayoon and Tatrahun (2008) applied C_{18} silica based adsorbent for the simultaneous SPE procncentration of eleven polycyclic aromatic hydrocarbons namely; naphthalene, acenaphthylene, acenaphthene, fluorene,phenanthrene, anthracene, fluoranthene, pyrene, benzo[b]fluoranthene, benzo[a]pyrene and benzo[ghi]perylene after which they were analyzed by gas chromatograph. Kouzayha et al., (2011) applied silica-based C_{18} cartridge for the preconcentration of the 16 US EPA priority PAHs in aqueous samples. Though the authors examined the parameters affecting the extraction procedure such as type and volume of the elution solvent, breakthrough volume of the percolated water sample, drying of the sorbent, and evaporation of the elute. The authors concluded that their method was fast and reliable.

Andrade-Eiroa et al., (2010) also reported the application of C_{18} SPE phase for pre-concentration of PAHs from liquid ultrasonic extract of PAHs from soot samples. The authors applied ultrasonic extraction of the PAHs using acetonitrile, after which the extracts were purified and pre-concentrated with the C_{18} SPE sorbent, and thereafter analyzed by Liquid Chromatography with UV and fluorimetric detection. According to the authors, the method was satisfactorily applied to kerosene and bio-kerosene soot from atmospheric open diffusion flames (pool fires) and premixed flames achieving Quantification and Detection limits in the range ng mg^{-1} soot and recoveries about 90% for most of the PAHs studied. In another report, a solid-phase extraction (SPE) method using triacontyl bonded silica (C_{30}) as sorbent was developed by Li et al., (2007) for the determination of 16 US Environmental Protection Agency polycyclic aromatic hydrocarbons (PAHs) in airborne particulate matters quantitatively by gas chromatography-mass spectrometry (GC-MS). The authors carried out the routine method development optimization experiments, and concluded that the optimized method was successful for the determination of 16 PAHs in real airborne particulate matters.

In another study, Huang et al., (2014) prepared and applied graphene (Gr) functionalized silica gel ($Gr–SiO_2$) sorbent as a new sorbent for solid-phase extraction (SPE) of polycyclic aromatic hydrocarbons (PAHs) including naphthalene, acenaphthylene, fluorene, phenanthrene, fluoranthene, and pyrene. The analytes were separated and detected by high-performance liquid chromatography (HPLC) and UV detector, respectively. Under the optimized SPE conditions, the authors reported that the developed SPE phase exhibited a wide linear range (0.01–600 µg/ L), acceptable repeatability of the extraction (RSDs of 1.7–8.2%, $n = 3$), satisfactory detection limits (0.0029–0.052 µg L^{-1}), as well as good recoveries 89.0–115.4%) of analytes in environmental water and milk samples indicating the applicability of the developed method.

For the purpose of comparison, Sargenti et al.(1998) applied three different bonded silica sorbents - C_{18} , cyano and phenyl bonded silica, and reported that C_{18} proved to be the best based on their method performance.

For phthalates, Lu et al., (2011) developed a simple, sensitive, and eco-friendly monolithic silica spin column extraction (MonoSpin-SPE) method combined with ultra-fast liquid chromatography-mass spectrometry (UFLC-MS) to determine the levels of six phthalate esters, dimethyl-(DMP), diethyl-(DEP), dipropyl- [DPrP], butyl-benzyl-(BBP), dicyclohexyl(DcHP), and di- *n-octyl-(DOP)* phthalate in physiological saline samples. Under optimized experimental conditions, the method gave acceptable method performance indices, and was used to determine the levels of six phthalate esters in physiological saline samples with good recoveries.

In a related study, Liu et al., (2013) applied a novel mixed hemimicelles solid-phase extraction (MHSPE) method, based on mesoporous silica-coated magnetic nanoparticles (Fe_3O_4/meso-SiO_2 NPs) as adsorbent was developed for extraction of phthalate esters from water samples. The authors correlated the acceptable performance of the method to some physicochemical properties of the sorbents as evidenced in the result of the characterization tests.

In another study, Wu et al., (2012) adopted silica/N-(n-Propyl)ethylenediamine-mixed SPE column for preconcentration of 17 phthalate esters (PAEs) in edible vegetable oil prior to analysis with GC-MS. The authors reported that the developed material was successfully applied for analysis of 30 plastic buckets of commercially available brands of edible oil, having exhibited acceptable values of method performance indices.

In a relatively advanced study, Kato et al., (2005) developed an on-line solid-phase extraction (SPE) method, coupled with isotope dilution high-performance liquid chromatography/tandem mass spectrometry (HPLC/MS/MS) and with automated sample preparation, to simultaneously quantify 16 phthalate metabolites in human urine. The authors applied a silica-based monolithic column for the initial preconcentration of the phthalate metabolites from the urine prior to the analysis of these analytes of interest using a silica-based conventional analytical column for the chromatographic separation. The authors highlighted the superiority of the method on the basis of not being labor intensive, authomatic pretreatment of the urine samples using HPLC autosampler, and minimal sample handling which consequently minimized exposure to hazardous chemicals.

Despite their broad application in the pre-concentration of organic micro-pollutants, all silica-based sorbents suffer from certain chemical limitations, namely the presence of residual surface silanol groups (even after an end-capping treatment) and a narrow pH stability range. Considering this scenario, there has been continued effort by scientists to develop better alternatives (Masqueè et al., 1998).

2.7.1.2 Other inorganic oxides

Apart from silica sorbents, other inorganic oxides have been tested for the adsorption of organic and inorganic compounds. The acidic oxides (such as SiO2), due to its acidic properties, is expected to adsorb only cations, while basic oxides (such as magnesia MgO) should adsorb only anions. These oxides have been reported to exhibit acceptable SPE performance for polar organics like cephalosporins (Nabi et al. (2004). However, due to non-polar nature of PAHs and phthalates, these other inorganic oxides are considered unsuitable adsorbents for PAHs and phthalates, and hence there is paucity of information on the application of the unmodified form of these oxides in SPE applications for non-polar organics. Expectedly, modification of these oxides will increase their performance as SPE sorbents, but most of the literature reports on the use of these other inorganic oxides applied the nanomaterial forms of the oxides. They are therefore reviewed under nanomaterials.

2.7.2 Organic based sorbents

For the purpose of this review, organic based sorbents are divided into polymeric and non-polymeric sorbents.

2.7.2.1 Polymeric SPE sorbents

Polymeric sorbents have been used for pre-concentration of micro-pollutants, having the advantage over bonded silica in that they can be used over the entire pH range (Fontanals et al., 2010). Their disadvantage is that the conditioning step is more time consuming as they require extensive cleaning before use (Masque et al., 1998). This section summarizes the most frequently used organic based sorbents, as well as the more recently reported ones. In most applications, new sorbents have been synthesized by chemically bonding more chemically interacting groups to polymeric cross-linked chains and characterizing their ability to selectively adsorb analytes of interest. Most of the bonded groups reported have low water solubility to avoid their leaching from the sorbent, as most applications deal with aqueous samples. At the same time, a too hydrophobic group will hinder wettability of the sorbent by the aqueous sample, resulting in poor retention efficiency.

A compromise is thus necessary. In addition to the functional group, the efficiency of polymeric sorbents depends on various physico-chemical parameters, such as particle size, surface area, pore diameter, pore volume, degree of cross-linking and particle size distribution.

2.7.2.1.1 Polystyrene-Divinylbenzene (PS-DVB) based sorbents

The most widely used polymeric sorbents are the styrene-divinylbenzene copolymers (PS-DVB) (Poole, 2003, Żwir-Ferenc and Biziuk, 2006), due to the fact that PS-DVB sorbent overcame many of the limitations of bonded silica phases. Polystyrene-divinylbenzene resin copolymer is a hydrophobic resin which has greater analyte retention, mainly for polar compounds, than their hydrophobic surface containing a relatively large number of active aromatic sites which allow π-π interactions with unsaturated analytes.

The higher potential of PS-DVB resins, such as Amberlite XAD-type, over C_{18} silicas for trapping polar compounds was largely demonstrated but these sorbents were not available in prepacked cartridges because they required laborious purification steps before use (Chai et al., 2004). XAD resins have been used to extract a variety of organic pollutants from water. XAD-1, XAD-2 and XAD-4 are PS-DVB with a highly hydrophobic character. XAD-7 and XAD-8 are acrylic ester resins with a higher affinity for polar solutes. XADs based on PS-DVB have some drawbacks including lack of selectivity, low breakthrough volumes for very polar compounds, and low sampling rate, and they require extensive cleaning before use (Żwir-Ferenc and Biziuk, 2006).

Another widely used PS-DVB copolymer is the PLRPS resin. It has been used in the extraction of organic pollutants such as pesticides from natural waters. PLRPS has the same drawbacks as XADs: lack of selectivity and low breakthrough volumes for very polar compounds.

However, considering paucity of literature data on application of PS-DVB based adsorbents for SPE pre-concentration of PAHs and phthalates, it is obvious that these adsorbents are considered not to be suitable for extraction of these compounds. This is owing to the fact that PS-DVB exhibit π–π interactions, in addition to the hydrophobic interaction that also occurs with C_{18}-silica. These interactions become relatively stronger to the extent that it often leads to irreversible adsorption for non-polar unsaturated compounds like PAHs and phthalates. Hence, elution with normal organic solvents will likely give low recovery.

2.7.2.1.2 Molecularly Imprinted Polymers

Highly stable synthetic polymers that possess selective molecular recognition properties have been obtained through the process of molecular imprinting. Recognition sites within the polymer matrix are complementary to the analyte in the shape and positioning of functional groups. Molecularly imprinted polymers are made by synthesizing highly cross-linked polymers in the presence of a template molecule. After removal of this molecule, the polymer can be used as a selective binding medium for the template (analyte) or structurally related compounds.

The mechanisms, by which these polymers specifically bind the template and related ligands, are attributed to the formation of functional groups in a specific arrangement within the polymer. They correspond to the template and the presence of shape-selective cavities.

Some of these polymers have high selectivity and affinity constants, comparable with naturally occurring recognition systems such as monoclonal antibodies, which make them especially suitable as constituents in chemical (biomimetic) sensors for analytical chemistry or simply for enhancing the selectivity in SPE. There are already a few applications of these polymers (Masqué et al., 1998).

In this vein, Prasad and Banerjee, (2003) prepared an inorganic based sorbent obtained from silica gel-bound molecularly imprinted polymer to oxazolone(s) exclusively derived from certain cephalosporins (cefaclor) and penicillins (amoxicillin and ampicillin) using ethylacetate as a porogen, and applied it as packing material for solid phase extraction in column chromatography. In a similar study, Brüggemann et al., (2000) prepared an oxacillin imprinted polymer by the use of 4-vinylpyridine as functional monomer and trifluoromethyl acrylic acid as cross-linking agent. The sorbent was applied for the separation of a mixture of penicillin V, penicillin G and the print molecule on an MIP utilizing an aqueous mobile phase. Baseline separation of the two penicillins from oxacillin was achieved using the molecularly imprinted polymer.

Recently Qi et al., (2011) reported the application of MIP as an SPE phase for analysis of monobutyl phthalate. The MIP was reportedly prepared using monobutyl phthalate (mBP) as template with different porogens and functional monomers, and thereafter as a selective sorbent in molecularly imprinted solid-phase extraction (MIP-SPE) for pre-concentration and determination of monobutyl phthalate (mBP) from bottled water. Control of the MIP-SPE process was seen as important in helping to facilitate the selective extraction of mBP from water samples. The authors reportedly concluded that the developed MIP-SPE method demonstrated to be applicable for the analysis of mBP in the bottled water.

2.7.2.1.3 Polyurethane Polymers

In recent years, cellular and foamed plastic materials such as modified and unmodified polyurethane foam (PUF) have received considerable attention for simple and fast separation and pre-concentration procedures. This renewed interest on PUF is as a result of several advantages over other solid phase sorbents viz; commercial availability, ease of preparation and handling, relatively high surface area, cellular structure, extremely low cost, stability in acids (except concentrated nitric and sulfuric acids), bases and organic solvents, and thermal stability up to about 180 ^{o}C. Moreover, the application of PUFs in column techniques in off – line or flow injection pre-concentration system is advantageous because it shows low resistance to passage of fluids and did not show any over-pressure nor swelling as commonly witnessed when using other sorbents (Lemos et al., 2007).

In this vein, Dmitrienko et al., (2002) developed a technique for the sorption pre-concentration of polycyclic aromatic hydrocarbons on polyurethane foams in the batch and dynamic modes providing their simultaneous quantitative extraction. Their procedure applied luminescence method for the determination of total amount of PAHs, desorption of adsorbed compounds with acetonitrile, and determination of individual compounds in the eluate by high-performance liquid chromatography with fluorescence detection. The authors concluded that their method can be applied for preconcentration of PAHs in aqueous systems based on the method performance indices both in model and real water samples. Also, polyurethane polymers have been applied for pre-concentration of trace metals in aqueous samples (Camel, 2003).

2.7.2.1.4 Miscellaneous polymer materials

Other polymer materials like divinylbenzene-vinylpyrrolidone, polyacrylate, polyethylene, polytetra-fluoroethylene, polystyrene, polyamide, iminodiacetate-type chelating resins, propylenediaminetetra acetate-type chelating resins, and polyacrylonitrile based resins ring-opening polymerisation-based polymers, have exhibited capacities to be applied as SPE sorbents for preconcentration of trace pollutants in aqueous media. However, literature reports showed that they are not suitable adsorbents for pre-concentration of neutral hydrophobic compounds like phthalates and PAHs (Camel, 2003).

2.7.2.2 Non polymeric SPE sorbents

2.7.2.2.1 Carbon Sorbents

The most widely used carbon-based SPE are graphitized carbon blacks (GCBs) which are obtained by heating carbon blacks at 2700–3000 °C in an inert atmosphere. These sorbents are non-specific and non-porous with surface area of about 100 m^2/g. Also, due to the presence of positively charged chemical heterogeneities on their surface, they are considered to be both reversed-phase sorbents and anion-exchangers (Hennion, 1999).

Carbon sorbents have been extensively used in the past few years for the SPE of polar organic pollutants from water samples like pesticides (Żwir-Ferenc and Bizuik, 2006), while it is still rare in trace elements SPE (Camel, 2003). The surface framework of GCBs used in SPE was shown to be contaminated by oxygen complexes. These groups are able to interact so strongly with sufficiently acidic compounds that conventional solvent systems are not able to desorb them. Hence, the main limitations are possible irreversible retention of analytes, which may be overcome by elution in the backflush mode, and poor mechanical stability.

2.7.2.2.2 Immunosorbents

One of the major problems encountered with SPE is the lack of selective sorbents when analyzing surface water. In this sense, the matrix of these samples is difficult to eliminate and it produces a noisy baseline and a large peak at the beginning of the chromatogram, thus making the determination of the most polar analytes laborious. Recently, new extraction sorbents involving reversible and selective antigen-antibody interactions, called immunosorbents (ISs), have been synthesized in order to trap structurally related pollutants. They give extracts which are free of interfering substances. Using ISs, extraction, enrichment and cleanup are accomplished in one step when surface waters are analyzed (Żwir-Ferenc and Bizuik, 2006; Pichon and Chapuis-Hugon, 2008).

Immunosorbents are obtained by covalently binding antibodies onto appropriate sorbents. The ideal support for an immune-affinity sorbent is supposed to be rigid and porous so that the flow rates of environmental samples can be high. Likewise, it should provide functional groups to enable appropriate coupling with a sufficient number of antibodies and be hydrophilic to prevent non-specific interactions with the analytes and the sample matrix (Martin Esteban et al., 1997; Żwir-Ferenc and Bizuik, 2006).

Immunosorbents (IS), have been used for selective isolation of PAHs from complex environmental samples. Perez et al. (2000) used sonication with dichloromethane/

methanol and an anti-fluorene immunosorbent followed by HPLC and diode array detection for determining PAHs from environmental sediments and a sludge reference material containing PAHs. Results showed a better selectivity since the chromatograms presented a clear baseline allowing the determination of PAHs at part per billion (ppb) levels. Also, good results were obtained when IS were used after SFE in order to increase the selectivity when soot samples were analysed (Marce and Borrull, 2000).

2.7.3 Nanomaterials

According to SCENIHR (2007), nanomaterials can be defined as natural, incidental or manufactured materials containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range of 1 nm–100 nm. They can be organic, inorganic, or hybrid materials. Compared with traditional SPE sorbents, nanomaterials possess large surface area, short diffusion route, and good mechanical stability which may result in high extraction efficiency and rapid extraction dynamics. In a bid to explore these advantages there have been several attempts in developing nanomaterials based SPE sorbents for pre-concentration of several micro-pollutants including PAHs and phthalates. Literature data revealed that among the existing nanomaterials, carbon and iron oxide based nanomaterials are the major class of materials applied for pre-concentration of PAHs and phthalates in water samples.

2.7.3.1 Nanomaterial SPE phase for PAHs

In one of the earliest recorded studies, Wang et al., (2007) applied multiwalled carbon nanotubes (MWCNTs) as SPE phase for preconcentration of PAHs in environmental water samples, after which they were analyzed with HPLC. After optimization of the relevant SPE operation parameters, the characteristic data of analytical performance were determined to investigate the sensitivity and precision of the method, and thereafter, the method was applied for the determination of PAHs in river, tap and wastewater samples. The authors reported that the SPE method exhibited good performance indices in terms of linear range (0.04–100µg/L), recovery (78.7–118.1%), precision (RSD=1.7–4.8%) and detection limit (0.005–0.058µg/L), and therefore concluded that MWCNTs packed cartridge coupled with HPLC was an excellent alternative for the routine analysis of PAHs at trace level. In a related study, Ma et al., (2010) utilized MWCNTs as SPE phase coupled with gas chromatography–mass spectrometry (GC–MS) for the determination of 16 polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. After optimization of the relevant SPE operation parameters, the characteristic data of analytical performance were determined to investigate the sensitivity and precision of the method, and thereafter, the method was applied for the determination of PAHs in river, tap and wastewater samples. The authors reported that the SPE method exhibited good performance indices in terms of recovery (70.0–125.5%) linearity (r^2=0.9848–0.9991)/linear range (20–5000 ng/L), precision (RSD=1.2%–12.1%) and detection limit (2.0–8.5 ng/L), and therefore recommended MWCNTs as suitable SPE phase for the routine extraction and analysis of PAHs at trace level.

In a somewhat novel study, Zhang et al., (2010) synthesized carbon coated Fe_3O_4 nanoparticles (Fe_3O_4/C) via a simple hydrothermal reaction and applied it as solid-phase extraction (SPE) sorbents for the first time, to extract trace polycyclic aromatic hydrocarbons (PAHs) from environmental water samples. The Fe_3O_4/C sorbents possess high adsorption capacity and extraction efficiency, high breakthrough volumes, convenient extraction procedure, and short extraction times, as well as good stability to changes in salinity and solution pH. Under the optimized SPE operation parameters, the authors reported that the developed SPE method exhibited good performance indices in terms of recovery (76–110%) linearity (r^2=0.9848–0.9991)/linear range (20–5000 ng/L), precision (RSD=0.8–9.7%) and detection limit (0.2–0.6 ng/L), and hence advocated for the use of Fe_3O_4/C nanoparticles for the pretreatment of environmental water samples.

In another study by Kefi et al., (2011), a TiO_2 nanotubes SPE combined with gas chromatography (GC) was established for the analysis of seven polycyclic aromatic hydrocarbons (PAHs). Under the relevant SPE operation conditions, the authors reported that the SPE method showed good linearity in the range of 0.01–0.8 µg/mL, precision (RSD=6.7–13.5%, n = 5) and satisfactory detection limits (0.017–0.059 ng/mL). Also, the developed method was successfully applied to the analysis of surface water (tap, river and dam) samples, where it exhibited good recoveries (90% to 100%). Having been successfully applied for analysis of surface water (tap, river and dam) samples, the authors concluded that titanate nanotubes is a potential SPE alternative phase for pre-treatment of PAHs polluted water samples. In a related study, Pan et al., (2011) developed Titanium wire-based SPE phase coupled to HPLC for analysis of six different PAHs in water samples. The adsorbent was a Ti wire on which TiO_2 nanotubes were first formed by anodization and thereafter coated with gold nanoparticles and n-octadecanethiol. Under the optimum SPE operation parameters, their method exhibited good linearities (r^2=0.9964–0.9999)/linear range (0.025–30mg/L), and low limits of detection in spiked water samples. Furthermore, this method was successfully applied in the analysis of real river water samples with recoveries (75.33–115.83%) and precision (4.85–10.77%). In conclusion, the authors recommended the developed SPE as a convenient means of sample pretreatment for environmental water samples.

Recently, Long et al., (2012) developed a magnetic solid-phase extraction (MSPE), which was an improved SPE method based on Triphenylamine (TPA)-functionalized magnetic microspheres (Fe_3O_4/SiO_2/TPA) adsorbent, for preconcentration, prior to HPLC analysis of PAHs in environmental samples. The improvement in their development was in terms of the sample loading/percolation and separation of the loaded adsorbents after sample loading, where the authors introduced magnetic separation (due to magnetic properties of Fe_3O_4/SiO_2/TPA). Under the relevant optimized SPE operation parameters, the authors reported that the developed SPE method exhibited good performance indices in terms of recovery (80.21–108.33 %) linearity (r^2>0.999), precision (RSD<10%) and detection limit 0.04–3.75 ng/L), and hence advocated for the application of their method in routine analysis based on the achieved performance indices.

2.7.3.2 Nanomaterial SPE phase for phthalates

Phthalate esters being one of the environmental pollutants of concern, was not left out in the exploration of obvious inherent advantages of nanomaterials based SPE adsorbents. In this guise, Cai et al., (2003), in one of the earliest reports on the enrichment of phthalates using nanomaterials, applied multi-walled carbon nanotubes (MWCNTs) packed cartridge for preconcentration of phthalates in water samples, prior to analysis using HPLC. Under the optimized conditions, detection limits of 0.18–0.86 ng/mL and the recoveries of 80.3–104.5% were achieved for four phthalate esters. The authors reportedly used their method to successfully determine di-ethyl-phthalate, di-n-propyl-phthalate, di-iso-butyl-phthalate, and di-cyclohexyl-phthalate in tap water, river water, and sea water samples. In another study, Xu et al., (2010) developed a combined Nylon6 nanofibre mat-based SPE and HPLC method for simultaneous determination of five phthalate esters. Under optimized conditions, the detection limits found for DMP, DEP, DBP, DEHP and DOP were 3, 2, 6, 10 and 33 pg/mL, respectively, while analysis of various water samples gave recoveries in the range of 86.9–101.9%, with relative standard deviations of less than 7.0%. The authors went further to carry out performance based comparative studies between Nylon6 nanofibres mat as sorbents, and C_{18} cartridges as well as other kinds of SPE sorbents with respect to recovery, sensitivity, and precision, and concluded that the Nylon mat was a viable material for the enrichment and determination of phthalate esters in environmental water samples.

In a recent study, an improvement was carried out on the application of carbon nanotubes by Wang et al., (2012). In their study, a layered-carbon-Fe_3O_4 (LC-Fe_3O_4) hybrid material was synthesized through a facile one-pot solvothermal method and used as the adsorbent for the preconcentration (prior to HPLC analysis) of some phthalate esters in water samples. The incorporation of Fe_3O_4 into the hybrid material conferred some magnetic properties, and hence enabled separation to be done by magnetic mechanism. Under the optimum conditions, their method exhibited enrichment factor (161 to 180) good linear range (0.5−100 ng /L), and low limits of detection (0.08−0.1 ng/mL) spiked water samples. Based on the performance indices of their method, the authors concluded that their method was suitable for the determination of trace levels of phthalate esters in environmental water samples.

Considering the array of literature reports on the development and application of nanomaetrials as SPE adsorbents, one would expect it to be the expected solution to high performance SPE adsorbents. However, continued application of these novel materials is being limited by some unavoidable difficulties when nanomaterials are applied to extract target compounds from large volumes of water samples. For instance, if column dynamic extraction mode is used, it consumes plenty of time for water samples to percolate through nanoparticle packed SPE columns due to the high backpressure. Also, when static batch mode is used, centrifugal separation is inapplicable for large volumes of samples, and filtration will encounter the same problem as column dynamic extraction mode (Zhang et al., 2010).

2.8 Options in removal of PAHs and phthalates in aqueous systems

More often, the outcome of water assays demands that necessary remediation action be taken to remove the micro-pollutants in the monitored water systems, where their presence have been confirmed to be above the maximum permissible limits. In this case, environmental scientists are faced with making the right choice, as literature has described various treatment options which are typically considered for the removal of emerging contaminants from drinking water as well as wastewater.

One of the most frequently applied methods is degradation processes. In this guise, several degredation processes like advanced oxidation processes and biodegradation, capable of degrading PAHs and phthalates with varied efficiency have been applied.

Advanced oxidation processes (AOPs) are used in wastewater to oxidize complex organic compounds that are difficult to biologically degrade into simpler by-products. AOPs involve the generation of hydroxyl and other free radicals that enhance the degradation process, achieving the complete conversion of the target pollutant species to CO_2, H_2O and mineral acids (Vilhunen and Sillanpää, 2010). Because of the ability of AOPs to convert pollutants into less harmful chemicals, they have been proposed as a potential alternative approach for the treatment of bio-recalcitrant organic pollutants (Oller et al., 2011). AOPs include different combinations of ozone, hydrogen peroxide, sonolysis, ultraviolet (UV) radiation and photocatalysis, among other treatments. Phthalate esters are more prone to advanced oxidative degradation process than PAHs because of their chemistry.

The literature describes, for example, photochemical degradation of diethyl phthalate and di-(2-ethylhexyl) phthalate via UV/H_2O_2 (Xu et al., 2007; Chen, 2010); photochemical degradation of dimethyl phthalate by Fenton’s reagent (Zhao et al., 2004); photochemical mineralization of di-n-butyl phthalate with H_2O_2/Fe^{3+} (Chiou et al., 2006); photocatalytic ozonation of dimethyl phthalate, dibutyl phthalate or di-(2-ethylhelxyl) phthalate over

TiO_2 film (Li et al., 2005; Jing et al., 2011) Also, several researchers have addressed the photolysis of phthalates by using artificial irradiation sources such as mercury lamps (Mailhot et al., 2002), Xenon arc lamps (Bajt et al., 2001), and ultraviolet light (Lau et al., 2005). In the study of PAE biodegradation under aerobic and anaerobic conditions, pure (Chang et al., 2004; Chao et al., 2006) and heterogeneous microbial cultures (Marttinen et al., 2003) have been used.

Although PAH may undergo photolysis, chemical degradation (Wild and Jones, 1995), and sonolysis (Laughrey et al., 2001), microbial degradation is the major degradation process (Kanaly and Harayama, 2000; Ebihara and Bishop, 2002; Holman et al., 2002). Review of previous studies had shown that PAH degradation depends on the environmental conditions, number and type of the microorganisms, nature and chemical structure of the chemical compound being degraded. They are biodegraded/biotransformed into less complex metabolites, and through mineralization into inorganic minerals, H_2O, CO_2 (aerobic) or CH_4 (anaerobic). The rate of biodegradation depends on pH, temperature, oxygen, microbial population, degree of acclimation, accessibility of nutrients, chemical structure of the compound, cellular transport properties, and chemical partitioning in growth medium. A number of bacterial species have been reported to degrade PAHs (Kanaly and Harayama, 2000). Lignolytic fungi too have the property of PAH degradation. Enzymes involved in the degradation of PAHs are oxygenase, dehydrogenase and lignolytic enzymes. Fungal lignolytic enzymes are lignin peroxidase, laccase, and manganese peroxidase. They are extracellular and catalyze radical formation by oxidation to destabilize bonds in a molecule (Haritash and Kaushik, 2009). Acevedo et al., 2010 evaluated the degradation of three and four-ring polycyclic aromatic hydrocarbons (PAHs) in Kirk medium by Anthracophyllum discolor, a white-rot fungus isolated from the forest of southern Chile. Anthracophyllum discolor was able to degrade PAHs in Kirk medium with the highest removal occurring in a PAH mixture, suggesting synergistic effects between PAHs or possible cometabolism. In another study, Zhang et al., (2010) investigated a bacterial isolate, designated as DQ8, and reported that DQ8 wa capable of degrading diesel, crude oil, n-alkanes and polycyclic aromatic hydrocarbons (PAHs) in petroleum. The authors assigned strain DQ8 to the genus Pseudomonas aeruginosa based on biochemical and genetic data. The authors reported that the metabolites identified from n-docosane as substrate suggested that *P. aeruginosa* DQ8 could oxidize n-alkanes via a terminal oxidation pathway. In their study, Afzal et al., (2011) investigated Enterobacter *ludwigii* and reported that all strains were capable of degrading hydrocarbon. The authors inferred that the presence of CYP153 gene in the microorganisms conferred them the ability to degrade these recalcitrant organic substances since the two strains that exhibited efficient biodegradation had the CYP153 gene in all plant compartments.

A new trend in bioremediation of micro-organic pollutants is the impregnation of adsorbents with bioactive micro-organisms which are capable of degrading the adsorbed pollutants once they are adsorbed. In recent times, remediation of PAHs polluted water has exploited this technique by immobilizing micro-organisms on polyurethane foam (Quek et al., 2006), polyvinyl alcohol algineate beads (Partovinia and Naeimpoor, 2013) and calcium (Feijoo-Siota et al., 2009).

Phytoremediation has also found an application in PAH removal from wastewater. The intensive biological activities in such an ecosystem lead to a high rate of autotrophic and heterotrophic processes. Aquatic weeds Typha spp. and Scirpus lacustris have been used in horizontal–vertical macrophyte based wetlands to treat PAHs (Haritash and Kaushik, 2009), but this technique was only effective for remediation of sediments.

Based on the recorded successes in the application of degradation processes so far, many authors considered degradation of PAHs and phthalates a realistic means of removing these pollutants from a contaminated environment. However, these methods require a long time to render these pollutants harmless. Also, another major challenge is that the pollutants are being broken down to potentially dangerous metabolites, that may be produced by oxidative and reductive processes, instead of being wholesomely removed from the aqueous media (Roy, 2005; Zhang et al., 2007; Valderrama et al., 2007).

Physico-chemical unit operations like coagulation, flocculation, ultrafiltration, and nanofiltration have proved to be effective for the treatment of some micro-organic pollutants. However, despite successful attempts in understanding the removal mechanism of coagulation and flocculation for phthalate removal, coagulation has proved ineffective at degrading phthalates (Thebault et al., 1981; Zhang et al., 2007). In a similar vein, though coagulation has been reported as one of the major synergistic processes for removal of PAHs in water treatment plants, there is paucity of data on the independent study for application of any of these physicochemical unit operations on the treatment of PAHs aqueous pollution. Hence, they may not be effective in aqueous PAHs removal.

As stated earlier, adsorption has proved to be the method of choice for treatment of PAHs, phthalate and other micro-organic pollutants in aqueous environment due to obvious advantages in terms of its convenience, easy operation, efficiency and effectiveness, and simplicity of design when compared to other water treatment options. Also, adsorption processes do not add undesirable by-products/degradation intermediates which could be harmful, and have been found to be superior to other techniques for wastewater treatment in terms of insensitivity to toxic substances (Julinováa and Slavík, 2012). However, full utilization of adsorption process for tackling chemical water pollution by PAHs and phthalates is being hampered by some observed inadequacies of the commonly used adsorbents like activated carbons and synthetic polymer resins. Hence, the development of low-cost adsorbent is not only a subject of interest, but that of necessity to the global science community.

However, both application of adsorption technology in water treatment, and subsequently the development of the much needed low cost adsorbents, require in-depth knowledge of the basic principles and operation of adsorption, as well as the theories guarding adsorption process in aqueous systems. In this vein, it is pertinent to briefly introduce these important concepts to this review.

2.9 Fundamental Principles and Operation of Adsorption

Principle: Adsorption is the concentration of ions, atoms, or molecules of gas, liquid, or dissolved solids, otherwise known as adsorbates (in this case, pollutants) on the surfaces of solid materials, otherwise known as adsorbents from its liquid or gaseous surrounding. Though the phenomenon of adsorption has been observed by many scientists as early as eighteenth century, it was Kayser who introduced for the first time in 1881 the term adsorption to differentiate surface accumulation from intermolecular penetration (Gupta and Suhas, 2009). He postulated that the basic feature of an adsorption process is surface accumulation of material. It is now customary to differentiate between two types of adsorption. If the attraction between the solid surface and the adsorbed molecules is physical in nature, the adsorption is referred to as physical adsorption. Generally, in physical adsorption, the attractive forces are van der Waals forces, and as they are weak, the resulting adsorption is reversible in nature. On the other hand, if the attraction forces between adsorbed molecules and the solid surface arise due to chemical bonding, the adsorption process is called chemisorption. In view of the higher strength of the bonding in chemisorption, it is difficult to remove chemisorbed species from the solid surface.

Operation: Adsorption from solution is usually conducted using either the column or the batch operation. In a batch operation, fixed amount of adsorbent is mixed all at once with specific volume of adsorbate (with the range of initial concentration), after which the system is agitated for a convenient period of time for the system to attain equilibrium. Separation of the resultant equilibrium solution is usually done by filtration, centrifugation, or decanting. In a column operation, the solution of adsorbate such as heavy metals (with the range of initial concentration) is allowed to percolate through a column containing adsorbent usually held in a vertical position. The influent solution is allowed to pass through the column at constant flow rate, in down flow manner with the help of a metering valve, while the effluent solution is collected at different time intervals. The equilibrium (for batch) and breakthrough (for column) adsorption capacity of adsorbate are usually obtained by mass balance using appropriate equations.

Ideally, it should be possible to characterize a given solution - adsorbent system by both techniques and still arrive at the same result, since the same physical and/or chemical forces are applicable in both cases. However, the results obtained from several studies have shown that data generated from batch experiment are somewhat more reliable (Al-Anber, 2011). In addition to this advantage, batch method is straightforward and less cumbersome.

Among the most serious limitations of the column experiments are: (1) the inherent difficulties associated to maintain a constant flow rate; (2) the difficulty of ensuring a constant temperature throughout the column; (3) the appreciable probability of presence of enough channels within the packed column; and (4) the relatively large expenditure both in time and manpower required for a column experiment. Hence, the wide reportage of batch technique being adopted for most adsorption studies is predicated on the foregoing (Bhatnagar and Minocha, 2006; Gupta and Suhas, 2009; Gupta et al., 2009; Julinová and Slavik, 2012).

In this vein, PAHs and phthalates adsorption studies were not left out in exploring the obvious advantages in batch adsorption techniques.

Regeneration of spent adsorbent: Adsorption is an unsteady process and regeneration or reactivation of the adsorbent is needed for recyclic use. The primary objective of regeneration is to restore the adsorption capacity of exhausted adsorbent while the secondary objective is to recover valuable components present in the adsorbed phase, if any. Since adsorption operations are a cyclic process composed of adsorption step and regeneration step, efficiency and cost of regeneration play important roles in the overall feasibility of an adsorption process (Suzuki, 1990; Roquerol et al., 1999;).

Among the several alternative processes available for the regeneration of spent adsorbents, desorption by changing affinity between adsorbate and adsorbent by chemical reagent, had remained the most effective option for liquid phase adsorption. This option conferred additional advantage when recovery of adsorbate is desirable. In this vein, the desorption of adsorbed micro-organic pollutants and hence, the regeneration of spent adsorbent for PAHs and phthalates has applied organic solvents (Olivella et al., 2011).

2.10 Theories of aqueous phase adsorption

The theories of aqueous adsorption are the pertinent concepts used in explaining the mechanisms, interactions, energy considerations, and other processes involved in adsorption. More often than not, most of these theories are represented with mathematical equations, otherwise known as models, which are used to test whether a given adsorption process is agreement with a given theory or not. In some cases, the theories corroborate and consolidate on themselves, while in others, they are exclusive. The theories that are often utilized explaining aqueous adsorption of organic micro-pollutants like PAHs are principally grouped into three viz: adsorption kinetic theories (or model), adsorption isotherm theories, and thermodynamic theory.

2.10.1 Adsorption Kinetics

The principal information obtained from analysis of kinetics data (data generated from the study of effect of time) is the type and processes of the overriding adsorption mechanism. Except for adsorption capacity, kinetic performance of a given adsorbent is of great significance for the pilot application. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established. Also, one can know the scale of an adsorption apparatus based on the kinetic information. Generally speaking, adsorption kinetics is the base to determine the performance of fixed-bed or any other flow-through systems.

Many attempts have been made to formulate a general expression describing the kinetics of sorption on solid surfaces for liquid-solid phase sorption systems. Several mathematical models have been proposed to describe adsorption data, which can generally be classified as adsorption reaction models and adsorption diffusion models. Both models are applied to describe the kinetic process of adsorption; however, they are quite different in nature.

2.10.1.1 Adsorption reaction models (Empirical or global kinetic rate models)

The sorption of organic compounds, such as phthalates and PAHs, onto natural sorbents has been described on a molecular level as a complex process by models which involve complicated mathematical computations (Valderrama et al., 2007). Thus, attempts at simplification have been considered on a macroscopic scale for practicality and ease of understanding the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes. From a macroscopic point of view, three global kinetic rate models are often used in the literature: pseudo-first-order kinetics; pseudo-second-order kinetics and the Elovich model (Awoyemi, 2011).

2.10.1.1.1 Pseudo-first-order

The pseudo-first-order equation was first represented by Lagergreen liquid phase adsorption and especially effective when regeneration of adsorbent as well as recovery of adsorbate is desirable, (Lagergren, 1898). The theory visualized adsorption as first order reaction, and hence the mathematical approach to the model derivation was based on this concept. The model is generally expressed as:

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \qquad 2.1$$

where q_e, and q_t are the sorption capacity at equilibrium and at time t, respectively (mgg^{-1}) and k_1 is the rate constant of pseudo-first-order sorption(min^{-1}).

The rate constant is obtained by a linear regression analysis of $\ln(q_e - q_t)$ as a function of t, as shown in equation 2.1 above. However, pseudo first order model had a major limitation arising from the fact that it does not fit well for the whole range of contact time, as observed by Ho and Mackay (1998). It was actually observed that the model is often generally applicable over the initial 20 to 30 minutes of the sorption process.

However, despite the observed shortcomings, pseudo first order model has been successfully applied in explaining some adsorption processes. For instance it has been reported that adsorption of dimethyl phthalate (DMP) onto XAD-4 polymer adsorbent fitted pseudo first order better than pseudo second order rate equations (Zhang et al., 2007). Also, though it exhibited lower fitting correlation, Chung et al., (2007) applied pseudo first order in fitting the kinetic adsorption data for PAHs. Hence, pseudo first order is still applied till date.

2.10.1.1.2 Pseudo-second-order

Due to the limitations of Lagergreen's pseudo first order, Ho and Mackay (1998) approached adsorption as obeying a pseudo second order rate law and derived the pseudo second order kinet model. The equation is of the form:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^{\,2}} \qquad 2.2$$

where k_2 is the pseudo-second-order rate constant ($gmg^{-1}min^{-1}$) and together with the qe is obtainable by a linear regression analysis of the $t / q_t = f(t)$ function. Ho and McKay (1998) introduced two new parameters viz: initial adsorption rate h_o (where $h_o = k_2 q_e^{\,2}$) which defines the rate of adsorption as time tends to zero; and adsorption half life $t_{1/2}$ (where $t_{1/2} = 1/k_2 q_e$ which defines the time required for adsorption to reach half of the equilibrium capacity.

Previous adsorption studies on PAHs and phthalates have shown that pseudo second order fitted the kinetic data better than the pseudo first order model (Zhang et al., 2007; Chung et al., 2007; Tang et al., 2010).

2.10.1.1.3 The Elovich Model

This model is based on adsorption capacity as established by the work of Zeldowitsch (1934). The simplified expression for this model is of the form:

$$q_t = \frac{1}{b}\ln t + \frac{1}{b}\ln(ab) \qquad 2.3$$

where q_t is the sorption capacity at time t (mg/g), a and b are the Elovich parameters referring to the initial sorption rate (mgg^{-1}min^{-1}) and the desorption constant (gmg^{-1}) during any one experiment, respectively. The Elovich model has proved effective in describing adsorption of metals and dyes (Gupta and Suhas, 2009; Gupta et al., 2009)

2.10.1.2 Mechanistic Models

Adsorption diffusion models were constructed on the basis that adsorption removal of pollutants molecules (and indeed any adsorbate) from aqueous phase system proceed via three successive steps (Qiu et al., 2009):

a) Transport of molecules from the bulk of the solution to the exterior surface of porous carbon particles through a boundary layer (liquid film or external diffusion);

b) Diffusion of the molecules through the interior pores of the adsorbent (intra particle or internal diffusion); and

c) Adsorption of molecules onto the active sites on the interior surface.

These steps are schematically represented in Figure 2.1. All the three steps could potentially affect adsorption kinetics, while the third step also controls the specific adsorption capacity and intensity. Generally, one of the 3 steps offers the greatest resistance and is thus referred to as the rate limiting step of the whole sorption process. In practice however, unless chemical modifications occur during the sorption, the third stage is assumed to be too fast to contribute significantly to the overall sorption rate (Valderrama et al., 2008). It is thus generally understood that slow sorption kinetics are

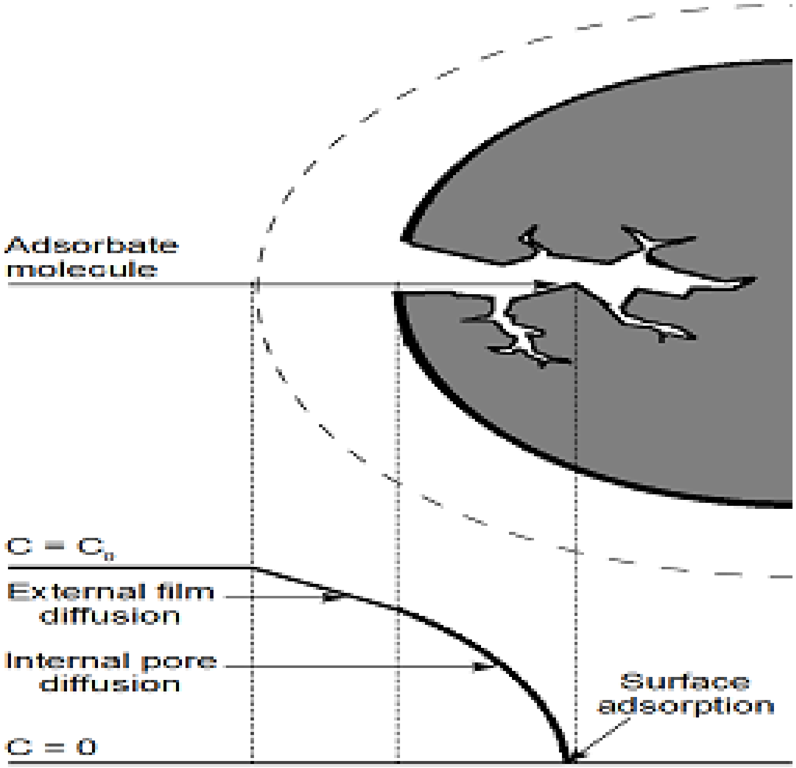


Figure 2.1. Schematic diagram of the three mechanistic stages of heterogeneous adsorption process (Adapted from Awoyemi, 2011)

caused by rate-limiting diffusive mass transfer (Wu and Gschwend, 1988; Brusseau et al., 1991).

2.10.1.2.1 Film Diffusion Model

The conditions under which the film diffusion controls the rate of adsorption as highlighted in the work of Mohan et al., (2001) are under-listed as:

i. Low adsorbate concentration;

ii. Poor mixing condition;

iii. Small adsorbent particle size; and

iv. Very high affinity of adsorbate for adsorbent surface.

It is worthy of note that even in the absence of these conditions, the film diffusion still controls the initial stage of any adsorption process, since the last two steps take some time to set in. The equation as proposed by Boyd et al., (1947) to govern a film diffusion controlled adsorption process is given by:

$$\ln\left(1-\frac{q_t}{q_e}\right) = -k_{fd}t \qquad 2.4$$

where k_{fd} (min^{-1}) is liquid film diffusion constant, and t is time (mins). k_{fd} is related to the particle size (and hence the surface area) of the adsorbent according to equation 2.5

$$k_{fd} = \frac{3D_e^1}{r_o \Delta r_o k^1} \qquad 2.5$$

D_e^1($cm^2 min^{-1}$) is effective liquid film diffusion coefficient, r_o(cm) is radius of adsorbent beads, r_o(cm) is the thickness of liquid film, and k^1 is equilibrium constant of adsorption.

A plot of ln(1−qt /qe) against t is usually a straight line with a slope -k_{fd} if the film diffusion is the rate limiting step.

2.10.1.2.2 Intra-particle Diffusion Models

A number of models have been used to describe the intra-particle diffusion of adsorbates into the porous structure of activated carbons. Valderrama et al.(2008) fitted their PAHs adsorption experiment data to the homogenous particle diffusion model (HPDM) kinetic model based on solute extraction as discussed by Helfferich (Valverde et al., 2004) while another classical model employed by many researchers is the Weber-Morris intra-particle model (Weber and Morris, 1963)

The homogeneous particle diffusion model (HPDM)

A typical intra-particle diffusion model is the so-called homogeneous solid diffusion model (HSDM), which can describe mass transfer in an amorphous and homogeneous sphere (Qiu et al., 2009). This model applies the diffusion of adsorbates onto a homogeneous adsorbent surface, assuming infinite dilution, spherical particle geometry, and assumes that diffusion rate controls the adsorption process. The HSDM equation is presented in equation 2.6.

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r}\right) \qquad 2.6$$

where where D_s is intraparticle diffusion coefficient, r radial position, and q is the adsorption quantity of solute in the solid varying with radial position at time t.

Though Valderrama et al.(2008) gave the solution of the simultaneous set of differential and algebraic equations from this model, the complexity of the mathematical manipulation involved in the application of this model has limited its use in describing adsorption kinetics (Qiu et al., 2009).

Weber-Morris intra-particle diffusion model

Weber and Morris (1963) found that in many adsorption cases, solute uptake varies almost proportionally with $t_{1/2}$ rather than with the contact time t.

$$q_t = k_i t^{1/2} + C \qquad 2.7$$

where q_t is amount adsorbed (mg/g), k_i is intra-particle diffusion rate constant, (mg/gmin$^{-1/2}$) t is time, and C is the constant related to resistance offered by boundary layer.

According to equation 2.7, a plot of q_t against $t^{1/2}$ should be a straight line with a slope k_i when the intra-particle diffusion is a rate-limiting step. For Weber-Morris model, it is essential for the qt against $t^{1/2}$ plot to go through the origin if the intra-particle diffusion is the sole rate-limiting step. However, it is not always the case and adsorption kinetics may be controlled by film diffusion and intra-particle diffusion simultaneously. Thus, the plot might not always go through the origin.

The simplicity of this model has made it to be widely used in the literature for describing the adsorption of both metals and organic micro-pollutants (Venkata Mohan, 2007; Cabal et al., 2009; Valderrama et al., 2008; Qui et al., 2009; Hall et al., 2009).

2.10.2 Adsorption Isotherm

When an adsorbent is in contact with a surrounding fluid of a certain composition, adsorption takes place and after a sufficiently long contact time, equilibrium is reached between the sorbent and the surrounding fluid environment. At equilibrium, there is a defined distribution of solute between the fluid and solid sorbent phases. Isotherm, a curve describing the retention of a solute on a solid at various concentrations, is a major tool for the description and prediction of the mobility of this solute in the environment. These retention/release phenomena are sometimes strongly kinetically controlled, so that time-dependence of the sorption isotherm must be specified. In other words, the adsorption isotherm is a functional expression relating the amount of solute adsorbed (q_e) on the sorbent to the equilibrium concentration (C_e) of solute in the fluid at a given temperature and after a given time. To allow for comparison of different sorbent materials, the quantity adsorbed is always normalized by the mass of the sorbent used.

In the environmental application of sorbents, the predominant scientific basis for sorbent selection has been said to be the equilibrium isotherm, while the diffusion rate is generally secondary in importance (Yang, 2003). This is rightly so since often times, the diffusion rate is extremely fast, and as such a primary concern would be the capacity of the sorbent for the target compound within the operating temperature, concentration and pressure conditions as equilibrium is reached.

2.10.2.1 Isotherm Models

Adsorption isotherms are described in many mathematical forms often based on empirical fittings while simplifying the physical properties and processes involved in the adsorption. The two major models that have mostly been used in fitting equilibrium adsorption isotherm of PAHs and phthalates in the literature are Langmuir and Freundlich isotherms. However, that does not foreclose the application of other isotherms.

2.10.2.1.1 Langmuir Isotherm Model

Langmuir isotherm is the most commonly reported model applied in describing adsorption systems. It is a semi-empirical isotherm derived from a proposed kinetic mechanism (Langmuir, 1916). It is based on four assumptions all summed up in the sorbent being regarded as homogeneous: (i) molecules are adsorbed at a fixed number of well-defined localized sites (Localized adsorption). (ii) all surface sites are alike and can only accommodate one adsorbed atom. (iii) the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy (No interactions). (iv) adsorption is limited to monolayer coverage.

By applying these assumptions, and a kinetic principle (rate of adsorption and desorption from the surface is equal), the Langmuir equation can be written in the following linear form:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L}\left(\frac{1}{C_e}\right) \qquad 2.8$$

where q_e is the equilibrium sorbed concentration (in mg of adsorbate per g of sorbent); q_{max} (in mgg^{-1}) is the adsorption capacity; C_e (in mgL^{-1}) is the equilibrium solution phase concentration; and K_L (in Lmg^{-1}) is the affinity coefficient which is related to the energy of adsorption.

Adsorption process would be describable by the Langmuir model, when all the assumptions of the Langmuir model hold for the adsorption process. However, the good fitting of the model to experimental results does not necessarily mean that the underlying assumptions have been characterized by the sorbent as evidenced by El-Dib et al.(1975). Also, it is unlikely to have the assumption of all sites being energetically equivalent even when the model fits experimental results well (Weber and Benjamin, 1980). This deviation thus limits the interpretation of values of q_{max} and K_L, although the value of q_{max} would nevertheless represent a practical limiting adsorption capacity for the sorbent under investigation. Also, it should be realized that the Langmuir isotherm offers no insights into the mechanism aspects of adsorption. Langmuir isotherm has been adopted by some authors to describe the adsorption of PAHs and phthalates (Den et al. 2006).

2.10.2.1.2 Freundlich Isotherm Model

Freundlich isotherm is an empirical model. This model isotherm equation is the most widely used isotherms for the description of adsorption of PAHs and other organic moieties possessing π-electrons (Chen et al., 2011).

Contrary to the monolayer and localized adsorption assumptions of Langmuir model, Freundlich (1926) derived an empirical model with an exponential distribution of site energies and immobile adsorption. It suggests there exist multiple sets of sites on the surface of the adsorbent which is heterogeneous (Ahn et al., 2005). The model is of the form:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad 2.9$$

where qe is the equilibrium sorbed concentration (in mg ofadsorbate/g of sorbent), and C_e (in mg/L) is the equilibrium solution phase concentration. K_f is the Freundlich constant related to the adsorption capacity, and 1/n is the intensity of adsorption. The Freundlich equation however does not give a limit of adsorption capacity (due to the 1/nth power of concentration), making the amount adsorbed go to infinity when concentration increases. This limits its application to concentrations below saturation where adsorption phenomena would no more be significant (Suzuki, 1990).

2.10.2.1.3 Temkin Isotherm

At first, Temkin equation was proposed to describe adsorption of hydrogen on platinum electrodes within acidic solutions. The derivation of the Temkin isotherm is based on the assumption that the decline of the heat of sorption as a function of temperature is linear rather than logarithmic, as implied in the Freundlich equation which is stated in linear form as:

$$q_e = B \ln A + B \ln C_e \qquad 2.10$$

where $B = \frac{RT}{b}$

R, T and b is the gas constant, the absolute temperature in Kelvin, and the constant related to the heat of adsorption, respectively. C_e and q_e are the same as above, and A is the Temkin isotherm constant.

Temkin isotherm model has been successfully applied in describing liquid phase chemisorption of some heavy metals (Febrianto et al, 2008; Dundar et al, 2008). However, adsorption in the liquid phase is a more complex phenomenon than gas phase adsorption due to complexities emanating from the presence of solvent molecules. Numerous factors including pH, solubility of adsorbate in the solvent, temperature and surface chemistry of the adsorbent influence the adsorption from liquid phase. Since the basis of derivation for Temkin equation are a simple assumption, it has been suggested that the complex phenomenon involved in liquid phase adsorption would not be adequately described by this equation (Febrianto et al, 2008).

2.10.2.1.4 Brunauer–Emmer–Teller (BET) model

Langmuir model assumed that adsorption only occurs on the unoccupied adsorption sites, but in BET model, this restriction is removed. Supposing that the initial adsorbed layer can act as a substrate for further adsorption; then the isotherm, instead of leveling off to some saturated value, at high concentrations is able to rise indefinitely (Foo and Hammed, 2010). The same kinetics concept proposed by Langmuir is applied to this multiple layering process, that is the rate of adsorption on any layer is equal to the rate of desorption from that layer. The simplified form of BET equation can be written in the following linear form

$$\frac{C_e}{(C_s - C_e)q_e} = \left(\frac{K_B - 1}{K_B Q^o}\right)\frac{C_e}{C_s} + \frac{1}{K_B Q^o} \qquad 2.11$$

where *Cs* is the saturation concentration (solubility limit) of the solute in mg/L, K_B is a constant related to the energy of interaction with the surface and the subsequent layers of adsorbates and Q^0 is the amount of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface.

BET isotherm is often applied for the interpretation of gas adsorption on surfaces. The most common application is in the determination of surface area of adsorbents and other porous solids, where the adsorption characteristics of nitrogen gas, N_2 are applied in estimating the surface area of porous solids.

2.10.2.1.5 The Dubinin-Radushkevich isotherm model (D-R model)

The D-R model is often employed to give insight into the adsorption mechanism by obtaining the apparent free energy of adsorption. Dubinin and his co-workers conceived this equation for sub-critical vapors in micropore solids where the adsorption process follows a pore filling mechanism onto energetically non-uniform surface. The model is given by (Dubinin, 1960):

$$q_e = q_{\max} \exp\left(-\left(\frac{RT\ln\left(C_e/C_e\right)}{\beta E_o}\right)^2\right) \qquad 2.12$$

In the above equations, q_e , and q_{max} are the equilibrium adsorption capacity, and the maximum adsorption capacity under optimized conditions in the D-R isotherm model in mg/g, respectively; C_e is the equilibrium concentration in mg/L; β is a constant related to energy in mol^2/kJ^2 and ε is the polanyi potential.

DR equation is rarely applied onto liquid-phase adsorption due to the complexities associated with other factors such as pH and ionic equilibria inherent in these systems. Additionally, the solute-solvent interactions often render the bulk solution non-ideal.

The linearized form of equation is used in obtaining the parameter β from which the mean adsorption free energy in kJ/mol is obtained.

2.11 Review of adsorption removal of PAHs and phthalates from water

Several adsorbents have been tested for the sorption removal of PAHs and phthalates from polluted water. For the purpose of this review, these adsorbents are categorized into the following groups: (i) Activated carbon and related materials (ii) Biomass/Biosorbents (iii) Clay materials (iv) Coal based materials and (v) Miscellaneous materials.

2.11.1 Activated carbon and related materials

Activated carbon (AC) is a carbonaceous material with large internal specific surface area and highly developed porous structure which has been successfully employed as a pollutant adsorbent from air and water, as well as an energy storage device, and a catalyst support due to its characteristically high surface area. In particular, water treatment accounts for the largest application of activated carbon, and in the estimate given by Awoyemi (2011), nearly 350,000 tonnes of activated carbon is being consumed on a yearly basis.

AC in different forms (powder, granular, or brittle) has been employed over the years in the treatment of both industrial and municipal waste water due to its ability to adsorb a wide variety of both organic and inorganic compounds to non detectable trace levels. In this vein, the adsorption removal of PAHs and phthalates by AC adsorbents has been extensively studied by scientists.

2.11.1.1 Adsorption of PAHs using activated carbon adsorbents

Walters and Luthy (1984) was one of the earliest reports of application of activated carbon for sorptive removal of PAHs from environmental waters. The authors applied batch experimental procedure for investigating the adsorption isotherm of 11 PAHs onto Filtrasorb activated carbon at 25°C. The authors reported that an evaluation of the equilibrium data with Henry's law, Langmuir, Freundlich, Redlich-Peterson, and BET isotherms, indicated that the Langmuir isotherm best described the adsorption data. The authors concluded that (1) the adsorption of PAHs on AC was much stronger than adsorption on soil, sediment, and suspended organic matter, and (2) comparable to or greater than adsorption of other hydrophobic compounds on AC. However, their report on Langmuir being the best isotherm attracted much comment that the authors had to write a rebuttal to that effect, on the processes that justified their assertion (Walters and Luthy, 1985).

Valderrama et al., (2008) evaluated the adsorption performance of granular activated carbon (GAC) for polycyclic aromatic hydrocarbons (PAHs) removal from aqueous solutions. The authors paid special attention to the surface morphology and its effect on kinetics of the adsorption process. Analyses of the batch rate data for five PAHs using two kinetic models: the homogenous particle diffusion model (HPDM), shell progressive model (SPM), and Weber and Morris intraparticle diffusion model, revealed that the apparent surface diffusivities are in the same order of magnitude as the values for the sorption of functionalized aromatic hydrocarbons (phenols and sulphonates) that are described in the literature.

In a similar study, Cabal et al., (2009) explored and compared the kinetics of naphthalene adsorption on an activated carbon from aqueous and organic solutions. Kinetic curves were fitted to different theoretical models, and the results were discussed in terms of the nature and properties of the solvents, the affinity of naphthalene to the solutions, and the accessibility to the porosity of the activated carbon. Data was fitted to the pseudo-second order kinetic model with good correlation coefficients for all the solution media. The authors reported that the faster adsorption rate was obtained for the most hydrophobic solvent (heptane), and that the overall adsorption rate of naphthalene was controlled simultaneously by external (boundary layer) followed by intra-particle diffusion in the porosity of the activated carbon when water, ethanol and cyclohexane were used as solvents.

Considering the strength of PAHs adsorption on AC, and both commercial and operational cost of using AC adsorbents, scientists have made spirited effort in generating activated carbon from locally available materials like agricultural residues. In this regards, Kong et al., (2011) applied soybean stalk-based carbons prepared by phosphoric acid activation at different carbonization temperatures, for the removal of PAHs from aqueous solution. Their results indicated that the specific surface area, iodine number, and amount of methylene blue sorption had positive correlation with an increase of carbonization temperature. The authors reported that the removal efficiencies of PAHs tended to increase with increasing carbon amounts and carbonization temperature, and concluded that the performance of the prepared carbon was superior to that of commercial activated carbon. Results obtained from their work provided some insights into the reuse of an agricultural residue, and also provide a new application for the treatment of PAHs in contaminated water utilizing activated carbon prepared from agricultural residues.

In a related study, though for a different purpose, James et al., (2005) applied both laboratory and field produced biochars to study the uptake of phenanthrene in aqueous solution. The study was reported to have been carried out to study the role of wood char or soot (in a soil or sediment) in determining the environmental fate of PAHs. The authors reported that the variation in sorption potential can be attributed to heating temperature and starting material, and that both the quantity and heterogeneity of surface-area impacts the sorption capacity. In a similar development, Sun et al., (2011) applied thermal and hydrothermal biochars for adsorption of bisphenol A (BPA), 17a-ethinyl estradiol and phenanthrene to investigate the sorption characteristic difference between the two types of biochars. According to the authors, thermal biochars were composed mostly of aromatic moieties, with low H/C and O/C ratios as compared to hydrothermal ones having diverse functional groups, and that X-ray diffraction and solid state nuclear magnetic resonance results suggested that hydrothermal biochars consisted of more amorphous aliphatic-C, possibly being responsible for their exhibiting high sorption capacity for phenanthrene. Their study demonstrated that hydrothermal biochars could adsorb a wider spectrum of both polar and non-polar organic contaminants than thermally produced biochars, suggesting that hydrothermal biochar derived from poultry and animal waste is a potential sorbent for agricultural and environmental applications.

2.11.1.2 Adsorption of phthalates using activated carbon adsorbents

Venkata Mohan et al. (2007) focused in their paper on the study of DEP sorption on activated carbon from the aqueous phase, using activated carbon of the geometric mean size of 70mm (surface area 500 m^2/g) as adsorbent. Principally, they studied the influence of various parameters such as contact time (sorption kinetics), initial concentration, carbon dosage and operational pH. The result of the study showed that activated carbon had good sorption capacity for DEP, with sorption rising with rise in the initial concentration of

DEP. The authors reported that the rate of DEP removal from the aqueous environment was initially rapid, reaching equilibrium within 120 minutes, while DEP adsorption had negative correlation with the pH of the aqueous media, with optimum adsorption occurring at pH of 2.

In another study carried out by Fang and Huang (2009), the adsorption of DBP onto nutshell-based activated carbon, NAC (BET area 1224 m^2/g) was investigated. The authors reported that the rate of sorption of DBP had a positive correlation with the initial DBP concentration, indicating that the interaction between DBP and NAC are weak at low DBP concentration levels. Also, the sorption capacity increased with increment in temperature, which is suggestive of an endothermic process. To gain more insight into the mechanism of the adsorption process, the authors applied the three isotherm: Langmuir, Freundlich and Temkim in describing the adsorption data. The experimentally measured isotherms featured S-type, with the Freundlich model being the most convenient. The result also gave the equilibrium time to be 30 hours. The study equally revealed that the initial concentration had a positive correlation with the adsorption rate, and pH of 5 was reported as optimum pH. In another study, Fang and Huang (2010) investigated the effect of salinity (using NaCl) and humic acid (HA) on the adsorption of DBP. The authors reported that both salinity and HA had negative correlation with DBP adsorption.

Julinova and Slavik (2012) have reported in their review paper that active carbon has proved to be an inefficient adsorbent for removing phthalates from contaminated water due to the low solubility and high hydrophobicity. However, it is known that the capacity of active carbon for adsorbing hazardous substances may be enhanced through modification with suitable chemicals, thus scientists have made several attempts in this regard.

Adhoum and Monser (2004) studied the adsorption performance of active carbon (serving as a comparative standard) and active carbon modified with tetrabutylammonium iodide (TBA) or cupric nitrate. The sorption capacity was tested on a model solution of phthalates prepared in the form of phthalic anhydride. The result showed that Cu-modified active carbon possessed an adsorption capacity for phthalate of approximately 2.12 times greater than pure active carbon. Similarly, the capacity increased 1.67 times with TBA-modified active carbon as compared to pure active carbon. In conclusion the authors said that the modification of active carbon with Cu or TBA markedly improved the adsorption capacity of active carbon and thus brought about 98% removal of phthalates from actual waste-water. However, this measure causes a steep rise in the price of sorption material (Adhoum and Monser, 2004).

2.11.2 Clay materials (silica and alumina)

Silica and alumina are the most common clay materials that have been applied for water treatment (Gupta and Suhas, 2009). They are abundant in nature, and require little or minor pre-treatment.

2.11.2.1 Adsorption of PAHs using clay material adsorbents

Vidal et al, (2011) applied periodic mesoporous organosilica (PMO) to remove polycyclic aromatic hydrocarbons (PAHs) from aqueous solutions. Adsorption equilibrium isotherms and adsorption kinetics experiments were carried out in solutions of PAHs (2–60 mg L^{-1}), using the PMO as adsorbent. Adsorption models were used to predict the mechanisms involved. The adsorption kinetics data best fitted the pseudo-first-order kinetic model for naphthalene, and to the pseudo-second-order model for fluorene, fluoranthene, pyrene, and acenaphtene. The intra-particle model was also tested and pointed to the occurrence of such processes in all cases. The isotherm models which best represented the data obtained were the Freundlich model for fluoranthene, pyrene, and fluorene, the Temkin model for naphthalene, and the Redlich–Peterson model for acenaphtene. In conclusion, PAHs showed similar behavior regarding kinetics after 24 hours of contact between adsorbent and PAHs.

2.11.2.2 Adsorption of phthalates using clay material adsorbents

Das and Mahiuddin (2005) studied the adsorption of benzoate and phthalate on α-alumina with the sole purpose of investigating the effect of functionality on the adsorption performance. Kinetics results of the study showed that the rate of adsorption of phthalate was approximately 2 times more than that of benzoate. The authors reported that the adsorption isotherms for both the systems were found to be Langmuir in nature with the maximum adsorption capacity of phthalate being 1.1–5.1 times more than that of benzoate on the same adsorbent under similar condition. This difference was attributed to the functionality of the adsorbates, which was the presence of adjacent COOH group in phthalate.

2.11.3 Chitin and chitosan

Chitin and chitosan are mechanically tough polysaccharides with chemical structures similar to cellulose, studied as adsorbents. Chitin is a fairly abundant natural biopolymer and is generally found in the exoskeletons of crabs and other arthropods and also in the cell wall of some fungi whereas chitosan or glucosamine is a deacetylated derivative of chitin and can be chemically prepared from it. Both chitin and chitosan are being used as an attractive source of adsorbents, especially for metal removal. Nevertheless, they are versatile materials and have also been used successfully for the removal of organics (Crini and Badot, 2008; Gupta, 2009)

2.11.3.1 Adsorption of PAHs using chitin and chitosan based adsorbents

Despite the success recorded in using chitin and chitosan for the sorption of dyes and other organic pollutants, there is limited information on the use of these low cost materials on the adsorption of PAHs. In this guise, Crisafully et al., (2008) investigated the removal of polycyclic aromatic hydrocarbons (PAHs) from petrochemical wastewater using various low-cost adsorbents of natural origin which included chitin and chitosan as well as other low cost agricultural waste materials like sugar cane bagasse, and green coconut shells. The adsorption experiments were designed to investigate the adsorption isotherm and dynamics using mixtures of PAHs (5.0–15.0 mg/L) at ambient temperature (28 ± 2 °C) and pH 7.5. The adsorption isotherms of PAHs were best described by Freundlich model, which signified multi-layer adsorption, while the uptake capacity of PAHs on chitin was greater than that of chitosan. The study also investigated the relationship between the partition coefficient and equilibrium adsorption constant, and concluded that the partition coefficients in acetone:water, the adsorption constants at equilibrium, and the molecular masses of the PAHs could be linearly correlated with octanol–water partition coefficients.

2.11.3.2 Adsorption of phthalates using chitin and chitosan based adsorbents

The adsorption removal of phthalates with chitosan from aqueous system was studied by Chen and Chung (2006) using real industrial wastewater samples from plastic manufacturing (Tainan, Taiwan). The following phthalates were studied: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-propyl phthalate (DPP), di-n-butyl phthalate (DBP), diheptyl phthalate (DHpP) and di-2-ethylhexyl phthalate (DEHP), in the midst of other organic and inorganic pollutants. The authors reported that the adsorption of phthalate by chitosan depended on temperature, pH and the concentration of Ca^{2+} ions, with optimal condition for greatest adsorption efficiency being the temperature of 15°C and at pH of 8. The authors reported efficient regeneration of the adsorbent with 50% methanol which they observed to be dependent on the physico-chemical properties of individual phthalates.

In another study, the adsorption of PAEs and their degradation products, such as phthalate monomers (MPEs) and phthalic acid (PA), from the aqueous environment on chitosan was investigated by Salim et al., (2010). The results of their kinetic experiments indicate that DBP was adsorbed to a greater extent than DEHP and DMP. Adsorption capacity for the tested MPEs declined in the following order: monobuthyl phthalate > monomethyl phthalate > monoethyl hexyl phthalate, with the highest adsorption capacity recorded for the sorption of PA. The results of the study of Salim et al. (2010) indicate that chitosan adsorbed PAEs primarily because of hydrophobic interactions, and interacted with PA mainly due to interaction between polar active groups. The authors opined that the monomers, especially monomethyl phthalate and monoethyl hexyl phthalate were less adsorbable, since they have lower hydrophobicity than phthalate esters and higher hydrophilicity than phthalic acid.

Not satisfied with the adsorption performance of unmodified chitosan for phthalates in their earlier work (Chen and Chung, 2006), Chen et al., (2007) conceived the idea that modifying the surface of the chitosan would improve the adsorption performance towards phthalates. In this vein, the authors modified chitosan with α-cyclodextrin, and thereafter applied it for adsorption of dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-propyl phthalate (DPP), di-n-butyl phthalate (DBP), diheptyl phthalate (DHpP) and di-2-ethylhexyl phthalate (DEHP). Kinetic adsorption tests determined the adsorption efficiency of individual phthalates in the sequence as follows: DHpP > DBP > DEHP > DPP > DEP > DMP. The authors attributed trend to hydrophobic interaction, as it is obvious from the sequence that adsorption capacity increases with the hydrophobicity of individual phthalates. Adsorption equilibrium of phthalates was reached after 6 hours, the same as when unmodified chitosan was employed. It was found that adsorption efficiency decreases with a corresponding increase in temperature. It was also observed from the study that there was no significant effect of pH on phthalate adsorption.

In another development, Chen and Chung (2007) studied the adsorption of phthalates from aqueous solution by molybdate-impregnated chitosan beads (MICB). The results of kinetic tests demonstrate that DHpP was the most adsorbed compound of the six phthalates studied (the same as in previous studies by these authors). MICB has proven to be a suitable sorbent even in the dynamic arrangement. For sorbent regeneration, recoverability of 92.5% has been achieved; this via a desorption solution of methanol:water - 4:6. The authors reported that regenerated MICB may be used up to 15 times, just as in the case of DEHP. As in previous works by Chen and Chung, (2006); and Chen et al., (2007), this research investigated the influence of pH, temperature, the concentration of Ca^{2+} ions and salinity of aqueous solutions on the efficiency of phthalate adsorption onto modified chitosan. It was found that the quantity of phthalates adsorbed decreased with increases in temperature; whereas the pH level, concentration of Ca^{2+} ions and salinity exerted no influence on adsorption.

2.11.4 β-cyclodextrin polymer

β-cyclodextrin polymer has proved to be one of the most frequently applied polymer adsorbents for water remediation. Murai et al., (1998) studied the removal of phthalates from aqueous solutions through forming inclusion complex compounds during adsorption onto β-cyclodextrin (β-CD) or to its epichlorhydrin cross-linked polymer (β-CDP). Based on the increasing values of stability constants, the authors reported that phthalate types containing longer alkyl groups were able to form more stable complexes than less hydrophobic phthalates with short alkyl groups. The sole exception was DEHP, whose greater hydrophobicity may be caused by ethyl groups present that sterically hinder the access of DEHP into the cavity of β-CD. The adsorption isotherm was reportedly described by Freundlich adsorption model. The values of adsorption capacity had a positive correlation with the stability constants of phthalates, and this was attributed to the inclusion of PAEs onto β-CD. Also, the authors studied the possibility of reclaiming phthalates and recycling β-CDP via an 80% aqueous solution of methanol, and it was confirmed that the β-CDP can be efficiently regenerated.

2.11.5 Biomass/Biosorbents

Also, considering the fact that most biosorbents are mostly produced from waste biomas, the application of this class of materials as adsorbent makes them to be valuable as industrial raw material.

2.11.5.1 Adsorption of PAHs using biomass/biosorbents

Olivella et al. 2011 evaluated the application of cork waste adsorbent for treatment of aqueous PAHs pollution, by studying the sorption-desorption behavior of a mixture of thirteen aqueous PAHs on cork waste at a particle of size 0.25–0.42 mm. Characterization tests of the selected cork revealed that suberin (38.5 %) and lignin (31.6%) were the main structural components of the cell wall. The high efficiency of cork as a biosorbent of PAHs was shown by the fact that just over 80 % of adsorption occurred during the first two minutes of contact time. Both Freundlich's and Langmuir's isotherms gave good fits to the sorption process. The highest adsorption affinities were exhibited for pyrene, anthracene, and phenanthrene. The authors also reported that desorption studies revealed a high degree of irreversibility for all PAHs, and especially so in the case of high molecular PAHs. The correlation with K_F and low molecular weight PAHs was the most significant. The authors showed that the quantity of cork required to reduce water pollution was estimated to be between 3 and 15 times less than the quantities required in the case of other materials like aspen wood and leonardite, and hence demonstrated for the first time that cork is a potential biosorbent for PAHs.

In a related study, Chen et al., (2011) investigated the applicability of plant residue materials: wood chips (WC), ryegrass roots (RR), orange peels (OP), bamboo leaves (BL), and pine needles (PN); as adsorbents for the control of PAHs aqueous pollution. The study was designed to correlate PAHs sorption to the selected biosorbents with their structures, elucidate the biosorption mechanism and removal efficiency of these plant residues as biosorbents. The authors reported that biosorption isotherms fitted well with Freundlich equation and the mechanism was dominated by partition process. The magnitude of phenanthrene partition coefficients (K_d) followed the order of PN > BL > OP > RR > WC.

Except the WC sample, the K_d values were negatively correlated with sugar content and polarity index [(N + O)/C] of the biosorbents, while the aromatic component exhibited positive effects. For a given biosorbent of bamboo leaves, the carbon-normalized partition coefficients (Koc) were linearly correlated with octanol–water partition coefficients (Kow) of PAHs. The authors concluded that the structure–effect relationship provides a reference to select and modify plant residues as a biosorbent with high efficiency to tackle organic pollutants.

Li et al., (2010) demonstrated that the sorption performance of natural biosorbent for PAHs, can be enhanced by chemical treatment of these adsorbents. To enhance removal efficiency of natural sorbent with polycyclic aromatic hydrocarbons (PAHs), single solute and bi-solute sorption of phenanthrene and pyrene onto raw and modified pine bark were investigated. Pine bark was modified using Soxhlet extraction, saponification and acid hydrolysis, yielding six bark fractions with different chemical compositions. The authors reported that raw pine bark exhibited high affinities with PAHs, and sorption was dominated by partitioning. The relatively nonlinear sorption isotherms of modified bark were attributed to the specific interaction between sorbate and aromatic core of sorbent. In comparison with lipid and suberin, lignin was the most powerful sorption medium, but which was almost completely suppressed by coexisting polysaccharide. After consuming polysaccharide by acid hydrolysis, sorption of pine bark fractions reportedly increased (4–17 folds); and sorption of pyrene just decreased 16–34% with phenanthrene as a competitor. In conclusion, the study showed that lignin enrichment is a viable way of valorizing waste lignocellulosic biomass for water treatment.

2.11.5.2 Adsorption of phthalates using biomass/biosorbents

In the phthalate adsorption studies of Fang and Zheng (2004), two adsorbents were applied: (i) activated sludge from a municipal wastewater treatment plant, containing suspended solids and volatile suspended solids, and (ii) extracellular polymeric substance (EPS), including carbohydrate, protein, humic substance, uronic acid, DNA and unidentified substances, most of which were likely to be lipids or phenols extracted from activated sludge. The authors applied batch adsorption method to determine the adsorption capacity, while using sodium azide to eliminate any biodegradation activity. The efficiency of DEP adsorption onto activated sludge and EPS decreased in relation to an increasing initial concentration of phthalates. The adsorption efficiency of DBP, as expected, was considerably higher than that of DEP for activated sludge as well as EPS. The authors concluded by reporting that the adsorption of phthalates onto activated sludge increases with their hydrophobicity, with DBP being more hydrophobic than DEP.

Chan et al., (2004) evaluated seaweed biomass -S. siliquastrum, S. angustifolium, S. hemiphyllum-samples and beached sea weed, gathered from selected underwater locations, as adsorbent for sorption removal of DEHP as a model phthalate from aqueous systems. The sequence of adsorption capacity levels for four adsorbents was determined as follows: S. siliquastrum > S. angustifolium > S. hemiphyllum > Beached seaweed. The study proved that pH had a negative correlation with the adsorption capacity and efficiency with pH 4 being the optimum value. The stiring intensity was observed not to affect the adsorption capacity. Temperature had a positive correlation with adsorption capacity of the adsorbents. As usual, the adsorption capacity increased with increment in initial concentration. The authors also found out that the sea weed adsorbents could be efficiently regenerated. The authors concluded that the origin of the biomass exerts an influence on its sorption capacity and the efficiency of DEHP removal from an aqueous environment.

In a work by Wang and Grady (1994), a comparison of biosorption isotherms for di-n-butyl phthalate adsorption unto live and dead bacteria biomass was conducted. Bacterial culture P.fluorescens IFO 12055, which has been proven to lack the ability to biologically break down di-n-butyl phthalate (DBP), was applied as live bacterial biomass, while biomass autoclaved at 121°C for 20 min, was designated as dead biomass. The experimental results obtained from the biosorption study showed that the sorption capacity of dead biomass was about 50% greater than that of live biomass. This was also confirmed by the values of their Freundlich isotherm constants. The authors attributed the difference in adsorption to changes in biomass properties resulting from cells disintegrating during autoclaving process.

2.11.6 Nanomaterials

Considering the intrinsic properties of nanomaterials as ealier discussed in the review of SPE adsorbents, there were renewed interests in developing nanomaterials based adsorbents for water remediation.

In this guise, Deng et al. (2006) investigated the adsorption of DMP and DEP onto multi-walled carbon nanotubes (MWCNTs) and compared the adsorption performance with that of granular activated carbon. The authors reported that Langmuir's model best described the adsorption process. The equilibrium time increased with increment in the outer diameter of MWCNTs, but was still substantially lower than that of standard granular activated carbon. At the same time, the adsorption capacity of nanotubes was reported to be significantly higher than that of activated carbon. The authors observed that the adsorption process was an endothermic type, since the increase in temperature led to a rise in adsorption capacity. Also, the effects of pH on sorption of DEP on MWCNTs was not really pronounced as the authors observed little increment in adsorption efficiency with increment in pH. In a related study, Wang et al. (2010) compared the adsorption of three dialkyl phthalate esters (DPEs) with different chain lengths onto carbon nanotubes (CNTs), with detailed attention on describing the interactions between the DPEs and CNTs. The authors applied single-walled CNTs and three types of multi-walled CNTs as adsorbents, while DMP, DEP and DBP were selected as model DPEs. The experimental data were reportedly described with Freundlich and Dubinin-Ashtakh's model, while the adsorption efficiency was in accordance with the hydrophobicity of individual phthalates. The authors reported that the adsorption capacity for these materials were high, and dropped with increments in the external diameter of CNTs. The authors stated that the adsorption coefficient is much higher than that of DPE adsorption onto sediments, and attributed the observation to variety of mechanisms such as hydrophobic effect, π- π electron-donor-acceptor interactions.

2.11.7 Reactive and functional polymers

The removal of DEP from an aqueous environment using adsorption onto functional polymer resin (NDA-702), with macro porous polymer resin (XAD-4) and coal-based granulated activated carbon (AC-750) was investigated by Xu et al. (2011). The AC-750 served as comparative adsorbents. The results of their work showed that the adsorption capacity of individual adsorbents decreased in the following order: NDA-702 > AC-750 > XAD-4. Langmuir and Freundlich models were applied in explaining the mechanism of adsorption, with the latter being evaluated by the authors as the more appropriate. Adsorption capacity for NDA-702 and AC-750 were significantly higher than that of XAD-4, and the authors attributed the situation to high micropore content in the structure of NDA-702 and AC-750, where intensive adsorption of DEP occurred. Also, the authors explained that the presence of polar carbonyl and hydroxyl groups in NDA-702 and AC-750, where there was an occurrence of a hydrogen bond produced between the DEP ester and sorbent, might be additional reason for the observed trend. In the conclusion of the study, the authors reported that the pore-size distribution and particle size of the adsorbent exhibited a significant impact on the adsorption of DEP. The larger uptake and greater selection of NDA-702, compared with AC-750 and XAD-4, probably results from the microporous structure, phenyl rings and polar groups on the NDA-702 polymer matrix.

Zhang et al. (2008) tested the adsorption of DEP on aminated poly-styrene resin (NDA-101) and oxidized polystyrene resin (NDA-702). Just as in a work by the authors Xu et al. (2011), homogenous polystyrene resin (XAD-4), coal-based granulated activated carbon (AC-750) and acrylic ester resin (Amberlite XAD-7) were chosen as comparative materials. The authors reported that the experimental data was best described by Freundlich's model, with adsorption capacity for DEP decreasing in the following order: NDA-702>NDA-101>AC-750 > XAD-4 > XAD-7. According to the authors, analysis of adsorption mechanisms suggested that the adsorbents spontaneously adsorb DEP molecules, driven mainly by enthalpy change, and that the adsorption process was derived by multiple adsorbent-adsorbate interactions, such as hydrogen bonding, π-π stacking, and micropore filling. The papers of Xu et al. (2011) and Zhang et al. (2008, 2007) assess NDA-702 as well as NDA-101 as very good adsorption materials for eliminating DEP from contaminated wastewater.

2.11.8 Current state of adsorption in treatment of aqueous PAHs and phthalates pollution

The summary of reports published so far on the removal of PAHs and phthalates via adsorption shows that, despite the extensive knowledge assembled by scientific teams around the world over recent decades, research in this area should continue.

Based on the knowledge acquired, the use of different materials for adsorption is dependent on many factors as determined by the physico-chemical properties of not only pollutants (solubility in water), but also the matrix (pH, hardness, salinity, etc.) from which the former is being removed. With regard to the chemical structure of the pollutant, applying a single universal adsorbent with the potential to adsorb a wide range of pollutants is not possible, at least for the time being. So far, efforts in developing low-cost adsorbent materials for treatment of micro organic pollutants in water, have yielded good results, but there are still potentials of getting better results.

2.12 Adsorbent selection criteria for water treatment and SPE applications

As stated earlier the important attributes for an adsorbent for any adsorption process application are: adsorption capacity, selectivity, regenerability, kinetics, compatibility and cost. Rarely will a single adsorbent be optimal in all these respects. In practical applications, it will be possible to narrow the choice to one or two classes of adsorbents, but that still leaves a vast array of possibilities. Different approaches are taken to evaluate these criteria. This information can be obtained from vendors for commercial adsorbents, otherwise practical measurements are done.

Adsorption capacity is the most important characteristic of an adsorbent. Succinctly, it is the amount of adsorbate taken up by the adsorbent, per unit mass (or volume) of the adsorbent. It depends on the fluid-phase concentration, the temperature, and other conditions (especially the initial condition of the adsorbent). Typically, adsorption capacity data are gathered at a fixed temperature and various adsorbate concentrations (or partial pressures for a vapor or gas), and the data are plotted as an isotherm (loading versus concentration at constant temperature). Adsorption capacity is of paramount importance to the capital cost because it dictates the amount of adsorbent required, which also fixes the volume of the adsorber vessels, and both generally are significant if not dominant.

Selectivity is related to capacity, but they have several distinctions. In simple terms, selectivity is the ratio of the capacity of one component to that of another at a given fluid concentration. That ratio generally approaches a constant value as concentration drops towards zero. Of course, the concentrations of interest may not be near zero, so the choice of definitions becomes subtle. Ideal situation occurs when the major component is not adsorbed much (so it can be thought of as an inert "carrier"), which leads to a very large selectivity.

All cyclic adsorption applications rely on regenerability, so that the adsorbent can operate in sequential cycles with uniform performance. This means each adsorbable component (adsorptive or adsorbate) must be relatively weakly adsorbed (or physisorbed).

Kinetics has been exploited as the basis of adsorptive separations. Mass transfer kinetics is a catch-all term related to intra particle mass transfer resistance. It is important because it controls the cycle time of a fixed bed adsorption process. In simple terms, kinetics is applied in estimating the fastness of the adsorption process.

Compatibility covers various possible modes of chemical and physical attack that could reduce the life expectancy of the adsorbent, such as biological fouling or attrition. For example, the adsorbent, binder, and surface groups (depending on the type of adsorbent), should be inert to the carrier or solvent, and should not irreversibly react with (or chemisorb) the adsorbate(s) or contaminants. Likewise, operating conditions such as velocity, temperature , pressure, and vibration should not cause undue disintegration of the adsorbent particles. This could happen by crushing or abrasion, and there are standard methods for measuring these conditions.

Cost is perhaps the most subtle characteristic to understand. For commercial adsorbents, it may vary from week to week and from sales rep to sales rep, even for the same exact material. The continuous effort in developing new adsorbent has basically been predicated on achieving high performance at lowest possible cost. Hence, in the development of new adsorbents, low cost precursors are preferred.

2.13 Starch and cyclodextrin as potential precursors to low cost adsorbents

Starch is the second most abundant natural polymer after cellulose. Starch is derived from renewable resources such as corn wheat, potato, tapioca, and legumes. Starches are mixtures of two polyglucans, amylopectin and amylose, but they contain only a single type of carbohydrate, glucose. Due to its unique physical and chemical characteristics starch is increasingly viewed as a potential sustainable alternative to many petroleum-based polymers. Numerous efforts have been made to develop starch-based polymers for reducing environmental impact and in searching more applications. Particularly two features in a starch molecule make it a unique and versatile material. First, starch is naturally biodegradable and degrades into sugars and organic acids that serve as feedstock for manufacturing many industrial chemicals, thermoplastics, and biofuels. Second, due to its chemical structure, the starch polymer is amenable to a variety of chemical and enzymatic modifications that permits creating new and novel functionalities in starch polymer (Ahmed et al., 2012).

An important class of starch derivatives is the cyclodextrins or cycloamyloses. Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing six to twelve glucose units. The CD molecules are natural macrocyclic polymers, formed by the action of an enzyme on starch. The three smallest CDs, alpha-cyclodextrin, beta-cyclodextrin and gamma-cyclodextrin which consists of six, seven and eight α-1,4 linked D(C)-glucopyranose units respectively are well known and are available commercially. The most characteristic feature of cyclodextrins is the ability to form inclusion compounds with various molecules, especially aromatics: the interior cavity of the molecule provides a relatively hydrophobic environment into which an apolar pollutant can be trapped. Several review articles were devoted to the detailed description of the applications of cyclodextrins (Hedges, 1998; Szejtli, 1998; Crini and Morcellet, 2002; Gupta, 2009; Morin-Crini and Crini, 2013).

Starch and cyclodextrins are unique raw materials/precursors for adsorbents in that they are: very abundant natural polymers (they are referred to as biopolymers); inexpensive (low-cost polymers); widely available in many countries; renewable resources; stable and hydrophilic biopolymers; and modifiable polymers. They also have biological and chemical properties such as non-toxicity, biocompatibility, biodegradability, poly-functionality, high chemical reactivity, chirality, chelation and adsorption capacities.

The excellent adsorption behavior of this polysaccharides is mainly attributed to: (1) high hydrophilicity of the polymer due to hydroxyl groups of glucose units; (2) presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups); (3) high chemical reactivity of these groups; and (4) flexible structure of the polymer chain.

In spite of these properties and advantages, there exist some limitations on the application of these polysaccharides as adsorbent materials. For example, starch is relatively soluble in most aqueous media while cyclodextrins are water soluble in their native form, hence, cannot be used as an insoluble sorbent under these conditions, except after physical and chemical modifications to prepare new insoluble derivatives. Chemical derivatization has been proposed as a way to solve this problem and to produce water resistant materials. However, the strategy for modification depends on the final material's purpose. If a water soluble starch derivative is desired for application in waste water flocculation or as an additive in paper manufacturing, then a random conversion of hydroxyl groups to aminopropyl hydroxyalkyl or cationic group groups can be achieved. If the starch-based material is to be used as adsorbent resins, then a rigid macromolecular structure is necessary (Crini, 2005).

Due to their characteristic reactivity, starch and cyclodxtrin are amenable to a variety of chemical modifications which include: substitution, grafting, and cross-linking reactions to produce materials with novel properties (Ahmed et al., 2012). Among these methods, cross-linking process has proved to be the most effective way of developing starch and cyclodextrin based adsorbents, because modification of these polysaccharides by cross-linking of the glucose chains of starch polymer or that of cyclodextrin molecules not only increases hydrophobicity, but also provides opportunity for tuning the sorption properties of the adsorbent as a function of the nature of the cross linking agent as well as degree of cross linking process.

2.13.1 Insoluble crosslinked polysaccharides

Due to the unique structure of the macromolecule combined with their polyfunctionality, polysaccharides have the ability to form crosslinked networks, gels and macroreticular resins (Crini, 2005; Sajilata 2006; Gupta, 2009). Crosslinking occurs when a reagent (namely a crosslinking agent) introduces intermolecular bridges and/or crosslinks between polysaccharide macromolecules. The crosslinking step is a well-known and well-documented reaction, and a relatively easy method to prepare polysaccharide-based materials. The crosslinking agent can react with macromolecules linear chains (crosslinking step) and/or itself (polymerization step) in an alkaline medium. Crosslinking drastically reduces segment mobility in the polymer and a number of chains are interconnected by the formation of new inter-chain linkages. A three dimensional network is then formed. If the degree of reticulation is sufficiently high, the matrix of the polymers becomes insoluble in water (but swellable in water) and in organic solvents. The two most important factors controlling the extent of adsorption properties of polysaccharide-based materials are the hydrophilicity of the polymer and the crosslink density. When the cross-linking degree is high, the material is mostly amorphous, but when it is low, some degree of starch crystallinity will still be retained (Shiftan et al., 2000; Demirgöz, 2000; Crini. 2005)

The crosslinked polymers are obtained in homogenous or heterogeneous conditions by using reticulation with bi- or polyfunctional crosslinking agents such as epichlorohydrin (Gao and Zhao, 2004; Delval et al 2006), ethylene glycol diglycidyl ether, glutaraldehyde, benzoquinone, phosphorus oxychloride (Kim and Lim, 1999; Eguchi, 2006) carboxylic acids (Seidel, 2001; Lanthong et al., 2006; Reddy, 2010; Kwak et al., 2011) maleic anhydride (Girek et al., 2000) or isocyanates (Ohkita and Lee, 2004; Mocanu et al., 2009; Ozmen and Yilmaz, 2007; Ozmen et al., 2008). Other water-soluble crosslinking agents have been proposed, such as sodium trimetaphosphate, sodium tripolyphosphate (Singh et al., 2007), phosphorus oxy-chloride (Kim and Lim, 1999; Chung et al., 2004; Farhat, 2006), etc. Among these reagents, epichlorohydrin, EPI, is the most widely used cross-linking agent. EPI, a bifunctional molecule, which contains two functional groups, is highly reactive with hydroxyl groups. Another advantage of EPI is that it does alter the adsorption properties of the polysaccharide precursors. For instance, it does not eliminate the cationic amine function of chitosan, which is the major adsorption site attracting the pollutant during adsorption (Crini, 2005). Also, the isocyanates are interesting because they differ in the length of the spacer and in the kind and number of their carbon chain, hence providing better tuning options for adsorption purposes (Okoli et al., 2014).

Crosslinked materials possess several characteristics, properties and advantages.

- Homogeneous crosslinked materials are easy to prepare with relatively inexpensive reagents and are available in a variety of structures with a variety of properties, and also in numerous configurations, e.g. gels, particles of irregular shape or regular beads, membranes, coatings, films, fibers, capsules and sponges. They are insoluble in acidic and alkaline mediums as well as organic solvents. Crosslinked gels are very stable hydrophilic polymers. They become more resistant to shear, high temperature and low pH compared to their parent polysaccharide.
- After crosslinking, they maintain their properties, original characteristics (except the crystallinity) and strength in acidic and basic solutions. These characteristics are important for an adsorbent so that it can be used in a lower pH environment.
- Crosslinking reduces the amount of the crystalline domains in the polysaccharide and can then change the crystalline nature of the raw polymer. This parameter significantly influences the sorption properties because it may control the accessibility to sorption sites.
- Crosslinked beads also have other advantages such as faster kinetics, increased ease of operation and interesting diffusion properties. Due to the hydrophilic nature of their crosslinking units, these materials possess a remarkably high swelling capacity in water, and consequently their networks are sufficiently expanded as to allow a fast diffusion process for the pollutants
- After adsorption, the crosslinked materials can also be easily regenerated by washing with a suitable solvent or by solvent extraction.

These characteristics, properties and advantages attracted scientists for application of cross-linked starch and cyclodextrin polymer as adsorbents in the remediation of water for chemical pollution, and possibly as SPE sorbents for pre-concentration of micro-pollutants.

2.13.2 Challenges in utilizing cross-linked polymer adsorbents

One of the greatest challenges in the utilization of cross-linked biopolymers as adsorbents for water treatment is the choice of cross-linking agent. The choice of the cross-linking agent has a significant influence on the adsorption properties because the chemical structure of the synthesized adsorbents depends on the nature of the cross-linking agent and the degree of cross-linking (Crini et al., 2005). Seidel et al., (2001) showed that the cross-linking agent has a significant influence on the sturdiness of the material. Cross-linking alters both the physical properties and the thermal transition characteristics of the polymer (Chung et al., 2004). Until now, the sole approach to selection of cross-linking reagents is based on the known chemical properties of the potential cross-linking agents. This approach involves experimental synthesis of the adsorbent material and the subsequent batch adsorption tests to assess the adsorption performance. This approach is laborious, cumbersome, and most importantly, not cost effective.

Also, choosing the suitable rate and degree of cross-linking, which can be modulated by choice of cross-linking condition, is another serious challenge. The selectivity success also depends strictly on the degree of cross-linking, otherwise known as cross-linking density, and in this case diffusion of pollutants into the polymer matrix becomes slower as the crosslinking density increases. It is well-known that, generally, the adsorption capacity decreases with increment in the degree of cross-linking. At higher levels of cross-linking the adsorbents have lower swelling capacities. The accessibility decreases as a result of a more extensive three-dimensional network (Crini et al., 2005; Reddy, 2010; Kwak et al., 2011) and an increase in the hydrophobic character. This phenomenon can also be interpreted in terms of decreased hydrophilicity caused by the destruction of the crystalline structure. The characteristics of the particles (shape, size and density) can also introduce hydrodynamic limitations and column fouling, which limits the use of these materials for large-scale columns.

2.14 Adsorbent design and QSAR

The adsorption isotherm plays a dominating role in selection or design of adsorbents for a target adsorbate molecule. With the advent of high-speed computing, it is now possible to calculate the adsorption isotherms based on interaction potentials and structure/geometry of the adsorbent (Yang, 2003).

For adsorption in gaseous state, adsorption occurs when the interaction potential energy ϕ is equal to the work done to bring a gas molecule to the adsorbed state. As a first approximation, the adsorbed state is assumed to be at the saturated vapor pressure.

$$\phi = \Delta G = \int_{p}^{p_o} VdP = RT \ln \frac{p_o}{p} \qquad 2.13$$

where ΔG is the free energy change and P_o is the saturated vapor pressure.
Hence P is the pressure when adsorption occurs for the given ϕ (ϕ is actually the adsorbate -adsorbate interaction energy on the liquid surface).

The total potential between the adsorbate molecules and the adsorbent is the sum of the total adsorbate -adsorbate and the adsorbate -adsorbent interaction potentials:

$$\phi_{total} = \phi_{adsorbate\text{-}adsorbate} + \phi_{adsorbate\text{-}adsorbent} \qquad 2.14$$

Since the adsorbent has only a secondary effect on the adsorbate -adsorbate interaction, the second term, adsorbate-adsorbent potential is considered more relevant. For this reason, much attention is focused on the second term, adsorbate - adsorbent potential, and the term is commonly referred as ϕ. The simplest straight-forward way of predicting the interaction potential, and subsequently the adsorption performance of adsorbents is to evaluate the chemical activities of the adsorbents based on their molecular structures, which can be done through quantitative structure activity relationship (Yang, 2003).

The concept of Quantitative Structure Activity Relationship, QSAR, is to transform searches for optimal compounds/materials with the desired properties based on chemical intuition and experience into searches with a mathematically founded and computerized form of approach. In the simplest of terms, QSAR methods are the methods for estimating properties of a chemical/material from its molecular structure. Once a correlation between structure and activity/property is found, any number of chemical compounds/materials, including those not yet synthesized, can be screened on the computer in order to select structures with the desired properties. These methods have the potential to provide information on the activity of chemicals/materials, while reducing time, financial cost and laboratory testing currently needed. The information generated from QSAR studies, otherwise known as chemical descriptors are used for predicting, as well as describing the chemical activities/properties of materials.

Since adsorption is a surface phenomenon, molecular modeling of the adsorption activity is the sure approach of evaluating the interaction potential of adsorbents.

2.14.1 Molecular Modeling of Adsorption

Molecular modeling methods have gained acceptance as practical tools in a variety of industries, such as bioactive materials like pharmaceuticals, electronic and photonic materials, homogeneous reactions and heterogeneous catalysis, fuels and automotive chemicals (David, 2001; Li, 2006), and adsorption and adsorbent design (Todeschini and Consonni, 2000; Rafati *et al.*, 2008; Shirvani *et al.*, 2010; Udhayakala *et al.*, 2012).

These computational methods are being adopted because they are proving their value over time. They are useful in developing hypotheses and a rational, strategic approach to problem solving, providing understanding and design rules, stimulating new ways of thinking, aiming for predictive results, rather than descriptive results, and most invaluable — steering experimental development while eliminating dead end research (Fermeglia *et al.*, 2003). Even though there is still much development needed in computational quantum chemistry methods, better and more accurate algorithms are continuously being explored. As more advanced software and hardware are developed, the molecular modeling methods become more attractive and successful applications become more common.

All in all, understanding the adsorbents' surface properties theoretically will help in choosing the best adsorbent for certain adsorbates. In this case, this study is investigating the properties of cross-linking starch and cyclodextrin polymer adsorbent and the adsorption properties of aqueous PAHs and phthalate species toward these adsorbents.

For adequate understanding of the modeling approaches adopted for this study, a brief review of some of the different computational approaches for examining surface phenomena is necessary.

There are two areas within computational chemistry devoted to the structure of molecules and their reactivity: molecular mechanics and quantum mechanics. The basic types of calculations they both perform include computing the energy, or properties related to the energy, of a particular molecular structure; performing geometry optimizations; and, computing the vibrational frequencies of molecules resulting from inter-atomic motion within the molecule (Foresman and Frisch, 1996).

This section explored these methods and their limitations to highlight the choices made for the methods employed in this research.

2.14.1.1 Molecular Mechanics

Molecular mechanics is a mathematical procedure that has been applied to many classes of structure. Unlike quantum mechanical approaches, electrons are not explicitly included in these calculations. Hence, it does not use a wave function or total electron density, but rather adopts simple algebraic equations with their associated constants, otherwise called force field for calculating the energy of a compound (Young, 2004). This is possible due to the Born-Oppenheimer approximation, which states that the electronic and nuclear motions can be uncoupled from one another and considered separately. Molecular mechanics assumes that the electrons in a system find their optimum distribution, and approaches chemical problems from the standpoint of the nuclear structure. These methods are characterized by their particular force fields representing the interactions between atomic species. However, electron effects are included implicitly in the force fields through parameterizations. The fundamental assumption of the molecular mechanics method is the transferability of parameters. In other words, the energy penalty associated with a particular molecular motion, say, the stretching of a carbon-carbon single bond, will be the same from one molecule to the next. This gives a very simple calculation that can be applied to very large molecular systems. (Bowen and Allinger, 1991; Field, 1999).

The approximations in molecular mechanical calculations make the computations quite inexpensive, which allows the methods to be used for very large systems containing thousands of atoms (Lewars, 2010). However, there are two major drawbacks of these methods. Firstly, each force field achieves good results only for a limited class of molecules for which the force field is parameterized. No force field can be used for all molecular systems. Secondly, molecular mechanics methods cannot treat chemical systems where electronic effects dominate because of the neglect of electrons. For example, they cannot describe processes involving bond formation or bond breaking, like adsorption processes (Field, 1999; Lewars, 2010).

2.14.1.2 Quantum Mechanics

Quantum mechanics (QM) is the mathematical description of the behavior of electrons and thus of chemistry. Electronic structure theory based on quantum mechanics is one of the most fundamental tools for molecular and material modeling, and applies the laws of quantum mechanics rather than classical physics as the basis for the calculations (Shankar, 1994). Two equivalent formulations of QM were devised by Schrödinger and Heisenberg. However, the Schrödinger form is often adopted since it is the basis for nearly all computational chemistry methods. The energies and structures of molecules are obtained through the solution of the Schrödinger equation, which can be written as:

$$\mathrm{H}(r,R)\psi(r;R) = E(R)\psi(r;R) \qquad 2.15$$

E(R) in the Schrödinger equation stands for the energy of the system, which is also the eigenvalue solution of the equation; *Ψ(r; R)* is the wave function that determines the electron density and various properties, such as dipole moments and electrostatic potentials. *H(r, R)* in the Schrödinger equation is named the Hamiltonian, and it represents the sum of the total potential and kinetic energies of the system (Levine, 2000).

These terms can be written as:

$$H = \frac{h^2}{2}\sum\frac{1}{m_i}\left(\frac{\partial^2}{\partial x_i{}^2} + \frac{\partial^2}{\partial y_i{}^2} + \frac{\partial^2}{\partial x_i{}^2}\right) + \sum{}_{i<j}\sum\left(\frac{e_i e_j}{r_{ij}}\right) \qquad 2.16$$

The first term in equation (2.16) accounts for the kinetic energies, and the second term accounts for the potential energies, including attractions or repulsions between particles. Equations (2.15) and (2.16) are the time-independent Schrödinger equation because time-derivatives and time-dependent terms have been eliminated. The time-dependent form is usually used when one is concerned with transient phenomena such as rapidly oscillating electric fields or scattering (Levine, 2000). Since adsorption, which is the core subject of this research is not concerned with these phenomena; equations (2.15) and (2.16) are considered suitable.

In theory, QM can predict any property of an individual atom or molecule exactly, but in practice, the QM equations have only been successfully solved with exact solution for one electron systems (Teter et al, 1989; Young, 2004). In this regards, a myriad collection of methods has been developed for approximating the solution for multiple electron systems. These approximation methods ranged from molecular modeling, to semi-empirical molecular orbital (MO) methods, to ab initio MO methods, and density functional theory (DFT) methods. These approximations can be very useful, but this requires an amount of sophistication on the part of the researcher to know when each approximation is valid and how accurate the results are likely to be. A significant portion of this review section addresses these approximation options.

2.14.1.2.1 Semi-Empirical Molecular Orbital (MO) Methods

Semi-empirical MO methods neglect most of the two-electron integrals in solving the Schrödinger equation and use experimental results (parameters) to adjust integrals to obtain accurate results at very low cost. Some of the methods used in modeling, especially for large biological molecules, are MNDO/d (Thiel, 1996), AM1 (Dewar et al., 1985) and PM3 (Stewart, 1989). These approaches, with parameters readjusted especially for absorption spectra, are powerful tools for excited states of large molecular systems and molecules containing transition metals.

These inexpensive methods have been used to calculate nonlinear optical properties of large molecules, in particular for industrial applications (Westmoreland et al., 2002).

Summarizing semi-empirical MO methods, their largest merit is definitely low computational cost. They are more expensive than the molecular mechanics (MM) methods, but they allow breaking of bonds and take electronic effects explicitly into account, which MM cannot do. Important shortcomings of semi-empirical methods are low reliability (qualitative at best, and particularly poor for transition states) for the energetic results and the lack of reliable parameters for transition metals (Foresman and Frisch, 1996; Levine, 2000).

Therefore, these approaches are not applicable to most homogeneous and heterogeneous catalysis or adsorption modeling efforts.

2.14.1.2.2 Ab initio MO Method

Ab initio quantum chemistry has long been applied as a major tool for investigating the structure, stability, reaction kinetics and mechanisms of different molecular systems (Zheng and Blowers, 2006). Ab initio calculations are based on the laws of quantum mechanics only and on the values of a small number of physical constants like the speed of light, the masses and charges of electrons and nuclei, Planck's constant, etc.

These methods compute solutions to the Schrödinger equation through a series of rigorous mathematical approximations. In the ab initio MO methods, the Schrödinger equation is solved "from the beginning" (which is not "from first principles", as ab initio is frequently translated) (Westmoreland et al., 2002). These methods usually express the molecular orbitals as linear combinations of a finite number of basis functions:

$$\varphi_i = \sum_{v=1}^{Nbaisi} C_{ir}\chi_r \qquad 2.17$$

where φ_i is the wave functions of the molecular orbitals, C_{ir} is the expansion factor and χ_r is one-electron spin orbital.

The difference between semi-empirical and ab initio methods lies in the trade-off between computational cost and the accuracy of results (Westmoreland et al., 2002).

With the availability of good parameters, semi-empirical calculations are relatively inexpensive and provide fairly accurate energies and structures. Ab initio methods, in contrast, provide highly accurate predictions for a broad range of systems (Frank, 1999). However, the chemical systems of interest are restricted to up to a few hundred atoms because of the high computational cost (Foresman and Frisch, 1996).

In summary, ab initio methods are the ultimate theoretical methods for electronic structure calculations, applicable to any atoms or molecules in both ground and excited states. The approximations can be systematically improved using better basis sets and better wave functions. The disadvantage of ab initio methods is their computational cost, much more demanding than semi-empirical and DFT methods (HeadGordon, 1996). Especially discouraging is the high-order power dependency on the size of the system, up to M^7 or M^8, where M is the molecular size (HeadGordon, 1996). The ab initio methods have been, and will be, used in industrial applications when the accuracy is needed or when inexpensive alternative methods, such as semi-empirical MO or DFT, do not work.

2.14.1.2.3 Density Functional Theory Methods

Density functional theory (DFT) calculations of the geometry optimization, single point energy and other properties of molecules are based on the fact that the properties of a molecule in a ground electronic state are determined by the ground state electron density (Westmoreland et al., 2002). At a very basic level, density functional methods are similar to some ab initio methods in many ways. DFT calculations have the same computational cost as Hartree-Fock theory, the least expensive ab initio method, but include the effects of electron correlation, which is the fact that electrons react to each other's motion (Zheng, 2007).

The electron density is defined in this context as:

$$\rho(r) = \rho(x, y, z) = N\int \psi^*(1,2,3,.....N)dx_1dx_2dx_3.....dx_N \qquad 2.18$$

where the ψ is the wave function of a molecule.

The electron density is a function of position only, that is, of just three variables, while the wavefunction of an N-electron molecule is a function of 4N variables. No matter how large the molecule is, the electron density is still a function of only three variables, while the complexity of the wave functions for the ab initio methods just described earlier increases with the number of electrons to powers up to 7 or 8. Therefore, DFT is less computationally expensive and more accessible than wave function computational methods with similar accuracy, especially for larger systems.

All in all, the greatest advantage of DFT is low cost (Koch et al., 2001; Westmoreland et al., 2002). On one hand, DFT methods could be as accurate as Moller-Plesset (MP2) if the proper functionals are used. The methods have a smaller M (molecular size) dependency than the comparable ab initio methods, and they are applicable to very large molecules, and electronic properties calculated with DFT are also reasonably reliable.

2.14.2 Molecular Modeling Approaches for Surfaces

Considering the large surface area of adsorbents, it is impossible to completely model the adsorption process on the entire surface in any surface calculation with density functional or ab initio methods, even with robust computer codes and highly efficient super computers (Hansen and Neurock, 1999; Neurock, 2003; Van Santen et al., 2009). In this guise, three approaches have been developed for handling the surface when an adsorbate is present, namely: cluster, embedded-cluster, and periodic methods.

2.14.2.1 Cluster approach

Cluster approach is a method for representing surfaces whereby a smaller cluster (Hoeft et al., 2001; Rantala et al., 1994) of atoms is used to represent the surface, often terminating unfilled valencies with hydrogen atoms or hydroxyl groups to mimic a continuous surface. The basic premise behind the approach is that reactions and adsorption are local phenomena, primarily affected by the nearby surface structure. The clusters can adopt different sizes and configurations depending on the specific system being examined and the accuracy of the desired results (Pacchioni, 1997). The advantage of the cluster approach is that the active site is described explicitly by the interactions between the local molecular orbitals of the adsorbate and the adsorbent. This enables one to probe bonding and reactivity and to formulate structure property relationships easily (Westmoreland et al., 2002). On the other hand, the disadvantage is the incomplete representation of the electronic system provided by the small size and the discrete nature of the cluster employed (van Santen and Neurock, 2009). Two possible underlying problems with the small clusters are their failure to describe the electronic band properties and in not converging properly (Hoeftet al., 2001). By carefully optimizing the adsorbate-cluster interactions, the lowest energy structures and electronic states can be calculated and used to predict reliable energetic data (Westmoreland et al., 2002). These cluster approaches normally allow one to use higher levels of theory and larger basis sets so one is able to obtain more accurate energetic results (Neurock, 2003).

The cluster approach has been used in the literature to model zeolites (van Santen and Kramer, 1995), metal oxides (Pacchioni, 1997; Hoeft et al., 2001; Rohrbach et al., 2004), metal sulfides (Neurock and van Santen, 1994), and some other catalysts (Hermann et al., 1996).

2.14.2.2 Embedded-cluster approach

Considering the operational features, the embedded-cluster approach is simply an extension of the cluster model (Neurock, 2003). In this method, a QM method is used to model the local region about the active site. This primary cluster is then embedded in a much larger system in order to simulate the external electronic environment. The outer model employs a much simpler quantum mechanical treatment to simulate the external environment.

Mostly, the molecular mechanics methods (MM) are used in embedded cluster approach. Therefore, the embedded-cluster method is commonly known as the QM/MM method (Raimondi et al., 2001).

The difficulties with this method involve accurately matching the electronic structure at the interface between the inner-cluster and the external model (Pisani, 1993). The newest methods treat the core region with DFT and the outer shell with MM, and can be carried out on systems that contain thousands to tens of thousands of atoms (Westmoreland et al., 2002). These approaches have been successfully applied in modeling metals, drugs, proteins and other biological systems (Pisani, 1993; Kruger and Rosch, 1994; Friesner and Beachy, 1998). This method has the potential to be applicable for systems with large number of molecules.

2.14.2.3 Periodic Quantum Mechanical calculations

Another method for handling surfaces is to use a periodic model to describe the surface where periodic boundary conditions are used to enable the code to rapidly calculate interactions (Neurock, 2003; Li 2006). One generally picks a cell unit size for the surface, which would include several layers of surface atoms and a vacuum space above the surface. The smaller the unit cell size is, the faster the calculation. Modeling chemisorption at higher coverages is therefore typically easier than modeling the low coverage situations where larger surfaces with only a few adsorbates would appear. The vacuum space needs to be set high enough to prevent the adsorbate from interacting with the periodic lower bound of the surface that would appear above the vacuum (Westmoreland et al., 2002).

The advantage of the periodic approach is that a much more complete electronic structure can be included. The disadvantage is that only systems with highly periodic structures can currently be examined within reasonable computational times (Zeigler et al., 2000). Industrial systems, however, in reality are often ill-defined supported particles, which are difficult to model using the periodic approach. Besides, very large CPU times are required for the calculations. Many of the current methods use ultrasoft pseudo potentials that cut down computational times by a factor of two or three, but this will only help so much in making the calculations feasible(Westmoreland et al., 2002). Considering these obvious limitations, the periodic approach is not considered suitable for the kind of surfaces under study.

All three approaches just discussed have all played important roles in understanding model chemistries over time. The method of choice for a particular problem clearly requires a careful consideration of the advantages and disadvantages of each method and their impacts on results. These trade-offs were considered in choosing the approaches used in this work.

2.15 State of the art on PAHs and phthalates pollution, treatment and SPE pre-concentration in aqueous media

PAHs and phthalates are harmful to both humans and biota. Exposure to PAHs and phthalate polluted water is one of the common routes of exposure to these harmful micro-pollutants. Adsorption has been established as the most efficient and effective ways of removal of PAHs and phthalates from water systems. However, some identified challenges with the available adsorbents have posed strong limitations to the continued application of adsorption technology as a treatment method of choice. This scenario has necessitated the continued search for efficient, effective, and low cost biodegradable adsorbent for these pollutants of interest.

In a similar vein, robust pre-concentration method is central to routine analytical methods for water pollution control and management. Solid phase extraction, SPE, has proved to be extraction method of choice for micro-organic pollutants like PAHs and phthalates. However, the narrow pH stability (for silica based adsorbent), low recovery and non-biodegradability challenges (for synthetic polymers) for the most commonly used adsorbents, have posed serious limitation for continued efficient application of the common adsorbents as SPE phase for preconcentration of micro-organic pollutants. This situation has also necessitated the need for development of solid phase sorbent that will be able to surmount these challenges.

Cross-linking process confers tunable adsorption properties to cross-linked adsorbents. Cross-linked starch and cyclodextrin polymer have shown potential characteristics, properties, and advantages that make them suitable for utilization as adsorbents both for adsorption removal and preconcentration of PAHs and phthalates in water systems. Previous studies on the application of cross-linked polysaccharides as adsorbents both in batch and column showed that the major challenge in utilization of cross-linked adsorbents is the difficulty associated with the selection of suitable cross-linking agents and the right cross-linking density. Hence, starch and cyclodextrin can serve as good precursors of adsorbents for PAHs and phthalates if these challenges are addressed.

CHAPTER THREE

Materials and Methods

3.1 Materials

3.1.1 Chemicals

Materials and reagents for synthesis of cross-linked adsorbents: Epichlorohydrin and aqueous ammonia were supplied by Aladdin Chemistry Company Ltd. Shanghai, China, while monomethyl amine was supplied by Tianjin Yongda, China. N,N-Dimethylformamide (DMF), 2,2-Methylene diphenyl diisocyanate (MDI) and 1,6-Hexamethylene diisocyanate (HDI) were supplied by Aladdin Chemistry Company Ltd. Shanghai, China. Corn starch (soluble starch) was supplied by Guangfu Research Institute, Tianjin; β-cyclodextrin (analar) was supplied Tianjin Kermel Fine Chemical Company, Tianjin

Reagents and standards for adsorption study: The acenaphthylene, phenanthrene, benzo[a] anthracene (BaA), and benzo[a]pyrene (BaP) PAH standards were supplied by Dr. Ehrenstorfer GmbH, Augsburg, Germany. Fluorene was supplied by Aladdin, China. Diethyl phthalate (DEP) standard was supplied by Tianjin Yongda Chemical Reagent Company Limited China, while that of Dimethyl phthalate (DMP) was supplied by Aladin Chemistry Company Ltd, Shanghai, China. Sodium Azide (NaN_3) was supplied by Amresco, USA. Anhydrous Calcium chloride was supplied by Sinopharm, China. Granulated Activated Carbon (Charcoal activated carbon) was supplied by Beijing Daling Xihuagong Chang.

Reagents and standards for Solid Phase Extraction/High Performance Liquid Chromatographic method development study: The US EPA PAH mix standard stock solution (PAH solution 16-22, 200 mg/L) was obtained from O2Si smart solution$^{®}$ South Carolina, USA, and supplied by ANPEL Scientific Company Limited China. The US EPA PAH mix had the following PAHs at the given concentration of 200 mg/L dissolved in Acetonitrile; Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]Perylene, Benzo[k] Fluoranthene, Benzo[a]pyrene, Dibenzo[b]anthracene, Benzo[g]Perylene, indeno[c]perylene. LC grade of Acetonitrile and Methanol were purchased from Fisher Scientific, New Jersey, USA and MREDA Technologies Inc. USA, respectively. Analytical grades of Acetone, Dichloromethane (DCM), and Hexane were purchased from Beijing Modern Fine Chemical Company, Beijing. Ultrapure water was prepared using Milli-Q water purification system (Bed-ford, MA, USA).

3.1.2 Instruments

Perkin Elmer Spectrum 1 FTIR spectrophotometer, Elementar (Germany) Vario Macro Cube elemental analyzer, Micromeritics ASAP 2020 Model surface area analyzer, Hitachi S4800 model Scanning Electron Microscope (SEM), Perkin Elmer Pyris 1 Thermogravimetric /Differential thermal Analyzer, Water bath temperature controlled horizontal shaker, 12 column capacity SPE manifold and PTFE suction tube (Agilent Technologies, USA), Air Cadet Model 420-1902 Vacuum Pump (Thermo Fisher Scientific, USA). 6 ml capacity polypropylene SPE column (Polypro, 2.CR0006.0001) and polyethylene frits for SPE columns (6ml PE frits 20 µm, 2.CR06PE.0001) (purchased from CNW Technologies, Shanghai ANPEL Science Instruments Company Limited), PerkinElmer (USA) Series 200 HPLC system having Brownlee Analytical PAH reverse phase column (150 x 3.2 mm, 5 µm, 110Å) equipped with Fluorescence and UV Detectors in series connection, TotalChrom (PerkinElmer) software for HPLC data capture and handling (provided by PerkinElmer).

3.2 Molecular Studies using Density Functional Theorem Computational Model

3.2.1 DFT quantum calculation

Based on the proposed synthetic scheme and the likely structure of the surfaces of the cross-linked polymer (Figure 3.1), cluster method was adopted to simulate the surfaces of the cross-linked polymers. In this vein, monomer units of Epichlorohydrin, 1,6-Hexamethylene diisocynate, and 2,2-Methylene diphenyl diisocyanate cross-linked polymer adsorbents (Figure 3.2) were adopted as representative structural models for the

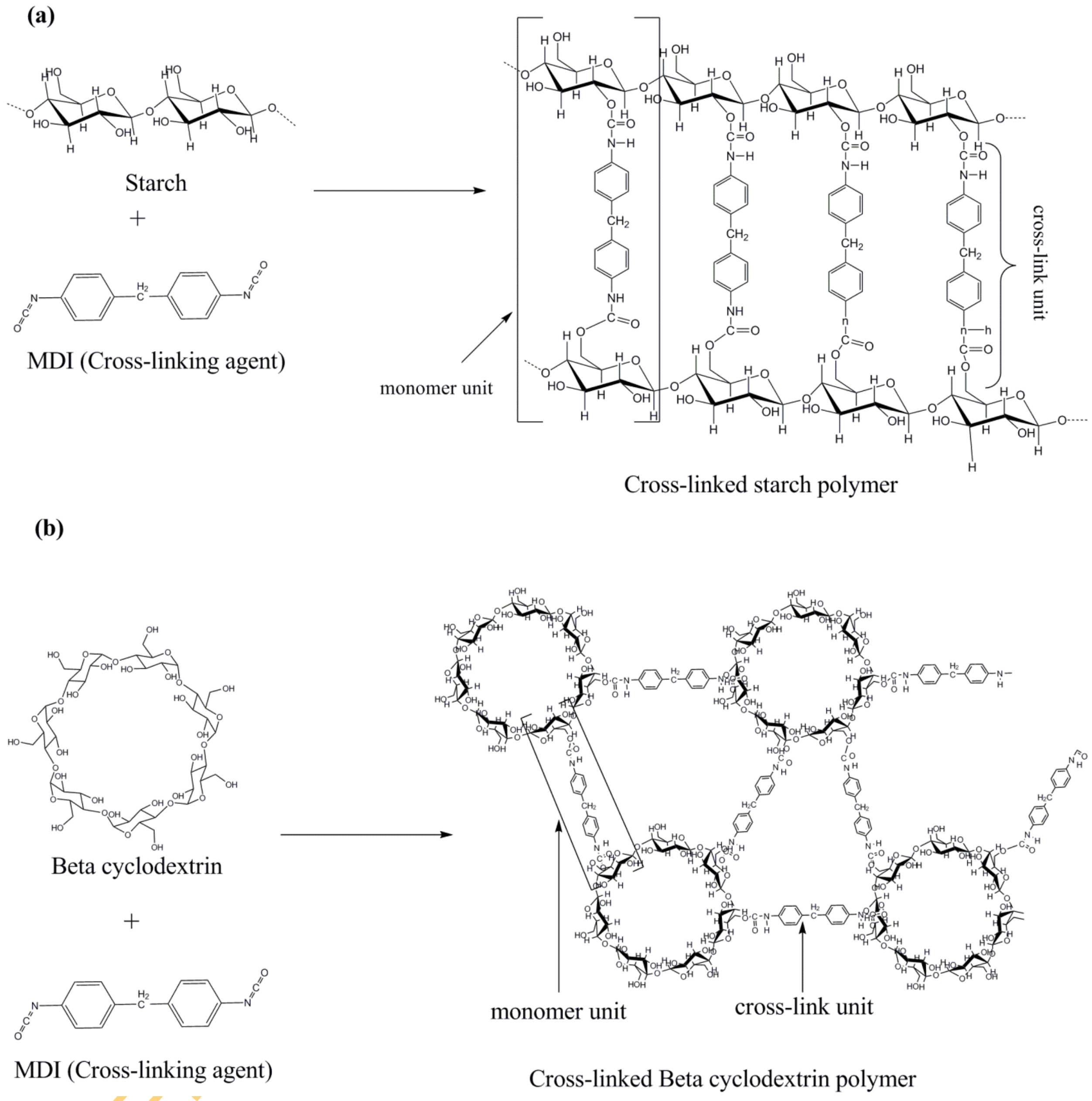


Figure 3.1. Proposed reaction scheme for the synthesis of (a) cross-linked starch polymer and (b) β-cyclodextrin polymer, using 2,2-methylene diphenyl diisocyanate (MDI) as cross-linking agent

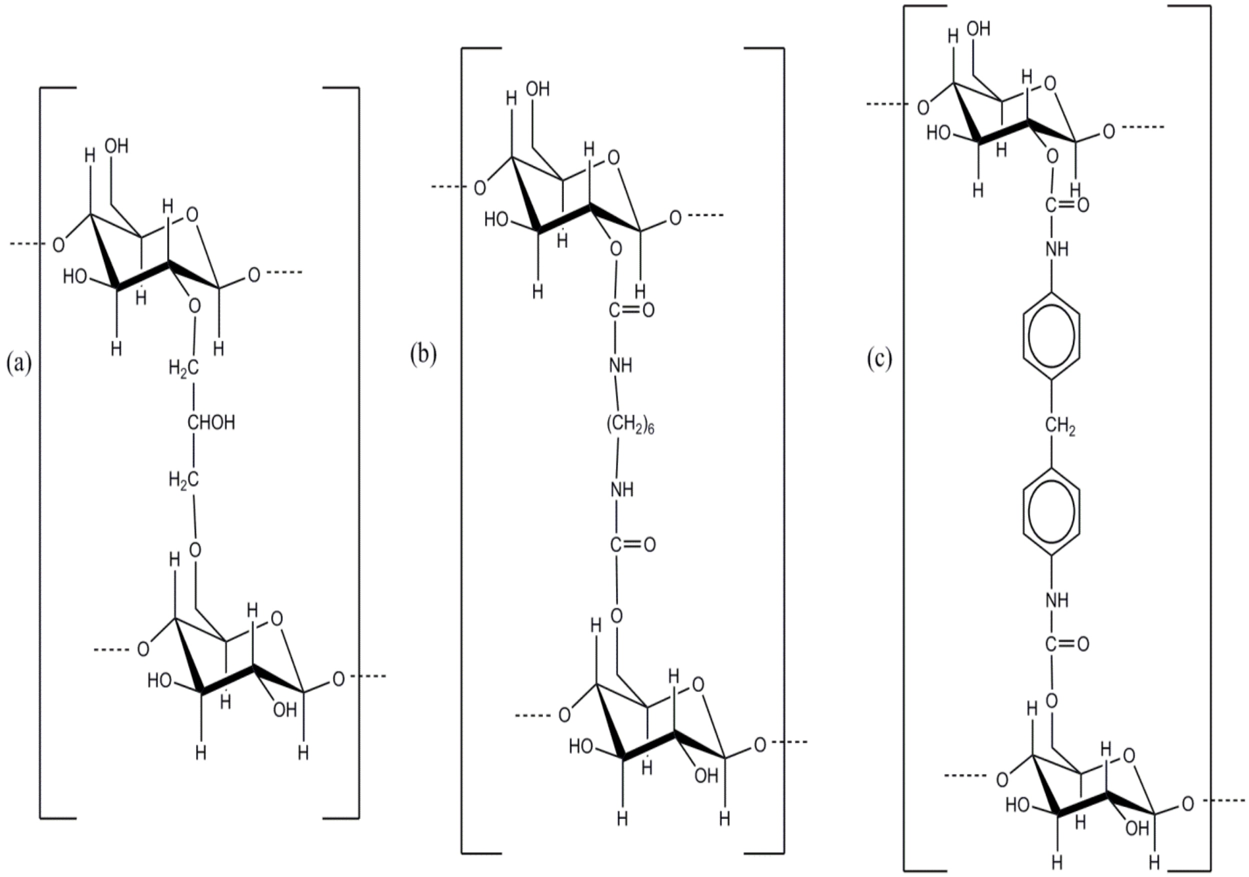


Figure 3.2. Monomer structures of (a) epichlorohydrin (EPI) cross-linked starch/cyclodextrin (b) 1,6-hexamethylene diisocyanate (HDI) cross-linked starch/ cyclodextrin, and (c) 2,2-methylene diphenyl diisocyanate (MDI) cross-linked starch/cyclodextrin

adsorbents, while the full molecular structures of the adsorbates (acenaphthylene, phenanthrene, Benzo[a]Anthracene (BaA), and diethyl phthalate (DEP)) were adopted for the computational studies. Conformer distribution study was first carried out on the molecules, to obtain the conformer or structure with the lowest energy. All the quantum calculations with full-geometry optimizations were performed using Spartan 10v1.0.1. suite of programs. Geometry optimizations and calculation of energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), dipole moment, and Quantitative Structure Activity Relationship (QSAR) volume of adsorbents and adsorbates were performed with the DFT method at B3LYP level of theory with the 6-31G basis set.

3.2.2 Data treatment for DFT computational study

Quantum chemical descriptors such as ionization potential (I), electron affinity (A), energy gap (ΔE), chemical hardness (η), softness (S), chemical potential (μ) and fractional number of transferred between the adsorbent and adsorbate (ΔN) were respectively calculated according to equations 3.1 – 3.7 (Ebenso et al., 2010).

$$I = -E_{HOMO} \qquad 3.1$$

$$A = -E_{LUMO} \qquad 3.2$$

$$\Delta E = E_{HOMO} - E_{LUMO} \qquad 3.3$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} = \frac{I - A}{2} \qquad 3.4$$

$$S = \frac{1}{\eta} = \frac{2}{I - A} \qquad 3.5$$

$$\mu = -\frac{(I + A)}{2} \qquad 3.6$$

$$\Delta N = \frac{\mu_B - \mu_A}{2(\eta_A - \eta_B)} \qquad 3.7$$

where E_{LUMO} and E_{HOMO} are the energies of Lowest Unoccupied Molecular Orbitals and Highest Occupied Molecular Orbitals respectively, generated from the DFT calculations, μ_A and μ_B are the chemical potentials of the adsorbent (A) and adsorbate (B), and η_A and η_B are chemical hardness of the adsorbent (A) and adsorbate (B).

3.3 Preparation of adsorbents

The cross-linked polymers were prepared by reticulation (one step direct reaction) of the precursors/mixture of the precursors (starch, β-cyclodextrin, and γ-cyclodextrin) with respective cross-linking agents. The summary of the quantities of precursors and cross-linking agents are as shown in Appendix I. The details of the synthetic processes and reaction conditions are reported below.

3.3.1 Preparation of Starch Based Adsorbents

The cross-linked starch polymers were prepared by reticulation of starch with different cross-linking agents.

Epichlorohydrin cross-linked starch adsorbents (EPICS)

For the synthesis of epichlorohydrin cross-linked starch (EPICS), seven variants of these adsorbents were prepared namely: EPICS1, EPICS2, EPICS3, EPICS4, EPICS5, EPICS6, and EPICS7. The synthetic process adopted the procedure introduced by Simkovic (Simkovic,1996; Simkovic et al., 1996) was modified by increasing the amount of EPI added, in order to obtain mechanically stable polymers. 15.0 g of starch was added into 100 ml of a 20% NaOH solution heated to 50°C in a thermostated reaction vessel, and the mixture was stirred using magnetic stirrer, until a uniform jelly-like suspension was obtained. Then the desired amount of epichlorohydrin (10.0, 20.0, 30.0, 40.0, 50.0, 60.0, and 70.0 ml for EPICS1, EPICS2, EPICS3, EPICS4, EPICS5, EPICS6, and EPICS7, respectively) was slowly added in a dropwise manner, and the stirring continued for 10–30 minutes (depending on the quantity of EPI added) at 60–70°C. The viscosity of the solution increased so strongly and rapidly that it could not be stirred, and after about 10 to 30 minutes (depending on the quantity of epichlorohydrin) a pale-yellow solid polymer was obtained. Then the pH was adjusted to neutral with 0.05M hydrochloric acid and cooled. The ready material was filtered off, washed copiously with distilled water, and further purified by soxhlet extraction using acetone for 12 hours. The polymer was finally lyophilized and kept in a desiccator prior to use.

Aminated epichlorohydrin cross-linked starch adsorbents (EPIACS)

The aminated EPI cross-linked starch adsorbents (EPIACS: EPIACS1, EPIACS2, and EPIACS3) was synthesized by adding 15.0 g of starch and the desired quantity of aqueous amonia (10.0, 20.0, and 30.0 ml for EPIACS1, EPIACS2, and EPIACS3, respectively) into 100 ml of a 20% NaOH solution, and thereafter adding 20.0 ml of EPI following the same procedure adopted for EPICS group of adsorbents.

Methyl aminated epichlorohydrin cross-linked starch adsorbents (EPIMACS)

The methyl aminated EPI cross-linked starch adsorbents (EPIMACS: EPIMACS 1, EPIMACS 2, and EPIMACS 3) were synthesized by adding 15.0 g of starch and the desired quantity of monomethyl amine (10.0, 20.0, and 30.0 ml for EPIMACS 1, EPIMACS 2, and EPIMACS 3, respectively) into 100 ml of a 20% NaOH solution, and thereafter adding 20.0 ml of EPI following the same procedure adopted for EPICS group of adsorbents.

Preparation of starch-based polyurethane adsorbents

For the synthesis of starch-based polyurethane adsorbents (diisocyanates cross-linked starch), the cross-linked polymers were prepared in one step by singly cross-linking starch with 1.6-hexamethylene diisocyanate (HDI) and 4,4-methylene diphenyl diisocyanate (MDI) according to the synthetic method described by Ozmen *et al.*, (2007), with increment in the ratios of the cross linking agent to improve the mechanical strength of the polymer.

1,6-Hexamethylene diisocyanate cross-linked starch (HDICS) adsorbents

For HDI cross-linked starch (HDICS: HDICS1, HDICS2, HDICS3, and HDICS4), a typical reticulation reaction was carried out as follows. 8.0 g of starch was added into 40 ml of dry DMF in 100 ml round bottom flask at room temperature. The mixture was stirred, while the temperature was gradually raised and later maintained at 60°C until complete dissolution. Thereafter, a given quantity of HDI (1.18, 3.50, 5.90, and 11.80 ml for HDICS1, HDICS2, HDICS3, and HDICS4 respectively) was added drop-wise, and the resulting solution was stirred at70^{o}C until solid formation which occurs at about 1 hour (depending on the quantity of the cross linking agent) after the addition of the cross-linking agent. Then acetone was added to stop the reaction, and the precipitated polymer was filtered off, washed copiously with distilled water, and further purified by soxhlet extraction using acetone for 12 hours. The polymer was finally lyophilized, and kept in a desiccators.

2,2-Methylene diphenyl diisocyanate cross-linked starch adsorbents

The synthesis of MDI cross-linked adsorbents (MDICS: MDICS1, MDICS2, MDICS3, and MDICS4) was carried out in a similar procedure with that of HDICS by replacing HDI with MDI as cross-linking agent. The quantities of MDI applied for the synthesis of MDICS1, MDICS2, MDICS3, and MDICS4 polymers were 1.70, 5.28, 8.81, and 17.61 g, respectively.

3.3.2 Preparation of Cyclodextrin Adsorbent

3.3.2.1 Preparation of β -Cyclodextrin polymers

Epichlorohydrin cross-linked β-cyclodextrin adsorbents (EPIBCD)

Epichlorohydrin cross-linked β -Cyclodextrin polymer (EPIBCD: EPIBCD1, EPIBCD2, EPIBCD3, and EPIBCD4) was synthesized following the method developed by Solms and Egli (1965), and extended by Komiyama et al. (1985) with some minor modifications consisting of increment in the amount of crosslinking agent in order to obtain mechanically stable polymers. The details of the synthetic procedure are as follows; 12.5 g of β-cyclodextrin was dissolved in 40 ml NaOH (50% w/w) containing 8 mg/L of $NaBH_4$ in a thermostated reactoer vessel maintained at 50-60^{o}C. The mixture was vigorously stirred with a magnetic stirrer until the reactants were dissolved (in approximately 2 hours). The desired amount of EPI (30.0, 40.0, 50.0, and 60.0 ml for EPIBCD1, EPIBCD2, EPIBCD3, and EPIBCD4, respectively) was thereafter added slowly in a drop-wise manner, while stirring continued for about 1 hour later when solid polymer was formed (to the extent that stirring could not be continued in some cases). Thereafter, 40 ml of acetone was added and further stirred for about 5 minutes. Mixtures were allowed to cool, after which the insoluble polymer was poured into a large beaker of water, filtered, and the resulting polymer purified using soxhlet procedure with acetone for 24 hours. The purified polymer was lyophilized and stored in a desiccator before use.

β-cyclodextrin adsorbents based polyurethane polymer adsorbents

For the synthesis of the β-cyclodextrin-based polyurethane polymer adsorbents (diisocyanates cross-linked polymers), a similar procedure with that of diisocyanates cross-linked starch modified by replacing starch with β-cyclodextrin, was adopted. The details were as earlier reported, and in accordance with the method of Ozmen et al., (2007), with the only difference being the replacement of starch with β-cyclodextrin. In this vein, 8.0 g of β-cyclodextrin was reticulated with 1.18, 3.50, 5.90, and 11.80 ml of HDI to produce HDIBCD1, HDIBCD2, HDIBCD3, and HDIBCD4 respectively. Similarly, 8.0 g of β-cyclodextrin was reticulated with 1.76, 5.28, 8.81, and 17.61 ml of MDI to produce MDIBCD1, MDIBCD2, MDIBCD3, and MDIBCD4, respectively.

3.3.2.2 Preparation of γ-cyclodextrin polymers

For the synthesis of epichlorohydrin cross-linked **γ**-cyclodextrin polymer (EPIGCD), 2.0 g of **γ**-cyclodextrin was dissolved in 10.0 ml of NaOH solution (50 % w/w), and stirred at a temperature of 60-70^{o}C for about 2 hours, after which 5.0 ml of epichlorohydrin was added in a dropwise manner, and the stirring continued. After about 4 hours of addition of epichlorohydrin, the reactants were allowed to cool to room temperature, and the **γ**-cyclodextrin polymer product was filtered off, washed copiously with distilled water, purified in a Soxhlet extractor for 12 hours, and dried by lyophilization.

For the synthesis of diisocyanate cross-linked **γ**-cyclodextrin polymer, (HDIGCD and MDIGCD) a similar method to the modified form of Ozmen et al., (2007) was adopted. The details are as follows; 4.0 g of γ-cyclodextrin was dissolved in 20.0 ml DMF in 50 ml capacity thermostated reactor connected to a condenser, and stirred for about 3 hours at 60-70 ^{o}C until the γ-CD dissolved. Thereafter, 1.75 ml (10.56 mM) of HDI and 2.64 g (10.56 mM) of HDI were added into reaction vessels for HDIGCD and MDIGCD polymers, respectively. The stirring was continued further for about 4 hours, after which the recticulation reaction was stopped with 10.0 ml of acetone, and the polymer products washed severally with ethanol and double distilled water. Further purification of the polymers was done with Soxhhlet apparatus using acetone as the purifying solvent for 24 hours, and thereafter the polymers were dried by lyophilization, and kept in a desicator prior to usage.

3.3.3 Preparation of cyclodextrin starch mixed polymers (CDS)

The synthesis of the starch-cyclodextrin mixed polymers was borne out of the thinking that when successfully done, the resultant polymer will possess the vital desirable qualities of both starch and cyclodextrin precursors. For example, starch has better swelling properties while CD has inclusion properties. It is therefore expected that copolymers synthesized from these two precursors will combine these two desirable qualities.

3.3.3.1 Epichlorohydrin based β-cyclodextrin-starch mixed polymers (EPICDS)

The synthesis of EPI based β-cyclodextrin-starch copolymer (EPIBCDS: EPIBCDS1 and EPIBCDS2) was done by copolymerization (co-crosslinking) of both β-cyclodextrin and starch with EPI in the same reaction vessel. The detailed procedure is as follows: 2.5 g of starch and 10.0 g of β-cyclodextrin were dissolved in 25ml of 20 % NaOH, and stirred in thermostated vessel at 50-70 ^{o}C until all the reactants were dissolved. 30.0 and 60.0 ml of EPI (for EPIBCDS1 and EPIBCDS2, respectively) was thereafter added into the solution in a drop-wise manner, and the copolymerisation products were formed in 30 minutes to 1 hour. After washing with double distilled water, the polymer was purified in Soxhlet apparatus for 12 hours and thereafter lyophilized. This same procedure was adopted for the synthesis of EPI based starch γ-cyclodextrin copolymer (EPIGCDS) by replacing the β-CD with γ-CD in the entire procedure. In this regards, mixture of 0.5 g of starch and 2.0 was copolymerized with 4.0 ml of EPI to produce EPIGCDS polymer.

3.3.3.2 Diisocyanates based starch cyclodextrin mixed polymer

The synthesis of this group of polymers [HDI γ-cyclodextrin starch polymer (HDIGCDS), HDI β-cyclodextrin starch polymer (HDIBCDS), MDI γ-cyclodextrin starch polymer (MDIGCDS), and MDI β-cyclodextrin starch polymer (MDIBCDS)] was done according to the method of Ozmen *et al.*, (2007) by cross-linking 1:4 mixture of starch and the respective cyclodextrin (β or γ) with HDI (HDIGCDS and MDIBCDS) and MDI (MDIGCDS and MDIBCDS). The details of the procedure is as follows; for the synthesis of HDIGCDS and HDIBCDS, mixture of 1.0 g of starch and 4.0 g of cyclodextrin (γ and β forms for HDIGCDS and HDIBCDS, respectively) was copolymerized with 4.41 and 2.64 g of MDI to produce HDIGCDS and HDIBCDS, respectively. In a similar vein, the synthesis of MDIGCDS and MDIBCDS applied a mixture of 1.0 g of starch and 4.0 g of cyclodextrin (γ and β forms for MDIGCDS and MDIBCDS, respectively) copolymerized with 4.41 and 2.64 g of MDI, to produce MDIGCDS and MDIBCDS, respectively.

3.3.4 List of the prepared adsorbents

In summary, the following adsorbents were successfully synthesized.

Starch based polymer adsorbents

EPICS (Epichlorohydrin crosslinked starch); variants: EPICS1, EPICS2, EPICS3, EPICS4, EPICS5, and EPICS6

EPIACS (aminated epichlorohydrin crosslinked starch); variants: EPIACS1, EPIACS2, and EPIACS3

EPIMACS (methyl aminated epichlorohydrin crosslinked starch); variants: EPIMACS1, EPIMACS2, and EPIMACS3

HDICS (1,6-hexamethylene diisocyanatecross-linked starch); variants: HDICS1, HDICS2, HDICS3, and HDICS4

MDICS (2,2-methylene diphenyl diisocyanate cross-linked starch); variants: MDICS1, MDICS2, MDICS3, and MDICS4.

β-cyclodextrin based polymer adsorbents

EPIBCD (Epichlorohydrin crosslinked β-cylodextrin); variants: EPIBCD1, EPIBCD2, EPIBCD3 and EPIBCD4.

HDIBCD (1,6-hexamethylene diisocyanate cross-linked β-cylodextrin); variants: HDIBCD1, HDIBCD2, HDIBCD3, and HDIBCD4.

MDIBCD (2,2-methylene diphenyl diisocyanate cross-linked β-cylodextrin); variants: MDIBCD1, MDIBCD2, MDIBCD3, and MDIBCD4.

γ-cyclodextrin based polymer adsorbents (one variant each)

EPIGCD (Epichlorohydrin crosslinked γ-cylodextrin)

HDIGCD (1,6-hexamethylene diisocyanate cross-linked γ-cylodextrin).

MDIGCD (2,2-methylene diphenyl diisocyanate cross-linked γ-cylodextrin).

Mixed polymers (one variant each)

EPIGCDS (Epichlorohydrin crosslinked γ-cylodextrin starch), EPIBCDS (Epichlorohydrin crosslinked β-cylodextrin starch), HDIGCDS (1,6-hexamethylene diisocyanate cross-linked γ-cylodextrin starch), HDIBCDS (1,6-hexamethylene diisocyanate cross-linked β-cylodextrin starch), MDIGCDS (2,2-methylene diphenyl diisocyanate cross-linked γ-cylodextrin starch), and MDIBCDS (2,2-methylene diphenyl diisocyanate cross-linked β-cylodextrin starch).

3.4 Characterization of adsorbents

The prepared adsorbents were characterized by IR spectrophotometer, elemental analyzer, surface area and porosity analyzer, scanning electron microscope, and thermogravimetric/differential thermal analyzer.

3.4.1 Fourier Transform Infra-red (FT-IR) spectrophotometry

Infra-red (IR) spectra of the synthesized polymer adsorbents were obtained using Perkin Elmer Spectrum 1 FTIR spectrophotometer, using the scanning frequency of 4000–450 cm^{-1}, to investigate the functional groups introduced as a result of the cross linking reaction. About 0.1 g of the dry adsorbent in powder form along with KBr were ground into fine particles and pressed to make pellets, which was used to obtain the IR spectra.

3.4.2 Elemental Analysis

Dry weight-based carbon, hydrogen and nitrogen contents of synthesized adsorbents were determined by Elementar (Germany) Vario Macro Cube elemental analyzer to investigate the percentage carbon (f_C), Hydrogen (f_H) and Nitrogen (f_N) contents. Since the content of other elements are negligible, the oxygen content (f_O) was calculated by equation of $f_O = 100 - f_C - f_H - f_N$. The data generated was used to comparatively assess the levels of hydrophobicity, polarity, aromaticity, polarizability, and the degree of the cross-linking of the various polymer adsorbents and their respective precursors.

3.4.3 Brunauer Emmett Teller (BET)

In this study, the surface area measurements were done on Micromeritics ASAP 2020 Model instrument. Approximately 0.5 g of the synthesized adsorbents was subjected to classical nitrogen gas adsorption surface area measurement at liquid nitrogen temperatures.

The surface areas were determined from the BET plot of the N_2 adsorption data at liquid N_2 temperature (77 K) and relative pressures (P/Po) between 0.05 and 0.20. Eight (8) data points were used to construct the plot to derive the monolayer adsorption capacity, from which the surface area was calculated using the N_2 molecular area of 16.2×10^{-20} m^2. The open surface areas and the micropore volumes were determined from t-plots (de Boer et al., 1966) by use of the N_2 adsorption data. The details for the plots and calculation of BET surface area using the N_2 adsorption data are shown in Appendix II.

3.4.4 Scanning Electron Micrographs (SEM images)

Hitachi S4800 model SEM instrument was used for visual characterization to obtain information of the surface characteristics and subsequently study the effect of the cross linking process on the surface morphology of the cross-linked polymer materials as against the starch and cyclodextrin precursors. Samples used in this study were used in the granular and powdery forms and in some cases, coated with gold to improve visibility. All samples were subjected to beam energy of 15 kV.

3.4.5 Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Perkin Elmer Pyris 1 TGA instrument was used for thermal analyses of the polymer materials to investigate the thermal behaviour, phase changes and decomposition pattern of the prepared adsorbents. The weight loss was measured on 10-20 mg of the polymer using linear temperature programming ($10^{o}C/min$) under air, and this enabled the determination of the stability of polymers at high temperatures.

3.5 Adsorption studies

Adsorption studies involved the application of the synthesized adsorbents in adsorption experiments for the removal of adsorbates (PAHs and phthalates) following standard adsorption procedures. The adsorption studies were done in three broad categories viz: (i) screening adsorption study (ii) study of PAHs adsorption onto the cross-linked adsorbents, and (iii) study of phthalates adsorption onto the cross-linked adsorbents.

3.5.1Adsorption procedure

The adsorption procedure consisted of the standard adsorption set-up and the instrumental determination of the levels of PAHs and phthalates in the aqueous solutions.

3.5.1.1Adsorption Setup

Batch adsorption method was adopted for this study using simulated PAHs/phthalates polluted water. The simulated PAHs (Acenaphthylene, Fluorene, Phenanthrene, and Benzo[a]Anthracene) and phthalates (DMP and DEP) polluted water samples were prepared in synthetic ground water (deionized water containing 44 mgl^{-1} $CaCl_2.H_2O$) to mimic environmental water. Due to low water solubility, PAH stock solutions were made at high concentrations in methanol, from which the working solutions of desired concentrations were obtained by serial dilution. Sodium azide was added at a concentration of 200 mg/L to prevent PAHs/phthalates biodegradation. The carrier solvent (methanol) was assumed to have no effect on solute equilibrium behavior due to its low concentration (< 0 .1% v/v) in the final experimental solution. Single solute PAHs/phthalates solutions were applied for all the adsorption studies, except for the competitive adsorption study where both single and binary PAHs solutions were applied. The working concentration was chosen with due consideration on the solubility of the respective polycyclic aromatic hydrocarbon.

Batch adsorption experiments were carried out by agitating aliquots (variable for different adsorption experiments) of simulated PAH/phthalate polluted water samples with desired dose of adsorbent in 100 ml capacity glass stopped Erlenmeyer flasks covered with aluminum foil, at 170 rpm at room temperature (25 ± 2^{o}C), except for thermodynamic study, using a horizontal shaker. After adsorption equilibrium was attained, the PAH/phthalate solution was separated from the adsorbent by centrifugation at 3500 rpm for 20 minutes, and the equilibrium PAHs concentration (the level of PAHs/phthalates remaining in solution) was determined using HPLC method. The quantity of PAHs/phthalates adsorbed at equilibrium (equilibrium sorption capacity) was estimated by mass balance as explained in data treatment section. All the adsorption experiments were performed in duplicates.

As a precaution, a blank study was done by carrying out adsorption study with a 20.0 mg of the adsorbent using 100 ml aliquots of Milli-Q water (organic-free water) to check whether the adsorbent could release PAHs/phthalates in the aqueous solution. Also, for every experiment, adsorbent free PAH/phthalate solutions (PAH/phthalate solutions without any adsorbent added to it) were subjected to the same experimental conditions to evaluate the loss of PAHs to factors, other than adsorption.

3.5.1.2 Instrumental Determination of Equilibrium Levels of PAHs/Phthalates

Equilibrium levels of PAHs/phthalates were quantified using PerkinElmer series 200 (USA) High Performance Liquid Chromatography (HPLC) system with Brownlee Analytical (PerkinElmer, USA) PAH reverse phase column (150 x 3.2 mm, 5 µm, 110Å) equipped with Series 200 Fluorescence and Series 200 photo diode array (PDA) UV

Detectors in series connection. Acenaphthylene was monitored with UV detector at UV absorbance of 254nm, while Fluorene, Phenanthrene, and Benzo[a]Anthracene were monitored with fluorescence detector at the excitation wavelength of 224, 252, and 238 nm and emission wavelength of 320, 370, and 398 nm respectively. Phthalates (DMP and DEP) were also monitored with UV at the absorbance of 254nm. Isocratic elution was adopted using acetonitrile and water in the ratio of 70:30

3.5.2 Screening adsorption study

This study was done to select the adsorbents (from the array of synthesized polymers) that exhibited good adsorption performance for detailed adsorption study. The screening study was also simultaneously applied to investigate the effect of chemical nature of the polymer adsorbents (effect of the nature of cross linking and amination agent, as well as the degree of cross linking and amination of the adsorbents) on the adsorption capacities of the various synthesized adsorbents.

The screening adsorption study for PAHs was done by agitating 50 ml aliquots of 3.0 mg/L, 1.0 mg/L and 1.0 mg/L of acenaphthylene, phenanthrene and Benzo[a]anthracene respectively, with 50 mg aliquots of all the synthesized polymers to select the ones with good sorption properties for further detailed studies. To compare the sorption capacities of the adsorbents to a standard, granulated activated carbon was subjected to this same adsorption condition to assess its capacity under these conditions.

For phthalates, the screening adsorption applied all the synthesized adsorbents with diethyl phthalate (DEP) as model phthalate. The study was done by agitating 50 ml aliquots of 4.2 mg/L DEP with 20 mg aliquots of all the synthesized polymers to select the ones with good sorption properties for further detailed studies. Similarly, granulated activated carbon was subjected to this same adsorption condition to assess its capacity under these conditions.

3.5.3 Study of PAHs adsorption onto the cross-linked adsorbents

After the screening adsorption studies, the adsorbents that showed high adsorption capacity (MDICS4, HDICS4, MDIBCD3, MDIGCD, MDIBCDS, and MDIGCDS) were selected for detailed adsorption studies. For ease of classification based on cross-linking agents and avoiding ambiguity in names of the adsorbents, MDICS4, HDICS4, and MDIβCD3 were re-designated as MDICS, HDICS, and MDIBCD respectively, since each of them represented their respective families.

In order to investigate the various factors that affect adsorption from aqueous solution, the standard adsorption set-up was adopted and only one factor was varied each time while others were kept constant. Several factors were investigated as detailed in the following sections.

Effect of Sorbent Dose

Batch adsorption study for effect of adsorbent dose was conducted by agitating variable doses of MDICS, HDICS, MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS (5, 10, 15, 25, 35, and 50 mg) of polymer adsorbents with 50 ml aliquot of 1.0 mg/L simulated phenanthrene solution.

Effect of contact time and kinetics study

The effect of contact time and kinetic experiment for all the adsorbents (MDICS, HDICS, MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS) was done by agitating 20.0 mg of adsorbent with 100 ml aliquots of 1.0 mg/L phenanthrene solution, while the residual phenanthrene concentration was monitored at contact times of 10, 30, 90, 180, 360, 720, and 1440 min. Similarly, 20.0 mg of adsorbents (MDICS, MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS) were agitated with 100 ml aliquots of 1.5 mg/L fluorene solution, and the residual fluorene concentration was monitored at contact times of 10, 30, 90, 180, 360, 720, and 1440 minutes. All the kinetics experiments were done at room temperature.

Effect of temperature and thermodynamics study

Study of the effect of temperature on the adsorption of phenanthrene for all the adsorbents (MDICS, MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS) was carried out by agitating 10.0 mg of the adsorbent with 50 ml aliquots of 1.0 mg/L phenanthrene solution for 12 hours at various temperatures (25, 45, 65, and 85 °C). In a similar experiment, the effect of temperature on the adsorption of acenaphthylene was studied by agitating 10.0 mg of the adsorbent with 50 ml aliquots of 1.5 acenaphthylene solution for 12 hours at various temperatures (25, 45, 65, and 85 °C).

In a somewhat different experiment, the effect of temperature on the rate of adsorption of PAHs was studied by agitating 10.0 mg of HDICS and MDICS adsorbents with 100 ml aliquot of 1.0 mg/L phenanthrene solution at three different temperatures of 25, 45, and 60°C, while the residual phenanthrene concentration was monitored at contact times of 10, 30, 90, 180, 360, 720, and 1440 minutes. This same procedure was repeated using 1.5 mg/L acenathylene solution.

Effect of initial PAHs concentration and isotherm study

Phenanthrene was adopted for a comparative assessment of the effect of initial concentration and isotherm studies of all the adsorbents (MDICS, HDICS, MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS). In this vein, the effect of initial concentration and isotherm study for adsorption of phenanthrene onto MDICS and HDICS was conducted with 10 mg and 20 mg of MDICS and HDICS, respectively, using 50ml aliquot of 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 mg/L phenanthrene solution. Similarly, the effect of initial concentration on adsorption of phenanthrene onto MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS adsorbents was investigated with 10 mg of adsorbents using 50 ml aliquots of 0.2, 0.35, 0.50, 0.65, 0.80, 0.95, and 1.10 mg/L phenanthrene solution. Experiments were carried out at phenanthrene concentrations of 0.2, 0.4, 0.6, 0.8, 0.1 and 1.2 mg/L, and at acenaphthylene concentrations of 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 mg/L.

Acenaphthylene was adopted for a comparative assessment of the effect of initial concentration on MDICS and HDICS (originating principally from different cross-linking agents). In this guise, the effect of initial concentration on adsorption of acenaphthylene onto MDICS and HDICS was conducted with 10 mg of MDICS and HDICS, using 50ml aliquot of 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 mg/L phenanthrene solution.

Fluorene was adopted for assessment of the effect of initial concentration on MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS. In this vein, the effect of initial concentration on adsorption of fluorene was conducted with 10 mg aliquot of MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS, using 50ml aliquot of 0.25, 0.50, 0.75, 1.0, 1.25, 1.5, and 1.75 fluorene solution.

Effect of pH of the aqueous solution

The study for the effect of pH of aqueous solution on the adsorption performance of the adsorbents was carried out by agitating 10 mg aliquot of MDICS and HDICS, respectively, using 50ml aliquot of 1.0 mg/L phenanthrene solution at pH values of 3.5, 5, 6.5, 8, 9.5 and 11. The pH adjustment of the phenanthrene solutions was done by adding drops of either 0.05M HCl or 0.05M NaOH. Phenanthrene solution without pH adjustment (6.2) was also used.

Effect of water hardness (Ca^{2+} ions) and salinity (Na^{+} ions)

Anhydrous $CaCO_3$ was used to prepare aqueous solution of 50.0, 75.0, 100.0, 125.0, and 150.0 mg/L as $CaCo_{3.}$ Effect of water hardness was studied by agitating aliquots of 10.0 mg of HDICS and MDICS adsorbents with 50ml aliquot of 1.0 mg/L phenanthrene solution having varying aqueous $CaCO_3$ concentration of 50.0, 75.0, 100.0, 125.0, and 150.0 mg/L.

For the effect of salinity, solutions of different Na^{+} ionic strength (0, 0.01 0.05, 0.10, 0.25, 0.5M of Na^{+}) were prepared using NaCl. Effect of salinity was studied by agitating aliquots of 10.0 mg of HDICS and MDICS adsorbents with 50ml aliquot of 1.0 mg/L phenanthrene solution having different Na^{+} ionic strength (0, 0.01 0.05, 0.10, 0.25, 0.5M of Na^{+}).

Effect of competition

The effect of competition on the adsorption capacity of the PAHs was investigated using binary solute solution system (phenanthrene/acenaphthylene and phenanthrene/fluorene). For each system, the solution concentration of analyte of interest (phenanthrene) was kept constant at 1.0 mg/L, while that of co-solute/competitor (acenaphthylene or fluorene) was adjusted from 0 .0, 0.4, 0.8, 01.2, 1.6, to 2.0. Batch experiments were conducted with the various concentration specifications of the binary solute solution system using adsorbent/solution ratio of 10 mg/50 ml.

Effect of particle size

Batch adsorption experiments containing 10 mg aliquots of adsorbents (MDICS and HDICS) in 50 ml aliquot of 1.8 mg/L fluorene solutions were performed using adsorbents of different particle sizes: size 1 (less than 0.125mm), size 2 (0.125 – 12.7mm), size 3 (12.7 – 25.4mm) and size 4 (above 25.4mm). The study was designed to elucidate the effects of particle size not just on equilibrium sorption capacity alone, but also on the rate of adsorption. Hence, the residual phenanthrene concentration was monitored at contact times of 10, 30, 90, 180, 360, 720, and 1440 min.

3.5.4 Study of phthalates adsorption onto the cross-linked adsorbents

The adsorbents studied for adsorption of phthalates (DMP and DEP) were MDICS, MDIGCD, and MDIGCDS polymer adsorbents. The parameters studied for the adsorption of phthalates were effects of contact time and kinetics, pH, salinity, temperature and thermodynamics, initial phthalate concentration and equilibrium, and sorbent dose.

Effect of contact time and kinetic study

The effect of contact time and kinetic experiment was done by agitating 50.0 mg of adsorbent (MDICS, MDIGCD, and MDIGCDS) with 100 ml aliquot of 8.0 mg/L DMP and DEP solution. while the residual phthalates concentration was monitored at contact times of 10, 30, 90, 180, 360, 720, and 1440 min.

Effect of pH, water hardness (Ca^{2+}) and salinity (Na^+)

The study for the effect of pH was carried out by agitating 20 mg aliquot of adsorbent (MDICS, MDIGCD, and MDIGCDS) and 50ml aliquot of 4.0 mg/L DEP solution at pH values of 3.5, 5, 6.5, 8, 9.5 and 11. The effect of water hardness (Ca^{2+}) and salinity (Na^+) were studied in a similar manner using solutions of different ionic strength (50.0, 75.0, 100.0, 125.0, and 150.0 mg/L of $CaCO_3$ for water hardness and 0, 0.01 0.05, 0.10, 0.25, 0.5M of Na^+ for salinity).

Effect of initial phthalate concentration

The effect of initial phthalate concentration was studied by varying the initial concentrations from 2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5, and 20.0 mg L^{-1} for both DMP and DEP. Study of the effect of temperature was carried out in a rate determination experiment at temperatures of 25, 45 and 60 °C using 8.0 mg L^{-1} of DMP and DEP.

Effect of adsorbent dose

The effect of adsorbent dose was studied by agitating 10, 20, 30, 40, 50, 70 and 100 mg of polymer adsorbents with 50 ml aliquot of 4.0 mg/L DEP solution.

Effect of temperature and thermodynamic studies

In order to investigate the effect of temperature both on the adsorption rate and adsorption capacity, this study was done kinetic wise. In this vein, the effect of temperature was studied by repeating the experimental procedure for effect of contact time and kinetics at temperatures of 25, 45, and 60°C.

3.5.4 Data treatment for adsorption studies

3.5.4.1 Batch adsorption study

The equilibrium PAHs/phthalate adsorption capacity (quantity of PAHs/phthalates adsorbed at equilibrium) was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{M} \qquad 3.8$$

where q_e is the equilibrium sorption capacity (mg/g); C_o and C_e (mg/L) are adsorbate (PAHs/phthalates) concentrations before and after adsorption, respectively; V is the volume of the experimental solution (L); M is the mass of adsorbent (g),

The mean adsorption capacity for each family of the adsorbents $\bar{q}_{eA}$, was calculated according to equations 3.9.

$$\bar{q}_{eA} = q_{eA1} + q_{eA2} + q_{eA3} + q_{eA4} \qquad 3.9$$

where $\bar{q}_{eA}$ is the mean adsorption capacity for each family of adsorbents (mg/g), q_{eA1}, q_{eA2}, q_{eA3}, and q_{eA4} are the sorption capacities of individual adsorbents that comprised each of the adsorbent families (A), thus A represents the following families of adsorbents: EPICS, HDICS, MDICS, EPIBCD, HDIB CD, and MDIBCD.

3.5.4.2 Study of correlation between the batch adsorption performance and the DFT theoretical predictions

Linear correlation analysis was applied for evaluation of the relationship between the batch adsorption performances of cross-linked adsorbents and the DFT theoretical predictions.

The values of DFT based quantum chemical descriptors reflect the nature of the cross-linking process. Therefore, to evaluate the correlation for the effect of nature of cross-linking process for starch adsorbents, the mean adsorption capacities $\bar{q}_{eA}$, for EPICS, HDICS and MDICS for a given adsorbate, were linearly correlated with the respective values of DFT quantum parameters for these adsorbents. To evaluate the correlation for the DFT quantum prediction based on ΔE, the values of $\bar{q}_{eA}$ for EPICS, HDICS and MDICS for acenaphthylene was correlated with the values of ΔE for these adsorbents. The $\bar{q}_{eA}$ values for phenanthrene, benzo[a]anthracene, and DEP were also similarly correlated with the ΔE of these adsorbents, to study the correlation between experimental adsorption of these pollutants and predicted trend based on energy gap. The same procedure was adopted for correlation of experimental adsorption and η, S and dipole moment predicted trend. The entire procedure was repeated for the study of β-cyclodextrin polymer adsorbents using the $\bar{q}_{eA}$ values for EPIBCD, HDIBCD and MDIBCD for a given adsorbate and the respective DFT quantum parameters.

To evaluate the correlation between theoretical prediction and experimental adsorption for the effect of degree of cross-linking process, the adsorption capacity q_e, for individual adsorbents was correlated with their respective values of arbitrary degree of cross-linking process for each family of adsorbents.

3.5.4.3 Study of the mechanism of adsorption

To study the kinetic mechanism of the adsorption process, the kinetic data generated were interpreted using the linear forms of pseudo first order, pseudo second order, liquid film diffusion, and Morris–Weber intra-particle diffusion kinetic equations as reviewed earlier (in chapter two) and repeated here (for clarity) as follows:

Pseudo First Order $$\ln(q_e - q_t) = -k_1 t + \ln q_e \qquad 2.1$$

Pseudo Second Order $$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$$ 2.2

where, q_e and q_t are the amounts of PAHs sorbed (mg/g) at equilibrium and at any time, t respectively, k_1 (l/min) is the pseudo-first order rate constant, and k_2 (g/mg/min) is the pseudo-second order rate constant. The initial rate constant h, is calculated as $h = k_2 q_e{}^2$. The values of k_2, h, and q_e for pseudo second order model were evaluated from the linear plots of t/q_t vs. t, while the values of k_1, and q_e for pseudo first order were evaluated from the linear plots of $\ln(q_e - q_t)$ vs. t.

Liquid Film Diffusion

$$\ln(1 - \frac{q_t}{q_e}) = -R^i t$$ 2.4

Morris-Weber Intra-particle Diffusion

$$q_t = k_{id} t^{1/2} + C_i$$ 2.7

where $\frac{q_t}{q_e}$ is the fractional attainment of the equilibrium, R^i is the diffusion rate parameter for film diffusion model, k_{id} is the diffusion rate parameter for intraparticle diffusion model, and C_i is a constant related to adsorption on the surfaces of the pores.

The surface properties and degree of affinity of the adsorbents were studied by fitting the adsorption data into four equilibrium isotherms: Langmuir, Freundlich, Tempkin and Brauner-Emmet-Teller (BET). The linear forms of these models (as reviewed earlier and restated here for clarity) were employed.

Langmuir Equation $$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L}(\frac{1}{C_e})$$ 2.8

Freundlich Isotherm $$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad 2.9$$

where q_{max} (mg/g) and q_e is the maximum adsorption and amount of solute adsorbed per unit weight of adsorbent (mg/g), respectively. C_e is same as above; K_L, K_f, and n are isotherm constants obtained from the slopes and intercepts.

Tempkin Isotherm $$q_e = B\ln A + B\ln C_e \qquad 2.10$$

$$\text{where} \quad B = \frac{RT}{b}$$

where R, T and b is the gas constant, the absolute temperature in Kelvin, and the constant related to the heat of adsorption respectively. C_e and q_e are the same as above, and A is the Temkin isotherm constant.

BET isotherm $$\frac{C_e}{(C_s - C_e)q_e} = \left(\frac{K_B - 1}{K_B Q^o}\right)\frac{C_e}{C_s} + \frac{1}{K_B Q^o} \qquad 2.11$$

where Cs is the saturation concentration (solubility limit) of the solute in mg/L, K_B is a constant related to the energy of interaction with the surface and the subsequent layers of adsorbates and Q^0 is the amount of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface.

The thermodynamic parameters of enthalpy (ΔH), entropy (ΔS) and free energy change (ΔG) of the adsorption process were evaluated with equations 2.9 and 3.0

$$\ln\frac{q_e}{C_e} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad 3.10$$

$$\Delta G = \Delta H - T\Delta S \qquad 3.11$$

where q_e and C_e are as explained initially, T is the absolute temperature in Kelvin (K) and R is universal gas constant (8.3144 J /mol/K).

3.6 Desorption and Regeneration Studies

100 mg of polymer adsorbent (HDICS, MDICS, MDIGCD, MDIBCD, MDIGCDS and MDIBCDS) was adsorbed with PAHs using 100 ml aliquot of multiple solute solution of 3.0, 1.5, 1.0, and 5.01 mg/L of acenaphthylene, fluorene, phenanthrene and DEP, respectively, under conditions of the equilibrium experiment in a 100 ml capacity Erlenmeyer flask. After sorption equilibrium was reached, the adsorbent was separated from the solution by suction filtration and thereafter dried by lyophlization, and the residual concentration of PAHs in the solution was determined. Thereafter, the Erlenmeyer flask was refilled with 100 ml of desorption solvent (organic solvent) and shaken with the loaded adsorbent at 180 rpm for 4 hours, after which the adsorbent was filtered off, and desorption equilibrium concentration $C_{desorbed}$, of PAHs and DEP, was determined.

To study the effect of desorption solvent, methanol, hexane, dichloromethane, and acetone were individually applied for the desorption study. Desorption kinetics was studied by determining the desorbed quantity at time of 2, 5, 10, 20, 30, 60, and 120 minutes. All the experiments were performed in duplicates.

The quantity of PAHs/phthalates adsorbed by the adsorbent q_e (or q_{ads}) was calculated as described earlier in equation 3.8 while the desorbed quantity q_{des} was calculated according to equation 3.12. Desorption efficiency was evaluated in terms of the ratio of the quantity desorbed q_{des} to that of the quantity adsorbed q_{ads}. Hence desorption efficiency DE was calculated according to equation 3.13.

$$q_{des} = \frac{C_{des}V}{m} \qquad 3.12$$

$$DE = \left(\frac{q_{des}}{q_{ads}}\right)\frac{100}{1} = \left(\frac{C_{des}}{C_o - C_e}\right)\frac{100}{1} \qquad 3.13$$

where $(C_o - C_e)$ and C_{des} represent the adsorbed and desorbed concentrations, respectively, and V and m are as explained earlier.

The regenerability test was done by loading (adsorption) the adsorbents with adsorbates (acenaphthylene, phenanthrene, fluorene and DEP) and regenerating (desorption) them following the procedure for the desorption studies, and thereafter applying these regenerated adsorbents for fresh adsorption studies. The adsorption capacities of the pristine and the regenerated adsorbents were evaluated to assess the regeneration efficiency. The regeneration efficiency was calculated as the percentage ratio of adsorption capacities of the regenerated adsorbent to that of the pristine adsorbent as shown in equation 3.14.

$$RE = \left(\frac{q_r}{q_e}\right)\frac{100}{1} \qquad 3.14$$

where q_e and q_r represent adsorption capacities for pristine and regenerated adsorbents, respectively.

3.7 Application of the developed adsorbents in real environmental water treatment

The applicability of the developed adsorbents for treatment of real water samples was tested with water samples collected from Sahe river (40°7'43.36"N, 116°19'9.43"E) and Shangzhuang (40°5'59.6"N, 116°12'17.3"E) reserviour of Beijing, China. The initial PAHs concentration was first determined following standard procedure, after which aliquots of the samples were spiked with 1.0 mg/L mixed concentrations of acenaphthylene, phenanthrene, and fluorene. Adsorption performance of the developed adsorbents was studied by applying 10 mg of the adsorbents on 100 ml of both spiked and un-spiked water samples following standard procedure.

3.8 Application of the developed adsorbents for preconcentration (SPE/HPLC method developement)

Solid phase extraction (SPE) was adopted as preconcntration method for this study. The SPE procedure involved the preparation of the SPE cartridges using the developed adsorbents, the optimization of the vital SPE parameters, evaluation and validation of the SPE method, and application of the developed method in real environmental samples. The application of the adsorbents as SPE phase for pre-concentration of PAHs (16 US EPA priority PAHs) and phthalates (DMP, DEP, and DEHP) in water samples was done separately for PAHs and phthalates.

3.8.1 Solid Phase Extraction pre-concentration study for PAHs

3.8.1.1 Preparation of the SPE cartridge

Polyethylene frit was first set at the bottom of polypropylene SPE column, after which a 250 mg aliquots of the adsorbent (MDICS, MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS) was packed into the 6 ml capacity polypropylene SPE column. Another polyethylene frit (guard frit) was set to hold the adsorbent in place, and thereafter, a subtle hand pressure was applied using a cylindrical glass rod, to make the packing compact. The prepared cartridge was thereafter considered to be ready for use in SPE studies.

3.8.1.2 Solid phase extraction standard procedure

In order to reduce the interferences of organic and inorganic contaminants, the entire SPE assembly was first successively washed with 50 mL each of dichloromethane, methanol, acetonitrile and 100 mL of ultrapure water before the first use. With the aid of adaptors, the outlet tip of the cartridge was connected to Solid-Phase Extraction Vacuum Manifolds (Agilent, USA), and the inlet end of cartridge was connected to PTFE suction tube of which other end was inserted into sample solution. The cartridge was first conditioned successively with 10 mL aliquots of methanol (to remove air and leach impurity), and ultrapure water (to equilibrate the solid phase), prior to sample loading. A known volume of water samples (simulated and real) was loaded at a known flow rate, immediately after conditioning. After loading, the cartridge was dried in vacuum (using negative pressure) at room temperature for 25 min to remove residual water. The analytes retained on the cartridge were eluted using aliquots of eluent (elution solvent) at a known flow rate. The eluates were collected into a test tube and evaporated to dryness using a rotary evaporator at 30^{o}C, and re-dissolved with 1 mL acetonitrile. The reconstituted extract was thereafter taken for HPLC-UV/FLD analysis.

HPLC instrumental analysis

All PAH extracts were analyzed using equipment from Perkin-Elmer (PE, Norwalk, CT, USA). The HPLC system consisted of a Series 200 analytical micro pump, Series-200 autosampler, Series 200 Fluorescence and Series 200 UV Detectors in series connection.

PAHs separation was done on a Brownlee analytical PAH reverse phase column (150 x 3.2 mm, 5 µm, 110Å), applying acetonitrile and water as mobile phase at the flow rate of 0.6 ml/min. The PAHs were separated with the following gradient program: maintaining 85% A for 8 min; followed by a linear gradient from 85% A at 8 min to 100% A at 30 min, and returning linearly to 85% A in 5 minutes, and thereafter maintaining 85% A for 5 min. The column temperature was 35^{o}C, and the chromatographic peaks for all the PAHs were detected at the wavelength of 254 nm for UV detector and the excitation and emission wavelengths shown in Table 3.1 for fluorescence detector. The excitation and emission bandwith applied for the fluorescence detector programme was 10 nm. The injection volume was 10µL. HPLC data acquisition and handling was managed with Totalchrom data acquisition program version 6.3.1 from PerkinElmer (USA).

3.8.1.3 Adsorbent selection

Some of the adsorbents that proved effective in the adsorption study for the remediation of PAHs polluted water were considered for their suitability as SPE adsorbents.

The adsorbents applied were MDICS, MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS. The adsorbent particle size was 60 mesh. To study the suitability of these adsorbents, each of the adsorbents was packed into SPE cartridge according the procedure explained earlier. The packed cartridges were subjected to SPE study following the SPE standard procedure as outlined earlier, and using simulated PAHs polluted water samples. The study was conducted according to the following conditions; Sample volume: 500 ml, Sample flow rate: 5 ml/minute, Elution solvent: DCM/Hexane mixture (50:50), Elution volume: 15 ml, Elution flow rate: 0.9 ml/minute. The selected adsorbent was further used for all the subsequent optimization studies.

3.8.1.4 SPE experiments for optimization of SPE parameters

MDICS polymer was selected from adsorbent selection experiment as the SPE for full optimization. The optimization experiments for SPE parameters applied the SPE standard procedure, and only one parameter was varied in each optimization experiment, while other parameters were kept constant.

Table 3.1. Excitation and emission wavelength for fluorescence detection

Constituent PAHs	Excitation wavelength	Emission wavelength
Naphthalene	224	330
Acenaphthylene	not detected	
Acenaphthene	234	320
Fluorene	224	320
Phenanthrene	224	320
Anthracene	250	370
Fluoranthene	252	402
Pyrene	238	398
Benzo (a) anthracene	238	398
Chrysene	238	398
Benzo(b)fluoranthene	268	398
Benzo(k)fluoranthene	268	398
Benzo(a)pyrene	268	398
Dibenzo(a,h)anthracene	234	420
Benzo(g,h,i)perylene	234	420
Indeno(1,2,3-cd)pyrene	300	466

Preliminary Experiments

The first preliminary experiment was designed to evaluate the pump pressure that will generate a given flow rate, and thus establish the pressure-flow rate relationship for the SPE set-up. This was necessary due to the fact that the vacuum pump was calibrated in pressure unit. The preliminary study therefore applied known pressure values for a given time duration, and estimated the flow rate based on the volume of water that flowed through the SPE column within this time duration.

This procedure was repeated three times, and thereafter, the mean value of flow rate per unit pressure was estimated. This mean value was used for calculating the corresponding pressure for a desired flow rate values for other experiments.

Another preliminary experiment carried out was the parameter of drying time of the sorbent after sample loading. Drying times of 15, 20, 25, 30, and 35 minutes were studied. To study the drying time, dichloromethane (DCM) was chosen as elution solvent, because it is immiscible with water.

Nature of elution solvent

To study the effect of nature of elution solvent, the packed SPE cartridges were loaded with spiked water samples containing 2.0 µg/L (0.002 mg/L) US EPA PAH mix following the SPE standard procedure, and the effect of nature of elution solvent was assessed by eluting the loaded cartridges with dichloromethane, acetonitrile, methanol, acetone, and 50:50 mixture of dichloromethane/hexane. Other parameters were fixed as follows; sample volume: 500 ml, sample flow rate: 4.5 ml/min, elution volume: 15 ml, and elution flow rate: 1.0 ml/min.

Effect of elution volume

To study the effect of volume of elution solvent, the packed SPE cartridges were loaded with spiked water samples containing 2.0 µg/L (0.002 mg/L) US EPA PAH mix following the SPE standard procedure, and the effect of volume of elution solvent was assessed by eluting the loaded cartridges with 5.0, 7.0, 10.0, 15.0, and 20.0 ml of dichloromethane. Other parameters were fixed as follows; sample volume: 500 ml, sample flow rate: 3.5 ml/min, ml, and elution flow rate: 0.7 ml/min.

Effect of elution flow rate

To study the effect of elution flow rate, the packed SPE cartridges were loaded with spiked water samples containing 2.0 µg/L (0.002 mg/L) US EPA PAH mix following the SPE standard procedure, and the effect of volume of elution flow rate was assessed by eluting the loaded cartridges with dichloromethane at flow rates of 0.456, 0.891 and 1.452 ml/minute. Other parameters were fixed as follows; sample volume: 500 ml, sample flow rate: 3.5 ml/min, and elution flow rate: 1.0 ml/min.

Effect of sample volume

To study the effect of volume of water samples, the packed SPE cartridges were loaded with 500, 1000 and 1500 ml of spiked water samples containing 2.0 µg/L (0.002 mg/L) US EPA PAH mix following the SPE standard procedure, and the loaded cartridges were eluted with dichloromethane. Other parameters were fixed as follows; sample flow rate: 3.5 ml/min, elution volume: 10 ml, and elution flow rate: 1.0 ml/min.

Effect of sample flow rate

To study the effect of the flow rate of the water samples, the packed SPE cartridges were loaded with 500 ml of spiked water samples containing 2.0 µg/L (0.002 mg/L) US EPA PAH mix at flow rates of 4.11, 4.55 and 5.47 ml/min, and the loaded cartridges were eluted with dichloromethane. Other parameters were fixed as follows; sample volume 500 ml, elution volume: 10 ml, and elution flow rate: 1.0 ml/min.

Effect of sample modifier

Methanol (analytical grade) was chosen as sample modifier since it is a good solvent for most PAHs of environmental relevance. To study this effect, the spiked water samples containing 2.0 µg/L (0.002 mg/L) US EPA PAH mix were first modified with 0%, 5%, 10%, 15%, and 20% of methanol before they were loaded on the SPE cartridges. Other SPE parameters were fixed as follows: sample volume: 500 ml; sample flow rate: 4.5 ml/min; elution volume: 10 ml; and elution flow rate: 1.0 ml/min..

3.8.2 Evaluation of method performance and validation

The performance of the developed pre-concentration method was assessed by evaluating linearity/ linear range, recovery, precision, and detection limit. These parameters were evaluated according to guidelines for single-laboratory validation of analytical methods for trace-level concentrations of organic chemicals (Fajgelj and Ambrus, 2007), while validation was based on parameters defined in standard protocols describing chromatographic methods (Thompson et al., 2002).

For the current study, these parameters were investigated by enriching real and US EPA PAH mix spiked water samples at suitable spike levels under the optimized SPE conditions: sample volume: 500 ml; sample flow rate: 5.5 ml/min; elution volume: 10 ml; and elution flow rate: 0.9 ml/min, sample modifier: 15% ethanol.

3.8.2.1 Method Detection Limit

To evaluate the method detection limits, the official method of the US EPA (1990) was applied.

Mathematically, method detection limit, MDL was calculated by the following expression:

$$MDL = t \times s \qquad 3.15$$

where t is the Student's t value for a 99% confidence interval and a standard deviation estimate with n–1 degrees of freedom, and s is the standard deviation of the replicate analyses.

For this study, six replicate analysis of laboratory tap water samples (isotope preparatory lab of centre for environmental remediation, IGSNRR, Beijing) were done. The spike level for the tap water was 0.5 µg/L for fluorescence detector, and 1.0 and 10 µg/L for UV detector.

3.8.2.2 Precision

The precision or repeatability was measured as the relative standard deviations (RSD) of the data obtained from the experiment for method detection limit. Mathematically, RSD was calculated using the following expression:

$$RSD = \frac{s}{\bar{\bar{x}}} \times \frac{100}{1} \qquad 3.16$$

where s is the standard deviation, and $\bar{x}$ is the mean value of the six replicate measurements.

3.8.2.3 Linearity and Linear range of the method

For this study, the water samples containing 0.5, 5.0, 25.0, and 50.0 µg/L of US EPA PAH mix were prepared, preconcentrated and analyzed. The peak response (peak area) was plotted against the corresponding concentration value. The linearity was assessed as r^2 values (with linear equations) of the straight line plots.

3.8.2.4 Recovery study

The water samples used for the recovery studies were tap water collected from the lab, and polluted water samples collected from Shahe river. The recovery study was done by analyzing the un-spiked and spiked water samples, and the percentage recovery was calculated as follows:

$$\mathrm{Recovery} = \frac{C_{SP} - C_{UP}}{SL} \times \frac{100\%}{1} \qquad 3.17$$

where C_{SP} is the concentration of the spiked sample, C_{UP} is the concentration of the unspiked sample, and SL is the spike level.

For the recovery study, the spike level for both tap and Shahe river samples was 10 µg/L. The optimum values of the SPE parameters as determined from the optimization experiments were applied for the SPE study.

3.8.3 Application of the developed method for analysis of PAHs in water samples

The applicability of the developed SPE method was tested in the analysis of water sample with/without spiking with PAHs/phthalates using the developed MDICS and commercial C_{18} (ENVI^{TM}18) SPE cartridges. The tested water samples include tap water from the lab (isotope preparatory lab of centre for environmental remediation, IGSNRR, Beijing), and river water from Shahe river of Beijing, China.

The sampling bottles were rinsed several times with the water to be analyzed and, therafter filled until water overflowed to prevent loss of volatile compounds in the presence of headspace. After being filtered through 0.22 µm cellulose membranes, the water samples were stored at less than 4ºC in the laboratory prior to analysis. Thereafter, the samples were extracted using the optimized SPE parameters and analyzed for PAHs.

3.8.4 SPE pre-concentration studies for phthalates

The SPE pre-concentration studies for phthalates applied similar conditions for optimization and validation parameters. DMP, DEP, and DEHP were applied for the preconcentration studies. MDICS was applied as the selected SPE adsorbent for full optimization.

3.8.4.1 Optimization experiments

The optimization experiments for phthalates adopted the same conditions applied for the optimization of SPE preconcentration of PAHs. Water samples containing 5.0 µg/L (0.005 mg/L) of DMP, DEP, and DEHP were used for the optimization studies.

3.8.4.2 Evaluation of method performance and validation

The method detection limit, precision, linear range, and recovery study were evaluated by enriching DMP, DEP and DEHP spiked tap water samples at certain spike levels under the optimized SPE conditions: sample volume: 500 ml; sample flow rate: 5.0 ml/min; elution volume: 10 ml; and elution flow rate: 0.6 ml/min, sample modifier: 10% ethanol.

The method detection limit and precision were evaluated using data generated from SPE preconcentration of water samples containing 1.0 µg/L (0.001 mg/L) of the phthalates (DMP, DEP and DEHP). The linear range was studied with aqueous standard concentrations of 1.0, 10.0, 50.0, and 100.0 µg/L, and the recovery study applied laboratory tap water at 10.0 µg/L spike level.

3.8.5 Application of the developed SPE method for analysis of phthalates in water samples

The developed MDICS and commercial C_{18} (ENVI^{TM}18) SPE cartridges were comparatively applied for replicate analysis of laboratory tap water (isotope preparatory lab of centre for environmental remediation, IGSNRR, Beijing), and river water from Shahe river of Beijing, China.

The sampling bottles were rinsed several times with the water to be analyzed and, therafter filled until water overflowed to prevent loss of volatile compounds in the presence of headspace. After being filtered through 0.22 µm cellulose membranes, the water samples were stored at less than 4 ºC in the laboratory prior to SPE preconcentration and analysis. Thereafter, the samples were extracted using the optimized parameters and analyzed for phthalates.

CHAPTER FOUR

Results and Discussion

4.1 Investigation of adsorption interaction using DFT molecular studies

Considering the array of cross-linking agents, polymer scientists face the challenge of selecting a suitable cross-linking agent that will be most effective for a given target pollutant. So far, the conventional approach for assessing the design and adsorption performance of these cross-linked polymer adsorbents has only been experimental studies. Based on this approach, the cross-linked polymers have to be synthesized using the various available cross-linking agents, characterized to confirm successful cross-linking process, and thereafter screened based on their respective adsorption performance. The obvious limitations of this approach have been discussed in details earlier. In addressing this challenge, this study developed a theoretical/computational approach for predicting the likely adsorption potential and/or trend which can serve as a feasibility guide in choosing a suitable cross-linking agent in the application of cross-linked polymer adsorbents for water treatment.

Density Functional Theorem (DFT) has become an attractive theoretical method for evaluation of molecular interaction (and consequently adsorption), because it has proved to be adequate for pointing out the changes in electronic structure responsible for chemical interaction, otherwise known as quantum chemical descriptors. It is against this backdrop that DFT quantum chemical descriptors have been successfully applied in assessing adsorption interaction (Todeschini and Consonni, 2000; Rafati *et al*., 2008; Hashemianzadeh and Nojini, 2008; Shirvani *et al*., 2010; Udhayakala *et al*., 2012).

The DFT descriptors explored for describing adsorption interactions in this study are Energy of the Highest Occupied Molecular Oritals (E_{HOMO}), Energy of the Lowest Unoccupied Molecular Oritals (E_{LUMO}), ionization potential (I), electron affinity (A), HOMO-LUMO energy gap (ΔE), chemical hardness (η), softness (S), electronegativity (χ), chemical potential (μ), dipole moment of the adsorbent molecules, and the fractional number of electrons transferred between the adsorbent and adsorbate (ΔN) (Ebenso *et al*., 2010; Peyghan *et al*, 2013).

Except dipole moment, all the quantum chemical descriptors applied in this study are directly based or derived from the orbital energies of molecular model structure of the adsorbents and adsorbates. Molecular orbital energies give information about reactivity/stability of specific regions of the molecule. Among the molecular orbitals, a fundamental role is played by the frontier orbitals (HOMO and LUMO), which are responsible for the formation of many charge transfer complexes such as those involved in adsorption interactions. Except dipole moment, all other descriptors discussed in this study were based on molecular orbital energies. Table 4.1 shows the computed values of these DFT molecular interaction parameters.

E_{HOMO} is the energy of the highest energy level containing electrons in the molecule. Molecules with high HOMO energy values can donate electrons more easily compared to molecules with low HOMO energy values, and hence are more reactive. Therefore, the E_{HOMO} descriptor is related to ionization potential (as explained previously in equation 3.1) which is a measure of nucleophilicity of a molecule. The low ionization potentials of the studied adsorbents indicate good adsorption interaction. Based on the values of I (Table 4.1), the expected trend of adsorption performance is MDI adsorbents > HDI adsorbents ≥ EPI adsorbents. E_{LUMO} is the energy of the lowest energy level containing no electrons in the molecule. Molecules with low LUMO energy values are more able to accept electrons than those with high values. Therefore, E_{LUMO} descriptor is related to electron affinity A (equation 3.2). Based on the values of A, the expected trend of adsorption performance is MDI adsorbents > HDI adsorbents > EPI adsorbents.

ΔE is a vital stability index which measures the difference between E_{HOMO} and E_{LUMO} (equation 3.3). Large values of ΔE translates to high stability of a molecule and consequently low reactivity, and vice versa. ΔE is an approximation of the lowest excitation energy of the molecule, and thus can be used for the definition of chemical hardness and softness. In simple terms, chemical hardness is a measure of the resistance to

Table 4.1. DFT model parameters for the cross-linked adsorbents using the cross-linking agents

Adsorbents/Adsorbates	EPI ads[†]	HDI ads[‡]	MDI ads[#]	Acy	Phe	BaA	DEP
E_{HOMO} (eV)	-6.45	-6.63	-5.57	-5.81	-5.73	-5.32	-6.95
E_{LUMO} (eV)	1.06	0.81	-0.18	-1.89	-0.99	-1.55	-1.40
Ionization potential, I	6.45	6.63	5.57	5.81	5.73	5.32	6.95
Electron affinity, A	-1.06	-0.81	0.18	1.89	0.99	1.55	1.40
Energy Gap, ΔE (eV)	7.51	7.44	5.39	3.92	4.74	3.77	5.55
Chemical Hardness, η (eV)	3.76	3.72	2.70	1.96	2.37	1.89	2.78
Chemical Softness S (eV^{-1})	0.27	0.27	0.37	0.51	0.42	0.53	0.36
Electronegativity, χ	2.70	2.91	2.88	3.85	3.36	3.44	4.18
Chemical potential, μ (eV)	-2.70	-2.91	-2.88	-3.85	-3.36	-3.44	-4.18
Dipole moment (Debye)	3.30	6.54	6.71	0.34	0.04	0.07	3.40
QSAR[*] volume (Ã)	NA[§]	NA	NA	171.66	201.68	253.06	232.46
Number of transferred electron, ΔN							
ΔN for Acy	-0.10	-0.08	-0.10	NA	NA	NA	NA
ΔN for Phe	-0.05	-0.04	-0.05	NA	NA	NA	NA
ΔN for BaA	-0.07	-0.05	-0.06	NA	NA	NA	NA
ΔN for DEP	-0.11	-0.10	-0.12	NA	NA	NA	NA

[*] Quantitative Structure Activity Relationship

[§] Not Applicable

[†] Epichlorohydrin cross-linked adsorbents

[‡] 1,6-Hexamethylene diisocyanate cross-linked adsorbents

[#] 2,2-Methylene diphenyl diisocyanate cross-linked adsorbents change in electron distribution or charge transfer. In DFT context, chemical hardness is mathematically defined as:

$$\eta = \frac{1}{2}(\frac{\partial^2 E}{\partial^2 N_e}) = \frac{1}{2}(\frac{\partial \mu}{\partial N_e}) = \int h(r)dr = \frac{1}{2S}$$

where μ, *h(r)* and S are electronic chemical potential, hardness density, and total softness respectively (Todeschini and Consonni, 2000).

However, on the basis of frontier molecular orbitals, chemical hardness and softness can be approximated on the bases of ionization potential and electron affinity. Considering the established relationship between *I* and *A* with ΔE and η, ΔE and η were expected to have positive correlation, while *S* was expected to have negative correlation with the adsorption performance of the adsorbents. Based on the values of ΔE, η, and *S;* the expected trend of adsorption performance is MDI adsorbents > HDI adsorbents > EPI.

Dipole moment has a positive correlation with adsorbent-adsorbate intereaction (Yang, 2003). Based on the values of the dipole moment generated from the DFT quantum calculations, the predicted adsorption trend is MDI adorbents > HDI adsorbents > EPI adsorbents. This trend was equally in agreement with those of I, ΔE, η, and S.

Global adsorption interaction, ΔN has been successfully applied in corrosion inhibition studies where it has proved to be very reliable for assessing and predicting adsorption interaction of the inhibitor molecules with steel surfaces (Ebenso *et al*., 2010). It has been established that a positive value of ΔN indicates that charge flows from adsorbate to adsorbent, thus the adsorbent acts as electron acceptor, whereas a negative value of ΔN indicates that charge flows from adsorbent to adsorbate and that adsorbent acts as electron donor. The calculated ΔN values (Table 4.1) for all the studied adsorbent-adsorbate pair were negative, an indication that the adsorbents were electron donors in the adsorption process. The computed ΔN values of the adsorbents predicted the adsorption interaction of MDI adsorbents > EPI adsorbents > HDI adsorbents for acenaphthylene and diethyl phthalates respectively, and EPI adsorbents ≥ MDI adsorbents > HDI adsorbents for phenanthrene and benzo[a]anthracene.

However, the reliability of ΔN as adsorption interaction descriptor has been found to be dependent on the magnitude of the fraction of transferred electrons. For corrosion studies, it has been established that ΔN values are reliable as adsorption interaction descriptors when $\Delta N < 3.6$ (Ebenso and Obot, 2010). Hence, considering the very small values of ΔN for this study, it may not be a reliable adsorption descriptor. On the basis of Frontier Molecular Orbital (FMO) theory (Musa et al., 2010), it was observed that access to the HOMO orbitals (Figure 4.1) of the cross-linked adsorbents were not the same, due to location and orientation of these orbitals. The orbitals of the MDI cross-linked adsorbents (MDICS and MDIBCD families) are more accessible due to their location on the cross-linker part of their representative model structure, while those of the EPI and HDI are substantially located on the glucose unit which forms part of the glucose chain of the polymer, and hence they are less accessible. Considering the foregoing, ΔN prediction of the adsorption interaction may not be reliable. Also, since the adsorbents were electron donors in the adsorption process, the chemical descriptors of electronegativity and chemical potential, that are based on electron acceptance were not considered as suitable descriptors.

From the fore going and based on the values of the studied DFT molecular interaction descriptors, the predicted trend of adsorption interaction was MDI adsorbents > HDI adsorbents > EPI adsorbents.

Also, considering the adsorption schemes as shown in Figure 4.2, increment in degree of cross-linking process leads to a corresponding increment in the number of interstitial spaces. Hence, the adsorption performance was expected to have a positive correlation with the degree of cross-linking process of the adsorbents.

However, prediction of adsorption performance based on interaction potentials assumes that the adsorbate molecules have uniform access to all the possible sorption/binding sites (Yang, 2003). Hence, surface area and pore characteristics equally play important contributory role in the real adsorption performance.

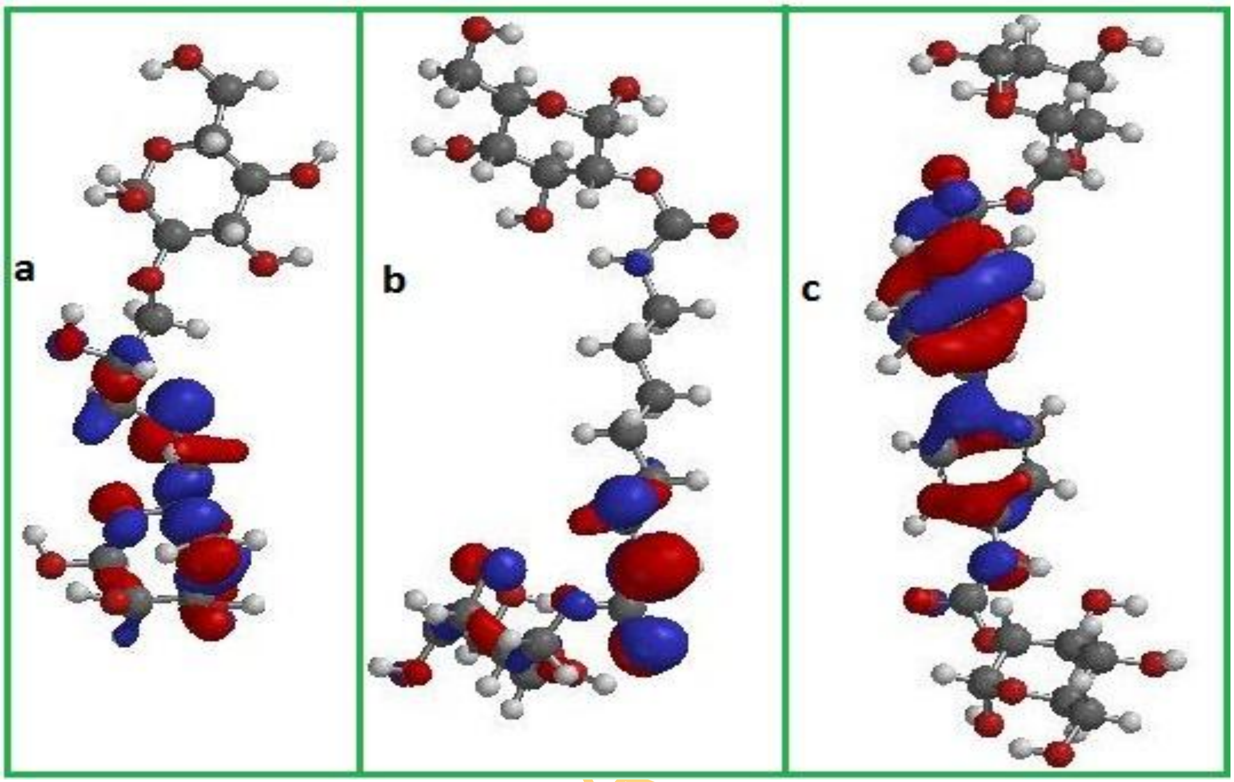


Figure 4.1. Frontier Molecular Orbitals of E_{HOMO} of the monomer models of (a) epichlorohydrin (EPI) (b) 1,6-hexamethylene diisocyanate (HDI), and (c) 4,4-methylene diisocyanate (MDI) cross-linked adsorbents

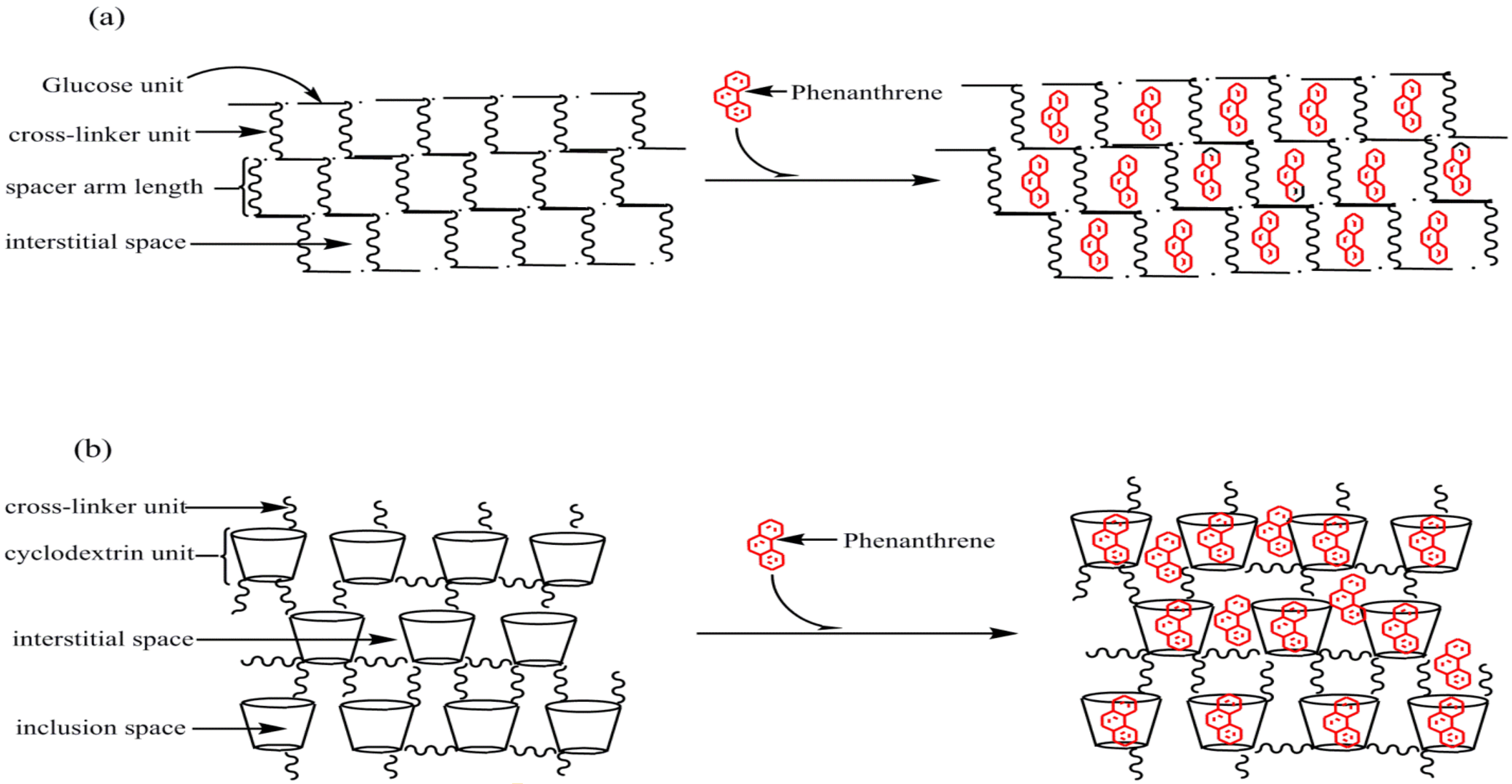


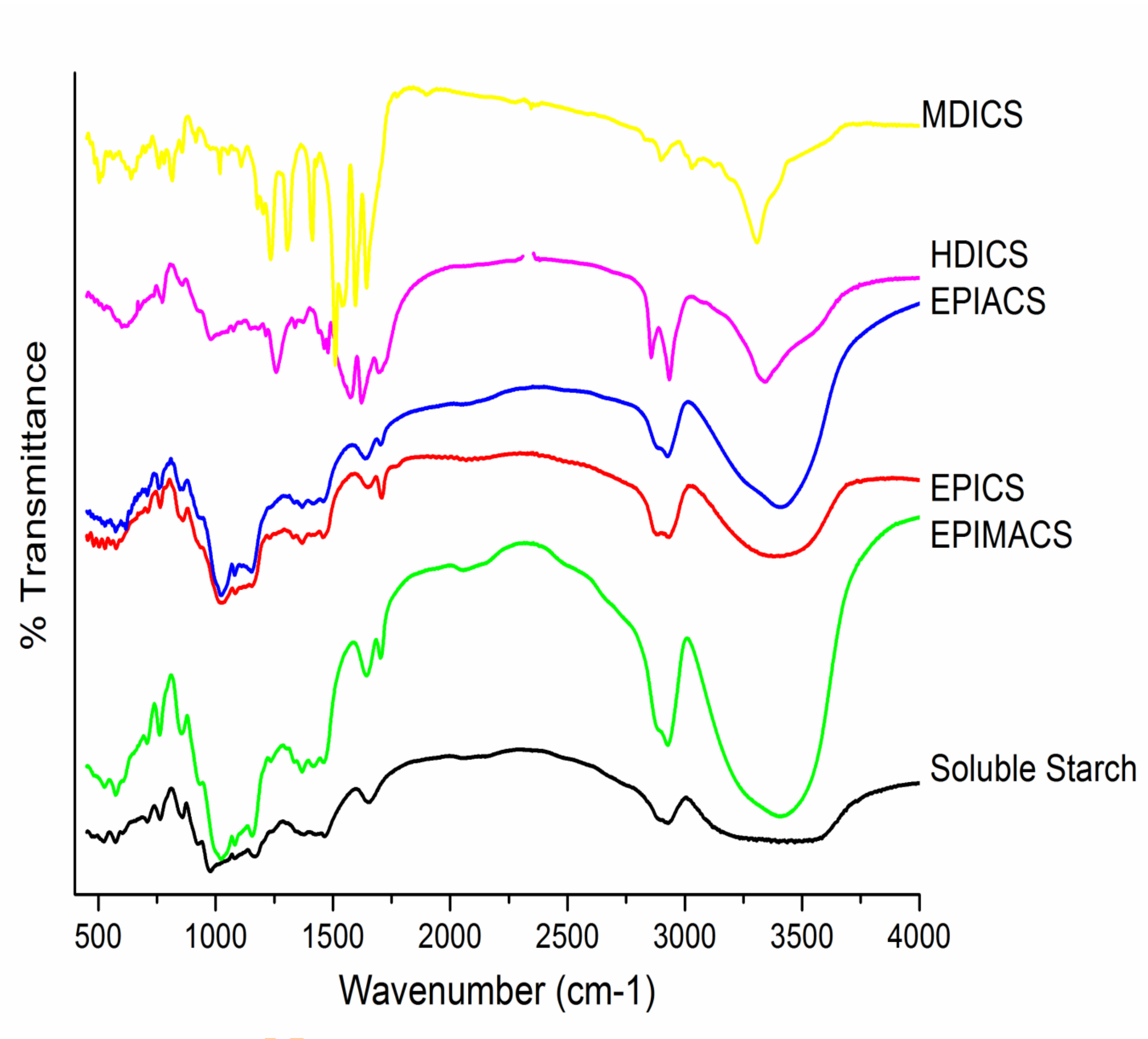
Figure 4.2. Adsorption schemes of (a) cross-linked starch adsorbent and (b) β-cyclodextrin polymer adsorbent for phenanthrene

4.2 Characterization of the synthesized cross-linked polymers

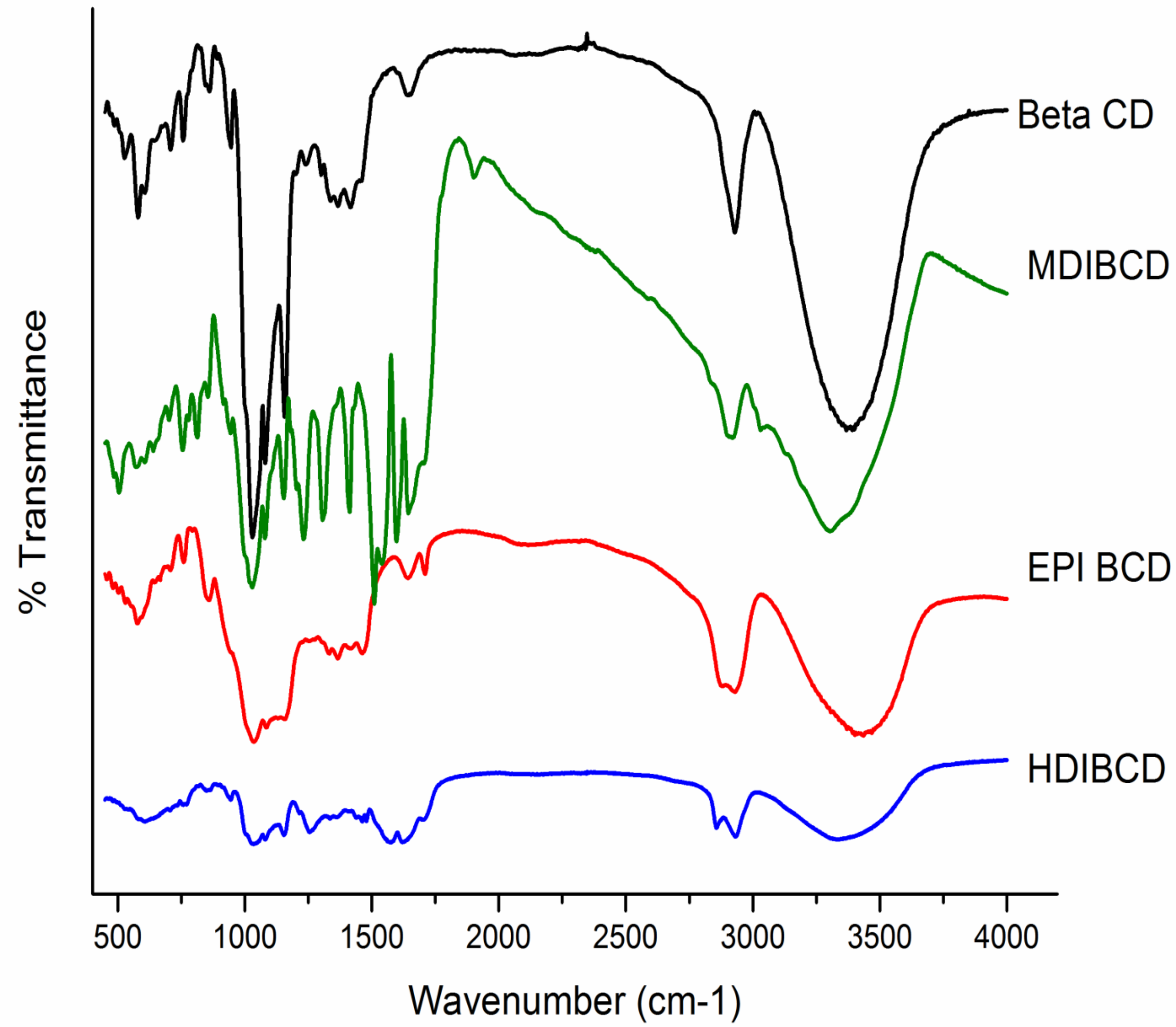
4.2.1 Fourier transform infra red spectroscopy (FT-IR)

The presence of relevant infra red peaks in the IR spectra of materials confirms the presence of certain bonds and consequently certain functional groups. The IR spectra of the cross-linked adsorbents (EPICS, EPIACS, EPIMACS, HDICS, MDICS, EPIBCD, HDIBCD, MDIBCD, EPIGCD, HDIGCD, MDIGCD, EPIGCDS, HDIGCDS, and MDIGCDS) and their precursors (starch, β-cyclodextrin, and γ-cyclodextrin) are as shown in figures 4.3, 4.4, 4.5 and 4.6 while the constituent IR peaks of each adsorbent for the relevant IR bands are as compiled in Tables 4.2 and 4.3.

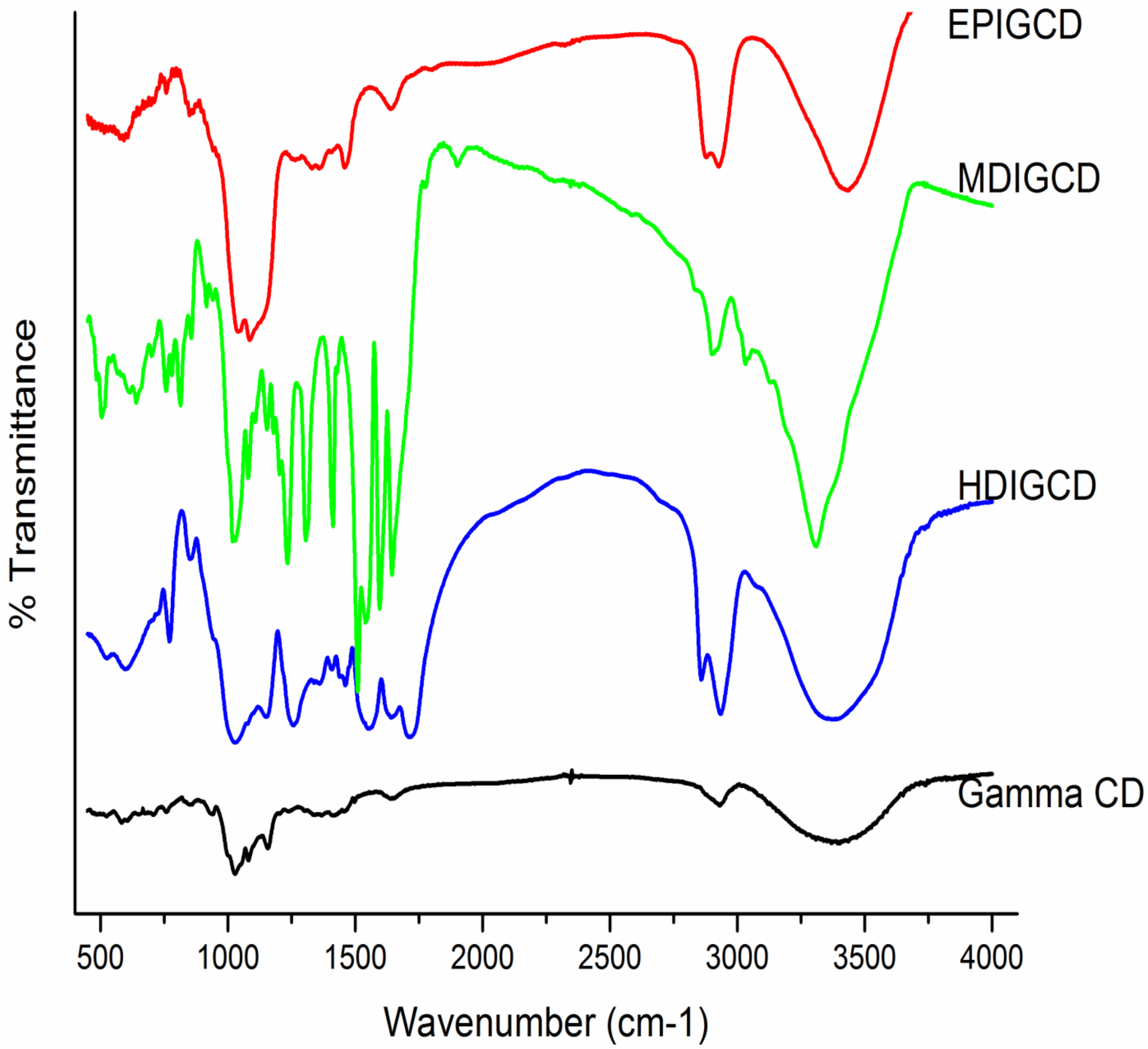
The IR spectra showed that both the adsorbent precursors (starch, β-cyclodextrin, and γ-cyclodextrin) and cross-linked polymer adsorbents exhibited the characteristic peaks of anomeric C-H ring deformations (900–550 cm^{-1}), C-O (1320-1000 cm^{-1}) and O-H (3500-3200 cm^{-1}) stretching vibrations of polymeric compounds especially polysaccharides, which implies that the starch structural backbone was retained in the these adsorbents. The presence of C-N (1721–1671 cm^{-1}) bands in the spectra of the epichlorohydrin aminated starch (EPIACS and EPIMACS) and polyurethane based cross-linked polymers (HDICS, HDIGCD, HDIBCD, HDIGCDS, HDIBCDS, MDICS, MDIBCD, MDIGCD, MDIGCDS, and MDIBCDS) confirmed the successful introduction of nitro group into the starch polymer matrix. This is a desirable property since the DFT model has shown that nitrogen being an electron rich centre, will increase the polarizability of the cross linked starch polymer, which is subsequently expected to enhance the sorption properties of the polymers. The spectra data of MDI cross-linked polymer adsorbents (MDICS, MDIBCD, MDIGCD, MDIGCDS, and MDIBCDS) showed presence of aromatic C-H (3100–3000 cm^{-1}), C-C (1500–1400 cm^{-1}), and C-N (1335–1250 cm^{-1}) stretch, and C-H (900–675 cm^{-1}) out of plane stretching (oops) vibration and plane bending bands (1250-1000 cm^{-1}) which confirms the successful incorporation of aromatic group into the cross-linked polymer.



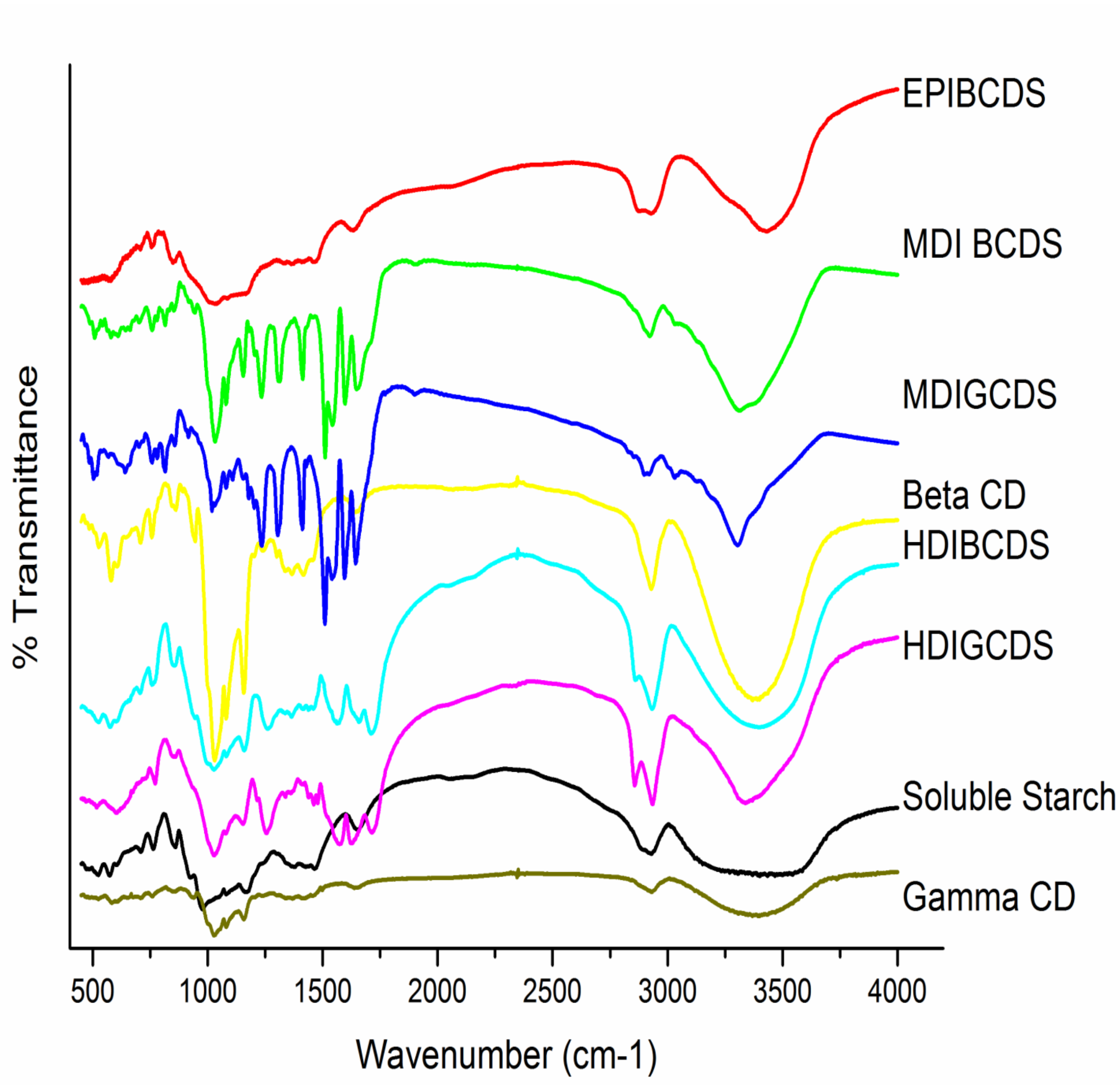
Figures 4.3. Infra-red (IR) spectra of cross-linked starch polymer adsorbents



Figures 4.4. Infra-red (IR) spectra of β-cyclodextrin polymer adsorbents



Figures 4.5. Infra-red (IR) spectra of γ-cyclodextrin polymer adsorbents



Figures 4.6. Infra-red (IR) spectra of cyclodextrin starch mixed polymer adsorbents

Table 4.2. Constituent FTIR absorption peaks of cross-linked starch polymer adsorbent

Functional Group	Band	Soluble Starch	EPI CS	EPIACS	EPIMACS	CSHDI	CSMDI
O-H stretch (cm^{-1})	3500-3200 (alcohols)	Present, broad	Present, broad	Present, broad	Present, broad	Present, narrow	Present, narrow
C-H stretch (cm^{-1})	3000-2850	2929	2909	2948	2906	2933	2890
Anomeric C-H deformations (cm^{-1})	900-550	561	554	552	557	596	662
C-H stretch (aromatic) (cm^{-1})	3100–3000	NA[*]	NA	NA	NA	NA	3036
C=O stretch (cm^{-1})	1760-1665 (Carbonyl)	NA	NA	NA	NA	1687	1671
Starch C-N vibrations (cm^{-1})		NA	NA	1719	1712	1721	1671
C-O stretch (cm^{-1})	1320-1000	1155	1145	1165	1286	1250	1315
C-H rock (cm^{-1})	1370–1350	NA	1353	1370	1363	1355	NA
Aliphatic C-N stretch (cm^{-1})	1250–1020	NA	NA	1167	1151	1247	1227
N-H wag (cm^{-1})	910–665	NA	NA	754	NA	775	751
Aromatic C-C (in ring) stretch (cm^{-1})	1500–1400	NA	NA	NA	NA	NA	1598
C-H "oop" (cm^{-1})	900–675	NA	NA	NA	NA	NA	819
Aromatic C-N stretch (cm^{-1})	1335–1250	NA	NA	NA	NA	NA	1303
Aromatic C-H plane bending (cm^{-1})	1250-1000	NA	NA	NA	NA	NA	1013

[*] Not Available

Table 4.3. Constituent FTIR absorption peaks of cross-linked β-cyclodextrin polymer adsorbent

Functional Group	Band	Pristine β-cyclodextrin	EPI BCD	HDIBCD	MDIBCD
O-H stretch (cm^{-1})	3500-3200 (alcohols)	Present, broad	Present, broad	Present, narrow	Present, narrow
C-H stretch(cm^{-1})	3000-2850	2923	2903	2920	2890
Anomeric C-H deformations (cm^{-1})	900-550	572	596	592	584
C-H stretch (aromatic) (cm^{-1})	3100–3000	NA*	NA	NA	3041
C=O stretch (cm^{-1})	1760-1665 (Carbonyl)	NA	NA	1714	1670
Polysaccharides C-N vibrations (cm^{-1})		NA	NA	1721	1673
C-O stretch (cm^{-1})	1320-1000	1023	1051	1247	1221
C-H rock (cm^{-1})	1370–1350	NA	1352	1353	NA
Aliphatic C-N stretch (cm^{-1})	1250–1020	NA	NA	1245	1160
N-H wag (cm^{-1})	910-665	NA	NA	776	745
Aromatic C-C (in ring) stretch (cm^{-1})	1500–1400	NA	NA	NA	1405
C-H "oop" (cm^{-1})	900–675	NA	NA	NA	746
Aromatic C-N stretch (cm^{-1})	1335–1250	NA	NA	NA	1318
Aromatic C-H plane bending (cm^{-1})	1250-1000	NA	NA	NA	1242

*Not Available

4.2.2 Elemental Composition

The elemental composition of materials is very vital in predicting the adsorption behaviour of materials (Cheng *et al*., 2011). The elemental composition of the cross-linked starch and cyclodextrin polymer adsorbents are as shown in Tables 4.4 and 4.5. For all the studied cross-linked starch polymers, there is a linear correlation between the carbon content and the quantities of cross linking and amination reagents (for aminated polymers only) used. The data for the polyurethane based polymers showed increase in nitrogen content, and consequently the degree of cross linking, as the quantity of cross linking agent was increased. Since there was an increase in the level of hydrophobicity, the solubility of the cross linked polymers changed from being less soluble to totally insoluble as the degree of cross linking increased. Similar trend was equally exhibited by the cyclodextrin polymer adsorbents. The observed trend is in agreement with what has been reported by Ozmen *et al*., (2007).

The (O + N)/C atomic ratios, otherwise known as polarity coefficient of the polymers, is an important parameter to predict sorption (Oliveila *et al*., 2011, Cheng *et al*., 2011). The values for this study (0.60–1.26 and 0.57–1.30 for cross-linked starch and cyclodextrin polymer adsorbents, respectively) is in range of some commercial lignins (0.33–0.94), which is a good sorbent for aromatic pollutants reported in literature (Wang, 2007). The values were relatively steady as the degree of cross-linking increased for all the cross-linked polymer adsorbents, except for those of MDICS group where there was a noticeable decrease. The N/C ratio is also an important factor that reflects the polarizability α, of the polymer adsorbents. The N/C values for all the polymers (except for the EPICS and EPIBCD groups) showed a positive correlation with the degree of cross linking and amination.

The C/H atomic ratio, which indicates aromaticity, for all the polymers showed no significant change except for those of MDICS and MDIBCD polymers, where a progressive increase was observed as the degree of cross-linking was increased. This observation is in consonance with a successful introduction of aromatic group into the

Table 4.4. Result of elemental analysis showing N, C and H content of the cross-linked starch adsorbents

Starch Adsorbent	N%	C%	H%	O%	C/H ratio	N/C ratio	(O+N)/C ratio
EPICS1	NA*	42.91	6.32	50.76	6.79	NA	1.18
EPICS2	NA	44.23	6.41	49.35	6.90	NA	1.12
EPICS3	NA	45.09	6.71	48.20	6.72	NA	1.07
EPICS4	NA	45.79	6.89	47.32	6.65	NA	1.03
EPIACS1	3.09	43.62	6.59	46.71	6.62	0.07	1.14
EPIACS2	5.79	44.24	6.60	43.38	6.70	0.13	1.11
EPIACS3	6.15	44.92	6.71	42.22	6.69	0.14	1.08
EPIMACS1	4.92	42.67	6.24	46.17	6.84	0.12	1.20
EPIMACS2	5.87	43.10	6.50	44.53	6.63	0.14	1.17
EPIMACS3	7.14	43.13	6.80	42.93	6.35	0.17	1.16
HDICS1	1.57	43.62	6.90	47.91	6.32	0.04	1.13
HDICS2	3.62	44.19	6.73	45.47	6.57	0.08	1.11
HDICS3	5.63	44.10	7.03	43.24	6.28	0.13	1.11
HDICS4	7.88	46.18	7.36	38.58	6.28	0.17	1.01
MDICS1	1.64	41.35	6.37	50.64	6.49	0.04	1.26
MDICS2	3.55	47.09	6.09	43.27	7.73	0.08	0.99
MDICS3	5.86	53.55	5.74	34.85	9.33	0.11	0.76
MDICS4	7.65	59.01	5.74	27.60	10.29	0.13	0.60

*Not Applicable

Table 4.5. Result of elemental analysis showing N, C and H content of the cross-linked β-cyclodextrin polymer adsorbents

Adsorbent sample	N%	C%	H%	O%	C/H ratio	N/C ratio	(O+N)/C ratio
EPIBCD1	NA*	41.02	5.74	53.24	7.15	NA	1.30
EPIBCD2	NA	41.56	5.86	52.58	7.09	NA	1.27
EPIBCD3	NA	42.08	5.97	51.95	7.05	NA	1.23
EPIBCD4	NA	42.67	6.08	51.25	7.02	NA	1.20
HDIBCD1	9.63	54.89	7.63	27.85	7.19	0.18	0.68
HDIBCD2	4.30	43.10	6.58	46.01	6.55	0.10	1.17
HDIBCD3	6.01	45.01	6.83	42.15	6.59	0.13	1.07
HDIBCD4	9.76	48.46	7.45	34.33	6.51	0.20	0.91
MDIBCD1	6.32	56.30	5.77	31.61	9.76	0.11	0.67
MDIBCD2	5.46	50.89	6.01	37.64	8.47	0.11	0.85
MDIBCD3	6.52	55.68	5.75	32.05	9.68	0.12	0.69
MDIBCD4	7.58	59.91	5.67	26.84	10.57	0.13	0.57

*Not Applicable

chemical structure of the starch polymer as was equally confirmed with IR absorption bands of MDI CS spectra.

4.2.3 BET Surface Analysis

Tables 4.6 and 4.7 show the BET surface characteristics of the polymers. The values of BET surface area for all the cross-linked polymers are higher than that of native starch and cyclodextrin. This is in tandem with the established principle that cross linking process increases the network of cross-linked polymers, thus increasing the surface area (Crini, 2005). It has also been reported that there is a positive correlation between the degree of cross linking and/or amination, and the surface area of cross-linked polymers (Deval *et al.*, 2005), hence the decision to choose the polymer with the highest degree of cross-linking as the representative for each group of the cross linked and aminated polymer adsorbents.

The data showed that the MDI cross-linked polymers had higher surface area values when compared to their EPI and HDI cross-linked counterparts. Analysis of the BET total surface area in relation to the adsorption surface area of pores is necessary for understanding the adsorption behavior of adsorbents, since the information reveals the extent of adsorption that takes place on the exterior, as well as the interior surfaces of the adsorbents. In this regards, the pore surface/total surface area ratio of the adsorbents shows that though MDICS might have had the highest total surface area, over 99% of the likely adsorption process will take place in internal pore surfaces. Hence, MDICS is predicted to have the slowest adsorption rate. The same effect and trend is therefore predicted for other polymers. Also, the study revealed that the average pore widths and pore volumes for most of the adsorbents are large enough to allow diffusion of adsorbate molecules into the internal surfaces of the adsorbents.

4.2.4 Scanning Electron Microscopy

The SEM images of the adsorbent precursors (soluble starch, β-cyclodextrin, and γ-cyclodextrin) and that of the cross-linked adsorbents are shown in Figures 4.7, 4.8, and 4.9. The images showed that the morphology of soluble starch particles appeared to be globular in shape and of different sizes while the cross linked counterparts appeared as agglomerates of irregular shapes and sizes, indicating the formation of bulkier polymer

Table 4.6. BET Surface and pore analysis of the starch adsorbents.

Adsorbent	EPICS	EPIACS	EPIMACS	HDICS	MDICS
BET surface area (m^2/g)	6.8091	9.7891	11.5713	3.2804	40.3858
BJH adsorption surface Area of pores (m^2/g)	3.9023	4.9237	5.8931	1.9820	40.0851
Pore surface/Total surface area	0.5773	0.5029	0.5093	0.6042	0.9925
Total pore volume (cm^3/g)	0.027281	0.04049	0.06047	0.007463	0.129811
BJH adsorption pore volume (cm^3/g)	0.03241	0.03562	0.10583	0.02361	0.188124
BET pore width (Å)	104.3561	110.6350	99.8130	91.0011	128.5709
BJH pore width (Å)	503.2710	497.4724	602.4732	476.473	187.7271

Table 4.7. BET Surface and pore analysis of cyclodextrin and cyclodextrin starch mixed polymer adsorbents

Adsorbent	MDIBCD	MDIGCD	MDIBCDS	MDIGCDS
BET surface area (m^2/g)	3.7814	15.2145	10.3255	7.6178
BJH adsorption surface Area of pores (m^2/g)	2.2640	10.6690	5.3320	5.3530
Pore surface/Total surface area	0.5987	0.7012	0.5164	0.7026
Total pore volume (cm^3/g)	0.0126	0.0373	0.0302	0.0266
BJH adsorption pore volume (cm^3/g)	0.0232	0.0623	0.0789	0.0478
BET pore width (Å)	133.1898	98.0814	116.8185	139.7694
BJH pore width (Å)	410.3700	233.7440	591.7510	356.8720

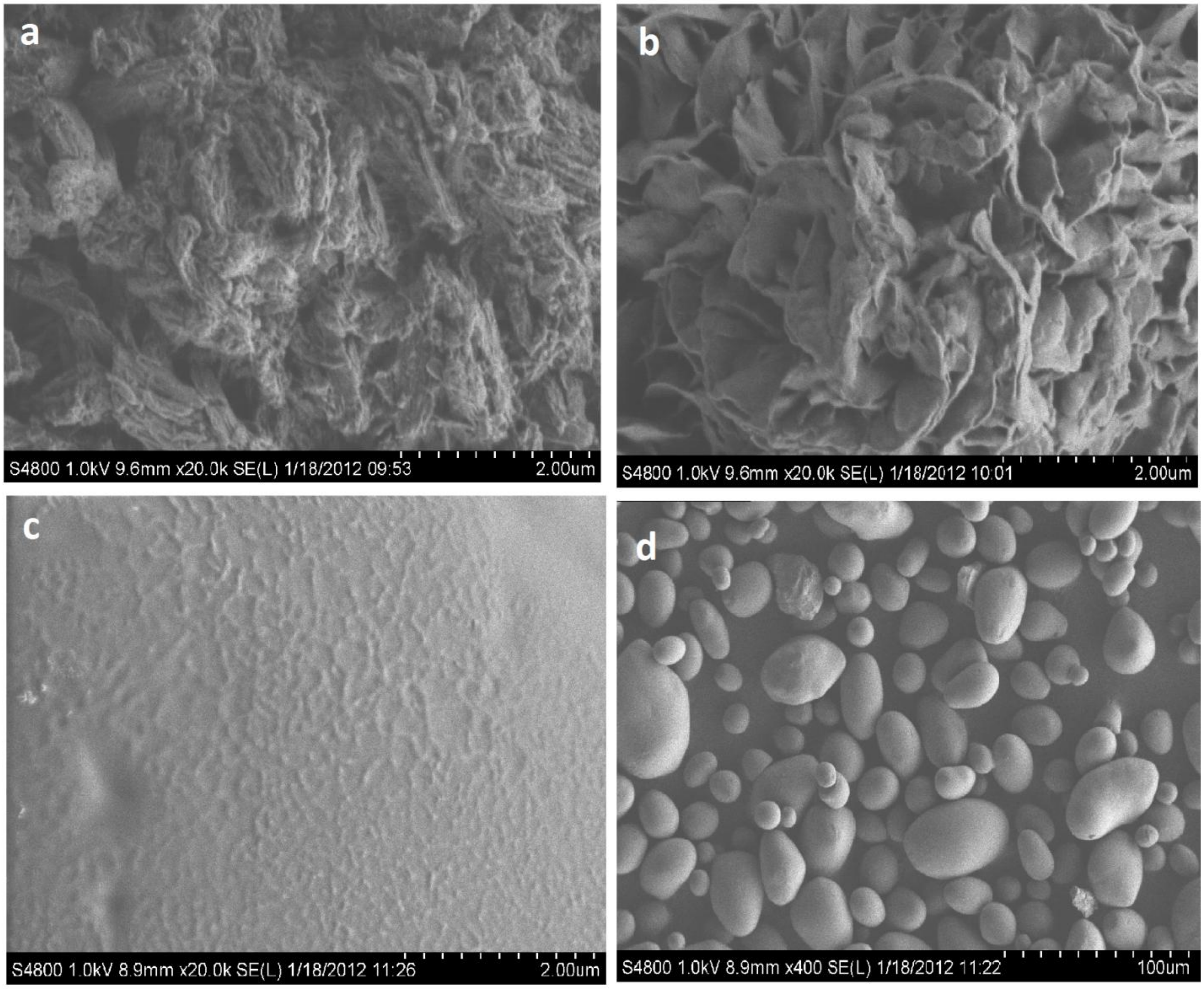


Figure 4.7. SEM images of (a) MDICS (b) HDICS adsorbents (c) pristine starch (x 20,000) and (d) pristine starch (x 400)

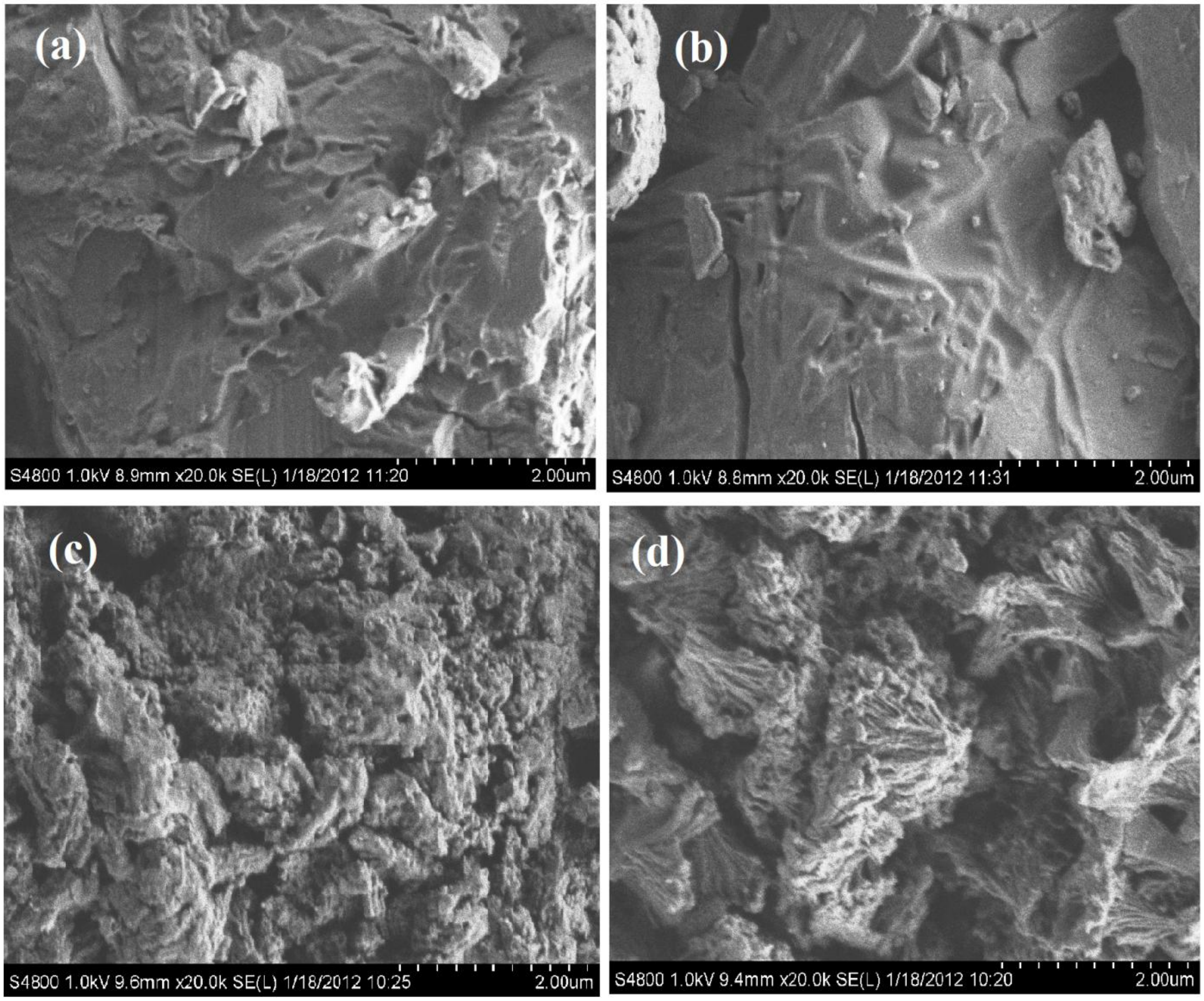


Figure 4.8. SEM images of (a) β-cyclodextrin, (b)γ-cyclodextrin, (c) MDIBCD and (d) MDIGCD

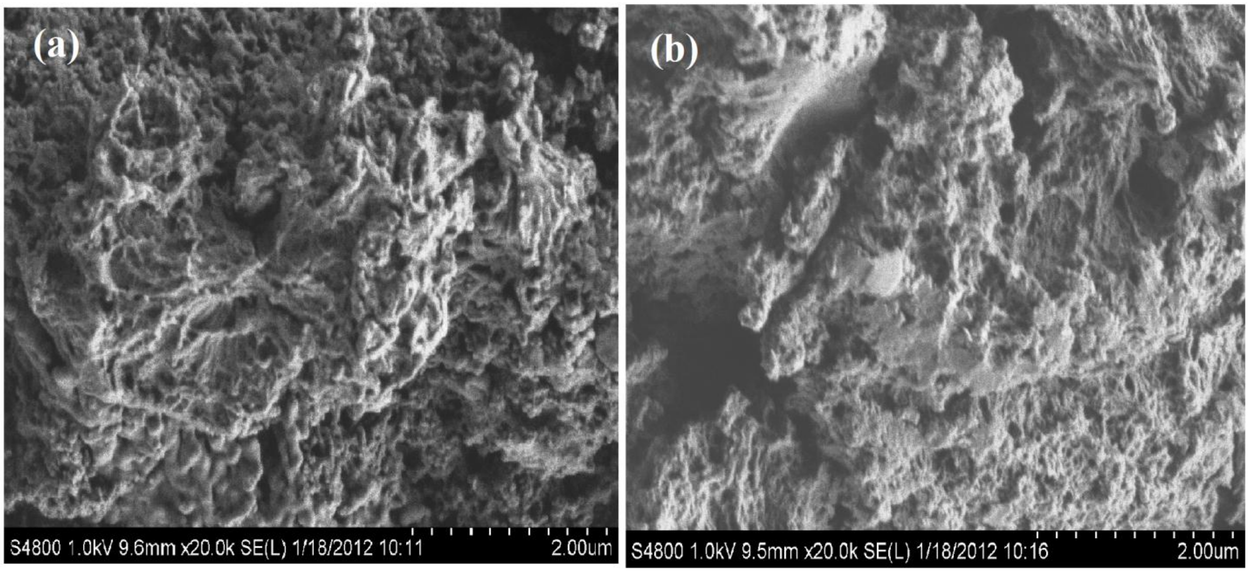


Figure 4.9. SEM images cyclodextrin-starch copolymer adsorbents (a) MDIBCDS and (b)MDIGCDS

units emanating from the cross linking process induced by the cross linking agents (Yang *et al*., 2010). A remarkable change on the morphology was very prominent on the surfaces of the cross linked starch when compared to the soluble starch precursors. While the surface of the soluble starch precursor appeared to be smooth with no noticeable pores, the surface of the cross linked counter parts appeared to be rough and porous with noticeable serrations, thus explaining why surface area of the cross linked starch polymers were higher than that of the soluble starch precursor. This observation is in agreement with the trend observed by Guo *et al*., (2002). Similar trend was equally observed for cross-linked cyclodextrin and starch-cyclodextrin copolymer adsorbents as shown by their respective SEM images (Figures 4.8 and 4.9).

4.2.5 Thermo-gravimetric analysis/Differential thermal analysis

The TGA and DTA plots of the cross-linked polymers are shown in Figures 4.10 and 4.11. For all the studied cross-linked polymers (HDICS, MDICS, MDIBCD, MDIGCD, MDIBCDS, and MDIGCDS), the TGA showed that mass losses occurred in three steps, while the DTA revealed the thermal events corresponding to these losses.

The TGA plot for MDICS showed that the first mass loss (3%) was between 30–104°C and correlated with the DTA peak at 47°C (Figure 4.10a). This is attributed to the dehydration that occurs in a single step. Once dehydrated, the polymer was stable up to 260°C and above this temperature the thermal decomposition occurred in two consecutive and/or overlapping steps between 260 and 670°C. The second mass loss (39.5%) (being the first mass loss of the anhydrous compound) was observed between 260 – 366ºC corresponding to the sharp exothermic DTA peak at 350ºC with oxidative process. The last mass loss (57.5%) was between 366–513ºC corresponding to the exothermic peak at 520°C, ascribed to the oxidation of the organic matter.

For HDICS, the first mass loss was between 30 – 99°C (2.5%) and corresponded to the peak at 91°C, which is attributed to the dehydration that occurs in a single step (Figure 4.10b). Once dehydrated, the polymer was stable up to 210°C and above this temperature the thermal decomposition occurred in two consecutive and/or overlapping steps between 210 and 620°C. The first mass loss (54.5%) of the anhydrous compound was observed between 260 – 352ºC corresponding to the sharp exothermic peak at 302ºC with oxidative

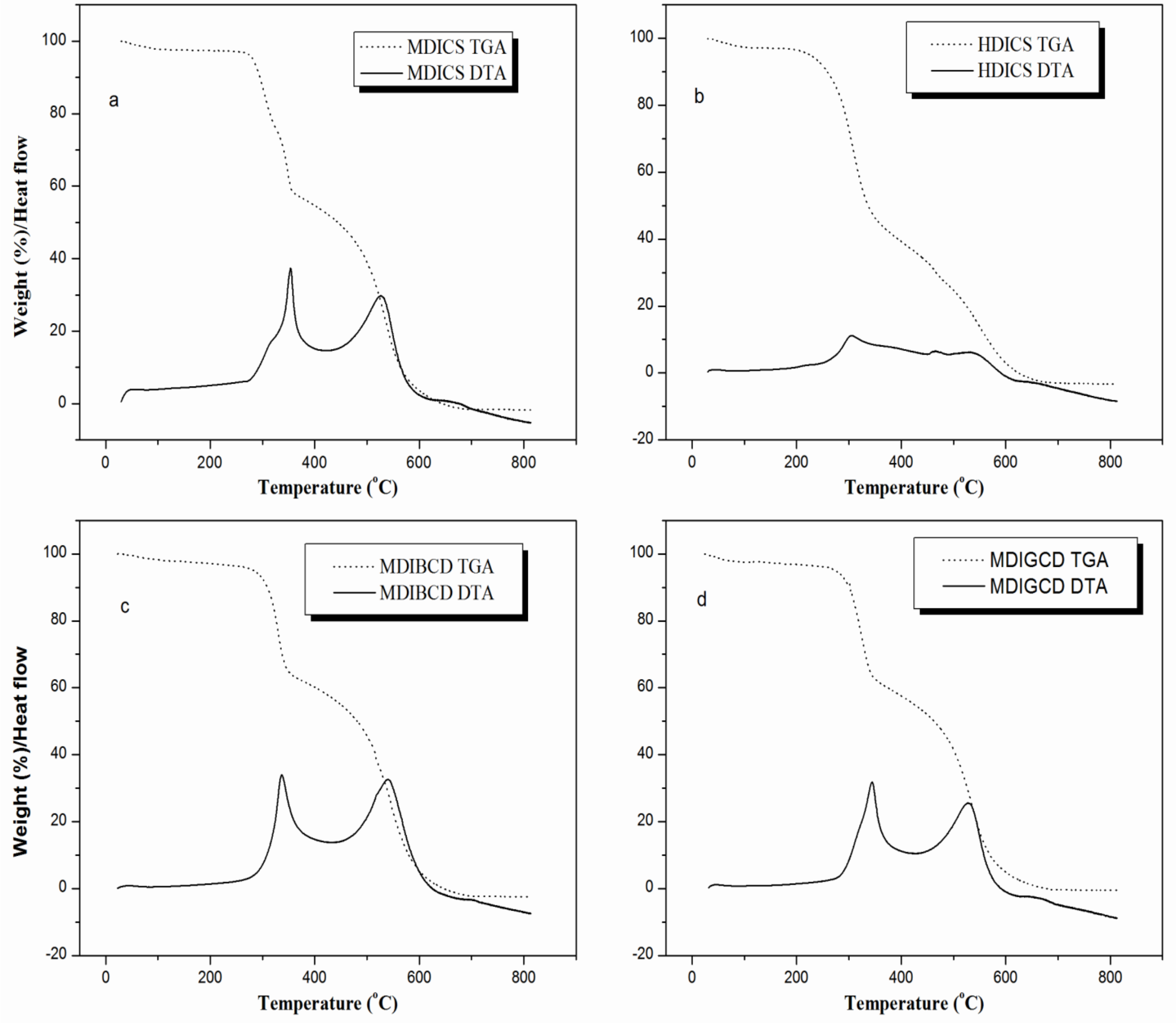


Figure 4.10. TGA/DTA plots of (a) MDICS, (b) HDICS (c) MDIBCD and (d) MDIGCD cross-linked adsorbents

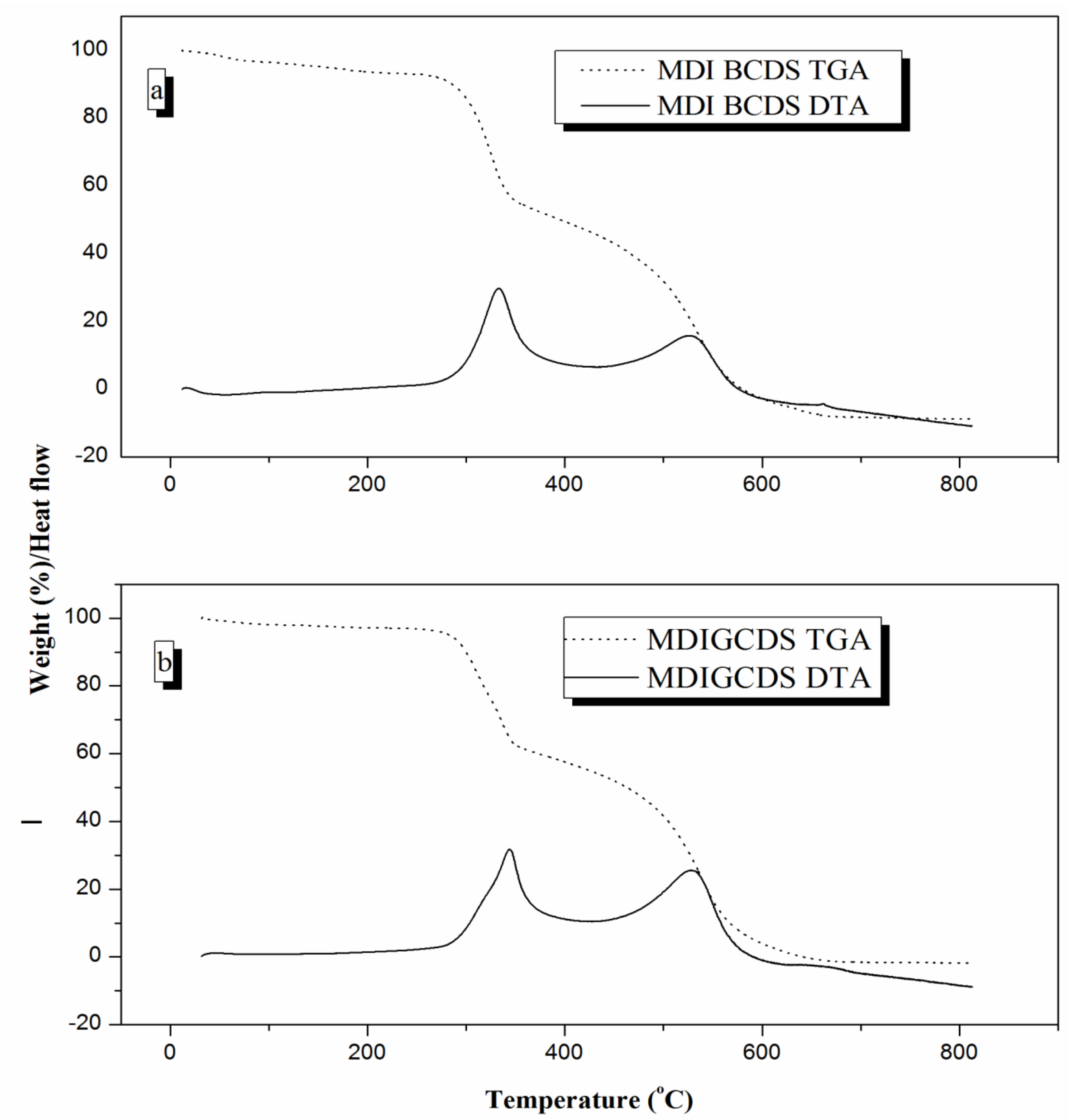


Figure 4.11. TGA and DTA plots of (a) MDIBCDS and (b) MDIGCDS polymer adsorbents

process. The last mass loss (42%) was between 352 – 620ºC corresponding to the broad exothermic peak at 520°C, ascribed to the slow oxidation of the organic matter.

All other MDI cross-linked adsorbents (MDIBCD, MDIGCD, MDIBCDS, and MDIGCDS) (Figures 10c, 10d, 11a, and 11b) exhibited a similar trend with that of MDICS. A similar trend has been recorded in literature (Costa *et al*., 2011).

4.3 Screening batch adsorption studies

Ultimately, the screening adsorption study was done to select the adsorbents with comparatively high sorption capacity, from the array of synthesized adsorbents for further studies, and thus develop them for subsequent use in water remediation and as SPE phase. The screening adsorption studies was also utilized to assess the correlation of the DFT predicted trend and the batch adsorption performance of the synthesized adsorbents, and thus assess the suitability of DFT quantum descriptors as a reliable tool for predicting adsorption performance of cross-linked starch and cyclodextrin adsorbents. In this vein, the data generated from the screening adsorption studies were evaluated to assess the effect of (i) nature of cross-linking agent (ii) degree of cross-linking (iii) nature of amination reagent and (iv) degree of amination on the adsorption capacity of the cross-linked starch adsorbents. Also, the screening adsorption study provided a veritable platform for comparing the adsorption performance of the adsorbents with that of Granulated Activated Carbon (GAC) standard, under the same experimental condition, since most literature citations might adopt different experimental conditions, which makes comparison to be difficult.

4.3.1Adsorption study using cross-linked starch polymer adsorbents

Figure 4.12(a, b, c, and d) showed the plots of adsorption performance against the arbitrary degree of cross-linking process. From the experimental results, it is observed that the trend of adsorption performance was MDICS > HDICS > EPICS. This was in tandem with the trend predicted by the DFT study. MDICS family of adsorbents had the highest adsorption capacity for all the studied PAHs of acenaphthylene, phenanthrene, and benzo[a]anthracene. This is attributed to high adsorbent-adsorbate interaction as predicted by DFT parameters. Another contributing factor for this observed performance was the π-π interaction which emanated from the fact that the target pollutants were aromatic

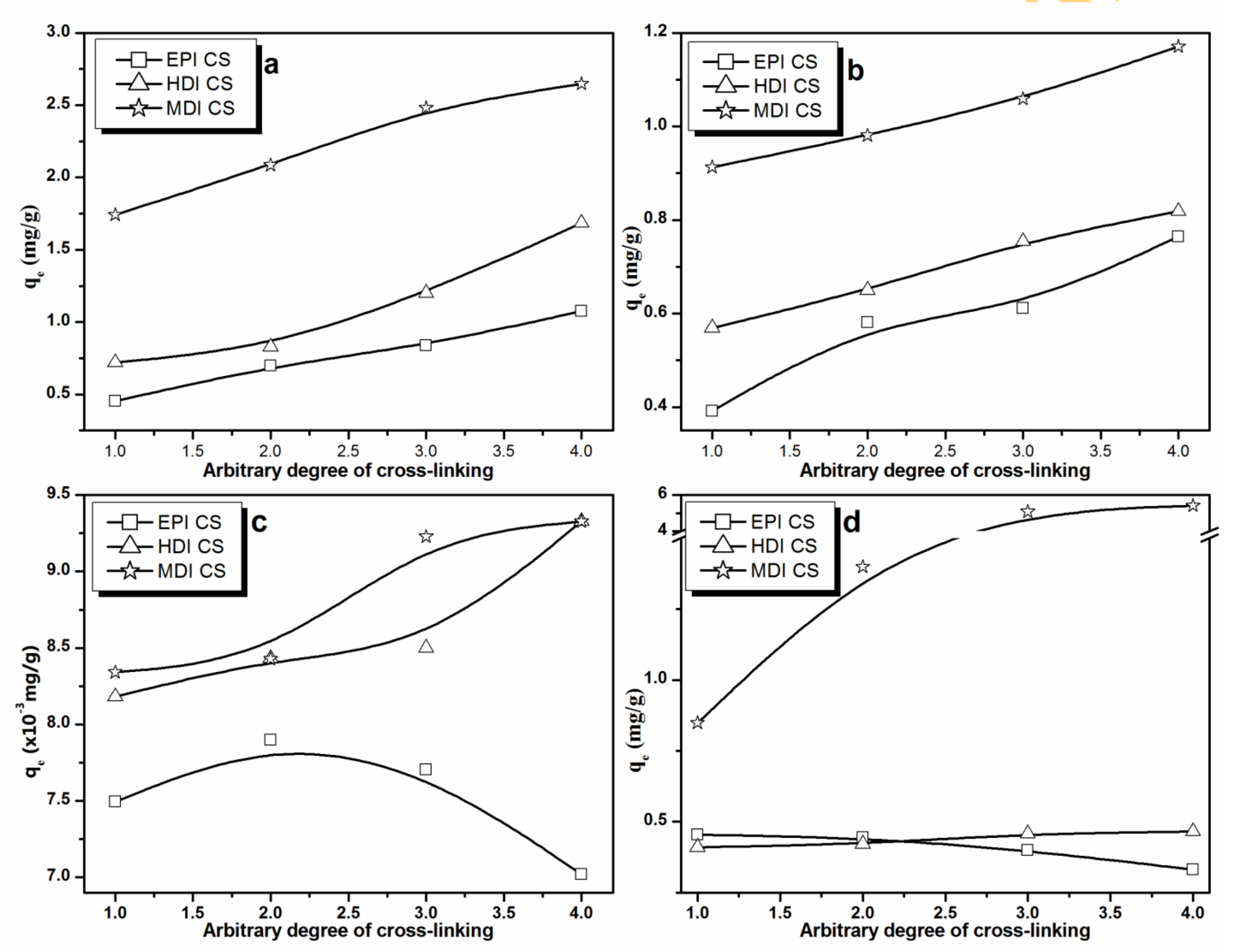


Figure 4.12. Effect of nature of cross-linking agent and the degree of cross-linking on the adsorption performance of cross-linked starch adsorbents for (a)acenaphthylene, (b) phenanthrene, (c) benzo[a]anthracene (BaA), and (d) diethyl phthalate (DEP)

compounds, and the MDICS set of polymers possesses aromatic properties as revealed by both their IR spectra and data from elemental analysis.

The HDICS family of adsorbents was the second in performance, as shown by their adsorption capacity for acenaphthylene, phenanthrene, and benzo[a]anthracene, while the EPI CS equally showed the least performance for all the studied PAHs. In addition to having the lowest values for most of DFT molecular interaction descriptors, the chemical structure of EPICS family was expected to have played a significant role in the adsorption process. Wilson *et al*., (2011) in explaining the adsorption performance of cross-linked β-cyclodextrin showed that the size of the interfacial spaces was directly dependent on the spacer arm length of the cross-link unit (Fig 4.2). Larger interfacial spaces translate to increased access to the binding sites and smaller spaces limit access due to steric hindrance. The adsorption performance of cross-linked adsorbents for a given molecule is therefore, expected to have a positive correlation with spacer arm length of the cross-link unit. Considering the chemical structure of the cross-linked adsorbents, it is obvious that EPICS has the shortest spacer arm length, and thus the smallest interfacial space.

DFT approach predicted positive correlation for degree of cross-linking and adsorption performance. The observed experimental adsorption of starch adsorbents for all the studied PAHs followed this prediction except the adsorption of EPICS adsorbents which did not strictly follow the trend. This observed deviation can be explained on the basis of steric effect which depends on two contributory factors viz: the spacer arm length of the cross-link unit and the molecular size of the adsorbates. Theoretically, the reduction in size of interfacial space is expected to be comparatively higher in EPICS than HDICS and MDICS, due to the fact that it has the shortest spacer arm length. Therefore, the effect of steric hindrance in the adsorption performance of the adsorbents, with a progressive increase in the degree of cross-linking, is expected to be stronger in EPICS family of adsorbents than others. The strength of this concept manifested in the experimental values and plots of the adsorption performance of the EPICS adsorbents. For acenaphthylene (Figure 4.12a), the effect of steric hindrance with a progressive increment in degree of cross-linking was not noticeable due to its small molecular size, however, for phenanthrene (Figure 4.12b), a relatively larger molecule, the effect of steric hindrance became noticeable at a very high degree of cross-linking. Benzo[a]anthracene (Figure 4.12c), which is the largest molecule among the studied PAHs (QSAR volume of 253 Ã), displayed the strongest effect of steric hindrance. Therefore, it can be said that for a given size of interfacial space, the effect of steric hindrance in adsorption increases with increment in molecular size. This observation is in tandem with what has been reported by Chao *et al*., (2008).

The result of the effect of nature and degree of cross-linking process on the adsorption of DEP on cross-linked starch adsorbent is shown in Figure 4.12d. The observed trend was only in agreement with the DFT prediction for the nature of the cross-linking process, while the observed trend for the degree of cross-linking was very much different. Considering the molecular structure of diethyl phthalate and the value of molecular dipole moment (3.40 Debye), it is expected that the adsorption interaction is controlled by two major contributing interactions of π-π and dipole-dipole interactions. For MDICS family of adsorbents, these two contributing interactions are in operation. However, due to the absence of aromatic group in EPICS and HDICS adsorbents, the π-π interaction is eliminated, and the dipole-dipole interaction dominates.

For the effect of degree of cross-linking on the DEP adsorption on cross-linked adsorbents, only MDICS set of adsorbents followed the trend predicted by the DFT quantum mechanical studies. This can be attributed to decrease in polarity index, (O+N)/C (Table 4.4), and the subsequent dominance of the π-π interaction over the dipole-dipole interactions with increase in the degree of cross-linking. For EPICS and HDICS, elemental analysis has shown that the polarity index, and subsequently dipole-dipole interaction decrease with increase in degree of cross-linking process. It is likely that this expected decrease in dipole-dipole interaction of these set of adsorbents manifested in the observed trend for the effect of degree of cross-linking on the adsorption performance.

4.3.2 Adsorption study using β-cyclodextrin polymer adsorbents

Figure 4.13 shows the plots for effects of nature and degree of cross-linking process on the adsorption capacity of β-cyclodextrin adsorbents for acenaphthylene, phenanthrene, benzo [a]anthracene and DEP.

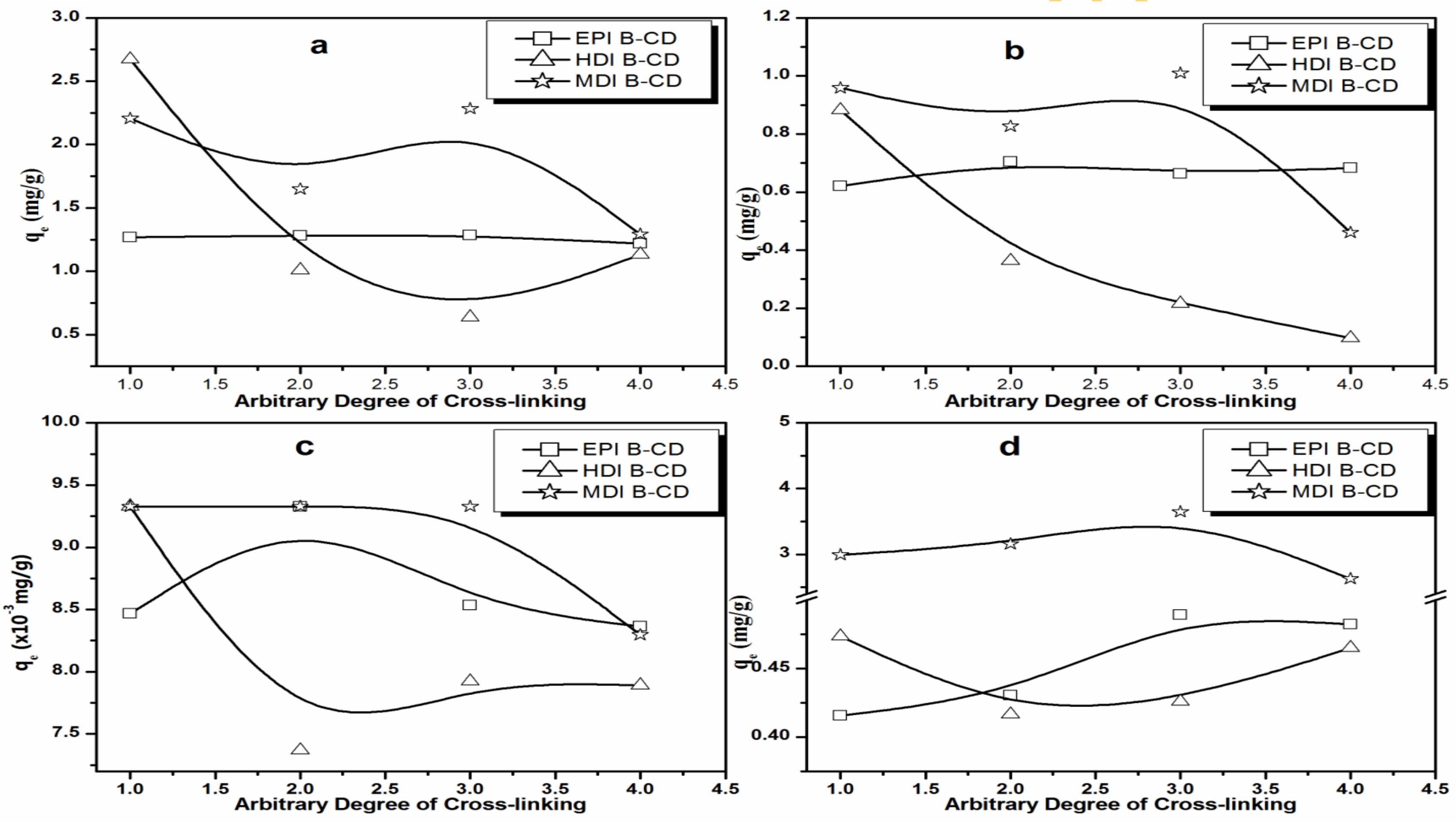


Figure 4.13. Effect of nature of cross-linking agent and the degree of cross-linking on the adsorption performance of β-cyclodextrin adsorbents for (a) acenaphthylene, (b) phenanthrene, (c) benzo[a]anthracene (BaA), and (d) diethyl phthalate (DEP)

The adsorption trend displayed by the β-cyclodextrin adsorbents for the effect of the nature of cross-linking process was in agreement with the DFT prediction, only at low degree of cross-linking process. This apparent deviation from the theoretical predictions is attributed to the type of the molecular interaction that is dominant in the adsorption process in each of the studied cases. Landy et al., 2012 has explained that the adsorption mechanism of cyclodextrin polymer adsorbents involved physical adsorption (dipole-dipole, van der Waal and π-π interactions) in the polymer network, hydrogen bonding, and formation of an inclusion complex on the cyclodextrin molecules through host–guest interaction (Fig. 4.2b). It is therefore obvious that the nature of cross-linking agent has great influence in determining the dominant adsorption interactions.

Considering the low dipole moment of PAHs, it is evident that only π-π interaction dominated the physical part of the adsorption process. Since MDIBCD has aromatic properites, both π-π interaction and host-guest interaction make significant contribution to the overall adsorption interaction of MDIBCD for PAHs. EPIBCD and HDIBCD adsorbents are non-aromatic, and therefore cannot have π-π interaction. Hence, host-guest interaction dominates the entire PAHs adsorption process by EPIBCD and HDIBCD adsorbents. However, DFT study only considered adsorption in the interstitial spaces of the cyclodextrin polymer adsorbents. Hence, the deviation of the experimental adsorption from the DFT prediction for effect of nature of cross-linking process is attributed to non consideration of host-guest interaction of cyclodextrin adsorbents in the DFT theoretical studies.

The effect of the degree of cross-linking on the adsorption performance showed entirely different trend from the DFT predicted trend. Due to the size of interfacial spaces and steric hindrance, the increment in degree of cross-linking leads to reduction in the contribution of host-guest interaction to the entire adsorption mechanism. Since host-guest interaction is the dominant adsorption mechanism for EPIBCD and HDIBCD, the adsorption performance is expected to decrease with increment in the degree of cross-linking. For MDIBCD adsorbents, the π-π interaction increased with increment in degree of cross-linking process, despite the decrease in host-guest interaction. The relatively steady adsorption performance observed for MDIBCD, with increment in degree of cross-linking process, is attributed to inverse relationship of these contributing interactions. However, at relatively high degree of cross-linking, the effect of steric hindrance led to the observed decrement.

The adsorption of DEP exhibited a somewhat different trend. For MDIBCD set of adsorbents, with a progressive increase in degree of cross-linking, there was an initial increment of adsorption performance to a certain maximum, after which subsequent increments resulted to decrease in adsorption. For EPIBCD and HDIBCD adsorbents, increment in degree of cross-linking did not result to reduced adsorption performance. These observations though not expected, can be explained on the basis of stability of host-guest inclusion complex of DEP. The stability of cyclodextrin host-guest inclusion complex has a negative correlation with the polarity of the guest molecule (Lichtenthaler and Immel, 1996). Considering the value of dipole moment of DEP (Table 4.1), it is obvious that the host-guest complex of DEP will be far less stable than those of PAHs. Therefore the adsorption contribution from physical adsorption will be the dominant adsorption mechanism. Since physical adsorption depends solely on the adsorption binding sites of the interstitial spaces, the adsorption performance increases with increase in the degree of cross-linking, until the certain maximum value where the effect of steric hindrance becomes dominant.

4.3.3 Effect of nature of amination reagent and degree of amination

In quantum chemistry, it has been shown that introduction of amino functional group (a nitrogen bearing group) in a molecule reduces the orbital energy band gap of the resultant molecule (Okoli *et al.*, 2014), and subsequently enhances the interaction potential of this molecule. In physical terms, it has also been observed that amination of cross-linked adsorbents improves the surface areas of these adsorbents (Deval *et al.*, 2005).

The plots of Figure 4.14 show the effect of nature and degree of amination on the adsorption performance of aminated cross-linked starch. For suitable comparison, low arbitrary degree of cross-linking was chosen in the synthesis of aminated cross-linked starch polymers (10 ml of epichlorohydrin per 15 g of soluble starch), to eliminate the effect of steric hindrance emanating from the degree of cross-linking, since earlier results have shown that steric hindrance was negligible at this level of reticulation. The plots of

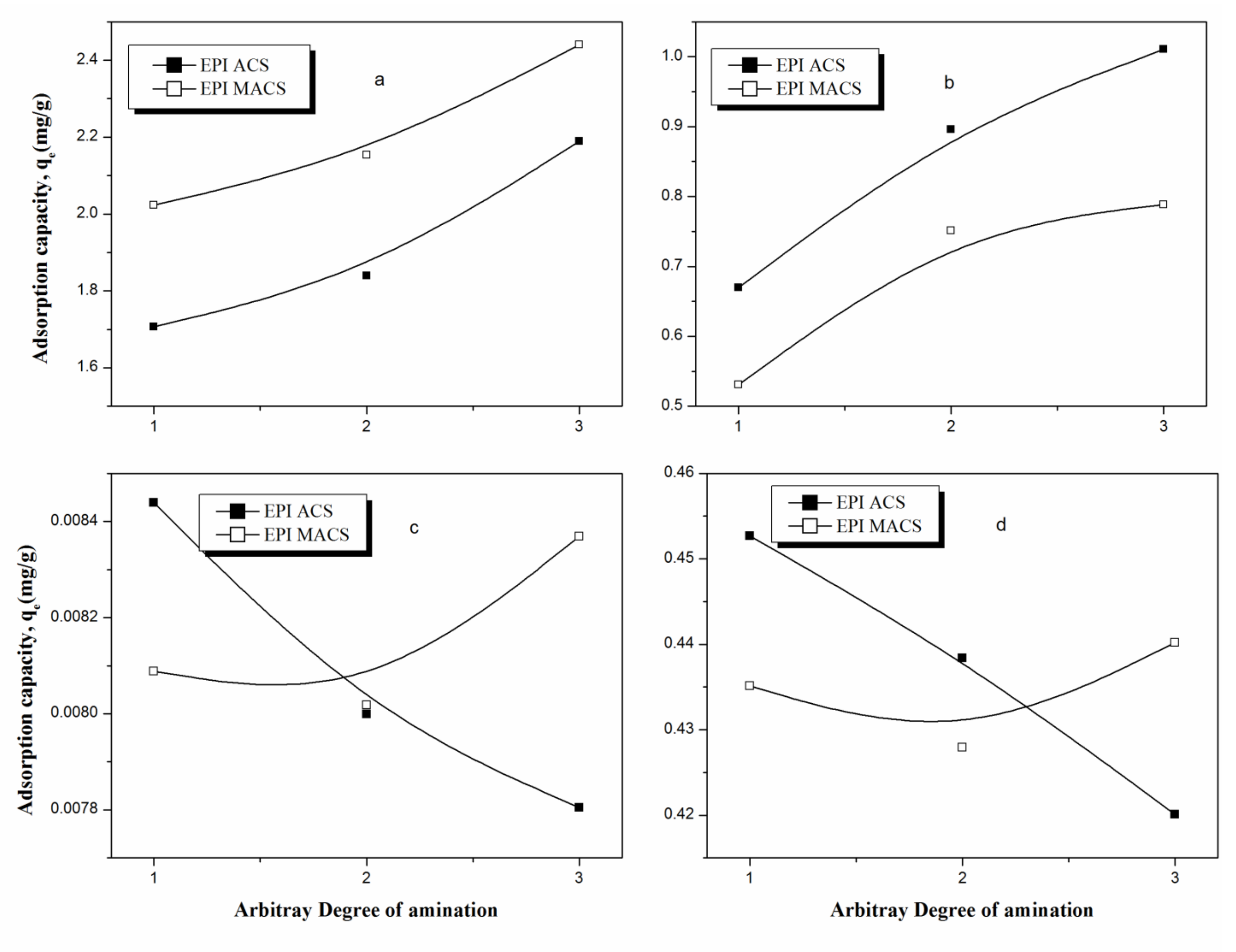


Figure 4.14. Effect of nature of amination agent and degree of amination on the adsorption performance of cross-linked starch adsorbents for (a) acenaphthylene (b) phenanthrene (c) benzo[a]anthracene (BaA) and (d) diethyl phthalate (DEP)

adsorption performance for acenaphthylene and phenanthrene indicated that the methyl aminated starch polymer (aminated with monomethyl amine reagent), EPIMACS set of adsorbents performed better than the ordinary aminated starch polymer (aminated with aqueous ammonia), EPIACS.

This observation can be explained on the bases of increment in the carbon content and subsequently the level of hydrophocity, as a result of additional methyl group on the EPIMACS set of adsorbents as revealed by their elemental analysis when compared to EPIACS set of adsorbents. The observed increase in the sorption performance of the adsorbents with increase in the degree of amination stems from the increase in the amine group which has been confirmed to increase the sorption of aromatic compounds (Deval *et al.*, 2005). However, the adsorption performance of EPIMACS for benzo[a]anthracene and diethylphthalate (DEP) exhibited a somewhat different trend from others. For benzo[a]anthracene, the adsorption performance decreased with successive increment in degree of amination within the investigated range of degree of amination, while that of DEP decreased first to a certain minimum, after which further increment in degree of amination resulted to increment in adsorption performance. The observed pattern displayed by benzo[a]anthracene and DEP can also be explained on the basis of steric hindrance as explained earlier.

4.3.4 Correlation between computational prediction and experimental adsorption

Since this study is the first to apply computational method for predicting adsorption trend of cross-linked starch and cyclodextrin polymers, it is necessary to study the extent of agreement of the experimental adsorption with the DFT predicted trend. Considering the fact that applying different cross-linking agents reflects different values of energy gap (ΔE), hardness (η), softness (S), and dipole moment, the relationship between the nature of cross-linking process/agent and adsorption performance was suitably evaluated by a correlation study between DFT parameters (ΔE, η, S, and dipole moment) and the mean adsorption capacity, $\bar{q}_e$ (see Table A4.9 of Appendix IV) of each family of adsorbents. Figures 4.15 and 4.16 showed the plots of DFT quantum chemical descriptors (ΔE, η, S, and dipole moment) against the mean adsorption performance of each family of adsorbents.

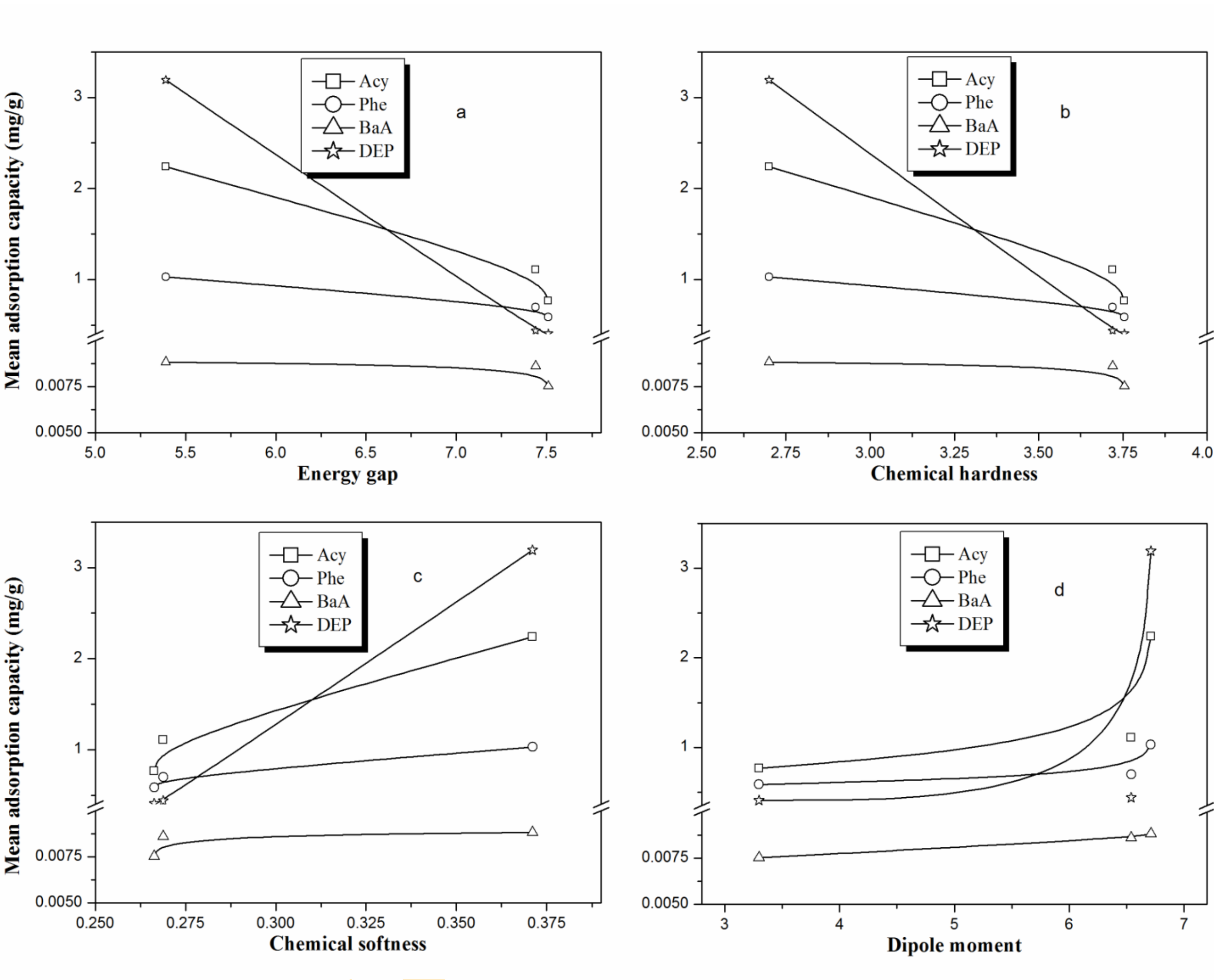


Figure 4.15. Plot of mean adsorption performance of families of cross-linked starch adsorbents vs (a) Energy gap, (b) Chemical hardness, (c) Chemical softness and (d) Dipole moment.

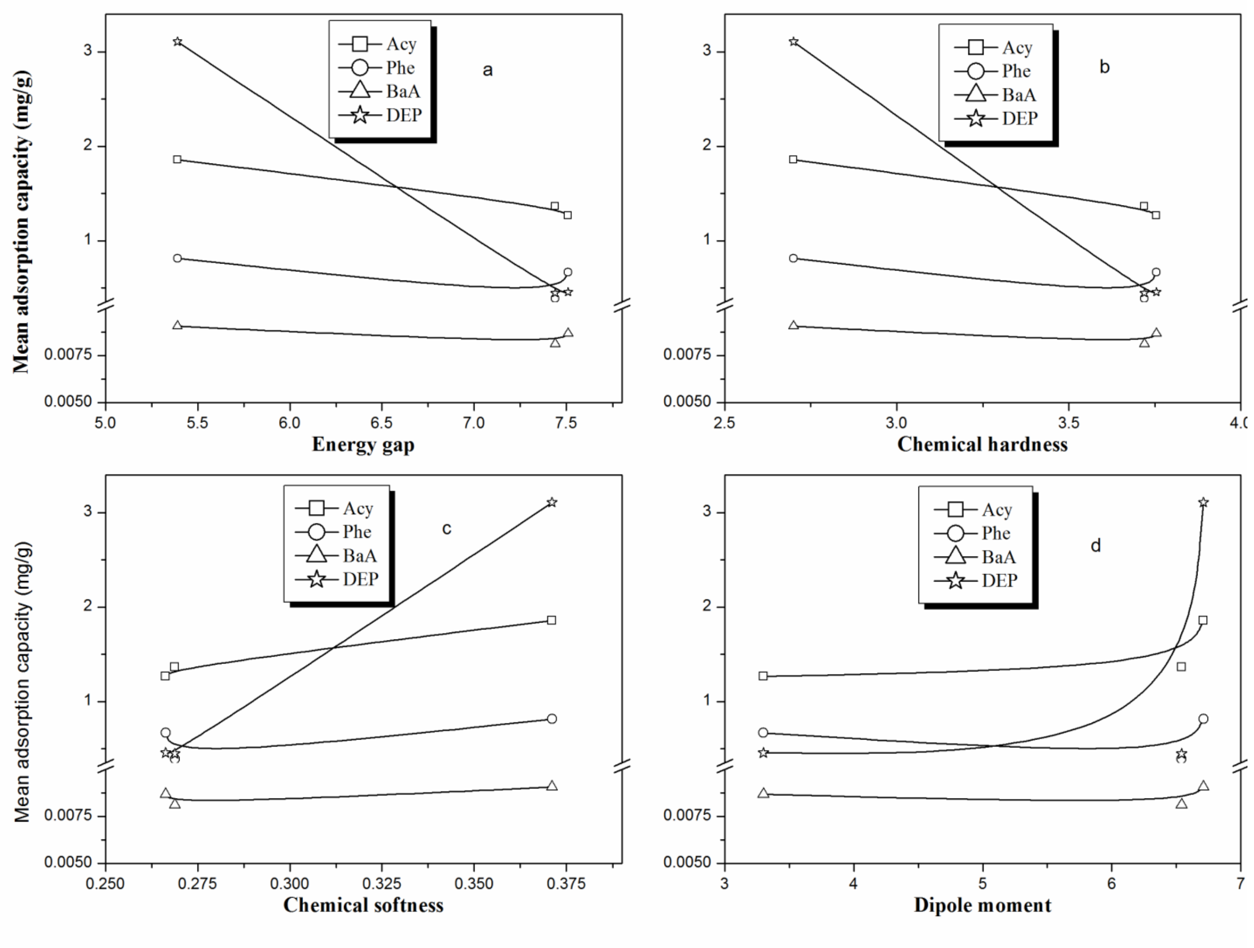


Figure 4.16. Plot of Mean adsorption performance of families of β-cyclodextrin polymer adsorbents vs (a) Energy gap, (b) Chemical hardness, (c) Chemical softness and (d) Dipole moment.

Table 4.8 showed the details of *r* values and linear equations of the correlation studies. ΔE, η and *S* gave better correlation coefficient ($r = 0.8849 \pm 0.1177$) than dipole moment ($R^2 = 0.3444 \pm 0.3000$). In a similar study, Shirvani et al, (2010) had observed poor correlation of dipole moment with adsorption, and explained that dipole moment correlates well with adsorption performance when electrostatic contribution plays a dominant role in the interaction process. The linear equation of the plots, $\bar{q}_e = mx + c$, (where $\bar{q}_e$ is the mean adsorption capacity for a given adsorbent family, *x* is the DFT parameter which translates to the nature of cross-linking process/agent, and m and c are constants that represent the slope and intercepts respectively) can be applied for estimating the mean adsorption capacity of each family of adsorbents, and subsequently the suitability of a given cross-linking agent for the synthesis of cross-linked starch and cyclodextrin adsorbents for a given pollutant (adsorbate).

The relationship between the degree of cross-linking and adsorption performance of the constituent adsorbents of each family of adsorbent has been explained earlier, as shown in figures 4.12 and 4.13. Linear correlation analysis for the plots (of Figures 4.12 and 4.13) indicated that the experimental trend for effect of degree of cross-linking process conformed better to theoretical predictions in starch adsorbents ($r = 0.9301 \pm 0.1218$) than the cyclodextrin adsorbents ($r = 0.7345 \pm 0.2068$) (see Table 4.9). Also, the analysis of the linear equation of the plots, $q_e = mx + c$, (where q_e is adsorption capacity for individual (constituent) adsorbents of each family, *x* is the arbitrary degree of cross-linking, and m and c are constants that represent the slope and intercepts respectively) showed that the values of *m* and *c* depended largely on the initial adsorbate concentration amidst other factors like the nature of adsorbents and adsorbates (Table 4.9). This situation primarily implied that the effect of degree of cross-linking process on adsorption capacity q_e, was more pronounced with increment in the initial adsorbate concentration. In summary, adsorption capacity of cross-linked starch and cyclodextrin polymer adsorbents has shown to be a function of the nature of cross-linking process/agent, degree of cross-linking, nature of adsorbates, and initial adsorbate concentration.

Table 4.8. Parameters for linear correlation study of DFT quantum descriptors and experimental adsorption performance

	Cross-linked starch adsorbents		Cyclodextrin adsorbents	
Adsorbates	Linear equation	r	Linear equation	r
Energy gap				
Acenaphthylene	$\bar{q}_e = -0.6283x + 5.6311$	0.9811	$\bar{q}_e = -0.2618x + 3.2694$	0.9921
Phenanthrene	$\bar{q}_e = -0.1874x + 2.0425$	0.9773	$\bar{q}_e = -0.1332x + 1.527$	0.7436
Benzo[a]anthracene	$\bar{q}_e = -0.0004x + 0.0109$	0.6536	$\bar{q}_e = -0.0003x + 0.0108$	0.8003
Diethyl phthalate	$\bar{q}_e = -1.3265x + 10.339$	0.9998	$\bar{q}_e = -1.2729x + 9.9654$	0.9995
Chemical Hardness				
Acenaphthylene	$\bar{q}_e = -1.2628\mathrm{x} + 5.6538$	0.9811	$\bar{q}_e = -0.5261\mathrm{x} + 3.2788$	0.9921
Phenanthrene	$\bar{q}_e = -0.3766\mathrm{x} + 2.0493$	0.9773	$\bar{q}_e = -0.2677\mathrm{x} + 1.5317$	0.7436
Benzo [a]anthracene	$\bar{q}_e = -0.0008\mathrm{x} + 0.0109$	0.6530	$\bar{q}_e = -0.0006\mathrm{x} + 0.0108$	0.8029
Diethyl phthalate	$\bar{q}_e = -2.558\mathrm{x} + 10.011$	0.9995	$\bar{q}_e = -2.558\mathrm{x} + 10.011$	0.9995
Chemical Softness				
Acenaphthylene	$\bar{q}_e = 12.641x - 2.4474$	0.9795	$\bar{q}_e = 5.2697x - 0.0974$	0.9911
Phenanthrene	$\bar{q}_e = 3.7693x - 0.3666$	0.9756	$\bar{q}_e = 2.7040x - 0.193$	0.7491
Benzo [a]anthracene	$\bar{q}_e = 0.0075x + 0.0060$	0.6475	$\bar{q}_e = 0.0064x + 6.6967$	0.8052
Diethyl phthalate	$\bar{q}_e = 26.733x - 6.7299$	0.9999	$\bar{q}_e = 25.655x - 6.4141$	0.9997
Dipole moment				
Acenaphthylene	$\bar{q}_e = 1.705x + 2.1067$	0.8873	$\bar{q}_e = 0.1094x + 0.891$	0.6614
Phenanthrene	$\bar{q}_e = 1.705x + 2.1067$	0.8873	$\bar{q}_e = -0.0151x + 0.7073$	0.1349
Benzo [a]anthracene	$\bar{q}_e = 0.0004x + 0.0063$	0.9933	$\bar{q}_e = -0.0001x + 0.0087$	0.0458
Diethyl phthalate	$\bar{q}_e = 0.454x - 1.1594$	0.5460	$\bar{q}_e = 0.4272x - 1.0216$	0.5353

Table 4.9. Parameters for linear correlation study of arbitrary degree of cross-linking and batch adsorption performance

Adsorbates	Adsorbents	Linear equation	r
Starch adsorbents			
Acenaphthylene	EPICS	$q_e = 0.2012x + 0.2625$	0.9951
	HDICS	$q_e = 0.3271x + 0.2901$	0.9674
	MDICS	$q_e = 0.3118x + 1.4598$	0.9881
Phenanthrene	EPICS	$q_e = 0.1149x + 0.3000$	0.9693
	HDICS	$q_e = 0.0853x + 0.4847$	0.9963
	MDICS	$q_e = 0.0852x + 0.8177$	0.9930
BaA	EPICS	$q_e = -0.0002x + 0.0079$	0.5530
	HDICS	$q_e = 0.0004x + 0.0077$	0.9105
	MDICS	$q_e = 0.0004x + 0.0079$	0.9355
DEP	EPICS	$q_e = -0.0416x + 0.5113$	0.9530
	HDICS	$q_e = 0.0204x + 0.3875$	0.9637
	MDICS	$q_e = 1.7413x - 1.1631$	0.9364
β-cyclodextrin adsorbents			
Acenaphthylene	EPIBCD	$q_e = -0.0149x + 1.3014$	0.57836
	HDIBCD	$q_e = -0.4991x + 2.6098$	0.717356
	MDICD	$q_e = -0.2112x + 2.385$	0.620645
Phenanthrene	EPIBCD	$q_e = 0.0144x + 0.6323$	0.521728
	HDIBCD	$q_e = -0.2502x + 1.0149$	0.933756
	MDICD	$q_e = -0.1313x + 1.142$	0.683228
BaA	EPIBCD	$q_e = -0.0001x + 0.0095$	0.374299
	HDIBCD	$q_e = -0.0004x + 0.0097$	0.577321
	MDICD	$q_e = -0.0003x + 0.0100$	0.774597
DEP	EPIBCD	$q_e = 0.0258x + 0.3899$	0.906808
	HDIBCD	$q_e = -0.0016x + 0.4493$	0.074162
	MDICD	$q_e = -0.0598x + 3.2558$	0.182757

4.3.5 Adsorption performance as basis for selection of adsorbents

The adsorption performance of the synthesized adsorbents from the screening adsorption study (see Appendix IV) showed that some of the adsorbents exhibited very good adsorption performance that is comparable to the performance of activated carbon standard. However, considering the adsorption performance of the various families of the synthesized adsorbents, and on individual basis, it was an onerous task to select the best among these families of adsorbents, because each of the families and even their constituent members has their own strengths and weaknesses. It is on this note that some desirable adsorption properties were laid down in their order of preference to serve as guide for selecting adsorbents for further studies. These desirable adsorption properties are: (i) high adsorption capacity (ii) wider spectrum of adsorption (iii) good physical properties and (iv) yield/efficiency of the synthesis.

In this regards, no member of EPICS, EPIBCD, HDIBCD, and HDIGCD sets of polymers was selected for further studies due to their low adsorption capacities and their narrow spectrum of adsorption as a result of steric hindrance. None of the aminated sets of polymers were considered for further studies mainly due to their low sorption capacities and synthetic inefficiencies. Similarly, EPIGCD was not selected despite having acceptable adsorption capacity, due to very low synthetic yield (<40 %).

For HDICS set of polymers, in addition to their relatively good adsorption capacity, their good physical properties like mechanical stability made them interesting. On this note, HDICS 4 was selected for further studies, and thereafter re-designated as HDICS since it represented this group of polymers. At low degree of cross-linking, MDICS polymers do not have good mechanical strength when wet, however, considering their very high adsorption capacity and their wide spectrum of adsorption for aromatic compounds, this set of polymers is adjudged to deserve further study. Therefore, MDICS4 was chosen and thereafter re-designated as MDICS to represent this group of adsorbents. In a similar vein, MDIBCD3 was selected to represent MDIBCD family. MDIGCD had only one variant, and hence was selected. Also, the MDIGCDS and MDIBCDS were selected to represent the mixed polymer adsorbents. In summary HDICS, MDICS, MDIGCB, MDIBCD, MDIGCDS and MDIBCDS were selected for further studies.

4.4 PAHs Adsorption studies

The detailed adsorption studies for PAHs were done using HDICS, MDICS, MDIGCD, MDIBCD, MDIGCDS and MDIBCDS.

4.4.1 Effect of contact time and kinetics study

The study for effect of contact time and kinetics is a useful parameter in the design of both the industrial adsorption columns and fluidized bed reactors. Except for adsorption capacity, kinetic performance of a given adsorbent is of great significance for the pilot application. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established. Also, one can know the scale of an adsorption apparatus based on the kinetic information. Generally speaking, adsorption kinetics is the base to determine the performance of fixed-bed or any other flow-through systems. In the current study, the rate of PAHs adsorption from solution can be used to assess the efficiency of the adsorbent to remove the pollutants from solution and thus can be applied in assessing its efficiency to clean up polluted water. Considering the fact that industrial wastewaters cannot be held in treatment plants for long periods, it is imperative that maximum sorption occurs in quick time, hence the need to establish the PAHs adsorption-time relationship for investigating various process conditions for the designing of water clean-up procedures.

Figure 4.17 showed the uptake rate for adsorption of phenanthrene, fluorene, and acenaphthylene onto cross-linked starch adsorbents (MDICS and HDICS) while figure 4.18 showed the uptake rate for adsorption of phenanthrene and fluorene onto cross-linked cyclodextrin (MDIGCD and MDIBCD) and cyclodextrin-starch mixed polymer (MDIGCDS and MDIBCDS) adsorbents. It was observed from the rate plots that time required to attain equilibrium was 720 minutes, however, a contact time of 1440 minutes has been employed for cross-linked starch adsorbents, just to monitor the possibility of further adsorption at this time. For adsorption of phenanthrene onto MDICS and HDICS, it was observed that there was a gradual increase in pollutant

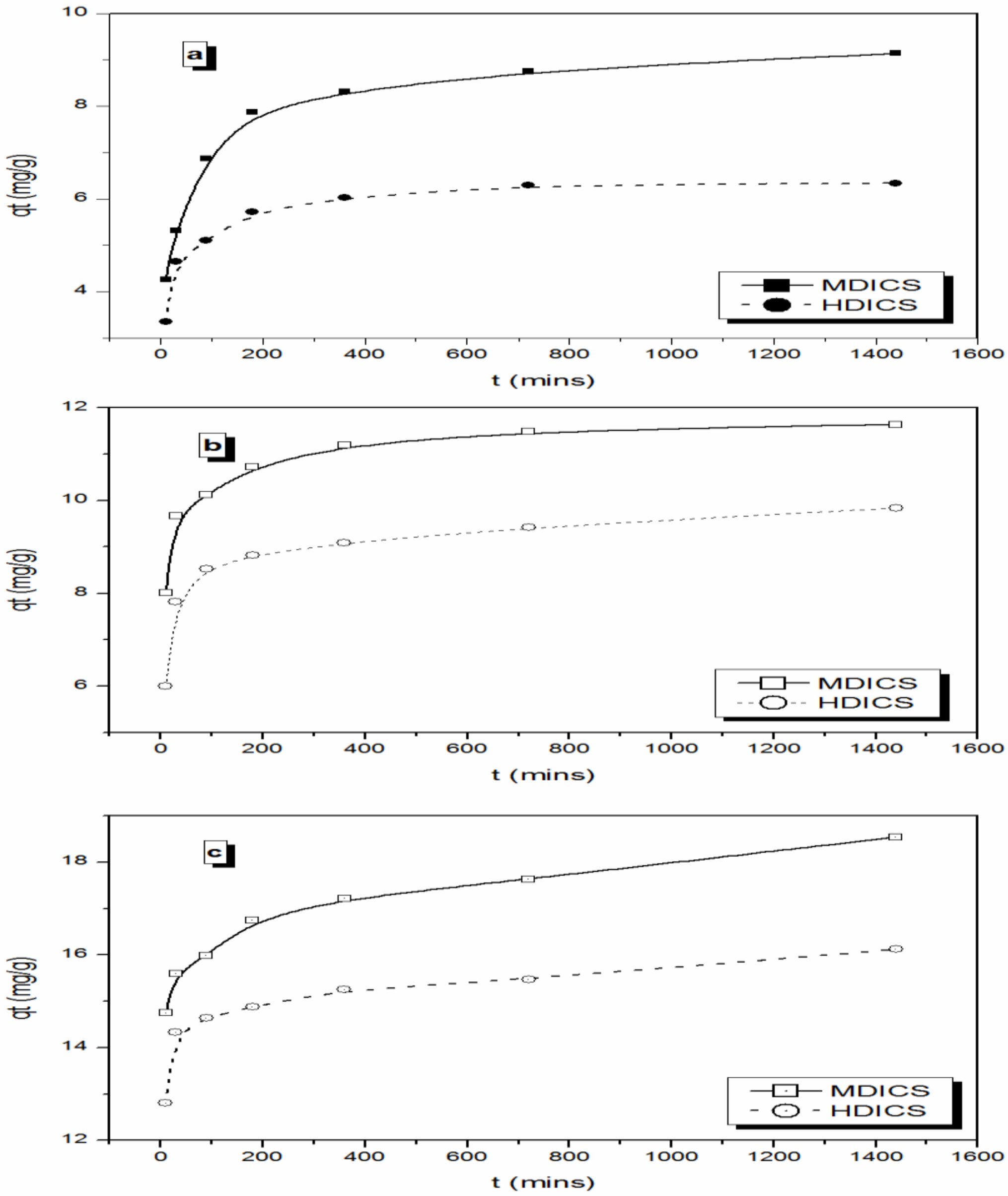


Figure 4.17. Rate plot showing the effect of contact time on the adsorption of (a) phenanthrene, (b) fluorene, and (c) acenaphthylene on MDICS and HDICS polymer adsorbents.

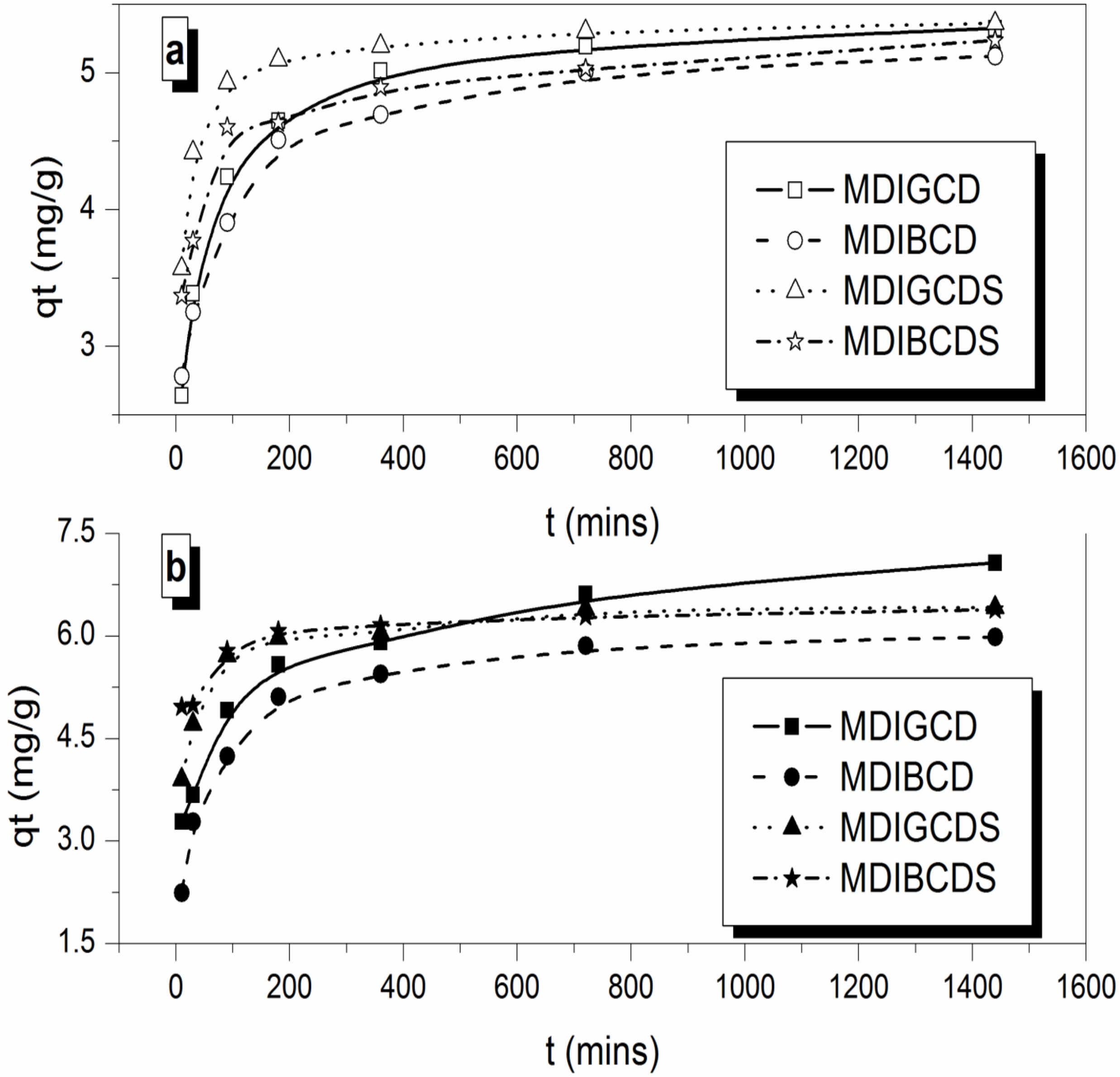


Figure 4.18. Rate plot showing the effect of contact time on the adsorption of (a) phenanthrene and (b) fluorene on MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS polymer adsorbents.

uptake from 42.7% (4.27 mg/g) and 33.5% (3.35 mg/g) at 10 minutes to a maximum of 87.6% (8.76 mg/g) and 63.0% at 720 minutes, and then the least increase to 91.50% (9.15 mg/g) and 63.4% at 1440 minutes for MDICS and HDICS, respectively. Acenaphthylene and fluorene followed a similar trend observed for phenanthrene. Also the adsorption of all the studied PAHs onto MDIGCD, MDIBCD, MDIGCDS and MDIBCDS followed a similar trend observed for phenanthrene. This observation can be attributed to the fact that a large number of vacant surface sites were available for adsorption during the initial stage, and with lapse of time, the remaining vacant sites would continually reduce.

It was observed from the rate plots that the cyclodextrin starch mixed polymer adsorbents (MDIGCDS and MDIBCDS) exhibited the fastest adsorption rate, with more than 90% of the total adsorption occurring in less than 3 hours, and attained equilibrium in less than 12 hours. The cyclodextrin polymer adsorbents (MDIGCD and MDIBCD) exhibited medium adsorption rate with over 80% of the total adsorption taking place within 3 hours, and also attained equilibrium in less than 12 hours. However, the cross-linked starch polymer adsorbents despite exhibiting over 90% of the total adsorption in less than 3 hours, it took more than 12 hours to attain equilibrium. This observation emanated from the pore distribution and surface area make-up of the adsorbents of the adsorbents. The surface area analysis (Tables 4.6 and 4.7) of the adsorbents showed that MDICS had highest ratio of surface area of pores to total surface area. The implication is that most of the adsorption sites for this adsorbent are located on the pore surfaces; hence these adsorbents have comparatively smaller external surfaces. Therefore more time is required to reach these sites than those on the external surfaces.

It has been shown that adsorption removal of adsorbate molecules from aqueous phase system proceed via three successive steps viz: (a) transport of molecules from the bulk of the solution to the exterior surface of porous adsorbent particles through a boundary layer (liquid film or external diffusion); (b) diffusion of the molecules through the interior pores of the adsorbent (intra-particle or internal diffusion); and (c) adsorption of molecules onto the active sites on the interior surface (Lazaridis and Asouhidou, 2003; Yuan et al., 2010). All the three steps could contribute to the overall adsorption kinetics, while the third step also controls the specific adsorption capacity and intensity. More often, one of the 3 steps offers the greatest resistance and is thus referred to as the rate limiting step of the whole sorption process. In practice however, unless chemical modifications occur during the sorption, the third stage is assumed to be too fast to contribute significantly to the overall sorption rate (Valderrama et al., 2008). It is thus generally understood that slow sorption kinetics are caused by rate-limiting diffusive mass transfer (Wu and Gschwend, 1988; Brusseau et al., 1991; Ball and Roberts, 1991). It is based on these concepts that the four kinetics models: two reactive (pseudo-first and pseudo-second order) and two diffusion based models (intra-particle and liquid film diffusion models) were used to test the mechanism that controlled the sorption process.

The comparative fit of the various models were as shown in Tables 4.10 and 4.11. A good correlation between the calculated and the experimental values of q_e, as well as the correlation coefficient (R^2) of pseudo-second order model for the kinetic data indicated that the adsorption of PAHs molecules onto cross-linked starch and cyclodextrin polymer adsorbent surfaces is governed by pseudo-second order kinetics model. This consistency of data indicates that PAHs sorption is controlled by physical adsorption (physisorption) involving hydrophobic, van der Waal and π-π interactions (for MDI cross-linked adsorbents only) between adsorbent and PAH molecules. This implied that adsorption capacity is proportional to the number of active sites occupied on the adsorbent surface (Olu-owolabi et al., 2012).

Liquid film and intra-particle diffusion models gave further insight into the controlling diffusion mechanism involved in the adsorption process. The fits of intra-particle diffusion curves indicate that diffusion of the phthalate molecules through the interior pores of the adsorbent had significant contribution to the overall adsorption kinetics. However, the fact that the curves did not pass through the origin (intercept not equal to zero) reveals that an initial boundary layer resistance existed, and equally indicates that the adsorption process was not solely dominated by pore diffusion (Fang and Huang, 2009). Hence, intra-particle diffusion was not the sole rate limiting step. The fits of liquid film diffusion model showed that transport of phthalate molecules from the bulk of the solution to the exterior

Table 4.10. Kinetic Parameters for the sorption of phenanthrene, fluorene and acenaphthylene onto MDICS and HDICS polymer adsorbents

Model parameters	MDICS			HDICS		
	Phenanthrene	Fluorene	Acenaphthylene	Phenanthrene	Fluorene	Acenaphthylene
Experimental q_e	9.1450	11.6370	18.5480	6.3380	9.8410	16.1220
Pseudo first order model						
K_1 (/min)(x10^{-3})	2.4415	2.6013	3.5407	2.4905	3.2407	4.6597
q_e(mg/g)	3.2144	2.8289	4.1915	1.494	1.8387	3.4613
R^2	0.9276	0.9376	0.9171	0.8099	0.224	0.8739
Pseudo second order model						
K_2(g/mg min)(x10^{-3})	3.8372	7.4959	3.4371	2.0842	5.8582	5.3434
q_e(mg/g)	9.2593	11.7054	18.5632	6.4103	9.8746	16.1238
h(mg/g min)	0.3292	1.0271	1.1844	0.8564	0.5709	1.3883
R^2	0.9994	0.9999	0.9992	0.9999	0.9993	0.9994
Morris-Weber Intra-particle Diffusion model						
K_{id}(g/mg min$^{1/2}$)(x10^{-2})	12.959	8.662	10.049	7.254	8.525	7.429
C	5.087	8.9806	14.9859	4.163	7.0983	13.5619
R^2	0.7311	0.6596	0.9212	0.6388	0.6278	0.7265
Liquid Film Diffusion Model						
K_{fd} (/min)(x10^{-3})	2.4400	2.5700	3.5400	2.4900	2.5804	4.6600
R^2	0.9276	0.9036	0.9171	0.8099	0.9393	0.8739

Table 4.11. Kinetic Parameters for the sorption of phenanthrene and fluorene onto MDIGCD, MDIBCD, MDIGCDS and MDIBCDS polymer adsorbents

Model parameters	MDIGCD		MDIBCD		MDIGCDS		MDIBCDS	
	Phenanthrene	Fluorene	Phenanthrene	Fluorene	Phenanthrene	Fluorene	Phenanthrene	Fluorene
Experimental qe	5.3270	7.0725	5.1235	5.9865	5.3625	6.4175	5.238	6.386
Pseudo first order model								
K1 (/min)($x10^{-3}$)	2.4600	2.3500	2.4300	2.3000	2.6700	2.5700	2.7400	2.6600
qe calc. (mg/g)	1.5573	3.1697	1.5623	2.2242	0.7655	1.2208	1.2776	0.9351
R^2	0.8840	0.9773	0.9100	0.8530	0.8513	0.7822	0.9442	0.9065
Pseudo second order model								
K_2(g/mgmin)($x10^{-3}$)	8.5610	3.2848	8.1522	5.2438	2.1504	1.1966	1.0960	1.6618
q_e calc. (mg/g)	5.3894	7.1865	5.1878	6.1039	5.3856	6.4712	5.2623	6.4111
h(mg/g min)	0.2487	0.1696	0.2194	0.1954	0.6237	0.5011	0.3035	0.6830
R^2	0.9998	0.9976	0.9996	0.9997	1.0000	0.9998	0.9995	0.9999
Morris-Weber Intra particle diffusion model								
K_{id} (g/mg $min^{1/2}$)($x10^{-2}$)	10.2000	14.0510	9.2180	14.4960	6.0940	9.3420	6.5960	5.9360
C (mg/g)	2.8743	3.1863	2.8361	2.4960	3.9677	4.2538	3.5344	4.9446
R^2	0.7844	0.8921	0.8477	0.8175	0.7011	0.6973	0.7240	0.7391
Liquid film diffusion model								
K_{fd} (/min)($x10^{-3}$)	3.5100	2.5600	3.4300	3.6300	3.7800	4.4900	2.6700	3.3500
R^2	0.8724	0.9254	0.9191	0.9168	0.7931	0.9009	0.7707	0.8091

surface of cross-linked adsorbents also contributed significantly to the rate controlling step. Hence, both intra-particle and liquid film diffusion contributed to the rate limiting steps.

4.4.2 Effect of adsorbent dose

Study of the effects of adsorbent dose is necessary for the optimization and selection of the best required dose for scale-up and designing large scale equipments. In this study, the effect of variation of the adsorbent dose for all the adsorbents was done with fixed phenanthrene solution concentration (1.0 mg/L) and volume (100 ml). Figure 4.19 showed the plots of q_e against adsorbent dose and % removal against adsorbent dose on the same x-axis, for MDICS and HDICS adsorbent. The result of MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS adsorbents (not shown) revealed a very similar trend with that of MDICS. This observation can be rationalized on the basis of similarity of the adsorption capacity of these adsorbents as earlier recorded in the batch screening adsorption study (see Appendix IV). In all the studied adsorbents, it was observed that increasing the dosage led to increment in percentage removal and decrement in equilibrium adsorption capacity. For instance, increasing the dose from a range 0.005 g through 0.050 g increased the percentage removal of phenanthrene from aqueous solution from 35.70% to 86.47%, and 83.78% to 97.10%, for HDICS and MDICS polymers respectively, while on the other hand, the equilibrium adsorption capacity, q_e, per unit mass of these adsorbents was found to decrease (3.57 mg/g to 0.86 mg/g and 8.38 mg/g to 0.97 mg/g for HDI and MDI polymers, respectively) with increased adsorbent dose as shown in Figure 4.19.

By increasing the amount of adsorbent, available sorption sites for sorbent- solute interaction is increased due to increased available surface functional groups, hence, leading to the increased percentage phenanthrene removal from aliquot solution. The q_e decrease with mass can be attributed to the decreasing total surface area of the adsorbent and an increase in diffusion path length due to aggregation of cross linked starch polymer particles. Also, as the weight of the polymer is increased, the aggregation becomes increasingly significant (Olu-owolabi et al., 2012), thus leading to the observed trend. Similar trends have been reported in literature (Farah et al., 2007; Ghanizadeh and Asgari, 2011) .

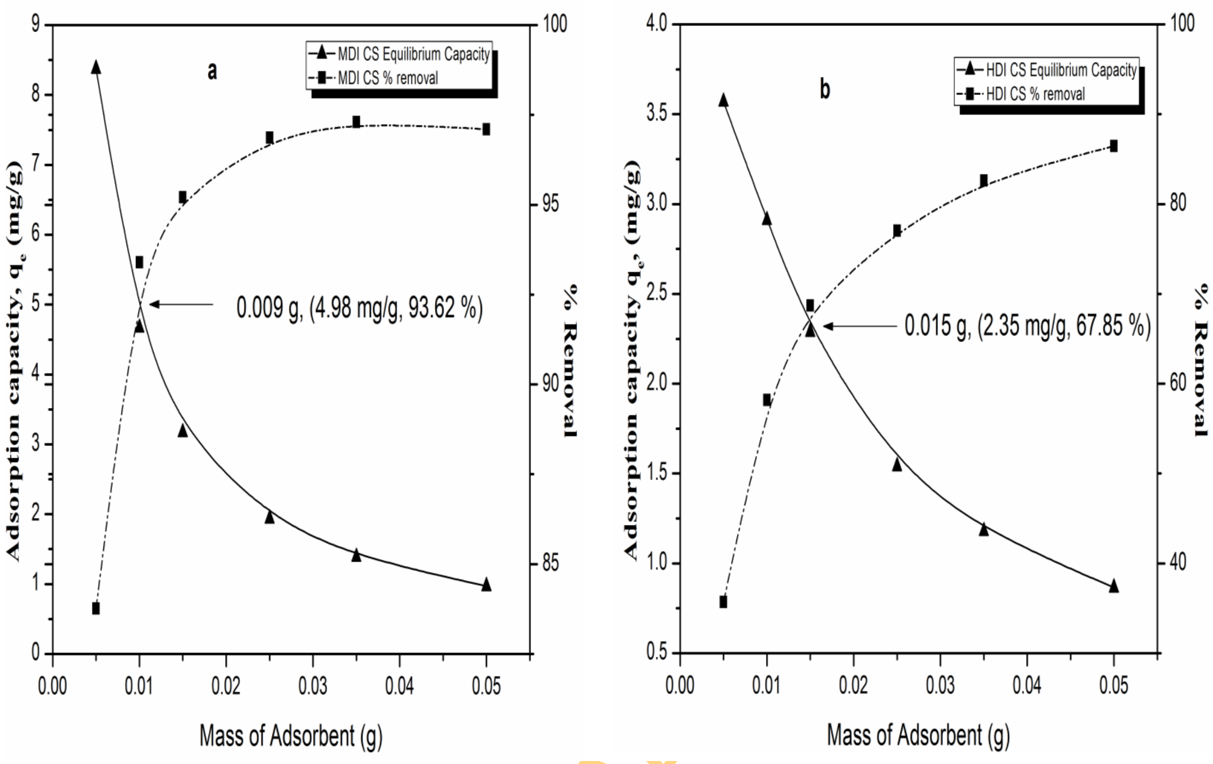


Figure 4.19. Effect of varying adsorbent dose on the sorption of phenanthrene

Considering the trend of % removal and q_e with increasing adsorbent dose, the optimum adsorbent dose was the point of intersection of their respective plots. Hence, the optimum adsorbent dose for HDICS was 0.015g (≈20mg), while MDICS (and similarly MDIGCD, MDIBCD, MDIGCDS and MDIBCDS adsorbents) was 0.009g (≈10mg). However, higher or lower adsorbent dose can still be applied depending on which of the measures (% removal or q_e) that needed to be maximized.

4.4.3 Effect of pH on the adsorption of PAHs

The study showed that pH changes did not significantly affect adsorption of phenanthrene (a model PAH) onto MDICS adsorbent from very low to moderately high pH values (Table 4.12). This observation is expected, and stems from the fact that both the surfaces of the adsorbents and the PAHs molecules are not charged, hence change in hydrogen ion concentration is expected to have minimum effect on the adsorbent-PAHs interaction. However, at very high pH values, there was a significant increment in adsorption performance. This can be explained on the basis that increasing pH induced deprotonation of the OH functional group on adsorbent surface and enhanced the π-electron-donor ability of the surface and, thus, strengthened π-π electron-donor-acceptor interactions of the aromatics. Similar trend has been observed in literature (Chen et al., 2008; Zeng et al., 2014).

Based on the foregoing, pH modification was not deemed necessary in the other adsorption experiments. Since the general pH value for freshwater aquaculture ranges from 7.0 to 9.0 (Adelekan and Ogunde, 2012), it is imperative that the adsorbents could be suitable for control of PAHs pollution in freshwater aquaculture systems.

4.4.4 Effect of water hardness (Ca^{2+} ions) and salinity (Na^{+} ions)

In Nigeria, groundwater is an important source for domestic and industrial use. Though Ca^{2+} was incorporated in all the working solution used for the adsorption studies to simulate environmental waters, independent study was necessary to investigate the effect of these ions on the PAHs removal. Groundwater is harder than surface water, so Ca^{2+} was used (the main component of hardness) as an indicator to evaluate the effect of Ca^{2+} coexistence on PAHs adsorption. The results showed that the adsorption efficiency of

Table 4.12. Effect of hardness (Ca^{2+}), salinity (Na^+), and pH on the adsorption of phenanthrene onto MDICS adsorbent

Ca^{2+} (mg/L $CaCO_3$)	q_e (mg/g)	Na^+ (Molarity)	q_e (mg/g)	pH	q_e (mg/g)
0.00	4.5505	0.00	4.5140	3.5	4.5395
75.0	4.5410	0.01	4.5020	5.0	4.5010
100.0	4.5795	0.05	4.4920	6.5	4.5495
125.0	4.5390	0.10	4.4520	8.0	4.5384
150.0	4.6045	0.25	4.6250	9.5	4.6254
175.0	4.7543	0.50	4.9770	11.0	4.8812

phenanthrene on the MDICS adsorbent was not significantly affected at any of the five different Ca^{2+} concentrations (Table 4.12). The predominant range of hardness in the groundwater in Nigeria was 70 – 140 mg/L as $CaCO_3$ (Adelekan and Ogunde, 2012), hence, using cross-linked starch as an adsorbent in a groundwater or freshwater system would be suitable.

To evaluate the feasibility of using the adsorbents to remove PAHs from a seawater system, information on the effect of NaCl (representative of salinity) on PAHs removal is vital. The average salinity in the Nigerian aquaculture system was 1500 mg/L (Adelekan and Ogunde, 2012), suggesting that the developed adsorbents might be applied in a seawater aquaculture system as well. Table 4.12 showed that alkalinity has no significant effect on the sorption of PAHs by cross linked starch adsorbents. This can be explained by the simple fact that neither the adsorbent nor the adsorbate increment in adsorption performance. This situation can be attributed to the principle of "salting out" which is predicated on the fact that solubility of non-polar organics decrease with increment in ionic strength.

4.4.5 Effect of initial PAHs concentration and isotherm study

Considering the fact that initial concentrations of the adsorbates that exist in real environmenatal water samples may be higher or lower than the ones chosen for the experimental adsorption study, the study of effect of initial adsorbate concentration is necessary in understanding the characteristics of the adsorbents, and hence the adsorption behaviour of these adsorbents in real life situations in the environmental media.

The influence of initial PAHs concentration on the adsorption performance of the cross-linked polymer adsorbents is shown on the plots of figure 4.20. The plots showed that the adsorption capacity of the adsorbents increased with increment in initial concentration of PAHs. The observed trend can be explained on the bases that as the initial adsorbate concentration increases, there will be higher availability of the PAHs molecules in solution. This provided increased driving force to overcome all mass transfer resistance of the adsorbates between the aqueous and solid phases. This situation resulted to higher probability of collision between PAHs and active adsorption sites of the adsorbent leading to higher pollutant uptake.

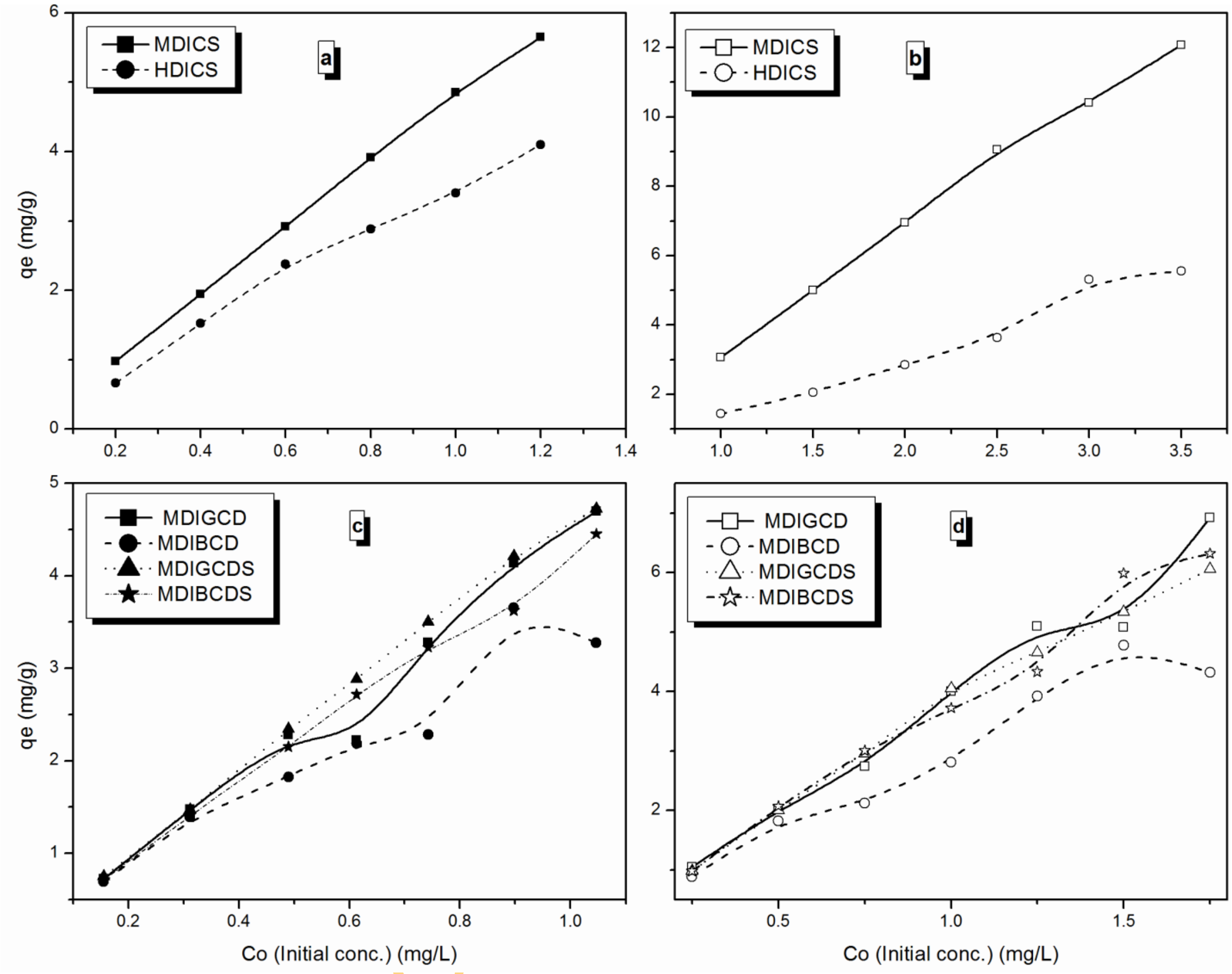


Figure 4.20. Plots showing the effect of initial concentration on the adsorption capacity of adsorbents for adsorption of (a) phenanthrene onto crosslinked starch adsorbents, (b) acenaphthylene onto crosslinked starch adsorbents (c) phenanthrene onto crosslinked cyclodextrin and mixed polymer adsorbents, and (d) fluorene onto crosslinked cyclodextrin and mixed polymer adsorbents

In the assessment of the adsorption capacity and surface properties of the adsorbents using the Langmuir, Freundlich, and Brauner-Emmet-Teller (BET) sorption isotherms, an isotherm is said to fit the adsorption data if the correlation coefficient (R^2) value is closer to unity than any other isotherm as well as the estimated adsorption capacity ($q_{e\ calc.}$) being close to the experimental value. The model parameters (Tables 4.13 and 4.14) showed that Langmuir model gave better R^2 values, however, the values of $q_{e\ calc.}$ were better correlated with the experimental q_e values for other isotherm models. The complexity of simultaneously comparing these variables (R^2 and q_e *calc.*) is made simpler by solving for $q_{e\ calc.}$ from the non-linear forms of these models using the model parameters obtained from their linear forms, and thereafter make a comparative plot of the experimental and isotherm model calculated values of q_e (Foo and Hameed, 2010).

The non-linear plots of the isotherm models are as shown in Figures 4.21, 4.22, and 4.23. The plots for starch based adsorbents (Figure 4.20) revealed that the experimental adsorption process for phenanthrene for both MDICS and HDICS were best described by BET isotherm and seconded by Freundlich, while that of acenaphthylene was best described by Freundlich and seconded by BET isotherms. In a similar manner, the adsorption of phenanthrene and fluorene onto the cyclodextrin polymers (MDIGCD and MDIBCD) and cyclodextrin-starch mixed polymer (MDIGCDS and MDIBCDS) adsorbents were either best described by BET isotherm, and seconded by Freundlich isotherm models, or vice versa. However, all the cases are still in tandem with the established fact that adsorption of PAHs occur via multilayer process (Olivella et al., 2011). Thus, this indicates that the adsorption of PAHs onto the studied cross-linked polymer surfaces obeyed both the Freundlich and BET multilayer adsorption isotherms. This can be explained by π-π stacking interaction that is being exhibited by PAHs. It was equally observed that all the MDI cross-linked adsorbents had higher adsorption capacities than HDICS. This situation can be attributed to the presence of aromatic rings in the structural make-up of these adsorbents. Also, the surface and pore characteristics of the adsorbents were expected to have played contributory role, as BET surface analysis showed that MDI cross-linked adsorbents had better surface and pore characteristics.

Table 4.13. Equilibrium model parameters for adsorption of phenanthrene and acenaphthylene onto cross-linked starch (MDICS and HDICS) adsorbents

Model	MDICS		HDICS	
Parameters	Phenanthrene	Acenaphthylene	Phenanathrene	Acenaphthylene
Langmuir Isotherm				
K_L	6.13424	0.509951	0.9486	0.22546
q_{max}	31.71583	13.55014	11.55135	13.3156
R^2	0.9669	0.9202	0.8223	0.8604
Freundlich Isotherm				
K_f	46.2732	12.1490	10.5548	4.0261
n	1.45601	0.76703	1.22574	0.80442
R^2	0.8219	0.9254	0.8304	0.7463
BET Isotherm				
K_B	45.6703	1.2594	4.6736	1.0700
Q	7.5239	25.6386	4.2087	10.7634
R^2	0.8728	0.2295	0.4889	0.2492
Tempkin Isotherm				
A	324.8162	3.6654	24.4784	3.2075
b	1284.3170	280.9808	1400.095	682.9052
R^2	0.9119	0.9779	0.9523	0.5940

Table 4.14. Equilibrium model parameters for adsorption of fluorene and phenanthrene onto cross-linked cyclodextrin (MDIGCD and MDIBCD) and cyclodextrin starch (MDIGCDS and MDIBCDS) polymer adsorbents

Model	MDIBCD		MDIGCD		MDIBCDS		MDIGCDS	
Parameters	Flu[a]	Phe[b]	Flu	Phe	Flu	Phe	Flu	Phe
Langmuir isotherm								
R^2	0.9336	0.9288	0.9587	0.8542	0.9336	0.9953	0.9797	0.9716
q_{max}	6.8488	3.3902	9.9502	6.6809	25.8598	6.8456	26.1300	6.8138
K_L	2.1108	15.9321	2.8645	12.2588	1.2832	8.6694	0.7501	20.8467
Freundlich isotherm								
R^2	0.8653	0.7671	0.8647	0.5654	0.8920	0.9598	0.9338	0.9449
K_f	5.4711	5.094	11.561	10.917	11.513	14.7072	11.0109	27.8285
n	1.5400	2.2600	1.3600	1.9300	1.2900	1.4700	1.3200	1.4500
Tempkin								
R^2	0.8689	0.60609	0.7141	0.42443	0.8352	0.9140	0.9781	0.9286
A	161.000	171.047	33.262	276.289	2.718	775.320	27.270	223.071
b	4595	3354	1160	2410	1099	3637	1124	1641
BET								
R^2	0.8132	0.8991	0.633	0.7128	0.7013	0.8905	0.9162	0.9079
K	20.0306	46.6553	11.2355	959.5931	7.8794	16.4919	9.0488	26.6061
Q	2.6056	2.1961	5.4304	2.3957	6.012	4.7483	5.5534	6.3596

[a] Fluorene

[b] Phenanthrene

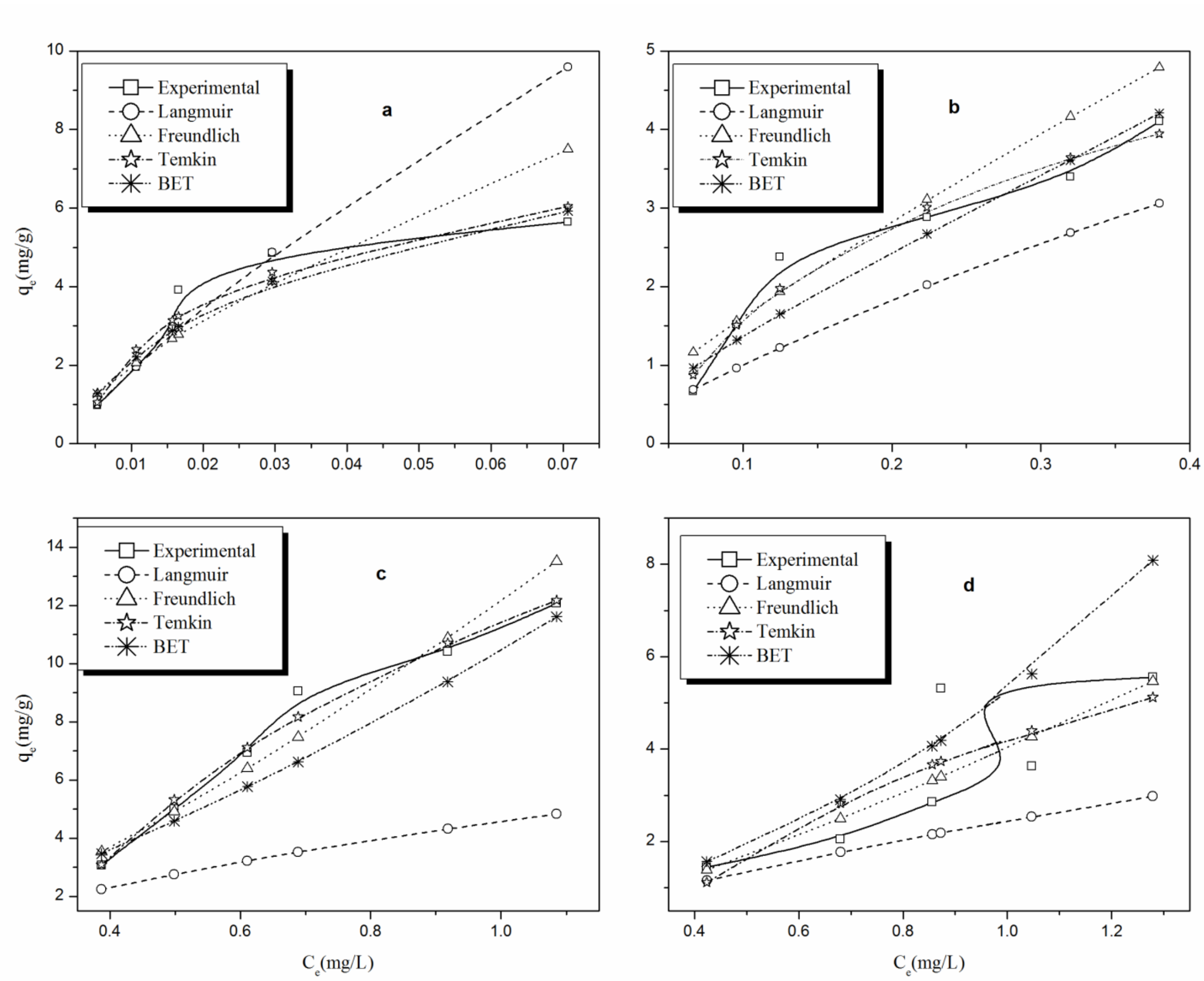


Figure 4.21. Plot of experimental isotherm (solid lines) and non-linear isotherm model fitting for the following adsorbent/adsorbate pairs: (a)MDICS/Phenanthrene (b)HDICS/Phenanthrene (c) MDICS/Acenaphthylene and (d)HDICS/Acenaphthylene

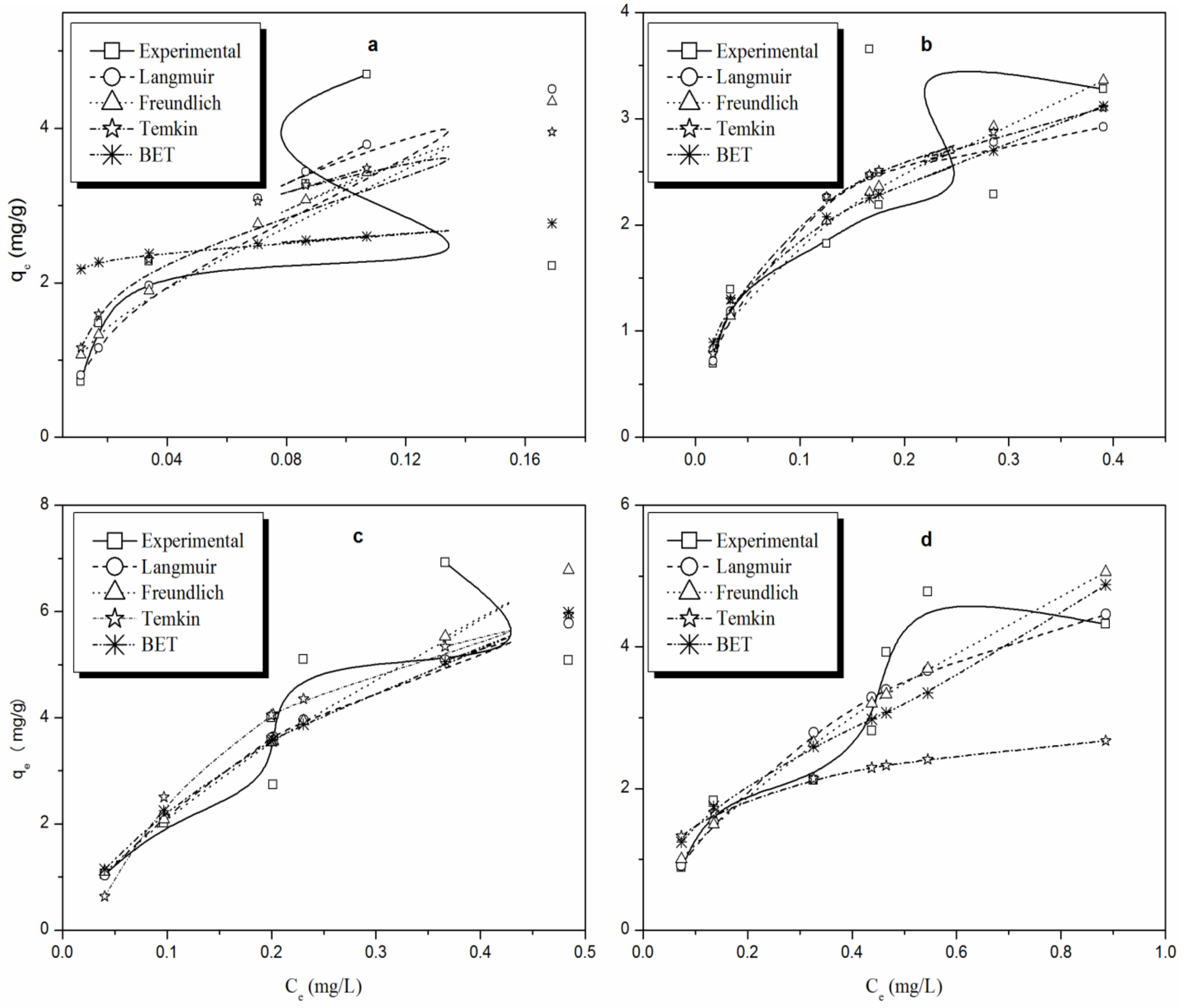


Figure 4.22. Plot of Experimental isotherm and non-linear isotherm model fitting for the cyclodextrin polymer adsorbent/adsorbate pairs: (a)MDIGCD/Phenanthrene (b)MDIBCD/Phenanthrene (c)MDIGCD/Fluorene and (d)MDIBCD /Fluorene

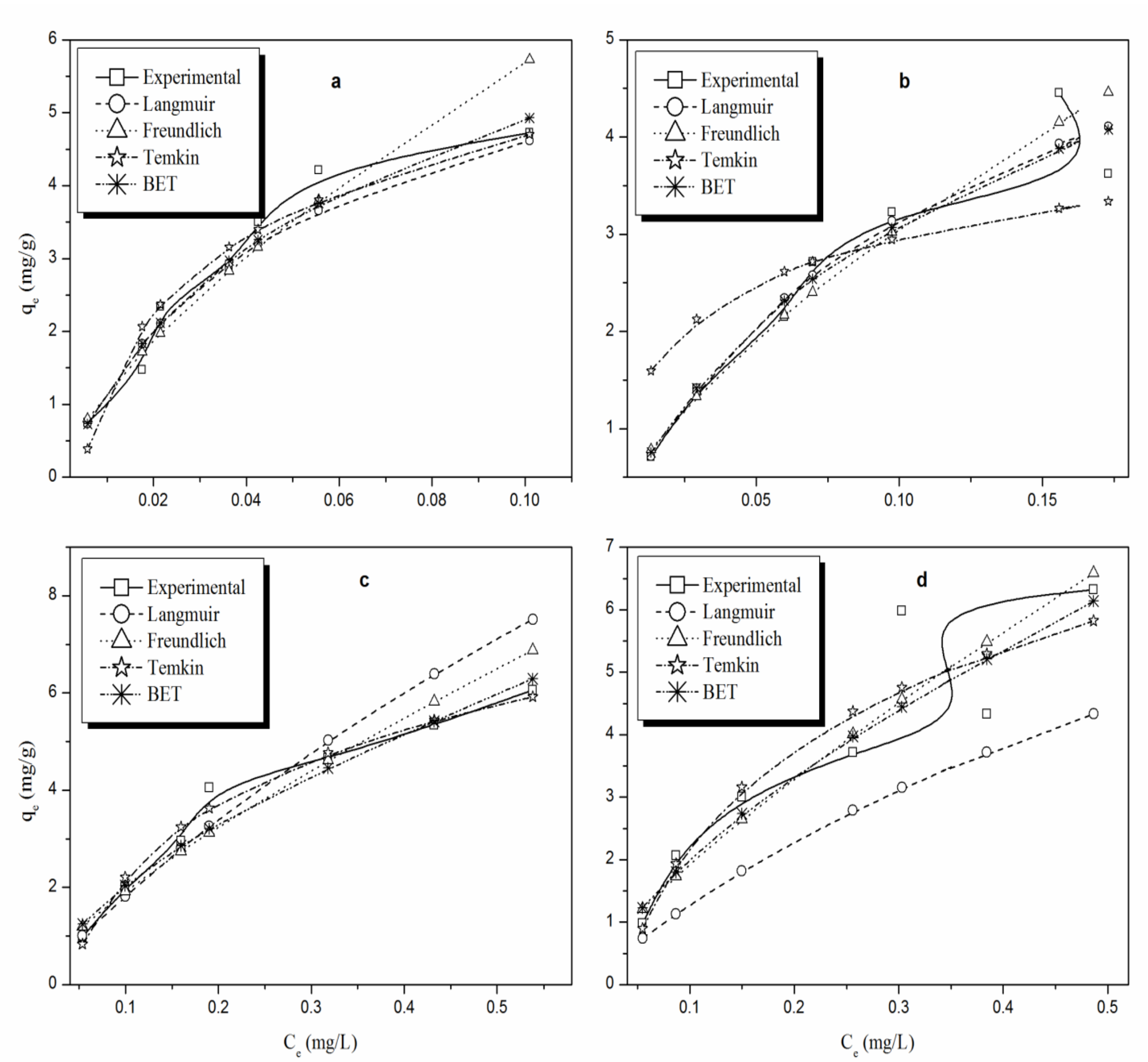


Figure 4.23. Plot of Experimental isotherm and non-linear isotherm model fitting for the cyclodextrin copolymer adsorbent/adsorbate pairs: (a)MDIGCDS /Phenanthrene (b)MDIBCDS /Phenanthrene (c)MDIGCDS /Fluorene and (d)MDIBCDS/Fluorene

The experimental adsorption isotherms of the studied PAHs for all the studied cross-linked starch and cyclodextrin polymer adsorbents were as shown in Figures 4.21, 4.22 and 4.23 (solid lines). According to the classification of Giles et al. (1960), convex initial curve of the adsorption isotherms indicate an L-type isotherm profile, while concave initial curve indicate an S-type of isotherm profile. Figures 4.21, 4.22 and 4.23 showed that the equilibrium sorption curves for the studied PAHs follow the L-type profile, S-type and borderline of L-type and S-type isotherm profiles in some cases. The sorption of phenanthrene by MDICS, HDICS, MDIBCD copolymer and MDIGCD copolymer showed L-type isotherm, while the borderline of L-type and S-type profiles were observed for MDIBCD and MDIGCD polymer adsorbents. For the sorption of fluorene, the MDIBCD and MDIGCD exhibited the borderline type of isotherm, while the MDIBCD and MDIGCD copolymer showed the L-type isotherm. Also, acenaphthylene adsorption by MDICS exhibited L-type isotherm, while HDICS exhibited S-type isotherm profile.

For the S-type adsorption isotherm, the initial direction of curvature shows that adsorption becomes easier as concentration rises. In practice, the S-type usually appears when the following three conditions are fulfilled: the solute molecule (a) is monofunctional, (b) has moderate inter-molecular attraction, causing it to pack vertically in regular array in the adsorbed layer, and (c) meets strong competition for substrate sites, from molecules of the solvent or of another adsorbed species. The definition of "monofunctional" in this context is that the solute molecule has a fairly large hydrophobic residue (>C_5,) and a marked localisation of the forces of attraction for the substrate over a short section of its periphery, and that it is adsorbed as a single unit and not in the form of a micelle (Giles et al., 1960). Since PAHs are non-polar and the solvent is polar, there is no likelihood of strong competition between the adsorbates (PAHs) and the solvent. Hence, only two conditions were met by the PAHs/adsorbent system, consequently the system did not exhibit complete S-type isotherm.

According to Giles classification, the initial curvature of the L-type isotherm profile shows that as more sites in the substrate are filled it becomes increasingly difficult for a bombarding solute molecule to find a vacant site available. This implies either that the adsorbed solute molecule is not vertically oriented (as against the S curve) or that there is no strong competition from the solvent (Giles et al., 1960). Since PAHs are non polar and the solvent is polar, there is no likelihood of strong competition between the adsorbates (PAHs) and the solvent. Hence, the only explanation for the exhibition of the L-type isotherm is that the PAH molecules were adsorbed flat. Though the current study is the first study on the adsorption of PAHs by cross-linked starch and cyclodextrin polymer adsorbents, previous studies on PAHs adsorption unto cork waste adsorbent by Olivella et al., (2011) had reported that PAH molecules were adsorbed flat.

On first approximation, all the observed isotherm profiles approaches linear isotherm, otherwise known as the C-type isotherm profile. The C-type isotherm is characterized by a constant partitioning of the adsorbate in the adsorbent and is obtained for solutes that penetrate into the solid more readily than the solvent. C-type isotherms have also been reported in different pesticides, phenols and chlorophenols.

Overall, the adsorption isotherm of PAHs for the studied adsorbents, were combinations of S-type and L-type isotherms, with elements of C-type in all the cases. This stems from the fact that the PAHs/adsorbent system did not completely meet all the conditions for any of the isotherm types, thus the implication of the partial fulfillment of the requirements for complete manifestation of these isotherms resulted to the exhibition of the borderline isotherm types of these principal isotherms. This observation indicated that (i) the adsorbates (PAHs) are monofunctional, (ii) PAHs have moderate inter-molecular attraction, causing it to pack vertically in regular array in the adsorbed layer and (iii) there was no strong competition from the solvent (ie water).

4.4.6 Effect of temperature and thermodynamic study

Considering the fact that solubility of organic compounds increase with increment in temperature, PAHs adsorption onto the adsorbents was expected to decrease with increment in aqueous temperature. However, it was observed that except for MDIGCD and MDIBCD polymer, the adsorption of other polymer adsorbents increased with increment in aqueous temperature until a certain maximum was reached, after which the adsorption decreased with increment in temperature (Figure 4.24). The phenanthrene adsorption by MDIGCD and MDIBCD polymer adsorbents decreased a little, and thereafter remained relatively constant as the temperature increased up to a certain point,

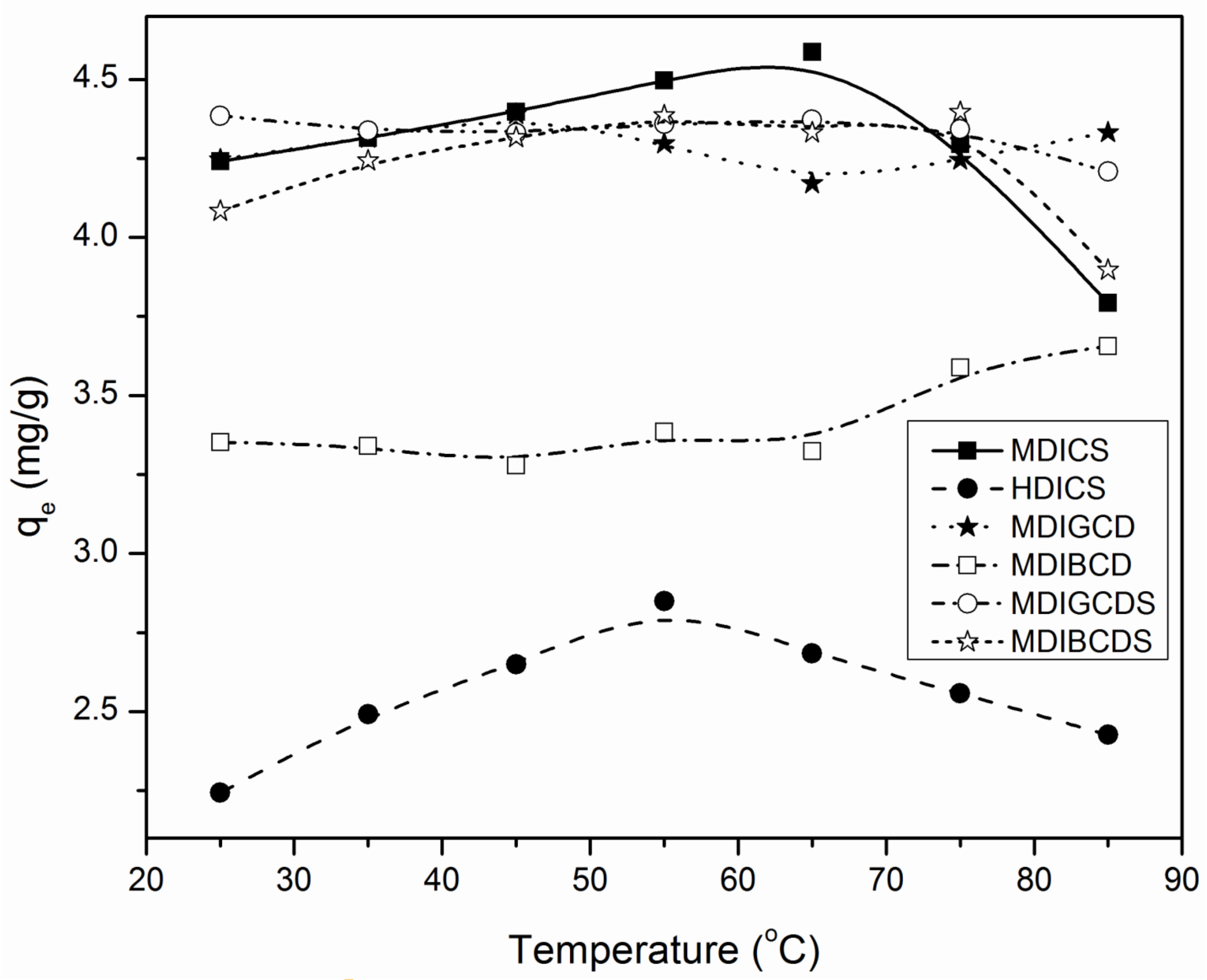


Figure 4.24. Effect of aqueous temperature on adsorption of phenanthrene on cross-linked starch and cyclodextrin polymer adsorbents

after which there were observable positive correlation with temperature. Overall, increase in temperature appeared not to have had any significant effect on the adsorption of phenanthrene onto the adsorbents. To gain more insights into the likely cause of the observed aberration, it became imperative to look at the mechanism of adsorption of PAHs onto these adsorbents under different temperatures. Since the experimental design of the first study only looked at the adsorption capacity (q_e) under different temperatures, the second study was designed to simultaneously investigate the effect of temperature on the kinetics (adsorption rate) as well as the equilibrium adsorption capacity. This was the rationale behind the thermodynamic study for adsorption of phenanthrene and acenaphthylene onto MDICS and HDICS adsorbents which was done in kinetic batch mode.

The result of the second thermodynamic study showed that increase in temperature led to a corresponding increment in the adsorption rate as evidenced in the values of rate constant, k_2 and initial reaction rate, h (Table 4.15). This effect may be due to the fact that at higher temperatures, the increase in heat and the subsequent kinetic energy leads to increased mobility of the solute, which results to higher adsorption rates. Also, the observed positive relationship between the temperature and k_2 and h still confirmed the fact that pseudo second order may not be the sole rate limiting step (Boparai *et al*., 2011)

The data showed that for phenanthrene, there was no significant change in equilibrium sorption capacity for MDICS polymer, whereas there was a noticeable increment in the sorption capacity values for HDICS. The trend became clearer with sorption data of acenaphthylene where the sorption capacity increased from 18.56 to 20.78 mg/g and 16.12 to 19.32 mg/g for MDICS and HDICS polymer adsorbents respectively, as the temperature increased from 25 to 60 °C. This observation can simply be explained by the fact that at higher temperature, starch based adsorbents swell in aqueous solution thus increasing access to more sorption sites that were hitherto inaccessible at lower temperatures. The marked difference in the magnitude of the increment of q_e for MDICS and that of HDICS can be explained in terms of the difference in their swellability as shown by a preliminary swellability test (result not shown). This study of effect of temperature showed that that the linearity of this observed trend was more visible for

Table 4.15. Kinetic model parameters for adsorption of PAHs at different temperatures

	Temp	k_2	R^2	q_e	h
Phenanthrene					
	25°C	0.0038	0.9994	9.2593	0.3292
MDICS	45°C	0.0054	0.9993	9.1600	0.4497
	60°C	0.0095	0.9996	8.9831	0.7682
	25°C	0.0208	0.9999	6.4103	0.8564
HDICS	45°C	0.0245	0.9998	6.7806	1.1255
	60°C	0.0253	0.9994	6.7159	1.1416
Acenaphthylene					
	25°C	0.0034	0.9992	18.5632	1.1844
MDICS	45°C	0.0058	0.9999	20.2061	2.3709
	60°C	0.0065	0.9999	20.7814	2.7899
	25°C	0.0053	0.9994	16.1238	1.3883
HDICS	45°C	0.0092	0.9999	18.4536	3.1227
	60°C	0.0153	1.0000	19.3237	5.7168

acenaphthylene than phenanthrene. This can as well be attributed to molecular size screening/steric effect, due to the fact that even with the swelling and the subsequent increase in pore size, the solutes with smaller molecular size will have more access to the hitherto inaccessible sorption sites than their bigger counterparts. This observation is another merit of these set of noble adsorbents, since it confers the adsorbents, the capacity to be applied for treating industrial effluents without compulsorily cooling them to ambient temperature unlike other adsorbents.

Investigations of the thermodynamic parameters of an adsorption process are necessary to ascertain the spontaneity of the process. The values of the thermodynamic parameters: free energy change (ΔG), enthalpy (ΔH) and entropy (ΔS) are shown in Table 4.16. The ΔG values for all the adsorbent-adsorbate systems were negative, indicating that the sorption process is spontaneous. It was also observed that as the temperature increases, ΔG decreases indicating the feasibility of adsorption at higher temperatures. ΔH values were positive, indicating endothermic process, except for adsorption of phenanthrene on MDICS which exhibited exothermic process with negative ΔH values (Table 4.16). ΔS values of sorption process were positive, which indicated increased randomness at the adsorbent/solution interface.

Since the temperature of Nigerian rivers and other water bodies generally remains below 40 °C throughout the year (Adebisi, 1981), cross-linked starch and cyclodextrin adsorbents can be applied in a Nigerian aqueous environment at ambient temperature.

4.4.7 Effect of competition

Knowledge of competitive sorption characteristics is critical for the environmental application of these adsorbents in wastewater treatment because real environmental water samples always contain potpourri of organic pollutants. Since all the MDI cross-linked adsorbents have exhibited similar characteristics MDICS and HDICS polymer adsorbents were selected for competitive adsorption studies. Result of the study showed that the presence of other aromatic compounds in the aqueous media enhanced the adsorption of PAHs, as evidenced by the values of the adsorption capacities in single and binary solutions (Table 4.17). This observation is predicated on π-π electron interaction between the PAH molecules. Recalling the fact that isotherm studies had confirmed that PAH

Table 4.16. Calculated values of thermodynamic parameters

Adsorbate/Adsorbent	ΔH	ΔS	ΔG(kJ/mol)		
	(kJ/mol)	(J/mol/K)	298K	318K	333K
Phenanthrene					
MDICS	-6.80	19.83	-12.71	-13.11	-13.4
HDICS	11.56	63.43	-7.34	-8.61	-9.56
Acenanphthylene					
MDICS	13.49	73.95	-8.55	-10.02	-11.13
HDICS	15.7	77.38	-7.36	-8.91	-10.07

Table 4.17. Model parameters for adsorption of PAHs from single and binary solutions

Adsorbents	PAHs solution	k_2	h		q_e
MDICS	Fluorene single	0.0075	1.0271	0.9999	11.7055
	Fluorene binary	0.0042	0.6368	0.9993	12.2594
HDICS	Fluorene single	0.0059	0.5709	0.9993	9.8746
	Fluorene binary	0.0055	0.5535	0.9992	10.0030
MDICS	Acy[a] single	0.0034	1.1844	0.9992	18.5632
	Acy binary	0.0021	0.8666	0.9989	20.4165
HDICS	Acy single	0.0053	1.3890	0.9995	16.1238
	Acy binary	0.0052	1.4619	0.9998	16.7757

molecules are adsorbed flat on the surfaces of these adsorbents, it is obvious that since these molecules are not chemically bonded to atoms of the adsorbents, the aromatic core of the adsorbed PAH molecules will exhibit stronger π-π interaction than free surface of the adsorbents. Hence, adsorbed PAHs molecules will act as better adsorption sites than vacant sites on the surfaces of the adsorbents. The resultant effect is that PAHs will prefer to adsorb in multi-layers than maintaining a monolayer. This is in consonance with the findings of the isotherm studies which confirmed that PAHs adsorption was best described by Freundlich and BET isotherm models, which are characteristics of multi-layer adsorption.

4.4.8 Effect of particle size

Difficulties in phase separation after adsorption have limited the application of powdered adsorbents in water decontamination (Cheng et al., 2007). Particles with bigger size are relatively easier to prepare than those of finer particles. However, for adsorbents with moderate porosity like the ones under study, increase in particle size reduces the accessible surface sorption sites. In some cases, adsorbents with low density float on water when the particles are too small. Particle size is therefore an important factor that needed to be moderated. Figure 4.25 showed that the effect of particle size had negative correlation to both the equilibrium sorption capacity and sorption kinetics for the two adsorbents under study. However, this effect was more significant on the equilibrium sorption capacity than the sorption kinetics. Considering the fact that the adsorption characteristics for sizes 1 and 2 were similar, size 2 was considered to be suitable as the optimum size.

4.5 Adsorption studies for phthalate esters

4.5.1 Effect of contact time and study of adsorption dynamics

The efficiency of the cross-linked adsorbent to remove phthalate esters from aqueous solution can be assessed by the rate of adsorption, and may be linked to its efficiency to cleanup waste water. From the adsorption rate curve (Figure 4.26), it was observed that adsorption for MDIGCD and MDIGCDS was rapid in the first 90 min with 72.9 % (6.7 mg/g) and 81.6 % (7.0 mg/g) respectively, of the total DEP adsorption occurring within

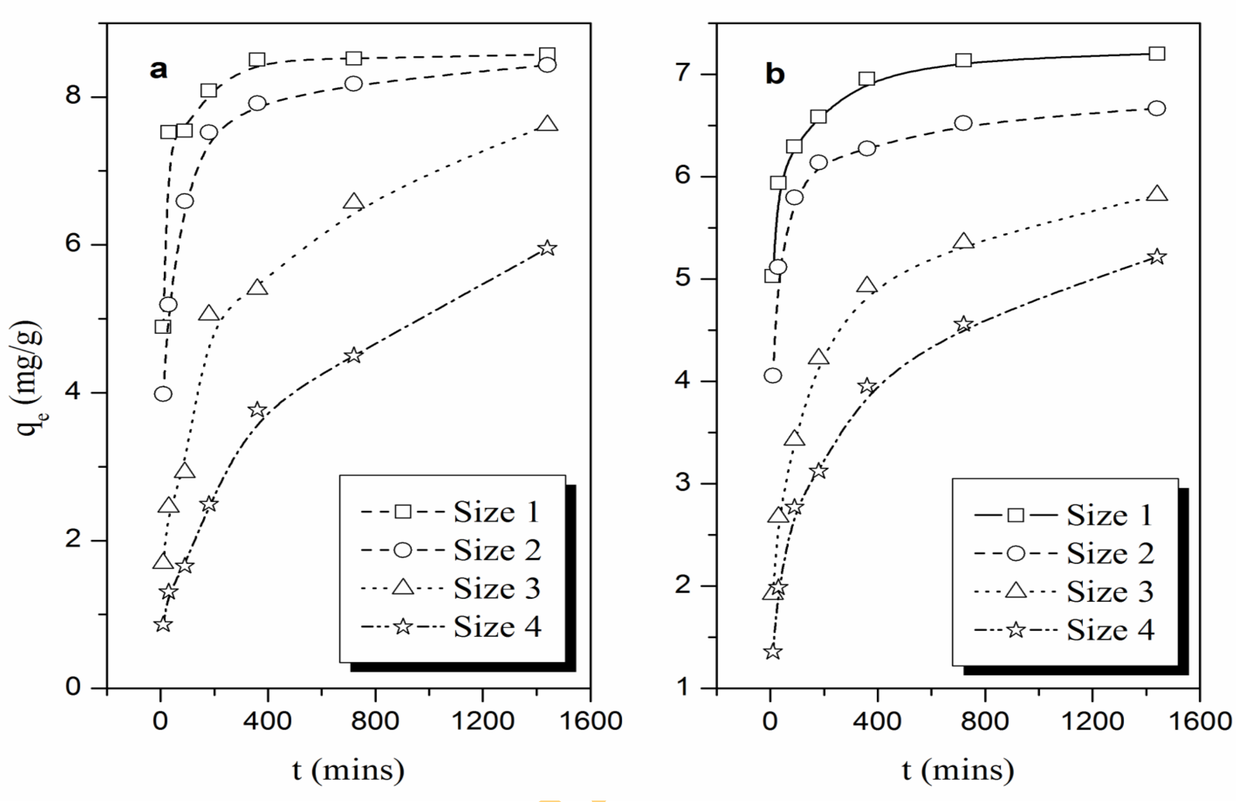


Figure 4.25. Kinetics plots of adsorption of phenanthrene by (a) MDICS and (b) HDICS adsorbents using different particle sizes.

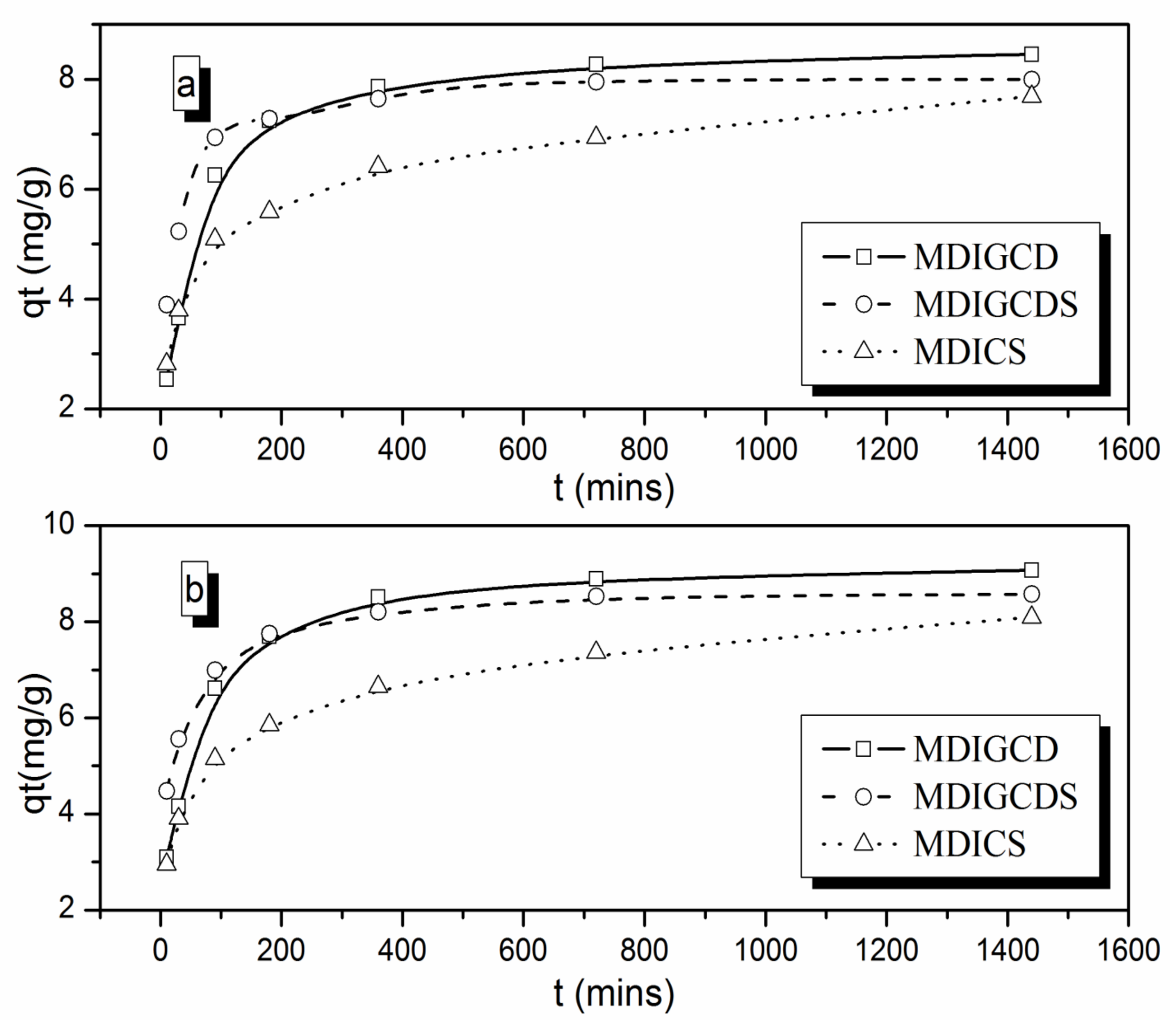


Figure 4.26. Rate plots showing the effect of contact time on the adsorption of (a) DMP and (b) DEP on MDIGCD, MDIGCDS and MDICS.

this time frame. As time elapsed, the rate decreased significantly until after 720 min when the percentage of DEP adsorption increased to 98.0 % (8.9 mg/g) and 99.9% (8.5 mg/g).

This trend of adsorption may be explained thus: the initial rapid increase in DEP uptake is due to the fact that a large numbers of vacant the cross-linked adsorbent surface sites are available for adsorption during the initial stage and since these have very high affinity for DEP, they are filled rapidly. After this initial rapid adsorption, it is likely that the remaining part of adsorption are dominated my micro-pore filing process, which is normally a gradual process. The fact that BET surface analysis has revealed the existence of significant level of micro-pores also laid more credence to the dominance of micropore filling at the later part of the adsorption process. However, the rate curve for the adsorption of MDICS adsorbent was somewhat different from that of MDIGCD and MDIGCDS counterparts (Figure 4.26). The rate curve showed that DEP adsorption for MDICS was less rapid than those of MDIGCD and MDIGCDS adsorbents, with more than 63.7 % (5.2 mg/g) of the total DEP adsorption occurring in the first 90 min. Unlike that of MDIGCD and MDIGCDS adsorbents, significant level of adsorption still occurred after the first 90 min, with adsorption increasing to 90.9 % (7.4 mg/g) in 720 min. Also, significant adsorption still occurred after 720min. Hence, the time required to attain a rapid equilibrium is 720 min. However, a contact time of 1440 min has been employed for every other study because of this possibility of further adsorption. The rate curves of DMP adsorption on the respective adsorbents also followed similar trends with that of DEP. Hence, the same explanation for DEP adsorption will suffix for these similar observations.

As explained earlier in the adsorption of PAHs, adsorption removal of adsorbate molecules from aqueous phase system proceed via three successive steps viz: (a) transport of molecules from the bulk of the solution to the exterior surface of porous adsorbent particles through a boundary layer (liquid film or external diffusion); (b) diffusion of the molecules through the interior pores of the adsorbent (intra particle or internal diffusion); and (c) adsorption of molecules onto the active sites on the interior surface (Lazaridis and Asouhidou, 2003; Yuan et al., 2010). The theory behind these concepts has been discussed in details for adsorption of PAHs. It is based on these concepts that the four kinetics models: two reactive (pseudo-first and pseudo-second order) and two diffusion based models (intra-particle and liquid film diffusion models) were used to test the mechanism that controlled the sorption process.

The comparative fits of the various models (Table 4.18) indicates that the adsorption of phthalate molecules onto the active sites on the surfaces of the adsorbents fit the pseudo-second-order kinetics better than for pseudo-first-order kinetics because the R^2 value as well as the experimental qe value of the pseudo-second-order is better correlated. Liquid film and intra-particle diffusion models gave further insight into controlling diffusion mechanism involved in the adsorption process. The fits of intra-particle diffusion curves indicate that diffusion of the phthalate molecules through the interior pores of the adsorbent had significant contribution to the overall adsorption kinetics. However, the fact that the curves did not pass through the origin ($C_{id} \neq 0$) indicates that intra-particle diffusion is not the only rate limiting step. The fits of liquid film diffusion model showed that transport of phthalate molecules from the bulk of the solution to the exterior surface of cross-linked adsorbents is the rate controlling step.

4.5.2 Effect of adsorbent dose

Figure 4.27 showed the plots of q_e and % removal against varying adsorbent dose (10 to 100 mg). It was observed that increasing the adsorbent dose in the studied range increased the % removal of DEP from 33.0-77.7, 31.0-92.3, and 30.7-93.4% for MDIGCD, MDIGCDS, and MDICS, respectively. On the other hand, the equilibrium adsorption capacity q_e per unit mass of the studied adsorbents was found to decrease 6.4-1.5, 6.0-1.8, and 5.9-1.8 mg/g for GPP, GSP, and SPP, respectively, with increasing adsorbent dose. Similar reports are found in literature (Chan *et al*. 2004). It is apparent that by increasing the amount of cross-linked adsorbent, available sorption sites for sorbent-solute interaction is increased due to increased available active surface adsorption sites, hence, leading to the noticed increased percentage phthalate removal from the aliquot solution. Olu-owolabi et al. (2012) have attributed the q_e decrease with increasing mass to the decreasing total surface area of the adsorbent and an increase in diffusion path length due to aggregation of adsorbent particles, and as the weight of the cross-linked adsorbents increased, the aggregation becomes increasingly significant.

Table 4.18. Kinetic Parameters for the adsorption of DMP and DEP onto MDIGCD, MDIGCDS and MDICS polymer adsorbents

Kinetic Model	MDIGCD		MDIGCDS		MDICS	
	DMP	DEP	DMP	DEP	DMP	DEP
q_e Expt	8.4574	9.072	7.9959	8.5726	7.688	8.0944
Psuedo First Order						
q_e calc	3.2160	3.3601	1.8288	2.0924	3.9743	4.2691
k_1	0.0023	0.0022	0.0025	0.0024	0.0024	0.0022
R^2	0.7941	0.7965	0.7629	0.7726	0.9749	0.9812
Psuedo Second Order						
$q_{e\ calc}$	8.6535	9.273	8.0854	8.6798	7.8162	8.2549
k_2	0.0034	0.0033	0.0078	0.0066	0.0023	0.0022
h	0.2546	0.2894	0.5099	0.5028	0.1507	0.1514
R^2	0.9999	0.9998	0.9999	0.9999	0.9963	0.9964
Intra-particle diffusion						
K_{id}	0.1581	0.1629	0.1001	0.1073	0.1302	0.1404
C_{id}	3.7239	4.1811	5.0568	5.3875	3.3314	3.3990
R^2	0.6454	0.6718	0.5695	0.6500	0.8543	0.8739
Liquid Film Diffusion						
K_{fd}	0.0023	0.0022	0.0025	0.0023	0.0024	0.0023
R^2	0.7940	0.7965	0.7629	0.7726	0.9749	0.98115

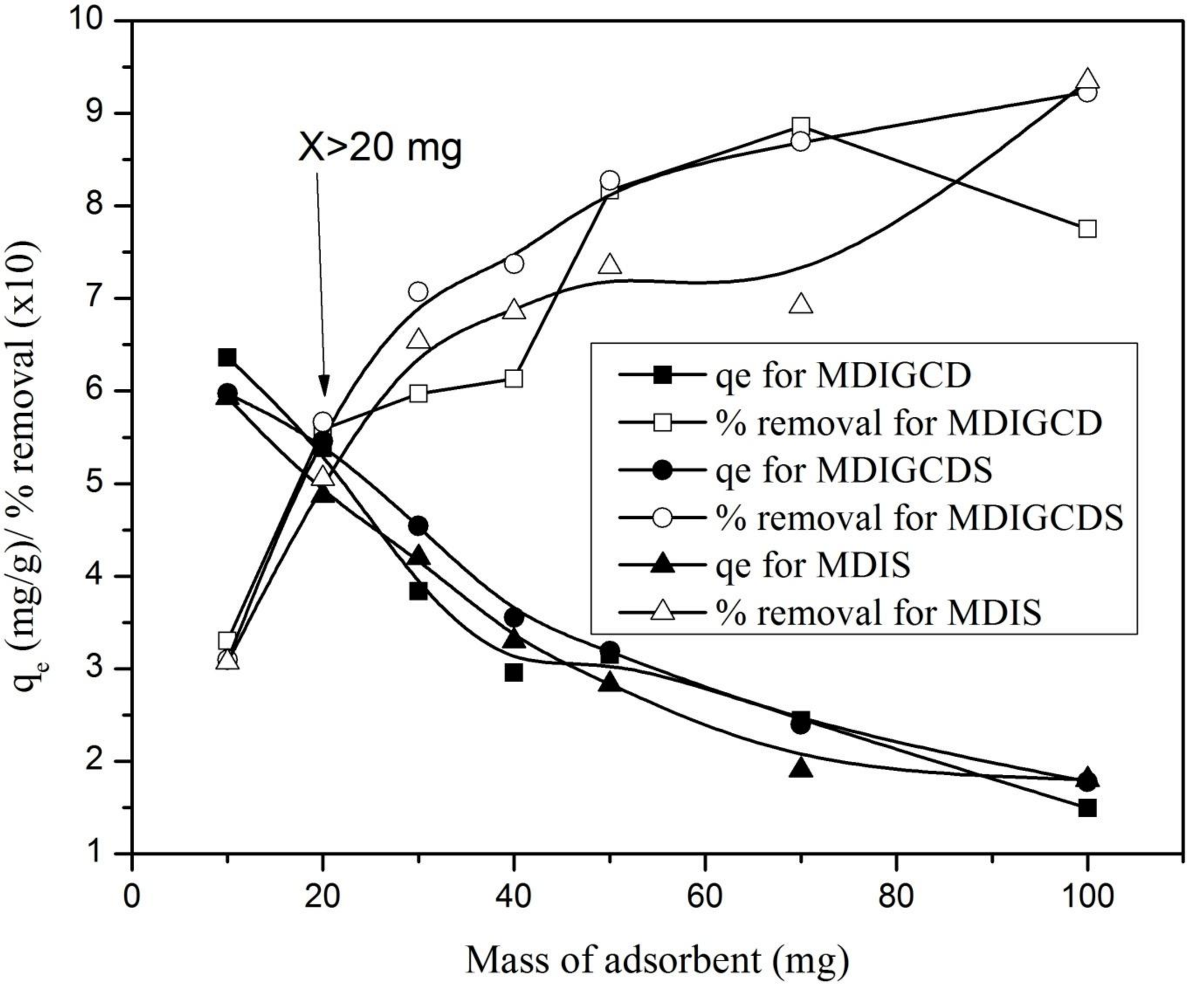


Figure 4.27. Effect of adsorbent dose on the adsorption capacity and % removal of DEP for the cross-linked adsorbents

4.5.3 Effect of pH and salinity (Na^+ ions) on phthalates adsorption

The result of study for effect of pH as shown in Table 4.19 indicated that changes in the aqueous pH did not affect adsorption of diethyl phthalate onto MDIGCD and MDIGCDS polymer adsorbents. However, the adsorption capacity of MDICS adsorbent increased with increment in the aqueous pH of the solution. Previous studies on adsorption of phthalates had established that the effect of pH on adsorption of phthalates often emanates from the pH effect on charge properties of the adsorbent surface, rather than the phthalate molecules (Staples et al., 1997; Cheng and Chung, 2007). Since none of the adsorbents under study has charged surfaces, pH was therefore supposed to have minimal effect on their adsorption performance for phthalates.

It has been observed earlier in this discussion that at relatively high pH, there appears to be de-protonation of the surface OH groups of the adsorbents which enhances adsorption. However, this effect is subject to the polarity of the surfaces. Considering the structure of cross-linked cyclodextrin and starch polymers, it is obvious that this effect will manifest more on starch polymers (in this case MDICS), since starch is more polar than cyclodextrin. Hence, this is the reason behind the observed difference in behavior of the studied adsorbents towards variation in pH.

The results on the effect of Na^+ (representative of salinity) on phthalate adsorption (Table 4.19) showed that increases in salinity (NaCl concentration) did result to corresponding increment in adsorption capacity of all the studied adsorbents. This can be attributed to the reductive effect of Na^+ on the solubility of phthalates, as Llompart et al., (2006) have reported negative correlation between solubility of phthalates and salt concentration. Hence, the reduction in the solubility of phthalates is what actually enhanced the adsorption process. This result suggests that MDIGCD, MDIGCDS, and MDICS adsorbents might be successfully used as adsorbents in freshwater and seawater aquaculture systems.

4.5.4 Effect of initial phthalate concentration and isotherm studies

The study for the effect of initial concentration showed that the adsorption capacity of the adsorbents increased with increment in initial phthalate concentration (Figure 4.28).

Table 4.19. Effect of pH and salinity on the adsorption of DEP onto cross-linked polymer adsorbents

Parameter	Adsorption capacity (qe) (mg/g)		
	MDIGCD	MDIGCDS	MDICS
pH values			
3.72	6.4355	6.2195	6.1585
5.10	6.5745	6.3590	6.2705
6.80	6.3645	6.1430	5.7515
8.40	6.4495	6.2490	6.2270
9.75	6.4650	6.3695	6.5765
Salinity [Na^+]			
0.00	5.9425	6.0655	5.9425
0.01	5.9630	6.052	5.9630
0.05	6.0775	6.1225	6.0775
0.10	6.0825	6.1655	6.0825
0.25	6.1035	6.0470	6.1035
0.50	6.4380	6.4055	6.4380

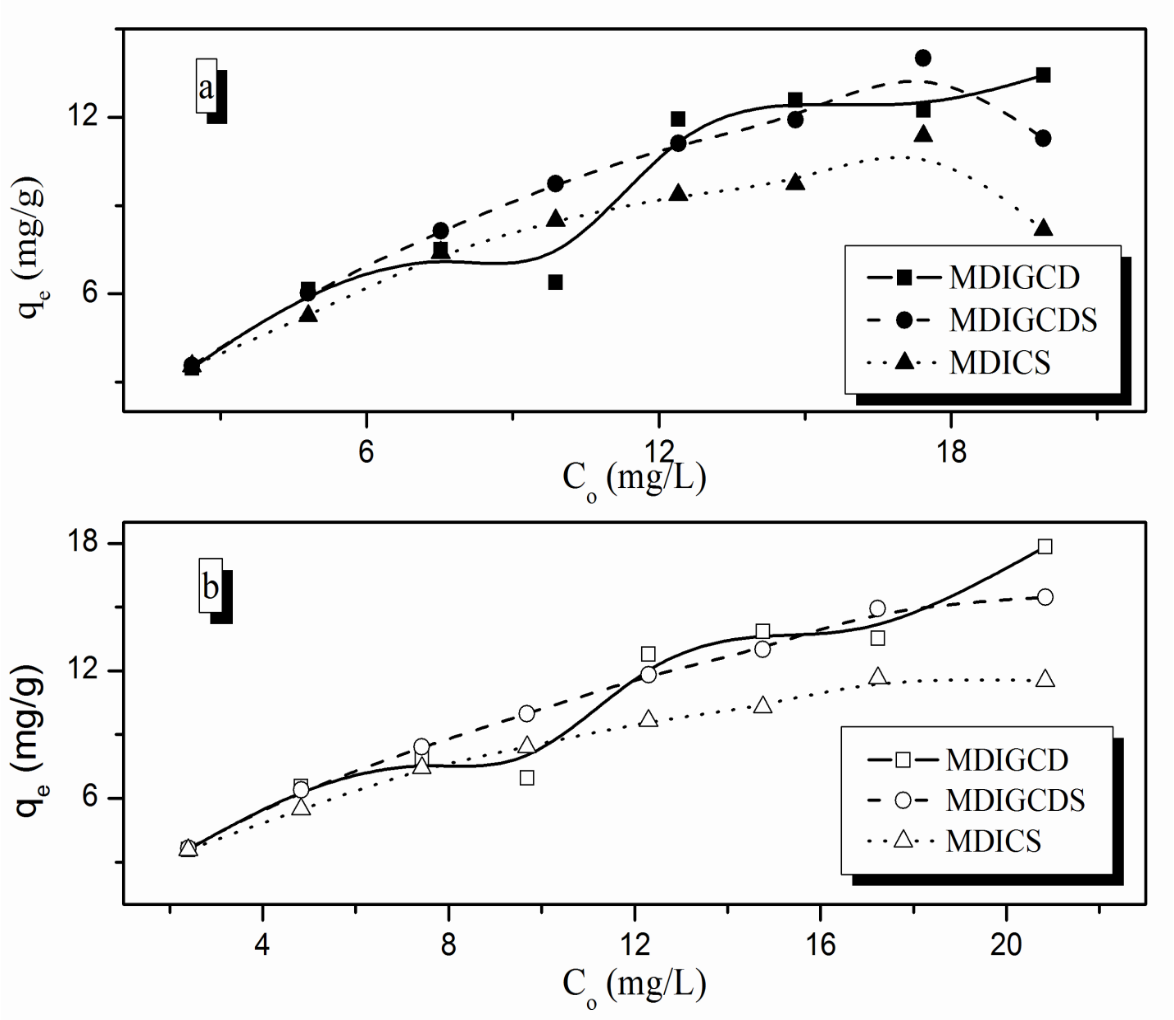


Figure 4.28. Effect of initial phthalate concentration $C_{o,}$ on adsorption capacities of the cross-linked polymer adsorbents for (a) Dimethyl phthalate and (b) Diethyl phthalate

The situation can be explained on the principle of increased number of effective collision of the adsorbate molecules with increment on the adsorbate initial concentration.

The experimental isotherm plots for the adsorption of phthalates onto the cross-linked starch and cyclodextrin polymer adsorbents were as shown in Figures 4.29 and 4.30 (solid lines). The plots showed that the equilibrium sorption curves for the studied adsorption mainly followed the L-type isotherm profiles. Detailed examination showed that the sorption of DMP and DEP by MDIGCDS and MDIS exhibited more of L-type isotherm, while that of MDIGCD adsorbent exhibited the borderline of L-type and S-type isotherm profiles, though the L-type was the dominant profile. The conditions for exhibition of this isotherm profile have been explained in the adsorption of PAHs. Hence, it can be concluded that there was no competition from the aqueous phase for the adsorption sites of the cross-linked adsorbents.

Isotherm model parameters of the equilibrium studies for phthalate adsorption unto the cross-linked adsorbents (Table 4.20) and non-linear isotherm plots (Figures 4.29 and 4.30) showed that adsorption isotherms fit well with the Langmuir and Freundlich models, which predicted the adsorption of phthalates with high correlation coefficients. However, the Langmuir model demonstrated to be better than the Freundlich model. The fact that both models are verified could indicate that the interactions that take place between adsorbent and adsorbate are weak interactions. This observation can be explained on the bases of π–π interaction and hydrogen bonding (Wu and Xu, 2010). The presence of phenyl ring on the cross-linked adsorbents is favourable to increase the adsorption capacity and affinity of the aromatic ring on DMP and DEP molecules by π–π interaction. On the existence of hydrogen bonding, the hydrogen atom of the hydroxyl group on the starch polymer chain of the cross-linked adsorbents can directly act as hydrogen bonding acceptor and form hydrogen bonding with the oxygen atom of the ester group of DMP and DEP molecules. Besides, the nitrogen atom of the amino group and the oxygen atom of the carbonyl group on the cross-linked adsorbents might also play a role of hydrogen bonding donator and can form hydrogen bonding with the oxygen atom of the ester group of DMP and DEP through the water molecules. Therefore, the conceptualized adsorption interaction is as shown in Figure 4.31.

Table 4.20. Isotherm model parameters for DMP and DEP adsorption using the studied adsorbents

Isotherm models	Parameters	MDIGCD		MDIGCDCS		MDICS	
		DMP	DEP	DMP	DEP	DMP	DEP
	Exp q_e	13.4278	17.8332	11.2869	15.4680	8.1765	11.54025
Langmuir	R^2	0.8767	0.8824	0.9858	0.9878	0.9364	0.9631
	q_{max}	13.6463	15.8200	15.1012	17.3800	10.8944	12.1374
	K_L	0.3329	0.3025	0.3073	0.2767	0.4691	0.4131
Freundlich	R^2	0.8281	0.8442	0.9292	0.9929	0.8385	0.9876
	K_f	3.6045	3.7300	3.9092	3.9400	3.8232	1.7600
	n	2.0400	1.8400	2.1100	1.8500	2.6500	2.2900
BET	R^2	0.6696	0.5211	0.9352	0.9779	0.9018	0.9857
	Q^o	200.2659	22.3625	358.5304	20.0868	719.0829	13.7770
	K_B	17.1055	81.9345	14.7149	115.4324	10.1574	163.5039
Tempkin	R^2	0.7586	0.7391	0.8943	0.9632	0.7728	0.9702
	A	2.1316	1.7230	2.6117	1.9700	4.4185	2.9000
	b	670.2400	530.3800	698.0700	554.7800	1023.5000	810.7700

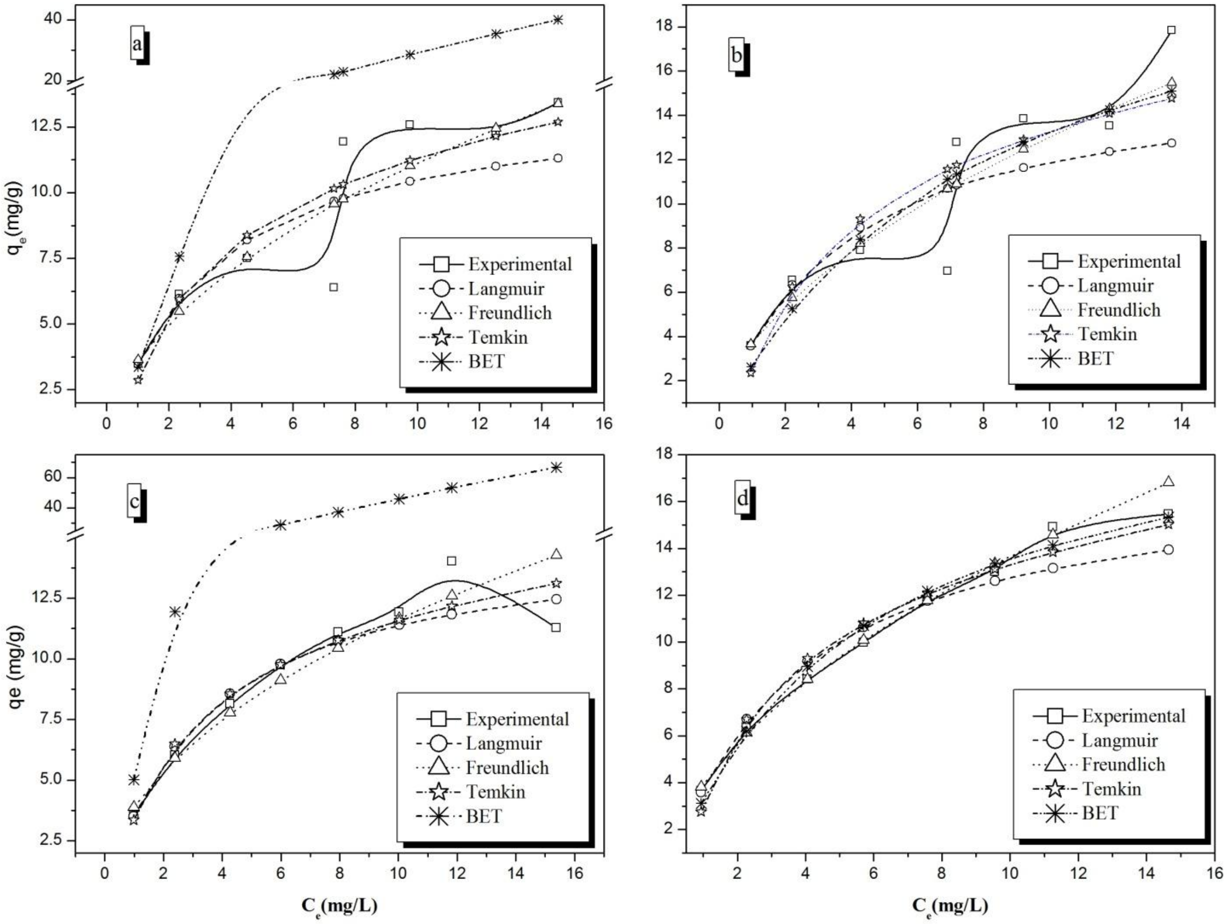


Figure 4.29. Experimental isotherm plots and non-linear isotherm model fitting for the adsorbent/adsorbate pairs of (a)MDIGCD/DMP (b)MDIGCD/DEP (c)MDIGCDS/DMP and (d)MDIGCDS/DEP

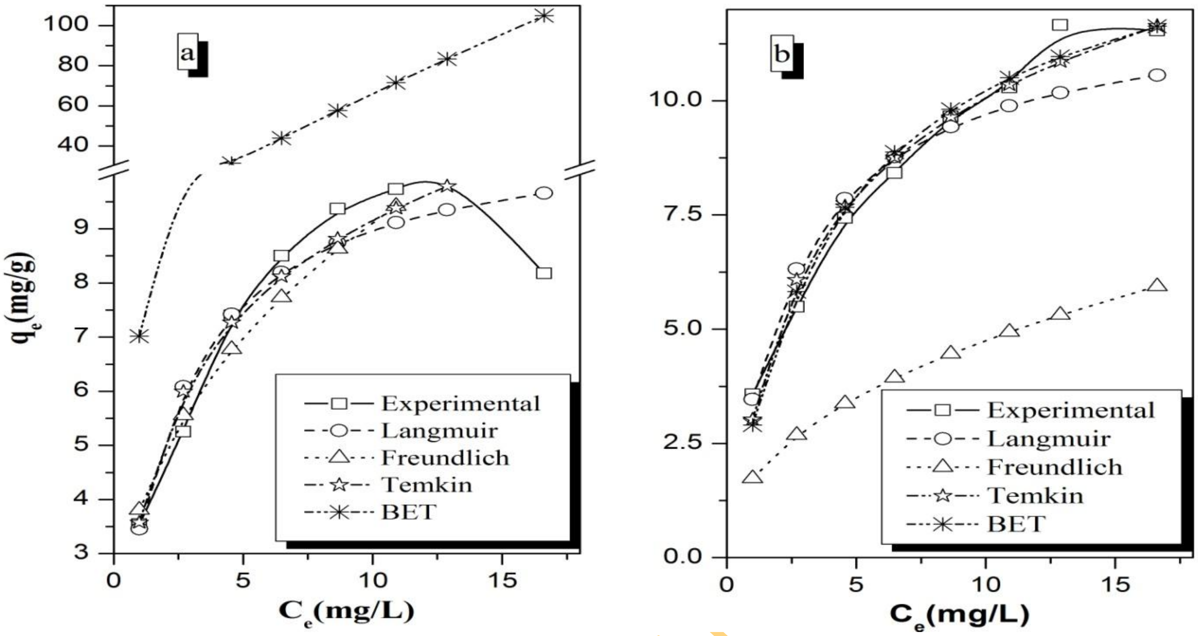


Figure 4.30. Experimental and non-linear plots of isotherm model fitting for the adsorbent/adsorbate pairs of (a)MDICS/DMP and (b)MDICS/DEP

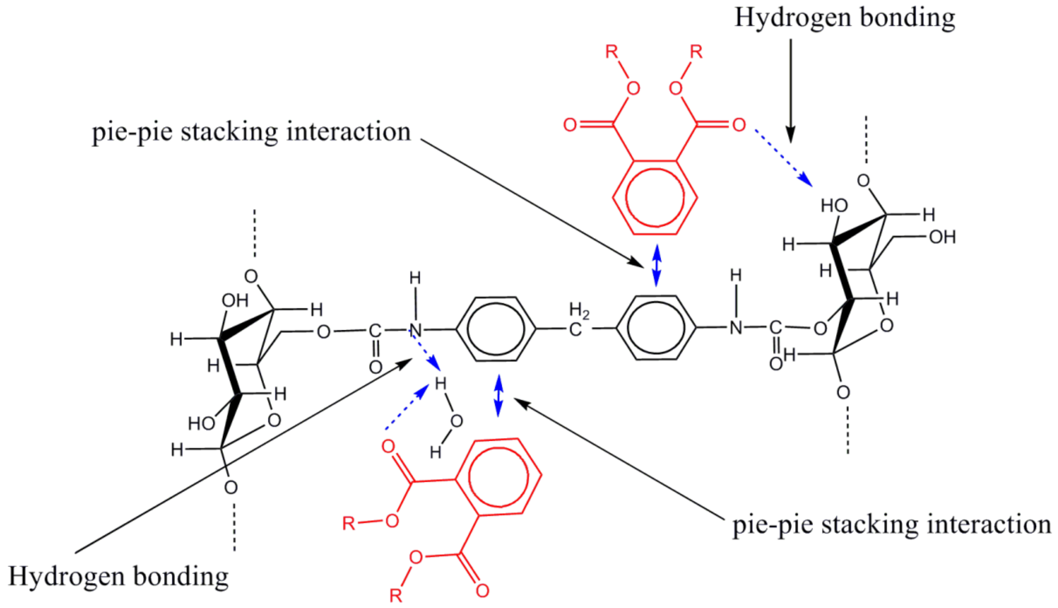


Figure 4.31. Schematic diagram of the adsorption interaction of phthalate molecules with cross-linked polymer adsorbents

The efficiency of the adsorption process can be predicted by the dimensionless equilibrium parameter R_L, which is defined as $R_L = 1/(1 + K_LC_o)$ (where C_o is the initial concentration of phthalate adsorbate). The R_L values (Table 4.21) ranged from 0.09 to 0.58, and suggested favorable adsorption ($0 < R_L < 1$) of phthalates onto the investigated adsorbent. Also, the Freundlich constants, K_F values, considered as a measure of the adsorption capacity, were higher for DEP than DMP. The reason for the higher affinity could be the higher hydrophobicity of DEP. The Freundlich isotherm indicated that *n* values ranged from 1.8 to 2.7, and this implied that the studied adsorption isotherms can be considered nonlinear because the *n* values were in general outside the $0.95 < n < 1.05$ range established by Pignatello et al., (2006) as suitable for an isotherm to be considered linear. This can be explained as the manifestation of aromatic interaction, as Xing et al. (2001) had observed that there was a positive relationship between aromatic carbons and isotherm nonlinearity for several soil humic acids. In this guise, nonlinear isotherms have been reported for the sorption of several aromatic compounds using aspen wood; using Spanish leonardite; using black, carbon-free biopolymers; using wooden chars of aspen wood; and using wood chars (Olivella et al., 2011).

4.5.5 Effect of temperature and thermodynamics analysis

The result of the study showed that aqueous temperature had a negative correlation with the adsorption capacities of the adsorbents (MDIGCD, MDIGCDS and MDICS). Hence, adsorption of phthalates decreased with increment in the temperature of the aqueous media. This is attributed to the reduced interaction of the phthalate molecules with the adsorbent, as a result of increment in the solubility of the phthalates with increment in temperature. Despite having negative correlation with the adsorption capacity, increment in aqueous temperature led to a corresponding increment in the adsorption rate as evidenced in the values of rate constant, k_2 and initial reaction rate, *h* (Table 4.22). This effect may be due to the fact that at higher temperatures, the increase in heat and the subsequent kinetic energy leads to increased mobility of the solute, which results to higher adsorption rates. Also, the observed positive relationship between the temperature and k_2 and *h* still confirmed the fact that pseudo second order may not be the sole rate limiting step (Boparai *et al*., 2010).

Table 4.21. Values of Separation factor R_L for the adsorption of DMP and DEP

DMP Co	MDIGCD /DMP	MDIGCDS /DMP	MDICS/ DMP	DEP Co	MDIGCD /DEP	MDIGCDS /DEP	MDICS /DEP
2.4098	0.5549	0.5745	0.4694	2.3980	0.5561	0.5757	0.4706
4.7977	0.3850	0.4041	0.3076	4.8270	0.3836	0.4027	0.3063
7.5204	0.2854	0.3020	0.2209	7.4242	0.2881	0.3047	0.2231
9.8775	0.2332	0.2478	0.1775	9.6875	0.2367	0.2514	0.1804
12.3951	0.1951	0.2079	0.1467	12.2981	0.1963	0.2092	0.1477
14.8007	0.1687	0.1802	0.1259	14.7567	0.1691	0.1807	0.1262
17.4303	0.1470	0.1573	0.1090	17.2323	0.1484	0.1588	0.1101
19.8962	0.1312	0.1406	0.0968	20.8362	0.1260	0.1351	0.0928

Table 4.22. Kinetic model parameters for DEP adsorption at different temperatures

Adsorbent	Temperature	k_2	PSO R^2	q_e
GCD MDI	25°C	0.0034	0.9998	9.2700
	45°C	0.0126	1.0000	6.9300
	65°C	0.2646	1.0000	4.7000
CS γ-CD MDI	25°C	0.0067	0.9999	8.6800
	45°C	0.0399	1.0000	6.8300
	65°C	0.0716	0.9999	4.9800
CS MDI	25°C	0.0022	0.9964	8.2500
	45°C	0.0041	0.9993	8.0900
	65°C	0.0196	1.0000	6.1500

The values of the thermodynamic parameters: free energy change (ΔG), enthalpy (ΔH) and entropy (ΔS) are shown in Table 4.23. The ΔG values for all the adsorbent-adsorbate systems were negative, indicating that the sorption process is spontaneous. It was also observed that as the temperature increases, ΔG increases indicating that the adsorption will be less feasibility at higher temperatures. ΔH values were negative, indicating exothermic process. ΔS values of sorption process were also negative, which indicated decreased randomness at the adsorbent/solution interface.

4.6 Evaluation of sorption performance

One of the suitable ways of evaluating sorption performance of adsorbents for a particular pollutant is by comparing the sorption coefficient of the adsorbent under investigation, to those of other adsorbents reported in literature. In this study, sorption coefficient, K_d was calculated from the slope of a plot of quantity adsorbed at equilibrium, q_e, against equilibrium concentration, C_e. ($K_d = q_e/C_e$). For ease of comparison, phenanthrene was chosen as a reference PAH, since its adsorption has been widely reported in literature.

In this vein, the values of sorption coefficient for phenanthrene using different adsorbents as reported in literature, and the values from this study were shown in Table 4.24. It has been observed from the data that MDICS, one of the novel adsorbents considered as cheap alternative to more costly materials like synthetic resins and activated carbons, developed from this study, is only second to activated carbon in terms of the values of their sorption coefficient while the value for HDICS showed that its sorption performance, though lower than the value for MDICS, is as good as that of lignin, which is equally accepted as good adsorbent for aromatic compounds.

In a similar manner, the values of sorption coefficient for diethyl phthalate (DEP) were applied for comparing the adsorption performance of the developed adsorbents with the ones reported in literature. In this regards, the values of $\log K_d$ for adsorption of DEP were 2.99, 2.94 and 2.72 for MDIGCD, MDIGCDS and MDICS, respectively. However, the $\log K_d$ values of the most common commercial polymer adsorbents and activated carbon as recorded by Zhang et al., (2008) were 3.30, 2.74, 2.73, 1.78, and 0.69 for NDA-702, NDA-101, AC750 (activated carbon), XAD-4 and XAD-7 respectively. Hence, the

Table 4.23. Thermodynamic parameters for adsorption of phthalates onto MDIGCD, MDIGCDS, and MDICS polymer adsorbents

Adsorbate/ adsorbent	ΔH (kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol)		
			298K	318K	338K
DMP					
MDIGCD	-8.63	-22.73	-1.85	-1.40	-0.94
MDIGCDS	-21.05	-64.53	-1.82	-0.53	0.76
MDICS	-10.79	-30.40	-1.73	-1.12	-0.51
DEP					
MDIGCD	-23.76	-71.76	-2.37	-0.94	0.50
MDIGCDS	-19.43	-58.29	-2.06	-0.90	0.27
MDICS	-10.26	-28.02	-1.91	-1.35	-0.79

Table 4.24. Sorption coefficient of phenanthrene as basis for comparing the sorption performance of the developed adsorbents and those previously reported in literature

Sorbents		log Kd	Source
Cross linked Starch Adsorbents			
	HDICS	3.97	Present study
	MDICS	4.79	
	MDIGCD	4.63	
	MDIBCD	4.31	
	MDIGCDS	4.68	
	MDIBCDS	4.56	
Algae			
	Botryococcus braunii	4.13	Salloum et al., 2002
	Sargassum hemiphyllum	3.83	Chung et al., 2007
Fungi			
	White-rot fungi	3.83	Chen et al., 2010b
Plant based materials			
	Wood chip	3.40	Chen et al., 2011
	Orange peel	3.47	
	Plant roots	3.32 – 3.70	Zhu et al., 2007; Chen et al., 2011
	Plant cuticles	4.21 – 4.73	Li and Chen, 2008
	Leaves	3.52–4.05	Lin et al., 2007; Zhu et al., 2007
	Pine bark	3.53	Li et al., 2010
Natural Organic Matter			
	Cellulose	2.98	
	Collagen	4.47	Salloum et al., 2002
	Lignin	4.03	
Modified Biosorbents			
	Aspen wood fiber	3.60–3.67	Huang et al., 2006
	Bleached wood	3.24–3.26	

Temperature hydrolyzed wood fibers	4.03–4.75	
Surfactant modified fibric peat	4.42	Tang et al., 2010
Acid hydrolysis of pine bark	4.23	Li et al., 2010
Geosorbents and Abiotic Sorbents		
Humic acid	4.45	Salloum et al., 2002
Pula kerogen	4.76	
Nature chars	4.83–6.31	
Fibric peat	4.11	Tang et al., 2010
Artificial wood chars	5.19–7.20	James et al., 2005
Active carbon	5.70–5.90	

adsorption performance of MDIGCD and MDIGCDS was better than most commercial adsorbents, and only second to the NDA-702 polymer adsorbent, while the adsorption performance of MDICS which seemed to be the least among the three studied adsorbents, was still comparable to the reported values for activated carbon.

4.7 Desorption Studies

It has been established that virtually all the industrial and natural applications of adsorbents involve both adsorption and desorption processes in one way or the other. In cases like pollutant immobilization in soil, adsorption is the preferred process while every effort is made to reduce or prohibit desorption through the treatment design. In agricultural practice, controlled release of pesticides and fertilizers involve fast adsorption and slow desorption process. It is worthy of note that in most cases, adsorption and desorption processes occur under different conditions. Hence, manipulation of these conditions is applied in controlling these processes. In certain cases where recovery of the adsorbates are desired (eg. solid phase extraction method of pre-concentration for analysis of organic micropollutants), fast adsorption and desorption processes are desired. Therefore, desorption kinetics is vital in the assessment of desorption processes.

It is therefore, imperative that efficient selection of adsorbents, for any given application cannot be suitably done on the basis of only adsorption characteristics. For all the adsorbent utilizations that involve both adsorption and desorption processes, desorption studies is the only way of assessing the regenerability of the adsorbents. Hence, desorption characteristics is very vital in the utilization of adsorbents for both water treatment and SPE pre-concentration technique.

4.7.1 Effect of nature of desorbing solvent

The desorption solvent creates the desired condition for desorption process to take place. Therefore the nature of desorption solvent has a dominant role in desorption process. The principle of “like dissolves like” is highly operational in desorption systems. In this vein, weakly polar to non-polar solvents are used for desorption of hydrophobic organic compounds. Figure 4.32 showed the desorption efficiencies for acenaphthylene, fluorene, phenanthrene, and DEP from MDICS, HDICS, MDIGCD, MDIBCD, MDIGCDS, and MDIBCDS adsorbents, using various desorption solvents. Calculations of desorption

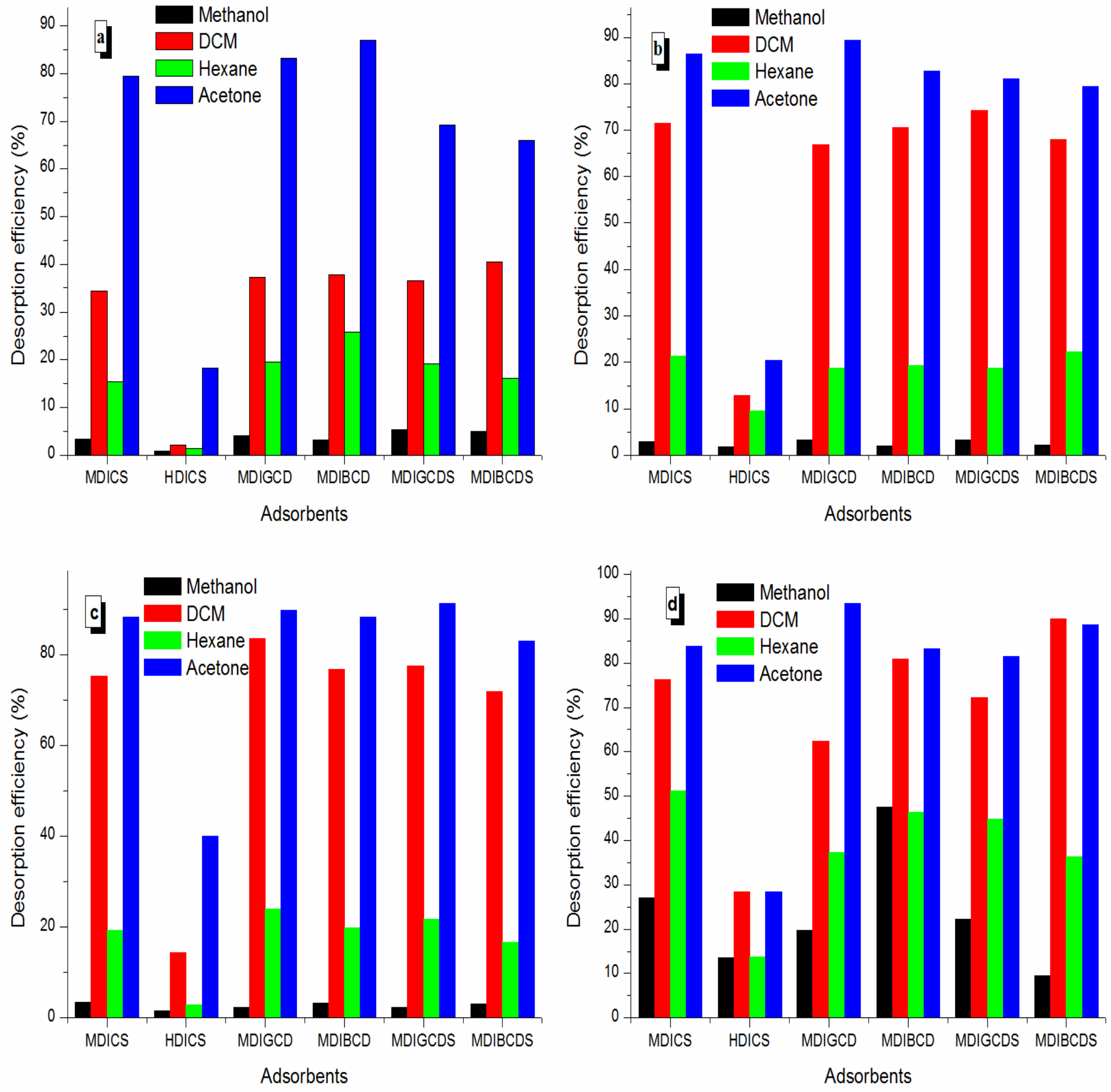


Figure 4.32. Desorption efficiencies of (a) acenaphthylene (b) phenanthrene (c) fluorene and (d) DEP using different desorption solvents

efficiency for each solvent were based on the ratio of the amount of desorbed PAHs to the amount of PAHs previously adsorbed on cross-linked adsorbents. The trend for all the studied adsorbent-adsorbate pairs was Acetone ≈ DCM >Hexane>Methanol. This trend can be explained on the basis of polarity, except for methanol which had the least desorption ability, despite having same polarity index value of 5.1 with acetone. This observation might likely be linked to the presence of different functional groups in acetone and methanol, and their associated interactions with the adsorbents. Hence, acetone which is an aldehyde (R-CHO) will likely interact more with the adsorbent than methanol which is an alcohol (R-OH). It was equally observed that HDICS had poor desorption efficiency, hence cannot be effectively regenerated.

4.7.2 Desorption kinetics

The desorption kinetics study utilized only HDICS and MDICS adsorbents, since previous studies revealed that all the MDI cross-linked adsorbents exhibited similar adsorption characteristics. The rate plot (Figure 4.33), showed that desorption process was fast and adjudged to be complete in less than 10 minutes. This is a pointer that the adsorbents have good potential for being utilized as solid phase in SPE pre-concentration procedure.

4.7.3 Regeneration efficiency

Effective and efficient regeneration of spent adsorbents is a desirable quality for development of low cost adsorbents. The regeneration efficiency tests showed that the adsorption performance of the regenerated adsorbent was still more than 70% of the original performance, even after four consecutive regenerations (Figure 4.34). This implied that these adsorbents could be advantageously recycled, and thus be reused several times. Hence, this is a very big comparative cost advantage over other common adsorbents for PAHs.

4.8 Application of the developed adsorbents for treatment of real environmentally polluted water samples

The adsorbents showed good adsorption performance for the treatment of spiked environmentally polluted water samples, though the values of adsorption capacities were slightly lower than the values obtained for simulated water samples. The drop in performance can be attributed to the presence of numerous other competing pollutants in

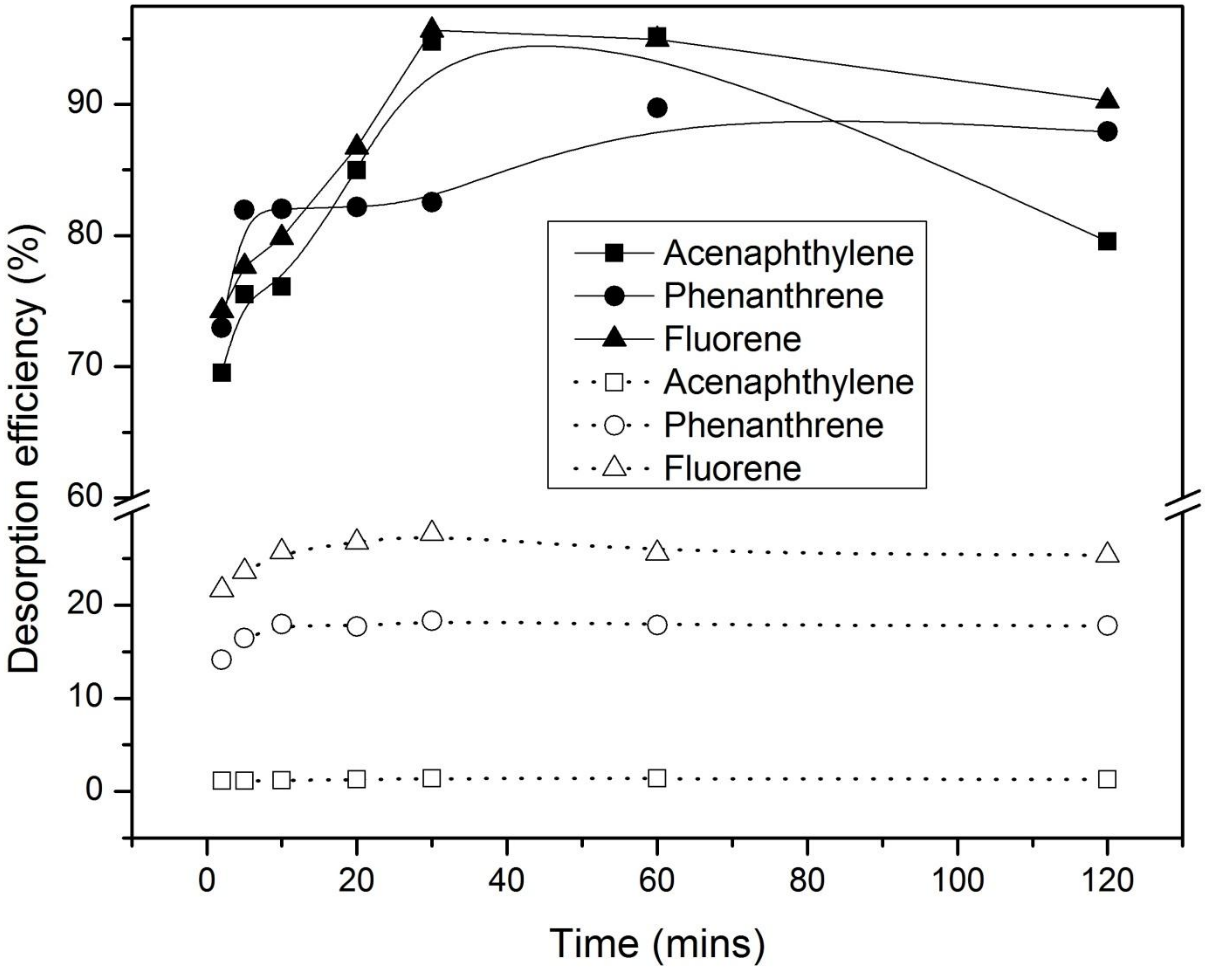


Figure 4.33. Plot of effect of contact time on the desorption efficiency of MDICS (solid lines) and HDICS (dotted lines)

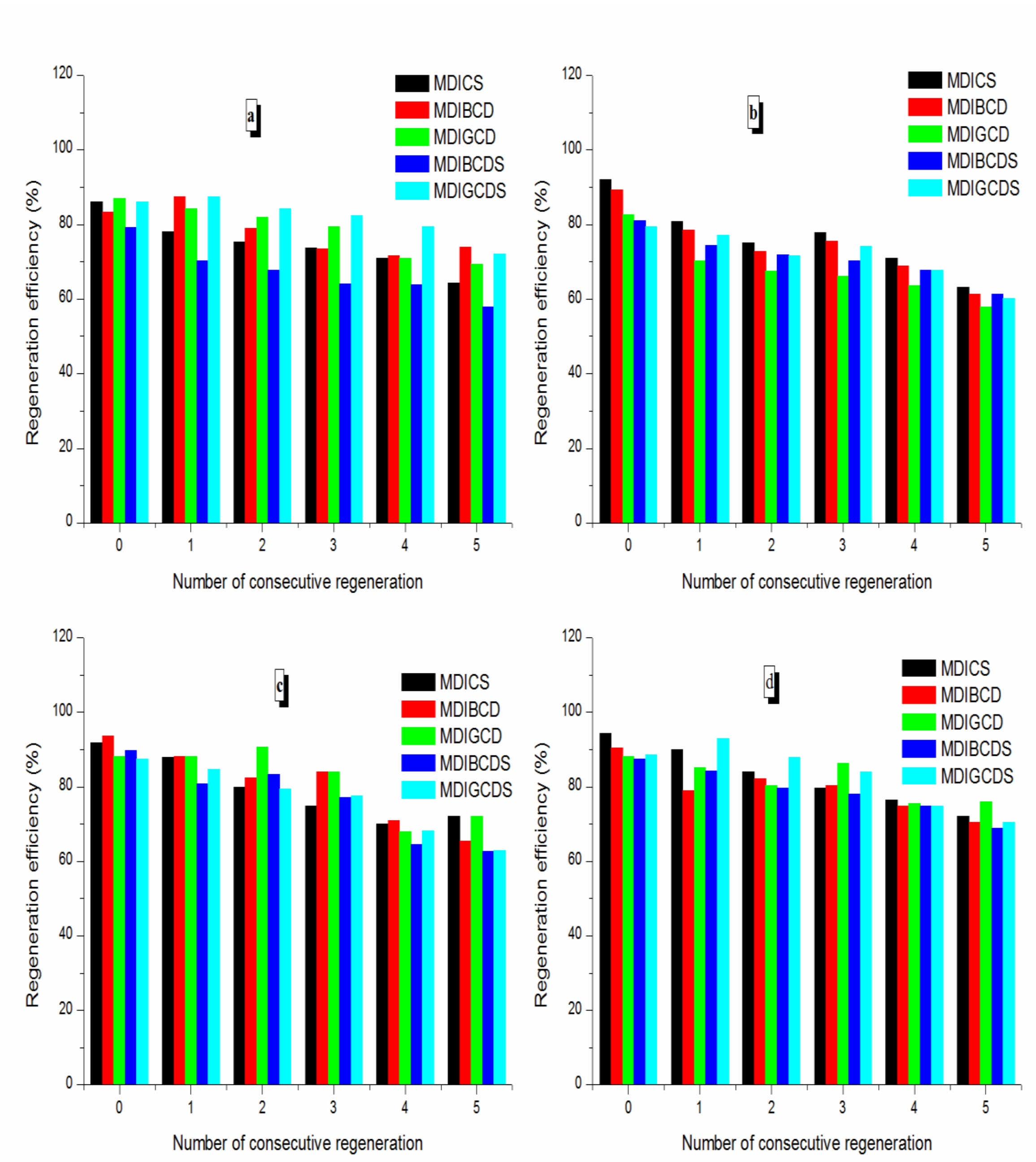


Figure 4.34. Bar chart showing the regeneration efficiencies of the adsorbents for (a) acenaphthylene (b) phenanthrene (c) fluorene and (d) DEP

real environmental water samples. PAHs were not detected after adsorption treatment of the un-spiked environmental water samples, which is adjudged to contain ambient (environmentally obtainable) levels of these pollutants, and thus confirmed the effectiveness of the adsorbents.

4.9 Method development for SPE pre-concentration procedure

4.9.1 Selection of adsorbent

The preliminary SPE studies showed that 1,6-hexamethylene diisocyanate (HDI) cross-linked adsorbents (HDICS, HDIBCD, HDIGCD, HDIBCDS and HDIGCDS) and epichlorohydrin (EPI) cross-linked polymers (EPICS, EPIMACS, EPIBCD, EPIBCD, EPIBCDS and EPIGCDS) showed very poor recoveries when they were applied as the SPE sorbents. However, the Methylene diphenyl diisocyanate (MDI) based polymers (MDICS, MDIBCD, MDIGCD, MDIBCDS and MDIGCDS) showed far better recoveries. This can be rationalized by the two obvious reasons. The PAHs belong to the class of non polar organic compounds. According to the rule of like dissolves like, the more non polar a sorbent is, the more likely it will facilitate enrichment of PAHs. Apart from the hydrophobic interactions which constituted of dipole-dipole and van der Waal interactions, the MDI cross-linked adsorbents has additional π-π interaction by the virtue of the presence of aromatic rings in the molecular structure of these polymers. It is this additional interaction that conferred higher adsorption potentials to the MDI cross-linked adsorbents (Guo and Lee, 2011). The delocalized π-bond interaction between PAHs and MDI based adsorbents is much stronger than the hydrophobic interaction between PAHs and HDI and epichlorohydrin based adsorbents. The second reason is the fact that the MDI based adsorbents possessed higher surface area and pore characteristics than their HDI and EPI counterparts as shown by the values of their BET surface characteristics, as discussed earlier. The observed SPE performance of the studied adsorbents based on the recovery values, also seemed to be in accordance with the sorption coefficient of these adsorbents, as elucidated in the adsorption studies. It was equally observed that this trend was more pronounced in MDI based adsorbents than the HDI and epichlorohydrin based adsorbents. The simple explanation for this observation still bordered on the surface and pore characteristics. With higher surface area, the elution solvent will have better access to the adsorbates (analyte of interest), thus conferring the potential of higher desorption (elution) efficiency, thus all the analytes adsorbed are likely going to be desorbed within the elution time frame. With poor surface characteristics, because of large volume of samples applied in SPE, analytes of interest will penetrate into the available few pores over time, however, during desorption (elution) due to the poor surface characteristics and the subsequent limitation of access of the elution solvent to the adsorbates (analytes of interest), the desorption efficiency will be low. Thus, all the analytes adsorbed are not likely going to be fully desorbed.

4.9.2 Optimization of SPE parameters for pre-concentration PAHs

The optimization of the experimental conditions was necessary since common sense has shown that the enrichment performance could be influenced by several of these conditions. The conditions optimized were elution parameters (nature of elution solvent, volume of elution solvent, and flow rate of elution solvent) and sample/loading parameters (sample volume, sample flow rate, and sample modifier).

4.9.2.1 Elution parameters

Nature of elution solvent

The type of elution solvent is vital for the extraction efficiency. A complete desorption of analytes from the adsorbent significantly affects the sensitivity, and is closely related to the desorption solvent. The solvent used for the PAH elution should be strong enough for the analytes to desorb the strongly bounded adsorbent. So the choice of elution solvent should be carefully taken into account. Figure 4.35 shows the recoveries obtained from five different organic solvents/solvent mixture, including acetonitrile, methanol, acetone, dichloromethane and dichloromethane/n- hexane mixture (50:50 v/v) tested as elution solvents. The mean recovery of PAHs eluted by acetone was 72.58% with RSD of 17.23%, dichloromethane gave the mean recovery of 71.57%, with RSD of 15.07%, while acetone/DCM mixture gave mean recovery value of 64.46% with RSD of 20.42%. However, using methanol and acetonitrile as elution solvents gave much lower recoveries, only 32.13% with RSD of 39.06 and 38.19.4% with RSD of 22.45%, for methanol and acetonitrile, respectively. Among the five solvents, acetone, dichloromethane and dichloromethane/n-hexane mixture provided the comparable results for PAHs, about 30–40% higher than the recoveries obtained by using methanol or acetonitrile. Though

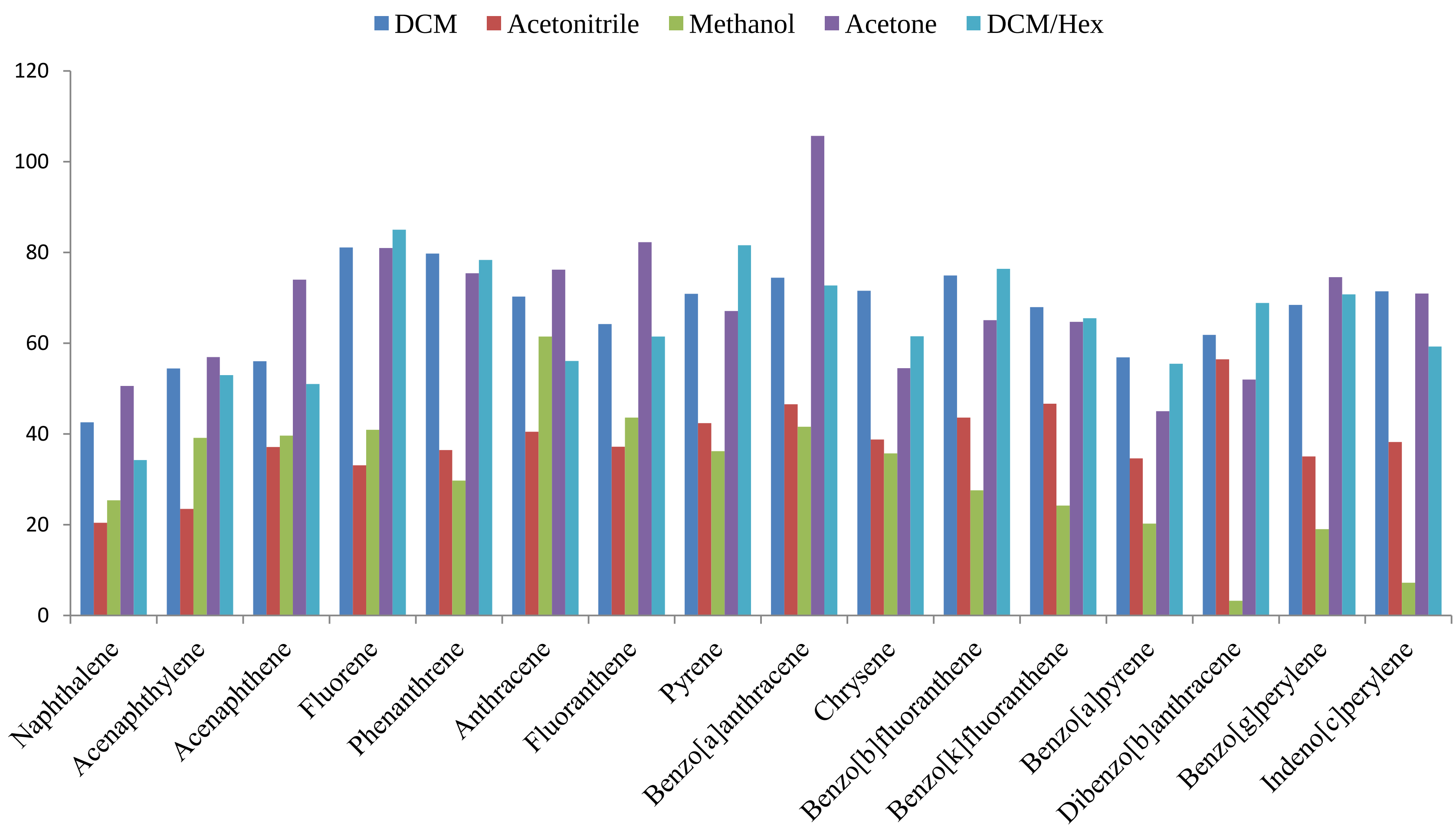


Figure 4.35. Effect of nature of elution solvent on analytical recovery of PAHs

acetone showed very good recovery, the acetone eluent seemed to have poor elution selectivity as indicated by multiple peaks in its chromatogram, and hence requires clean-up. In addition to the elution strength, DCM presents another advantage, which is the high vapor pressure necessary to achieve quick and effective solvent evaporation. Also, it was observed from recovery values of individual PAHs that DCM gave better recovery values for the high molecular weight PAHs than acetone. Considering the foregoing, DCM was selected as the best elution solvent.

Elution volume

It has been established that for a given elution flow rate, higher solvent volume translates to higher contact time and subsequently higher recovery, up to the optimum value after which further increment in volume does not result to a corresponding increment in analyte recovery (Poole, 1990). For small to medium molecular size PAHs, the recoveries increased with progressive increment of the eluent volume from 5 ml to 10 ml, after which increment in volume did not result to a reasonable increment in the recoveries, whereas the recoveries of higher molecular PAHs continued to increase with increment in elution volume up to 20 ml (Figure 4.36). This behaviour can be explained on the basis of PAHs hydrophobicity in aqueous media. The higher molecular weight PAHs are more hydrophobic as can be shown by their high octane-water partition coefficient (log K_{oc}) values. Hence they have stronger affinity towards the SPE phase, and therefore need more solvent to desorb (elute) them. Looking at this scenario, the choice of elution volume will be guided by the PAHs of priority concern, i.e. whether high or low molecular weight PAHs. However, since acceptable recoveries were recorded for the higher molecular weight PAHs when 10 ml elution volume was applied, 10 mL (5 mL each time and washed twice) dichloromethane was selected for this study.

Elution flow rate

Elution flow rate is an important parameter for enrichment efficiency and analyte recovery. The effect of the sample flow rate was investigated over the range from 0.45 to 1.45 mL/min. For a given elution volume, the analyte recoveries have been shown to have a positive correlation with the contact time of the solvent with the loaded SPE sorbent, up to a maximum (often referred as the optimum) value, after which further increment in the

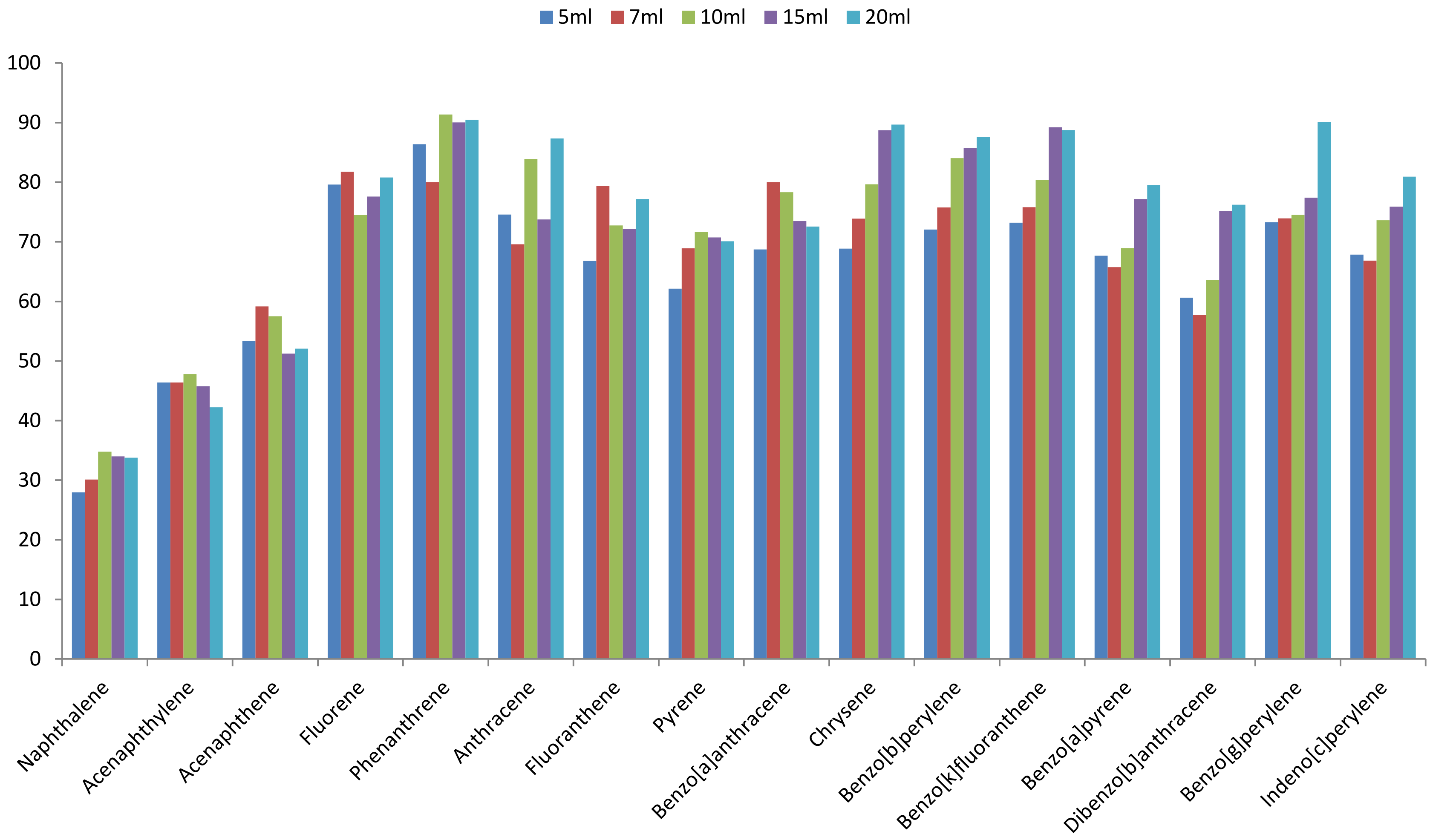


Figure 4.36. Effect of volume of elution solvent on the on analytical recoveries of PAHs

contact time does not translate to increment in analyte recoveries (Poole, 1990). However, high elution flow rate translates to shorter elution contact time, and vice versa. Alternatively, for a given solvent volume, higher elution flow rate translates to shorter contact time, and vice versa. Previous studies have shown that for a given solvent volume, higher molecular weight PAHs require high contact time for better recoveries (Kouzayha et al., 2011). Therefore, a compromise is always struck between flow rate (time) and solvent volume. Since the elution volume in SPE is always relatively small, the use of low flow rates does not necessarily translate to much time, and hence the application of low flow rates in this study is justified. As shown in Figure 4.37, elution flow rate of 0.891 mL/min (approximately 1.0 mL/min) was an optimal value for these 16 PAHs.

4.9.2.2 Sample/loading parameters

Sample Volume

The effect of sample volumes on the enrichment of PAHs is shown in Figure 4.38. For small molecular weight PAHs, it was found that the recoveries were steady in the range of 500–1000 ml but decreased when the sample volume exceeded 1000 ml. This may be attributed to the fact that in presence of larger amounts of solvent, it will result in less interaction between PAHs and the SPE sorbent. This effect was equally observed for high molecular weight PAHs, but was comparatively not as pronounced as those of small molecular weight. This can equally be attributed to the difference in the level of hydrophobicity between the PAHs. Overall, the effect of sample volume within the studied range (500–1000 ml) was minimal. On the basis of optimization, 500 ml was selected as the optimal sample volume.

Sample flow rate

Generally, sample loading time can be saved at a high flow rate while the possible analytes loss happens owing to an incomplete adsorption of PAHs by the sorbents; complete adsorption can be achieved at a low flow rate but it is time consuming. Therefore, a suitable flow rate for loading sample should be investigated to achieve high recovery and short loading time. Considering the sample volume applied for the study, relatively high sample flow rate is required to achieve enrichment in reasonable time,

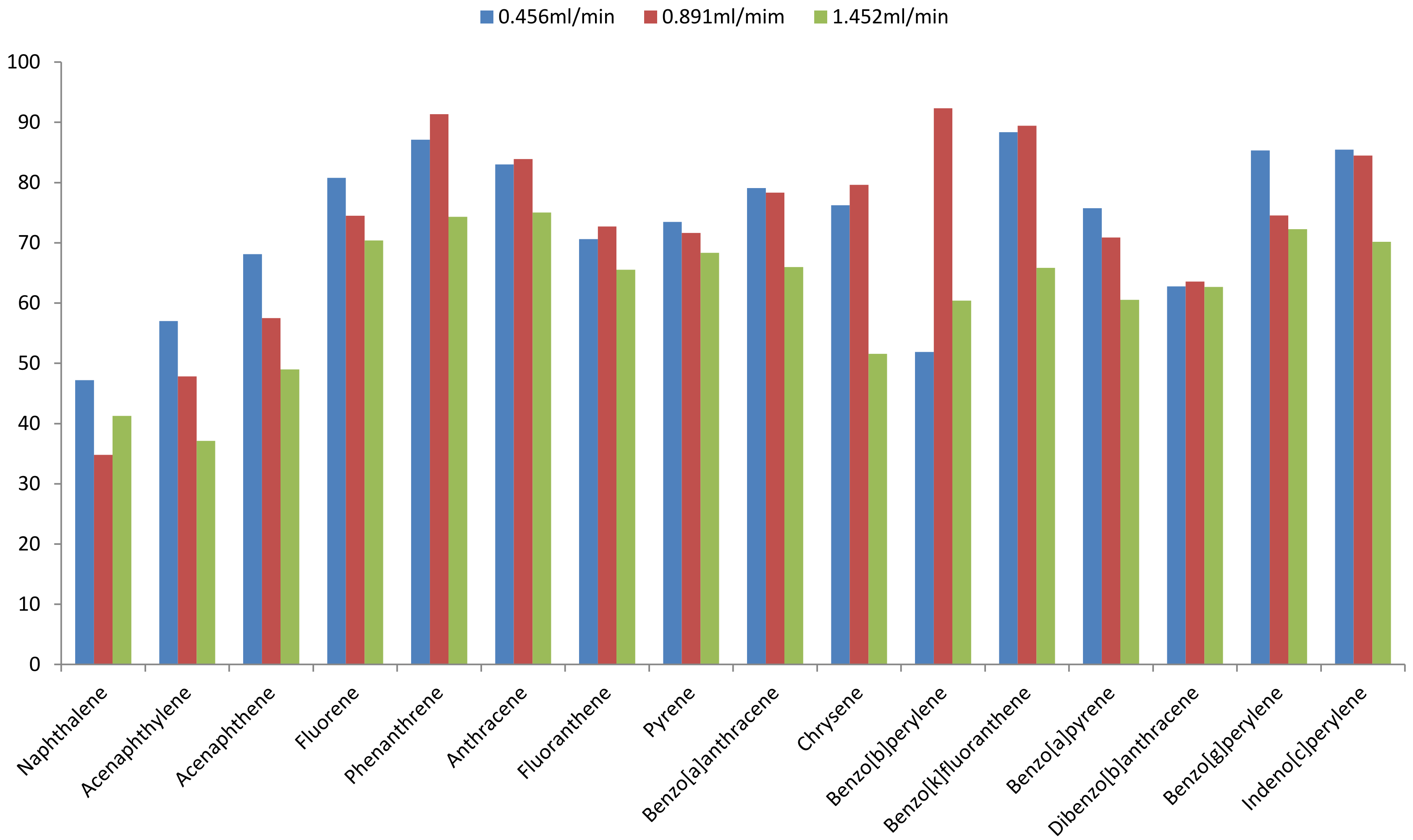


Figure 4.37. Effect of elution flow rate on analytical recovery of PAHs

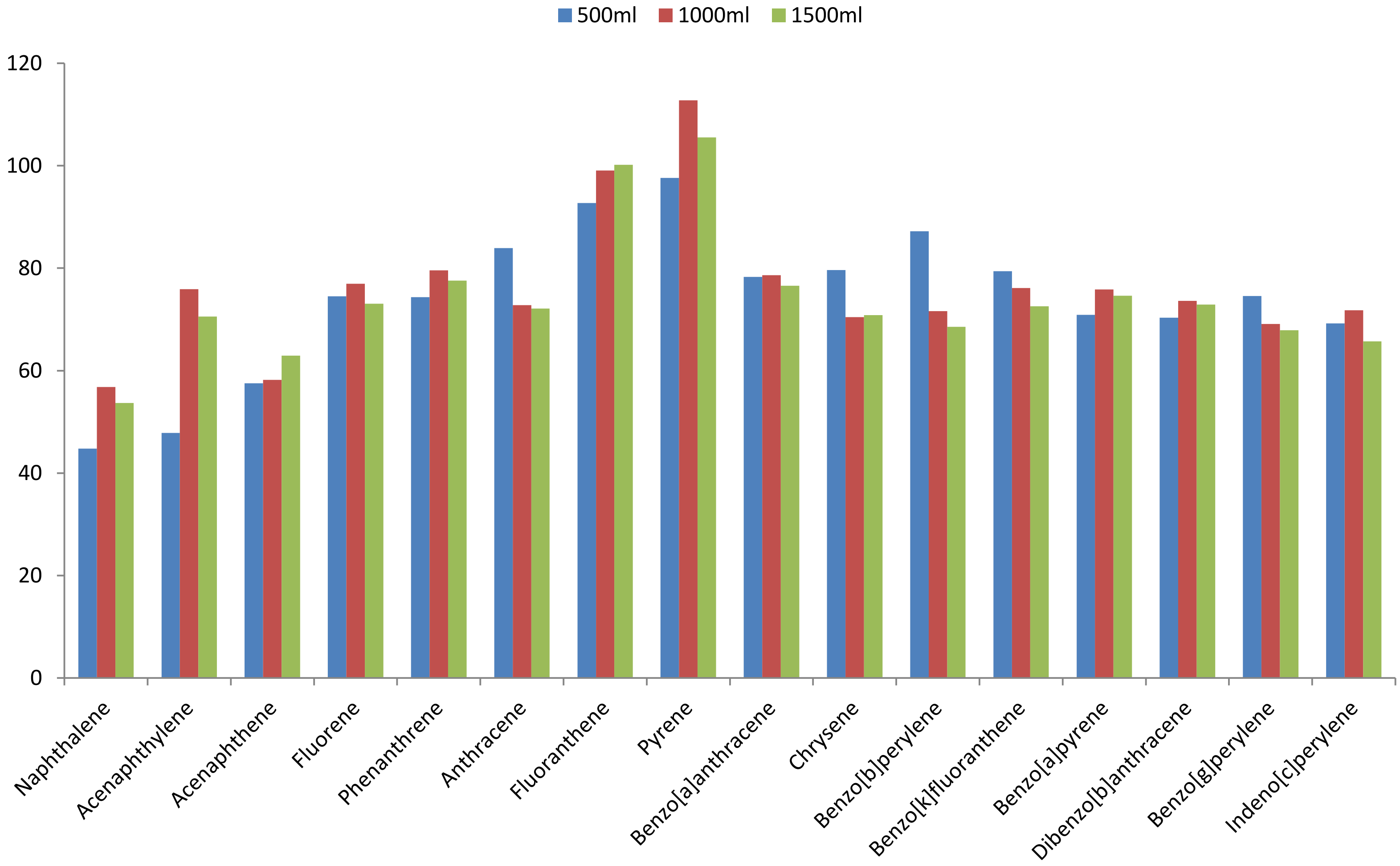


Figure 4.38. Effect of sample volume on analytical recoveries of PAHs

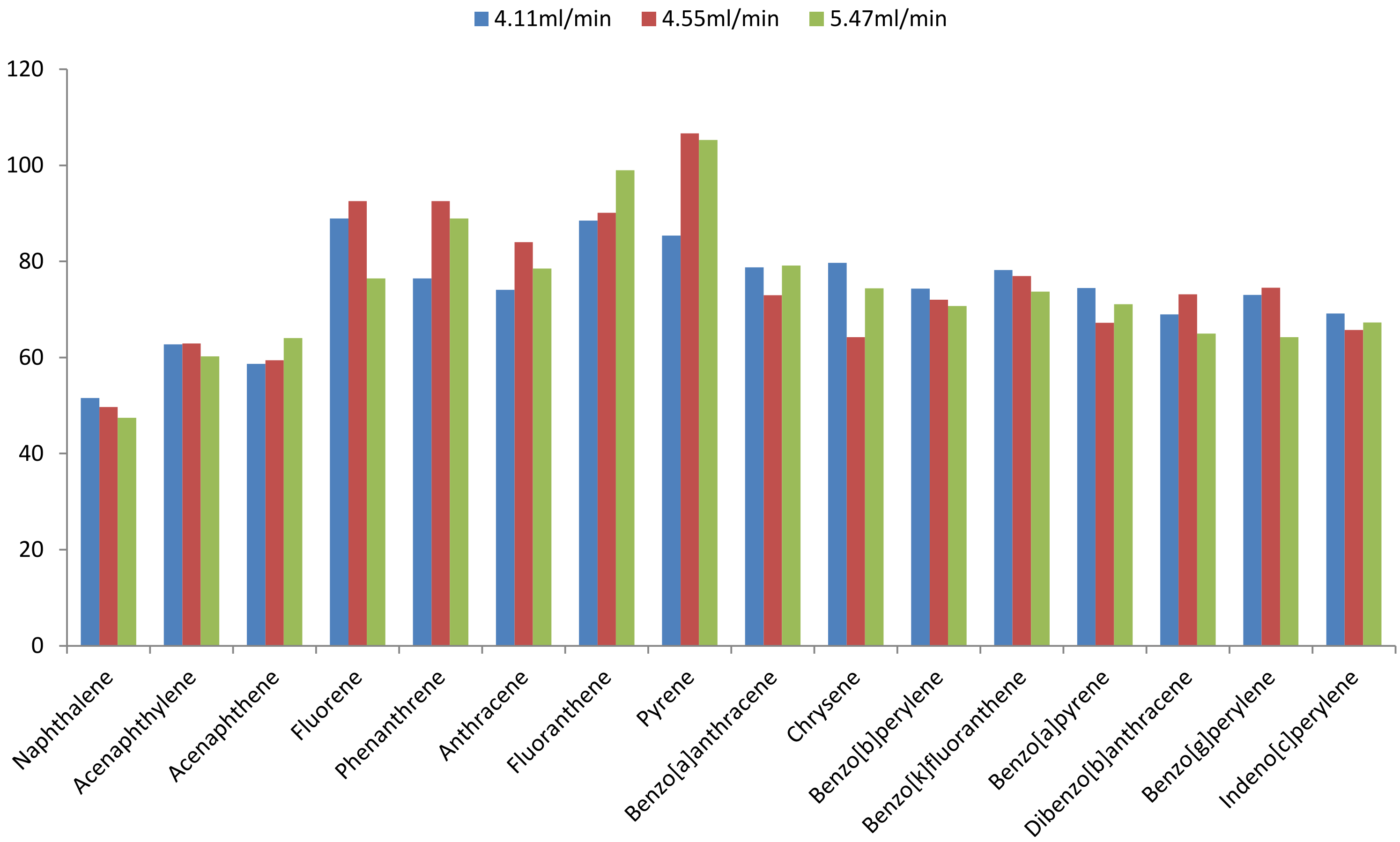


Figure 4.39. Effect of sample flow rate on analytical recoveries of PAHs

hence the choice of medium flow rate range of 4.1 – 5.5 ml/min. As shown in Figure 4.39, the PAH recoveries within the investigated flow rates were acceptable. Considering that all the 16 PAHs could be efficiently adsorbed within this time span, the sample loading flow rate of 5.5 mL/min was adopted as the optimum sample flow rate.

Sample Modifier

Due to the low solubility of PAHs in water, it is necessary to add organic solvent as an organic sample modifier to prevent PAHs from adsorbing on the walls of the glass sample containers. Methanol was chosen for this study because it is relatively a good solvent for the 16 PAHs under study, relatively cheap, and less toxic. The content of the organic modifier (concentration in 500 mL water sample) investigated for this study was 0–20%. It can be observed from Figure 4.40, that there was significant increment in the recoveries of the PAHs using organic solvent modified samples when compared to the recovery values of previous optimization experiments without organic solvent modification, as evidenced in the values of PAH recoveries. For small and medium molecular weight PAHs, Figure 4.40 showed that recovery of PAHs increased till it reached a maximum value, after which progressive increment in organic content led to decrease in recovery of PAHs.. However, there was continuous increment in recovery values within the entire range (0 – 20%) for high molecular weight PAHs.

The observed general increment in recovery of PAHs with increment in the percentage of sample modifier can be explained on the basis of reduction or elimination of PAHs that had hitherto adsorbed on the walls of sample containers. However, with continuous increment in the percentage of organic solvent, the solubility of PAHs (especially the low molecular weight PAHs) in the sample will be significantly enhanced to the extent that it will cause reduction in interaction (and subsequently adsorption) of PAH molecules with the solid phase sorbent, and hence cause reduction in recovery as observed for low molecular weight PAHs. Considering higher hydrophobicity of the high molecular weight PAHs, the increment in solubility as a result of increment in percentage of sample modifier might not be significant enough to induce reduction in PAHs interaction with the solid phase. Based on these facts, 15% (75 ml of methanol in 500 ml sample) was adopted as the optimum value of sample modifier to be added to enhance the recovery of PAHs.

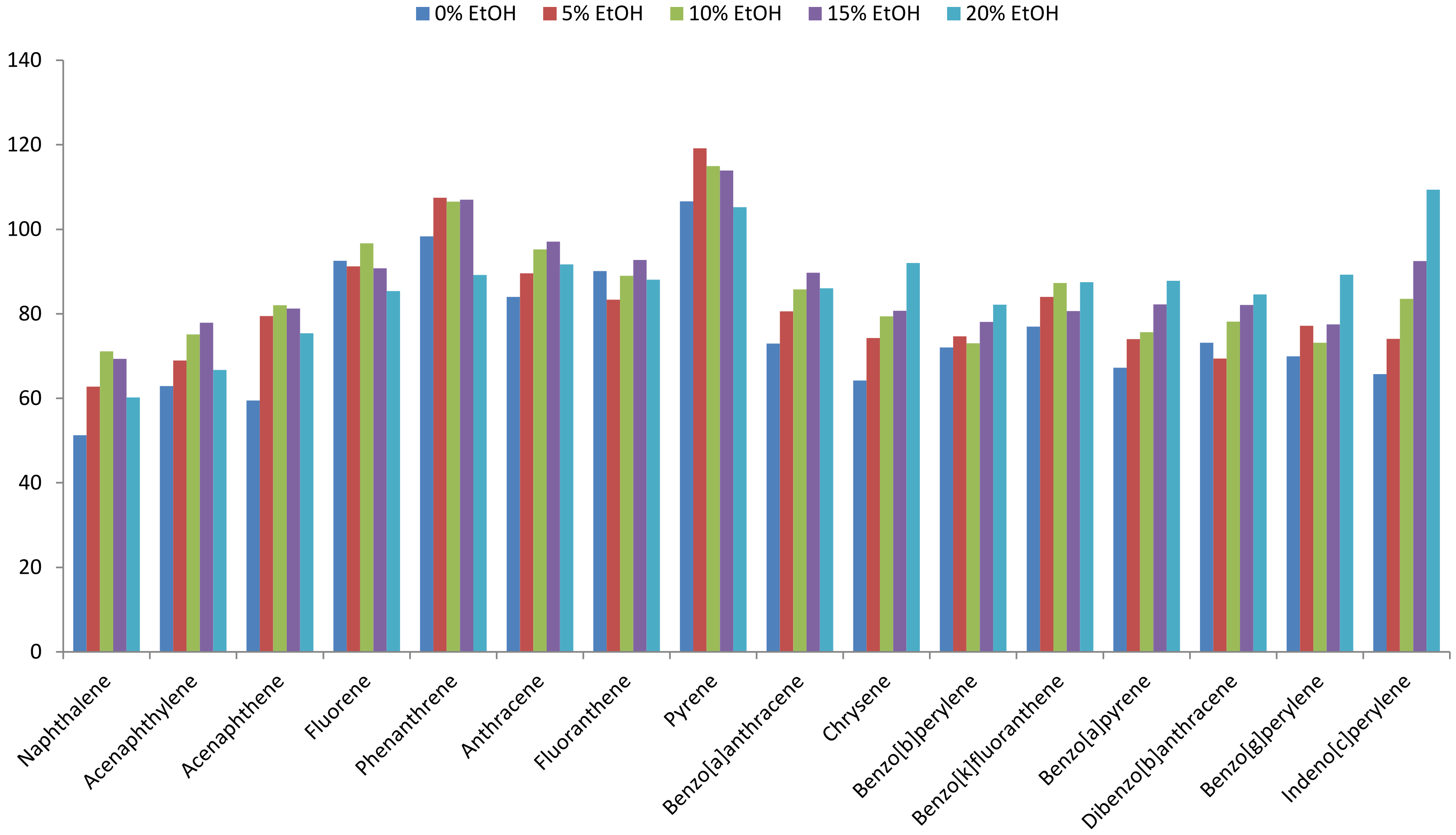


Figure 4.40. Effect of sample modifier on analytical recoveries of PAHs

4.9.3 Validation of SPE method

Validation was based on parameters defined in standard protocols describing chromatographic methods (Thompson et al., 2002).

4.9.3.1 Method detection limit (MDL)

Method detection limit is the lowest concentration level that can be determined to be statistically different from a blank at 99% confidence level. The relevance of MDL in SPE method validation cannot be over emphasized as it is one of the major selection guidelines for selecting a method in consideration with the expected concentration range of the analyte of interest. In the present study, method detection limit was determined using the standard deviation (n = 6) of the concentration at the selected low levels of enrichment.

As shown in Tables 4.25 and 4.26, detection limits for the developed method varied between 22.9 - 155.3 ng/L and 0.51 – 24.15 ng/L for ultra-violet and fluorescence detectors, respectively.

4.9.3.2 Precision

Precision is a measure of the random error associated with a series of repeated measurements of the same parameter within a sample. In other words, precision describes the closeness with which multiple analyses of a given sample agree with each other, and is sometimes referred to as reproducibility or repeatability.

In the validation study, precision was measured using relative standard deviations (RSD) at two concentration levels (1.0 and 10.0 µg/L) for UV detector, and one concentration level (0.5 µg/L) for fluorescenc detector. The RSD values ranged from 6.94% for Indeno[c]perylene to 25.69% for naphthalene when UV detector was used (Table 4.25), and from 0.41% for BaA to 16.60% for naphthalene for fluorescence detector (Table 4.26). All RSDs were below 30%, the value considered acceptable (Bispo et al., 2011).

4.9.3.3 Linearity/ Linear range

The performance evaluation of an analytical method using linearity and linear range evaluates whether the calibration curve of the method is linear within the concentration range upon which the analyte of interest is likely to be present in the media under

Table 4.25. Method validation data for PAHs using UV detector

PAHs	Regression Equation (y = a + bx)	Mean Recovery	R^2	MDL (ng/L)	Precision (RSD)	Fortification µg/L
Naphthalene	y = 25410x + 2034	67.69	0.9980	155.3	25.69	10.0
Acenaphthylene	y = 20657x - 8684	83.10	0.9988	123.6	21.19	10.0
Acenaphthene	y = 7926x - 4513	101.62	0.9976	157.3	26.02	10.0
Fluorene	y = 154517x - 39955	84.91	0.9991	94.3	13.00	10.0
Phenanthrene	y = 454750x - 27118	90.26	0.9991	63.7	20.97	1.0
Anthracene	y = 49796x + 281634	80.37	0.9980	23.6	8.71	1.0
Fluoranthene	y = 126437x - 39230	86.25	0.9968	50.7	17.47	1.0
Pyrene	y = 109378x - 53288	71.21	0.9945	47.3	19.74	1.0
Benzo[a]anthracene	y = 217338x -75594	84.61	0.9955	33.1	11.62	1.0
Chrysene	y = 404855x -30163	93.67	0.9998	66.2	21.01	1.0
Benzo[b]fluoranthene	y = 244919x - 110252	106.49	0.9926	70.8	19.76	1.0
Benzo[k]fluoranthene	y = 192612x + 34810	108.98	0.9994	61.8	16.86	1.0
Benzo[a]pyrene	y = 233160x - 116549	99.43	0.9946	35.7	10.68	1.0
Dibenzo[b]anthracene	y = 55464x - 19809	97.24	0.9992	32.6	9.95	1.0
Benzo[g]perylene	y = 94916x - 40744	100.31	0.9982	26.4	7.83	1.0
Indeno[c]perylene	y = 268245x - 119733	97.89	0.9962	22.9	6.94	1.0

Table 4.26. Method validation data for PAHs using fluorescence detector

PAHs	Regression equation (y = a + bx)	R^2	Mean recovery	MDL (ng/L)	Precision (RSD)	Fortification (µg/L)
Naphthalene	y = 3417x + 136	0.9969	73.13	24.15	16.60	0.5
Acenaphthylene	ND	ND	ND	ND	ND	0.5
Acenaphthene	y = 4922x - 1331	0.9934	81.49	16.74	12.21	0.5
Fluorene	y = 5519x - 5933	0.9999	71.68	6.47	5.36	0.5
Phenanthrene	y = 7559x - 17438	0.9996	81.36	3.50	2.55	0.5
Anthracene	y = 9096x + 151641	0.9989	88.09	4.24	2.86	0.5
Fluoranthene	y = 86434x - 23229	0.9969	118.44	6.20	3.11	0.5
Pyrene	y = 9373x - 23248	0.9995	94.29	1.94	1.22	0.5
Benzo[a]anthracene	y = 17532x -35794	0.9979	72.65	0.51	0.41	0.5
Chrysene	y = 314853x -30163	0.9998	86.38	0.88	0.60	0.5
Benzo[b]fluoranthene	y = 144013x - 71254	0.9997	83.91	1.04	0.74	0.5
Benzo[k]fluoranthene	y = 90212x +13410	0.9984	92.10	0.97	0.63	0.5
Benzo[a]pyrene	y = 17165x - 60149	0.9986	84.73	0.63	0.44	0.5
Dibenzo[b]anthracene	y = 25467x - 1180	0.9997	89.49	0.92	0.61	0.5
Benzo[g]perylene	y = 44532x - 51075	0.9968	102.49	2.41	1.39	0.5
Indeno[c]perylene	y = 128542x - 39735	0.9969	126.00	7.89	3.72	0.5

consideration. Linearity is more appropriately expressed by adjusted root mean square (R^2) values. However, it can still be expressed as an equation of a straight line describing the calibration curve, whereas linear range is expressed as numerical concentration range being considered.

A five-point calibration curve constructed for each PAH analyte over the concentration range of interest (0.5 - 50 µg/L), showed that the regression coefficients (R^2) of the calibration plots were higher than 0.99 in all cases (Tables 4.25 and 4.26). This indicated high level of linearity within the studied concentration range.

4.9.3.4 Recovery Studies

In SPE method development, recovery studies are used to measure the accuracy of the measurements, which reflects the closeness of a measured value to a true value.

In this study, recoveries were measured at two fortification levels, 1.0 and 10.0 µg/L for the UV detectors. At the first level (10.0 µg/L), recoveries varied from 67.69.0% for naphthalene to 101.62% for acenaphthene. At the second level (1.0 µg/L) recoveries were from 71.21% for pyrene to 108.98% for BkF (Table 4.25). For fluorescence detector, recoveries were measured at 0.5 µg/L fortification level. At this fortification level, the recoveries were from 71.68 to 126.00% (Table 4.26). In all the studies, the efficiency of the SPE method was satisfactory, with recoveries lying close to the range normally considered acceptable, between 70% and 130% (Bispo et al., 2011) (with the exception of naphthalene).

4.9.4 Application of the developed SPE method to real water samples

The levels of PAHs in the tap and ShaHe river water samples (unspiked samples), as analyzed using the cross-linked starch SPE, were as shown in Table 4.27. All the investigated PAHs were detected in Sahe river water samples, while nine of the US EPA were detected in the tap water samples. The performance of the SPE preconcentration method was assessed by evaluating the recovery of PAHs in spiked real water samples (0.5 µg/L spike level). Application of the developed method in the analysis of the spiked environmental water samples exhibited good recoveries in the range of 52.64-102.16%

Table 4.27. Analysis of unspiked and spiked environmental water samples for comparative evaluation of cross-linked starch and C_{18} (ENVI^{TM}) as SPE phases using fluorescence detectors.

PAHs	Conc. in Tap water (µg/L)	Recovery		Conc. in Sahe water (µg/L)	Recovery	
		Starch SPE	ENVI^{TM} (C_{18})		Starch SPE	ENVI^{TM} (C_{18})
Naphthalene	ND	73.29	69.35	0.0235	63.85	60.23
Acenaphthylene	ND	69.38	77.90	0.0012	74.50	66.71
Acenaphthene	ND	52.64	64.26	0.0340	74.31	75.40
Fluorene	ND	73.74	90.78	0.1500	67.74	85.37
Phenanthrene	ND	73.39	107.04	0.3410	71.68	89.18
Anthracene	0.0117	73.39	97.07	0.0215	77.64	91.68
Fluoranthene	0.1404	86.87	92.74	0.3580	82.65	88.09
Pyrene	0.0852	102.16	113.90	0.2680	84.65	105.25
Benzo[a]anthracene	0.1366	68.11	89.72	0.0645	78.93	86.03
Chrysene	0.0890	70.84	80.75	0.0925	85.84	92.04
Benzo[b]fluoranthene	0.1471	75.96	78.11	0.1735	109.31	82.20
Benzo[k]fluoranthene	0.0448	86.31	80.62	0.0840	106.92	87.52
Benzo[a]pyrene	0.0576	77.56	82.24	0.1310	95.80	87.85
Dibenzo[b]anthracene	ND*	81.48	82.11	0.1090	84.86	84.61
Benzo[g]perylene	ND	94.49	77.49	0.2010	86.60	89.29
Indeno[c]perylene	0.0642	77.81	92.46	0.0102	97.58	110.40
Range		52.64-102.16	64.26-107.04		67.74-109.31	60.23-110.40

* Not detected

and 67.74-109.31% for tap and Sahe water samples, respectively. The validity of the recorded levels of PAHs was evaluated by comparing the recoveries of starch SPE and that of standard C_{18} (ENVI^{TM}18) SPE. The recovery values for both cross-linked starch and C_{18} SPE indicated that the analytical performance of the developed method is comparable to that of commercially available C_{18} SPE phase.

Also, the performance of the SPE preconcentration method using the developed material was equally compared with the performance of other methods reported in literature. In this vein, Table 4.28 showed the recoveries of PAHs as performance indicator for similar studies reported in literature.

The merits of the present method are obvious including simple synthetic method for the adsorbents, high recoveries, low LODs, as well as fast and simple analytical procedure.

4.10 SPE studies for phthalate esters

The SPE studies for phthalates showed that MDICS polymer adsorbents is a suitable SPE phase for pre-concentration of phthalates in aqueous media.

4.10.1 Optimization of SPE parameters

The optimization experiments showed that optimum SPE operation parameters were as follows: elution volume: 10 ml; elution flow rate: 0.5 ml/min; sample volume: 500 ml; sample flow rate: 5.0 ml/min; and organic content (sample modifier): 10% v/v (50 ml of methanol in 500 ml of water sample). It was observed that sample modification of the water samples using methanol had significant negative effect on the recovery of DMP and DEP at all the studied levels, whereas the recovery of DEHP was greatly improved. This observation is attributed to the fact that DEHP is less soluble, and hence more hydrophobic than DMP and DEP. Therefore, the increment in solubility as the percentage content of the organic modifier increased was more significant in DMP and DEP than DEHP. However, considering the environmental relevance of DEHP, sample modification with 10% methanol was adopted.

Table 4.28. Comparative evaluation of the analytical performance of the developed method and the values reported in literature

Preconcentration method	SPE[1] Tap water	SPE[1] River water	SPE[2] Subsoil water	SPE[3] Milli-Q water	SPE[4] Sewage	SPE[5] Seawater	LLE[6] Seawater	LLE[7] Seawater	LLE[5] Seawater
Naphthalene	73.29	63.85	35	NR	99	ND	ND	NR	NR
Acenaphthylene	81.38	74.50	46	NR	104	ND	ND	NR	NR
Acenaphthene	52.64	74.31	105	NR	64	ND	ND	NR	NR
Fluorene	73.74	67.74	97	NR	93	ND	ND	NR	NR
Phenanthrene	73.39	71.68	102	NR	72	52	10	NR	NR
Anthracene	73.39	77.64	86	NR	82	10	3	NR	NR
Fluoranthene	86.87	82.65	113	NR	81	34	13	NR	NR
Pyrene	102.16	84.65	112	NR	90	32	13	NR	NR
Benzo[a]anthracene	68.11	78.93	68	NR	106	23	12	NR	NR
Chrysene	70.84	85.84	67	NR	96	18	13	NR	NR
Benzo[b]fluoranthene	75.96	109.31	86	NR	91	25	14	NR	NR
Benzo[k]fluoranthene	86.31	106.92	73	NR	87	18	13	NR	NR
Benzo[a]pyrene	77.56	95.80	61	NR	77	10	7	NR	NR
Dibenzo[b]anthracene	81.48	84.86	63	NR	81	22	13	NR	NR
Benzo[g]perylene	94.49	86.60	58	NR	72	20	16	NR	NR
Indeno[c]perylene	77.81	97.58	67	NR	69	16	13	NR	NR
Range	52-102	64-109	35-112	95-104	64-106	10-52	3-16	95-112	65-92

ND = not detected; NR = not reported; [1]Present study; [2]Martinez et al.(2004); [3]Garcia-Falcón et al.(2004); [4]Oleszezuk and Baran (2004); [5]Filipkowska et al., (2005); [6]Nemr and Abd-Allah (2003); [7]Anyakora et al.(2005).

4.10.2 Evaluation and validation of the phthalate SPE method

The developed starch based SPE phase performed creditably well in the pre-concentration and analysis of phthalates in environmental water as evidenced in the values of linearity, method detection limit, recovery and precision as shown in Table 4.29. The values for these parameters were within the acceptable values.

Table 4.29. Method performance for simulated and real environmental water samples for phthalate esters

Evaluation and validation of method performance				
Phthalates	R^2	MDL (ng/L)	Recovery (%)	Precision (RSD)
DMP	0.9983	117.48	81.44	15.14
DEP	0.9994	106.42	92.51	20.85
DEHP	0.9978	78.15	104.63	16.96

Analysis of real environmental samples				
Phthalates	Conc in tap water (µg/L)	Recovery (%)	Conc in SaHe river samples (µg/L)	Recovery (%)
DMP	0.245	81.21	0.403	74.83
DEP	0.173	79.54	0.349	78.01
DEHP	ND	86.45	0.109	79.46

ND: not detected

CHAPTER FIVE

Conclusions and Recommendations

5.1 Conclusions

This study has successfully introduced the application of computational chemistry using Density Functional Theorem quantum mechanical model in the study of the design and adsorption interaction potential of cross-linked starch and cyclodextrin adsorbents, as the observed experimental adsorption trend was highly in agreement with computational prediction. The import of this procedure is that the feasibility of using a given cross-linked adsorbent for a target analyte can be evaluated through computational simulation without necessarily going through synthesis and characterization of the adsorbents, as well as experimental adsorption studies. This approach saves cost, time and labour in the development of adsorbents that have definite molecular structures, like cross-linked polymers.

The screening adsorption studies showed that the adsorption performance of both cross-linked starch and cyclodextrin adsorbents depended largely on the nature of the cross-linking agent as well as the degree (extent) of the cross-linking process. Also, the screening adsorption studies showed that 2,2-methylene diphenyl diisocyanate (MDI) was the most suitable cross-linking agent. The results obtained from the detailed batch adsorption studies showed that the adsorption was very fast. After 1 hour, more than 50 % of all PAHs were removed and at a contact time of 3 hours, the percentage of the removal of PAHs exceeded 70%. The study revealed that external factors like temperature, pH, and salinity of the water samples, as well as competition from other pollutants, had minimal effects on the adsorption performance of the adsorbents. A similar trend was equally observed for phthalates. The desorption studies indicated that the spent adsorbents can be efficiently regenerated. The developed adsorbents exhibited acceptable adsorption performance in treatment of aqueous PAHs and phthalates pollution in model and real environmental water samples. Hence, the results obtained in this research indicate that the

MDI cross-linked starch/cyclodextrin based polymer adsorbents (MDICS, MDIGCD, MDIBCD, MDIGDS, and MDIBDS) could be used as effective and economical adsorbents for the removal of PAHs in PAH-contaminated waters.

All the MDI cross-linked starch and cyclodextrin polymer adsorbents (MDICS, MDIGCD, MDIBCD, MDIGDS, and MDIBDS) showed great potential as SPE phase, but only one of them, MDICS was selected for optimization. The SPE pre-concentration method using MDICS for enrichment of PAHs and phthalates showed good analytical method performance in terms of detection limits, precision, linearity and linear range, and recoveries. Interestingly, the values of method detection limit achieved in this study for both UV and fluorescence detectors are lower than the maximum allowable levels for PAHs set by most environmental regulatory bodies, which make them suitable for monitoring studies for wide concentration range of PAHs and phthalate pollution. The MDICS adsorbent performed creditably well when it was applied as a solid phase for enrichment of PAHs and phthalates in real (tap and river water) samples prior to HPLC analysis. The analytical performance of the SPE/HPLC method using the developed adsorbent is very much comparable with other standard methods adopted by environmental regulatory agencies. In most cases, the observed analytical performance were better than the performance of most of the SPE adsorbents reported in literature.

The availability of starch and cyclodextrin at relatively low cost, use of cheap and easily accessible cross-linking reagents, and very simple synthetic procedure showed that the developed adsorbents can be easily prepared in the laboratory at a reasonable cost, and therefore can be applied for routine laboratory analysis. The biodegradable nature of cross-linked starch and cyclodextrin adsorbents confers a great advantage to the adsorbents developed in this study, over Polystyrene Divinyl Benzene (PS-DVB) based adsorbents which are non- biodegradable, but have proved to be the choice adsorbent for most aromatic compounds including PAHs and phthalates.

The achieved results show that 2,2-methylene diphenyl diisocyanate (MDI) cross-linked starch and cyclodextrin (MDICS, MDIGCD, MDIBCD, MDIGDS, and MDIBDS) are excellent adsorbents to enrich PAHs and phthalate esters, and can be applied for the preconcentration of these compounds in water samples.

5.2 Recommendations

DFT computational approach developed in this study is recommended for screening/selection of cross-linking agents for synthesis of starch and cyclodextrin based polymer adsorbents. It is equally recommended as feasibility guide for predicting the adsorption performance of not only starch and cyclodextrin based adsorbents, but also for other cross-linked polymer based adsorbents with definite chemical structures. Hence, further studies is recommended to extend this approach to general polymer based adsorbents.

Based on their sorption performance, the adsorbents are recommended for treatment of PAHs and phthalates polluted water. In this vein, the data generated from this study are recommended as basic guide for the engineering design of pilot water treatment facilities that will apply these adsorbents.

Also, adsorbents developed in this study having displayed high analytical performance, are strongly recommended to be applied as solid phase for pre-concentration of PAHs and phthalates prior to their chromatographic analysis.

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APPENDICES

Appendix I

Quantities of Reactants used for the Synthesis of the Cross-linked Adsorbents

Table A2.1 Quantities of reactants for the synthesis of the cross-linked starch polymers

Adsorbent	Starch (g)	EPI (ml)	Ammonia	MMA (ml)	HDI (ml)	MDI (g)
EPI starch polymers						
EPICS 1	15.00	10.00	–[*]	–	–	–
EPICS 2	15.00	20.00	–	–	–	–
EPICS 3	15.00	30.00	–	–	–	–
EPICS 4	15.00	40.00	–	–	–	–
EPICS 5	15.00	50.00	–	–	–	–
EPICS 6	15.00	70.00	–	–	–	–
EPI Aminated polymers						
EPIACS 1	15.00	20.00	10.00	–	–	–
EPIACS 2	15.00	20.00	20.00	–	–	–
EPIACS 3	15.00	20.00	30.00	–	–	–
EPI MACS 1	15.00	20.00	–	10.00	–	–
EPI MACS 2	15.00	20.00	–	20.00	–	–
EPI MACS 3	15.00	20.00	–	30.00	–	–
HDI starch polymers						
HDI CS 1	8.00	–	–	–	1.18	–
HDI CS 2	8.00	–	–	–	3.50	–
HDI CS 3	8.00	–	–	–	5.90	–
HDI CS 4	8.00	–	–	–	11.80	–
MDI starch polymers						
MDI CS 1	8.00	–	–	–	–	1.70
MDI CS 2	8.00	–	–	–	–	5.28
MDI CS 3	8.00	–	–	–	–	8.81
MDI CS 4	8.00	–	–	–	–	17.61

[*] Not Applicable

Table A2.2 Quantities of reactants for the synthesis of β-CD polymers

Adsorbent	β-CD (g)	EPI (ml)	HDI (ml)	MDI (g)
EPI β-cyclodextrin polymers				
EPIBCD 1	12.50	30.00	–	–
EPIBCD 2	12.50	40.00	–	–
EPIBCD 3	12.50	50.00	–	–
EPIBCD 4	12.50	60.00	–	–
HDI β-cyclodextrin polymers				
HDIBCD 1	8.00	–	1.18	–
HDIBCD 2	8.00	–	3.50	–
HDIBCD 3	8.00	–	5.90	–
HDIBCD 4	8.00	–	11.80	–
MDI β-cyclodextrin polymers				
MDIBCD 1	8.00	–	–	1.76
MDIBCD 2	8.00	–	–	5.28
MDIBCD 3	8.00	–	–	8.81
MDIBCD 4	8.00	–	–	17.61

Table A2.3 Quantities of reactants for the synthesis of starch cyclodextrin copolymers

Adsorbent	Starch(g)	β-CD(g)	γ-CD(g)	EPI (ml)	HDI (ml)	MDI (g)
EPI based mixed polymers						
EPI γ-CDS	0.50		2.00	4.00		
EPI β-CDS1	2.50	10.00		30.00		
EPI β-CDS2	2.50	10.00		60.00		
HDI based mixed polymers						
HDI γ-CDS	1.00		4.00		2.95	
HDI β-CDS	1.00	4.00			1.75	
MDI based mixed polymers						
MDI γ-CDS	1.00		4.00			4.41
MDI β-CDS	1.00	4.00				2.64

Appendix II

Calculation of Surface Area from N_2 Adsorption Data

A3.1 Calculation of Surface Area using BET multipoint measurement method

The Brunauer-Emmett-Teller (BET) method being the most widely used procedure for the determination of the surface area of solid materials was employed in this study and involves the use of the BET equation:

$$\frac{1}{V\left(\left({}^{P_o}\!/_{P}\right)-1\right)} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m C}\right)\left(\frac{P}{P_o}\right) \qquad \text{A1}$$

where V is the volume of gas adsorbed at a relative pressure, P/P0; V_m is the volume of adsorbate constituting a monolayer of surface coverage; and C is the BET constant related to the energy of adsorption in the first adsorbed layer.

For the multipoint BET method, a linear plot of 1/[V*(P0/P)-1] vs P/P0 in the P/P0 range of 0.06 to 0.22 was employed from which the slope [(C-1)/(Vm*C)]and intercept [1/(Vm*C)] were used in evaluating the variable Vm. The BET total surface area was obtained from the expression:

$$S_{BET} = \frac{V_m * N * A_{CS}}{M} \qquad \text{A2}$$

where N is Avogadro's number (6.023x10^{23}molecules/mol); M is the molecular weight of the adsorbate (14 g/mol for N_2 used) and A_{cs} is the cross sectional area occupied by each molecule of the adsorbate (0.162 nm^2 for N_2 used). The specific surface area was obtained by dividing the BET total surface area by the weight of the outgassed adsorbent sample.

The BET plots for calculation of BET surface area of MDICS, HDICS, MDIGCD, MDIBCD, MDIGCDS and MDIBCDS are as shown in Figure A3.1

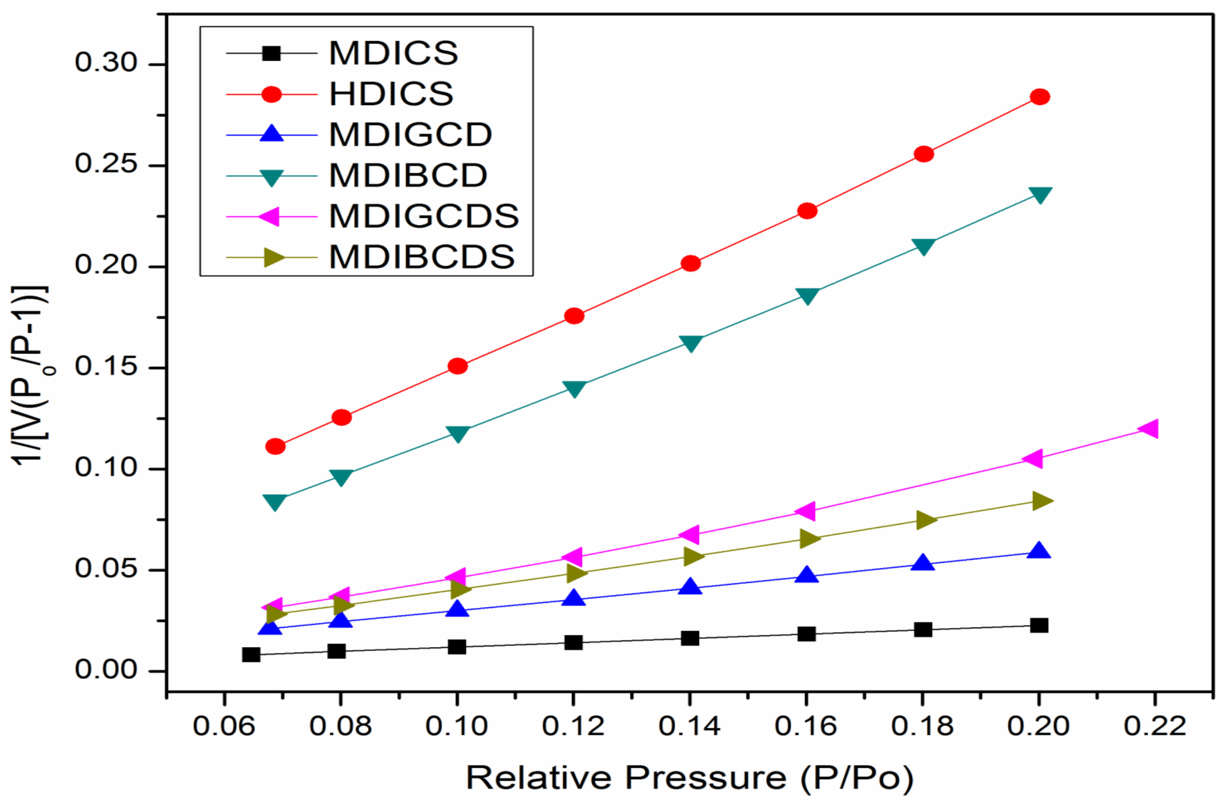

Figure A3.1 Linear plots of BET surface area

A3.1 Calculation of the pore width

Since the contribution of pores not filled below a relative pressure of 1 is negligible to the total pore volume and the surface area of the sample, the average pore size radius (rave) could be estimated from the total pore volume and the BET total surface area. By ssuming that all pores are cylindrical, the total pore volume and BET total surface area could be expressed as:

$$V_t = \pi r_{ave}^2 L \qquad \text{A3}$$

and

$$S_{BET} = 2\pi r_{ave} L \qquad \text{A4}$$

where L is the mean pore length. Thus, the average pore size width was calculated by dividing equation A3 by equation A4 to yield:

$$d = 2 * r_{ave} = 2 * \left(\frac{2 * V_t}{S_{BET}} \right)$$

Appendix III

Experimental Set-up for the Solid Phase Extraction (SPE) Preconcentration Studies

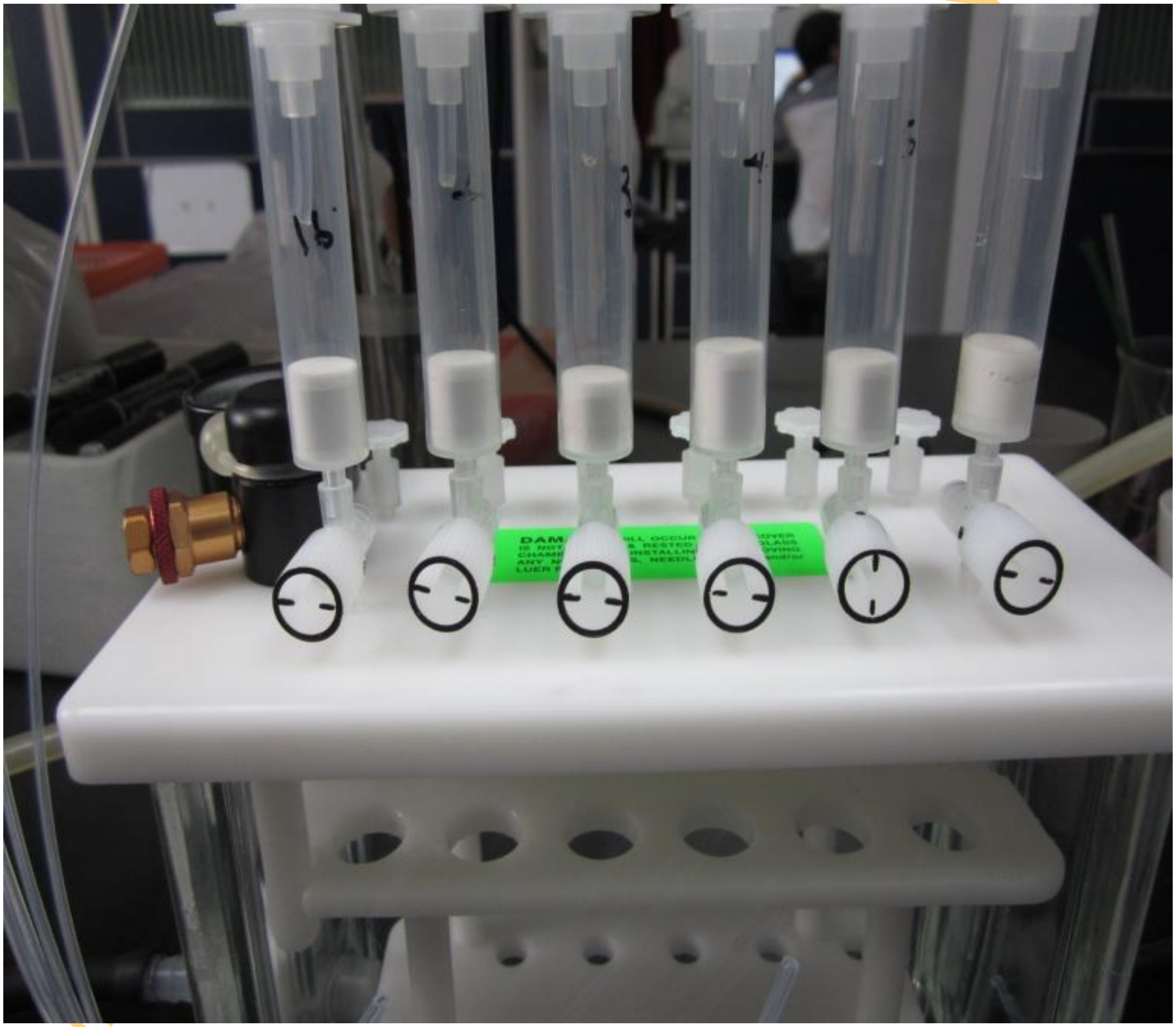

Plate A1: Set-up of the packed SPE cartridge on manifold

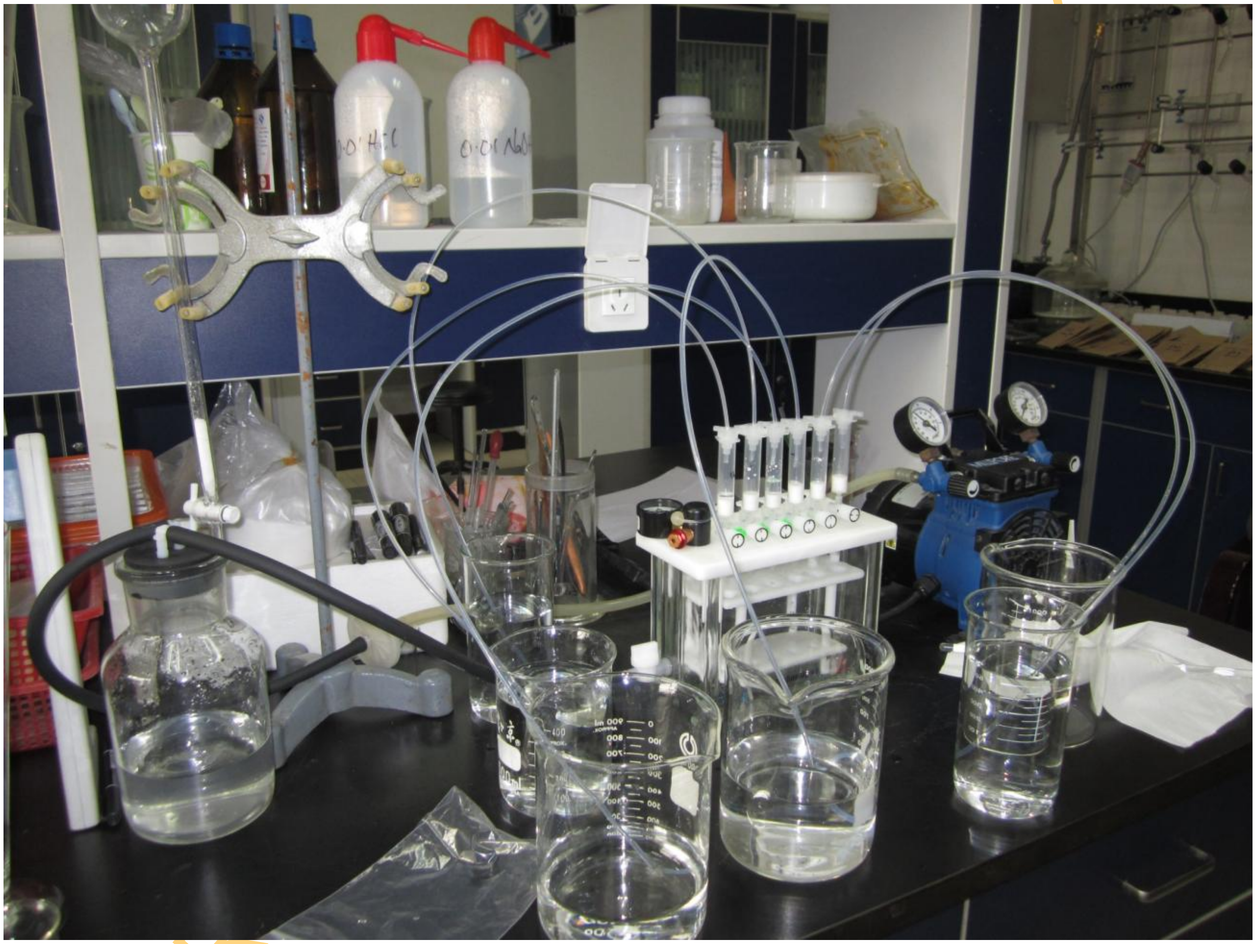

Plate A2: Experimental Set-up for Solid Phase Extraction

Appendix IV

Data for Screening Adsorption Study

Cross-linked starch adsorption

Table A4.1 Screening adsorption data for acenaphthylene

Adsorbent	C_o (mg/L)	C_e (mg/L)	C_o-C_e(mg/L)	q_e(mg/g)
EPICS 1	2.9386	2.4868	0.4518	0.4518
EPICS 2	2.9386	2.2419	0.6967	0.6967
EPICS 3	2.9386	2.1003	0.8383	0.8383
EPICS 4	2.9386	1.8633	1.0753	1.0753
EPICS 5	2.9386	1.5442	1.3944	1.3944
EPICS 6	2.9386	1.2219	1.7167	1.7167
EPIACS 1	2.9386	1.2319	1.7067	1.7067
EPIACS 2	2.9386	1.0987	1.8399	1.8399
EPIACS 3	2.9386	0.7499	2.1887	2.1887
EPIMACS 1	2.9386	0.9157	2.0229	2.0229
EPIMACS 2	2.9386	0.7851	2.1535	2.1535
EPIMACS 3	2.9386	0.4982	2.4404	2.4404
HDICS 1	2.9386	2.2194	0.7192	0.7192
HDICS 2	2.9386	2.1117	0.8269	0.8269
HDICS 3	2.9386	1.7382	1.2004	1.2004
HDICS 4	2.9386	1.2535	1.6851	1.6851
MD1CS 1	2.9386	1.1973	1.7413	1.7413
MD1CS 2	2.9386	0.8529	2.0857	2.0857
MD1CS 3	2.9386	0.4571	2.4815	2.4815
MD1CS 4	2.9386	0.2899	2.6487	2.6487
GAC*	2.9386	0.1914	2.7472	2.7472

*Granulated Activated Carbon

Table A4.2 Screening adsorption data for phenanthrene

Adsorbent	C_o (mg/L)	C_e (mg/L)	C_o-C_e(mg/L)	q_e(mg/g)
EPICS 1	1.1709	0.7792	0.3917	0.3917
EPICS 2	1.1709	0.5901	0.5808	0.5808
EPICS 3	1.1709	0.5592	0.6117	0.6117
EPICS 4	1.1709	0.4066	0.7643	0.7643
EPICS 5	1.1709	0.2047	0.9662	0.9662
EPICS 6	1.1709	0.5073	0.6636	0.6636
EPIACS 1	1.1709	0.5012	0.6697	0.6697
EPIACS 2	1.1709	0.2749	0.896	0.8960
EPIACS 3	1.1709	0.1605	1.0104	1.0104
EPIMACS 1	1.1709	0.6401	0.5308	0.5308
EPIMACS 2	1.1709	0.4197	0.7512	0.7512
EPIMACS 3	1.1709	0.3824	0.7885	0.7885
HDICS 1	1.1709	0.6017	0.5692	0.5692
HDICS 2	1.1709	0.5211	0.6498	0.6498
HDICS 3	1.1709	0.4166	0.7543	0.7543
HDICS 4	1.1709	0.3521	0.8188	0.8188
MD1CS 1	1.1709	0.2581	0.9128	0.9128
MD1CS 2	1.1709	0.1902	0.9807	0.9807
MD1CS 3	1.1709	0.112	1.0589	1.0589
MD1CS 4	1.1709	ND#	1.1709	1.1709
GAC*	1.1709	ND#	1.1709	1.1709

*Granulated Activated Carbon

Not Detected

Table A4.3 Screening adsorption data for Benzo[a]anthracene (BaA)

Adsorbent	C_o (µg/L)	C_e (µg/L)	C_o-C_e(µg/L)	q_e(µg/g)
EPICS 1	9.3278	1.8334	7.4944	7.4944
EPICS 2	9.3278	1.4303	7.8975	7.8975
EPICS 3	9.3278	1.6235	7.7043	7.7043
EPICS 4	9.3278	2.3071	7.0207	7.0207
EPICS 5	9.3278	2.7281	6.5997	6.5997
EPICS 6	9.3278	3.912	5.4158	5.4158
EPIACS 1	9.3278	0.8883	8.4395	8.4395
EPIACS 2	9.3278	1.3292	7.9986	7.9986
EPIACS 3	9.3278	1.5231	7.8047	7.8047
EPIMACS 1	9.3278	1.2392	8.0886	8.0886
EPIMACS 2	9.3278	1.3095	8.0183	8.0183
EPIMACS 3	9.3278	0.9586	8.3692	8.3692
HDICS 1	9.3278	1.1473	8.1805	8.1805
HDICS 2	9.3278	0.8979	8.4299	8.4299
HDICS 3	9.3278	0.8273	8.5005	8.5005
HDICS 4	9.3278	ND	9.3278	9.3278
MD1CS 1	9.3278	0.9864	8.3414	8.3414
MD1CS 2	9.3278	0.9012	8.4266	8.4266
MD1CS 3	9.3278	0.0987	9.2291	9.2291
MD1CS 4	9.3278	ND[#]	9.3278	9.3278
GAC[*]	9.3278	ND	9.3278	9.3278

[*] Granulated Activated Carbon

[#] Not Detected

Table A4.4 Screening adsorption data for Diethyl phthalate (DEP)

Adsorbent	C_o (mg/L)	C_e (mg/L)	C_o-C_e(mg/L)	q_e(mg/g)
EPICS 1	4.1609	3.9791	0.1818	0.4545
EPICS 2	4.1609	3.9833	0.1776	0.4440
EPICS 3	4.1609	4.0009	0.1600	0.4000
EPICS 4	4.1609	4.0287	0.1322	0.3305
EPICS 5	4.1609	4.0069	0.1540	0.3850
EPICS 6	4.1609	4.0154	0.1455	0.3638
EPIACS 1	4.1609	3.9798	0.1811	0.4527
EPIACS 2	4.1609	3.9855	0.1754	0.4384
EPIACS 3	4.1609	3.9929	0.1680	0.4201
EPIMACS 1	4.1609	3.9869	0.1740	0.4351
EPIMACS 2	4.1609	3.9897	0.1712	0.4279
EPIMACS 3	4.1609	3.9848	0.1761	0.4402
HDICS 1	4.1609	3.9971	0.1638	0.4095
HDICS 2	4.1609	3.9925	0.1684	0.4210
HDICS 3	4.1609	3.9777	0.1832	0.4580
HDICS 4	4.1609	3.9749	0.1860	0.4650
MD1CS 1	4.1609	3.8217	0.3392	0.8480
MD1CS 2	4.1609	3.6014	0.5595	1.3988
MD1CS 3	4.1609	2.1237	2.0372	5.0930
MD1CS 4	4.1609	1.9925	2.1684	5.4210
GAC*	4.1609	0.8767	3.2842	8.2105

*Granulated Activated Carbon

β-Cyclodextrin polymer adsorption

Table A4.5 Screening adsorption data for Acenaphthylene

Adsorbent	C_o (mg/L)	C_e (mg/L)	C_o-C_e(mg/L)	q_e(mg/g)
EPIBCD 1	2.9386	1.6691	1.2695	1.2695
EPIBCD 2	2.9386	1.6561	1.2825	1.2825
EPIBCD 3	2.9386	1.653	1.2856	1.2856
EPIBCD 4	2.9386	1.7198	1.2188	1.2188
HDIBCD 1	2.9386	0.2669	2.6717	2.6717
HDIBCD 2	2.9386	1.9304	1.0082	1.0082
HDIBCD 3	2.9386	2.3021	0.6365	0.6365
HDIBCD 4	2.9386	1.8065	1.1321	1.1321
MDIBCD 1	2.9386	0.7324	2.2062	2.2062
MDIBCD 2	2.9386	1.2902	1.6484	1.6484
MDIBCD 3	2.9386	0.6563	2.2823	2.2823
MDIBCD 4	2.9386	1.6477	1.2909	1.2909
GAC*	2.9386	0.1914	2.7472	2.7472

*Granulated Activated Carbon

Table A4.6 Screening adsorption data for Phenanthrene

Adsorbent	C_o (mg/L)	C_e (mg/L)	C_o-C_e(mg/L)	q_e(mg/g)
EPI β-CD 1	1.1709	0.5496	0.6213	0.6213
EPI β-CD 2	1.1709	0.4658	0.7051	0.7051
EPI β-CD 3	1.1709	0.5073	0.6636	0.6636
EPI β-CD 4	1.1709	0.4878	0.6831	0.6831
HDI β-CD 1	1.1709	0.2890	0.8819	0.8819
HDI β-CD 2	1.1709	0.8082	0.3627	0.3627
HDI β-CD 3	1.1709	0.9553	0.2156	0.2156
HDI β-CD 4	1.1709	1.0741	0.0968	0.0968
MDI β-CD 1	1.1709	0.2122	0.9587	0.9587
MDI β-CD 2	1.1709	0.3442	0.8267	0.8267
MDI β-CD 3	1.1709	0.1613	1.0096	1.0096
MDI β-CD 4	1.1709	0.7107	0.4602	0.4602
GAC*	1.1709	ND#	1.1709	1.1709

*Granulated Activated Carbon

Not Detected

Table A4.7 Screening adsorption data for Benzo[a]anthracene (BaA)

Adsorbent	C_o (μg/L)	C_e (μg/L)	C_o-C_e(μg/L)	q_e(μg/g)
EPI β-CD 1	9.3278	0.8609	8.4669	8.4669
EPI β-CD 2	9.3278	ND	9.3278	9.3278
EPI β-CD 3	9.3278	0.7952	8.5326	8.5326
EPI β-CD 4	9.3278	0.9643	8.3635	8.3635
HDI β-CD 1	9.3278	ND	9.3278	9.3278
HDI β-CD 2	9.3278	1.9602	7.3676	7.3676
HDI β-CD 3	9.3278	1.4050	7.9228	7.9228
HDI β-CD 4	9.3278	1.4370	7.8908	7.8908
MDI β-CD 1	9.3278	ND	9.3278	9.3278
MDI β-CD 2	9.3278	ND	9.3278	9.3278
MDI β-CD 3	9.3278	ND	9.3278	9.3278
MDI β-CD 4	9.3278	1.0300	8.2978	8.2978
GAC*	9.3278	ND#	9.3278	9.3278

*Granulated Activated Carbon

Not Detected

Table A4.8 Screening adsorption data for Diethyl pathalate (DEP)

Adsorbent	C_o (mg/L)	C_e (mg/L)	C_o-C_e(mg/L)	q_e(mg/g)
EPI β-CD 1	4.1609	3.9946	1.5978	0.4158
EPI β-CD 2	4.1609	3.9887	1.5955	0.4305
EPI β-CD 3	4.1609	3.9652	1.5861	0.4893
EPI β-CD 4	4.1609	3.9680	1.5872	0.4823
HDI β-CD 1	4.1609	3.9715	1.5886	0.4735
HDI β-CD 2	4.1609	3.9943	1.5977	0.4165
HDI β-CD 3	4.1609	3.9906	1.5962	0.4258
HDI β-CD 4	4.1609	3.9749	1.5899	0.4650
MDI β-CD 1	4.1609	2.9638	1.1855	2.9928
MDI β-CD 2	4.1609	2.8988	1.1595	3.1553
MDI β-CD 3	4.1609	2.7018	1.0807	3.6478
MDI β-CD 4	4.1609	3.1092	1.2437	2.6292
GAC*	4.1609	0.8767	3.2842	8.2105

*Granulated Activated Carbon

Table A4.9 Mean adsorption capacities ($\bar{q}_e$) of the major families of adsorbents

Adsorbents	Acenaphthylene (mg/g)	Phenanthrene (mg/g)	Benzo[a] anthracene (μg/g)	Diethyl phthalate (mg/g)
EPICS	0.77	0.59	7.53	0.41
HDICS	1.11	0.70	8.61	0.44
MDICS	2.24	1.03	8.83	3.19
EPIBCD	1.26	0.67	8.67	0.45
HDIBCD	1.36	0.39	8.13	0.45
MDIBCD	1.86	0.81	9.07	3.11

γ-Cyclodextrin polymer adsorption

Table A4.10 Screening adsorption data for Acenaphthylene, phenanthrene, BaA and DEP adsorption onto γ-cyclodextrin polymer adsorbents

Adsorbent	C_o (mg/L)	C_e (mg/L)	C_o-C_e(mg/L)	q_e(mg/g)
Acynaphthylene				
EPIGCD	2.9386	0.7843	2.1543	2.1543
HDIGCD	2.9386	1.6684	1.2702	1.2702
MDIGCD	2.9386	0.7843	2.1543	2.1543
Phenanthrene				
EPIGCD	1.1709	0.3017	0.8692	0.8692
HDIGCD	1.1709	0.4647	0.7062	0.7062
MDIGCD	1.1709	0.1865	0.9844	0.9844
DEP				
EPIGCD	4.1609	3.9801	0.1808	0.452
HDIGCD	4.1609	3.9629	0.198	0.495
MDIGCD	4.1609	1.6665	2.4944	6.236
Benzo[a]anthracene				
Adsorbent	C_o (µg/L)	C_e (µg/L)	C_o-C_e(µg/L)	q_e(µg/g)
EPIGCD	9.3278	1.3012	8.0266	8.0266
HDIGCD	9.3278	1.1511	8.1767	8.1767
MDIGCD	9.3278	0	9.3278	9.3278

Cyclodextrin starch mixed polymer adsorbents

Table A4.11 Screening adsorption data for Acenaphthylene

Adsorbent	C_o (mg/L)	C_e (mg/L)	C_o-C_e(mg/L)	q_e(mg/g)
EPIGCDS	2.9386	1.5189	1.4197	1.4197
HDIGCDS	2.9386	1.3283	1.6103	1.6103
MDIGCDS	2.9386	0.1864	2.7522	2.7522
EPIBCDS	2.9386	1.7198	1.2188	1.2188
HDIBCDS	2.9386	2.1491	0.7895	0.7895

MDIBCDS	2.9386	0.2650	2.6736	2.6736

Table A4.12 Screening adsorption data for Acenaphthylene

Adsorbent	C_o (mg/L)	C_e (mg/L)	C_o-C_e(mg/L)	q_e*(mg/g)*
EPIGCDS	1.1709	0.4541	0.7168	0.7168
HDIGCDS	1.1709	0.4678	0.7031	0.7031
MDIGCDS	1.1709	0.0529	1.1180	1.1180
EPIBCDS	1.1709	0.5674	0.6035	0.6035
HDIBCDS	1.1709	0.6717	0.4992	0.4992
MDIBCDS	1.1709	0.1681	1.0028	1.0028

Table A4.13 Screening adsorption data for BaP

Adsorbent	C_o (µg/L)	C_e (µg/L)	C_o-C_e(µg/L)	q_e*(µg/g)*
EPIGCDS	9.3278	0.8382	8.4896	8.4896
HDIGCDS	9.3278	2.6069	6.7209	6.7209
MDIGCDS	9.3278	ND	9.3278	9.3278
EPIBCDS	9.3278	0.9918	8.336	8.336
HDIBCDS	9.3278	1.2092	8.1186	8.1186
MDIBCDS	9.3278	ND	9.3278	9.3278

Table A4.14 Screening adsorption data for BaP

Adsorbent	C_o (mg/L)	C_e (mg/L)	C_o-C_e(mg/L)	q_e*(mg/g)*
EPIGCDS	4.1609	3.9197	0.2412	0.6030
HDIGCDS	4.1609	3.9277	0.2332	0.5830
MDIGCDS	4.1609	1.6948	2.4661	6.1653
EPIBCDS	4.1609	3.9372	0.2237	0.5593
HDIBCDS	4.1609	3.9399	0.2210	0.5525
MDIBCDS	4.1609	2.4201	1.7408	4.3520

Appendiix V
Publications and Presentations

Publications

1. Chukwunonso Peter Okoli, QingJun Guo, and Gregory O. Adewuyi (2014). Application of DFT Quantum Descriptors for Predicting Adsorption Performance of Cross-linked Starch and Cyclodextrin Adsorbents. *Carbohydrate Polymers*, Elsevier. Volume 101, pp 41 – 49. http://dx.doi.org/1016/j.carbpol.2013.08.065
2. Chukwunonso P. Okoli, Gregory O. Adewuyi, Zhu Guangxu, ChungYu Wang, Qian Zhang and Guo QingJun. Treatment of aqueous polycyclic aromatic hydrocarbons pollution using starch-based adsorbents. *International Journal of Environmental Science and Technology*, Springer Verlag. Under review
3. Chukwunonso Peter Okoli Gregory Olufemi Adewuyi Paul Nkem Diagboya and Qingjun Guo. Mechanism of dialkyl phthalates removal from aqueous solution using γ-cyclodextrin and starch based polyurethane polymer adsorbents. *Carbohydrate Polymers*, Elsevier. Under review
4. Chukwunonso Peter Okoli, Qingjun Guo, Qian Zhang, Paul Nkem Diagboya, and Gregory Olufemi Adewuyi. Application of QSAR in Selection of Starch-based Solid Phase Sorbent for HPLC Analysis of Aqueous Polycyclic Aromatic Hydrocarbons. *Journal of Chromatography A*, Elsevier. Manuscript submitted

Presentations

1. 41st International Symposium on High Performance Liquid Phase Separations and Related Techniques (HPLC 2014), May 11–15, 2014, New Orleans, Louisiana, USA. Poster Presentation: Chukwunonso Peter Okoli, Qingjun Guo, Qian Zhang, Paul Nkem Diagboya, and Gregory Olufemi Adewuyi. Application of QSAR in Selection of Starch-based Solid Phase Sorbent for HPLC Analysis of Aqueous Polycyclic Aromatic Hydrocarbons. Accepted.
2. 1st National Conference on Environmental Health Sciences, November 24 – 27, 2013, Ibadan, Nigeria. Oral presentation: Chukwunonso Peter Okoli, Guo Qingjun, Qian Zhang, Guangxu Zhu, ChungYu Wang and Gregory Olufemi Adewuyi.,Removal of polycyclic aromatic hydrocarbons from aqueous solution using cross-linked starch polymer adsorbents.