THE REMOVAL OF TOXIC ANIONS FROM WASTEWATER USING ELECTROSPUN NANOFIBERS

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By

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DEDICATION

This research is dedicated to the Almighty God, for His great protection and provision during the course of this study.

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everlasting desire, sacrifice, affection, blessing and help towards me from birth. Thank you ma.

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ABSTRACT

The presence of arsenic and phosphate in waters, especially wastewater, has become a worldwide problem even till the present time. The current regulation of drinking standard water has become more stringent and requires arsenic content to be reduced to a few parts per billion. Nevertheless, phosphorous pollution, known as the eutrophication, is regarded as one of the main causes of water quality deterioration. Hence, the decontamination of phosphorous from aqueous solutions is of importance for eutrophication control and phosphorous recovery. Efforts are being made to remove these contaminants, arsenic (v) and phosphate from wastewater using low cost adsorbents. In the present study, removal of arsenic(v) and phosphate from wastewater using two novel fabricated sorbent materials; polyvinylmethylketone functionalized 2-amino4,6-dihydroxylpyrimidine (APPMKNFs) prepared via a Schiff base condensation reaction and aminated polyvinylbenzylchloride (PVBC) prepared through a substitution reaction and then quaternized using three alkyl groups (R′ = CH_3, C_2H_5 and C_3H_7) were investigated. The experiments were carried out in batch and solid phase extraction mode. Preliminary experiments were done with series of four sorbent materials (APPMKNFs, R′ = CH_3, C_2H_5 and C_3H_7) in order to find out a suitable and low cost adsorbents for the effective removal of arsenic (v) and phosphate. The best sorbent materials were obtained after the optimization and preparation experiments. The APPMKNFs and R′ = CH_3 were effective for arsenic (v) and phosphate removal from wastewater. The effect of pH, initial sorbate concentration, amount of sorbent, effect of co-exisiting anions and the reusability in batch and solid phase extraction mode were

also investigated. From the experiment conducted, the pH shows a decisive factor on arsenic and phosphate removal. Analysis of adsorbent dosage, Kinetic studies and co-existing anions were carried out in order to evaluate sorption parameters. The adsorption isotherms were well fitted by Langmuir than Freundlch isotherm for (APPMKNFs).

The presence of other anions such as SO_4^{2-}, Cl^-, NO_2^- for arsenic (v) and SO_4^{2-}, Cl^- and NO^- for phosphate which are generally present in wastewater sources were also carried out on the arsenic and phosphate removal efficiency. Experiments were also conducted to evaluate the arsenic(v) and phosphate removal efficiency on APPMKNFs and PVBC (R′ = CH_3, C_2H_5 and C_3H_7). It was observed that, the removal was strongly affected because of the presence of these anions. SO_4^{2-} for arsenic(v) and $CO_3^{2-}$and SO_4^{2-} for phosphate were the most interfering ions. Exhausted APPMKNFs and PVBC (R′ = $CH_{3,}$ C_2H_5 and C_3H_7) were regenerated by using 0.1 M NaOH solution and regeneration efficiency was tested for repeated regeneration cycles. The results show that, arsenate and phosphate sorption on the fibers were achieved within 30 min at pH 3.0 via Hydrogen bonding (APPMKNFs), 40 min at pH 5 (PVBC R′ = CH_3, C_2H_5 and C_3H_7) for arsenic(v) and 20 min at pH 5.0 PVBC (R′ = $CH_{3,}$ C_2H_5 and C_3H_7) for phosphate by ionic interaction. Fourier transform infrared (FTIR) analysis for APPMKNFs shows peaks at 1696 cm^{-1} and 3139 cm^{-1} on the polymer and on the ligand respectively as the starting materials, these peaks however disappear to form a new band at 1613 cm^{-1} indicative of the presence of imine functional group on the synthesized product. The band assigned to 670 cm^{-1} $_v$(C-Cl) disappeared completely to form a new band at 1562 cm^{-1}

indicating the presence of NH group on the fibers. CHNS micro analysis of APPMKNFs shows the presence of functional groups of carbon and hydrogen with the absence of nitrogen before the synthesis and the presence of nitrogen after the synthesis. Energy dispersive x-ray spectrometer (EDX) for PVBC shows the presence of a broad peak for Cl on the unfunctionalized fiber and this peak disappears to form a sharp peak of nitrogen from the amine in EDA of the fibers. X-ray diffraction (XRD) analysis of the fibers reveals the sharp peak on 40 (2θ) degree axis on the surface of the functionalized fibers. The functional groups on the fibers played an important role in the removal of arsenate and phosphate from wastewater. The functionalized fibres reduced the concentrations of the analytes from 50 µg/l to 10 µg/l within the shortest possible time compared to the conventional methods attributed to the electrostatic interaction between the positive charge on the sorbent materials and the negative arsenate and phosphate ions.

DECLARATION

“I hereby declare that the work in this thesis is my own work (***Removal of toxic anions from wastewater using electrospun nanofibers***) and that, to the best of my knowledge, it contains no materials previously published or written by another person, or substantial proportions of materials which have been accepted for academic award at any other educational institution, except where due acknowledgment is made in the thesis. Any contribution made to this research by others, with whom I have worked with, at Rhodes University, or elsewhere, is explicitly acknowledged in the thesis. I also declare that, the intellectual content of this research is the product of my own work, except to the extent that, assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.” All the resources I have used or quoted have been indicated and acknowledged by complete references.

Moronkola, B. Adekemi

LIST OF ABBREVIATIONS

TDS	Total dissolved solid
NOM	Natural organic matter
SOCs	Synthetic organic compounds
MF	Micro filtration
UF	Ultrafiltration
NF	Nanofiltration
RO	Reverse osmosis
UV	Ultraviolet
PEUF	Polyelectrolyte enhanced ultrafiltration
EPA	Environmental protection agency
BET	Brunauer Emmett Teller
SEM	Scanning electron microscope
FTIR	Fourier Transformed Infrared
EDS	Energy dispersive X-ray spectroscopy
TMAO	Trimethylarsin oxide
AB	Arsenobetaine
AC	Arsenochlorine
US	United States
WHO	World Health Organization

BFD	Black foot diseases
HFO	Hydrous ferric oxide
HAO	Hydrous Aluminum Oxide
S/S	Solidification
DO	Dissolved oxygen
pH	$-\log [H^+]$
NTA	Nitrilotriacetate
HM-PLLA	High molecular weight poly-L-lactic acid
DMF	N,N'-dimethyl formamide
THF	Tetrahydrofuran
PVA	Polyvinyalcohol
ICP-OES	Inductively coupled plasma optical emission spectrometry
APPMKNFs	Amino polyvinylpyrimidinemethylketonenanofibers
NaOH	Sodium hydroxide
PVBC	Polyvinylbenzylchloride
EE	Extraction efficiency
HCl	Hydrochloric acid
PO_4^{3-}	Phosphate
ASO_4^{3-}	Arsenate
$FeCl_3$	Iron(lll)chloride

HPO_4^{3-}	Hydrogen phosphate
$H_2PO_4^-$	Dihydrogen phosphate
H_3PO_4	Trihydrogen phosphate
$Na_2S_2O_5$	Sodium metabisulphide
H_2SO_4	Sulfuric acid
K_2HPO_4	Dipotassium hydrogen phosphate
SPE	Solid phase extraction
Mg	Milligram
Mg/L	Milligram per liter
Min	Minute
mL	Milliliter
EtOH	Ethanol
PMMA	Poly(methyl methacrylate)
MEK	Methyl ethylketone

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CHAPTER 1

1.0 Introduction

Water scarcity and water pollution are crucial issues in today's world (Green Arth, 2012). One of the ways to reduce the impact of water scarcity and pollution is to expand water and wastewater reuse. The increasing scarcity of water in the world along with rapid population increase in urban areas gives rise to concern about appropriate water management practices (Looker, 1998). In the context of trends in urban development, wastewater treatment deserves greater emphasis. Currently, there is a growing awareness of the impact of sewage contamination on rivers and lakes. Accordingly, wastewater treatment is now receiving greater attention from the World Bank and government regulatory bodies. (Green Arth, 2012; Ng, 2006)

Wastewater constitutes a major ecological problem: It is a leading cause of death and diseases worldwide. Wastewater is produced when there is the alteration in physical, chemical and biological characteristics of water, which has a resultant harmful effect on human and aquatic biota (Armienta *et al*., 2008). The toxic effect of wastewater is on the increase due to rapid population growth, industrial exploitation, urbanization, increasing living standards and wide spheres of human activities (Armienta *et al*., 2008). It is anticipated that, in the near future, pure and clean water (particularly in densely populated and industrialized areas) may be inadequate for maintaining normal living standards (Kimiko, 2001). However, wastewater contamination has been shown to be reversible (Huang and Fu 1984). Nevertheless, if wastewater contaminates ground water, it is difficult to restore it to the original water quality of the aquifer that is supplied by good water.

According to the World Bank, "The greatest challenge in the water and sanitation sector over the next two decades will be the implementation of low cost sewage treatment that, will at the same time, permit selective reuse of treated effluents for agricultural and industrial purposes" (Green Arth, 2012). It is crucial that, sanitation systems have high levels of hygienic standards to prevent the spread of diseases.

For instance, functionalized polyvinylmethylketone has shown about 99.90% of arsenic(v) removal from wastewater. The World Health Organization's guideline for arsenic in drinking water was lowered from 50 μg/L to 10μg/L in 1993. The European Union followed suit in 1998 and the United States in 2001 (USEPA, 2001).

1.1 Arsenic

An estimated 30 to 35 million Bangladesh people are exposed to arsenic concentrations above 50 $\mu g l^{-1}$ (World Health Organization (WHO) guideline value prior to 1993), and the number of people exposed to more than 10 $\mu g l^{-1}$ (current WHO guide line value) is 46 to 57 million (Kelly and Tarek, 2005). The problem of wastewater is acute among developing and industrialized countries that are still struggling with the toxic effect of waste water (Armienta *et al.*, 2008).

Arsenic is an aubiquitous element that ranks 20th in abundance in the earth's crust, 14th in sea water and 12th in the human body (Badal *et al.*, 2002). It comprises about five hundred-thousand of 1 % (0.00005%) of the earth's crust (Miteva, *et al.*, 2005). It is widely distributed in nature in the form of either metalloids or chemical compounds, primarily present in inorganic forms and exists in two predominant species: arsenate and arsenite. Arsenite is much more toxic (Ferguson and Gavis, 1972; Shailendran *et al.*, 1978), soluble and mobile than arsenate. Arsenate ($H_2AsO_4^-$ and $HAsO_4^{2-}$) is the predominant form of arsenic in well-oxidized waters, while arsenite occurs predominantly as H_3AsO_3 and $H_2AsO_3^-$ in reduced environments (Shailendran *et al.*, 1978).

1.1.2 Speciation of Arsenic(As)

The speciation of inorganic arsenic, As species is important when considering toxicological studies and remediation techniques, particularly since the latter is highly species dependent. Two factors (pH and redox potential) are very important in controlling As speciation (Mohan *et al.*, 2007). As^{5+} species (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}) are dominant under oxidising conditions, with $H_2AsO_4^-$ dominates at low pH ($pH < 6.9$) and $HAsO_4^{2-}$ at higher pH, while H_3AsO_4 and AsO_4^{3-} may occur in extremely acidic and alkaline conditions, respectively. On the contrary, As^{3+} species (H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$) are stable under reducing (or anoxic) conditions, with the most common being the uncharged species H_3AsO_3 at $pH < 9.2$ (Smedley *et al.*, 2002).

The ratio of As^{3+} to As^{5+} in groundwaters is highly unstable due to the variations in the availability of redox active solids, especially organic carbon, the activity of micro organisms, and the extent of convection and diffusion of oxygen from the atmosphere. For example, the proportion of As^{3+} in As-rich reducing groundwater of Bangladesh is about 10–90% of the total As concentration, which typical ranges from 50–60% (Smedley *et al.*, 2002). Due to the presence of uncharged As^{3+} species in reducing environments under a wide range of pH values (0–9), most of the sorption techniques can hardly remove As^{3+}. In this regard, the contaminated water, where As^{3+} is the dominant species needs to be pre-treated by oxidation. Moreover, As reacts with iron and manganese hydroxides, when these oxides are present in both groundwater and surface water, and subsequently is immobilized through adsorption-coprecipitation or released from the precipitate surfaces in the presence of orthophosphate and natural organic matter (NOM) due to competition for sorptive surface sites (Jiang 2001).

The primary forms of arsenite are unchanged below pH 9.2 because the pK_a of arseneous acid is 9.2. On the other hand, the primary form of arsenate is anionic above the pH 2.5, because the first pK_a for arsenic acid is 2.2 while, the second and third pK_a values of arsenate are 7.0 and 11.4 respectively. This is why arsenite is more mobile than arsenate (Smedley and Kinnibug, 2002). Typically, the primary method for removing arsenite from water is to convert it to arsenate, because arsenate is usually in ionic form in water. The dominant species at each pH of arsenate are presented in Figure 1.1.

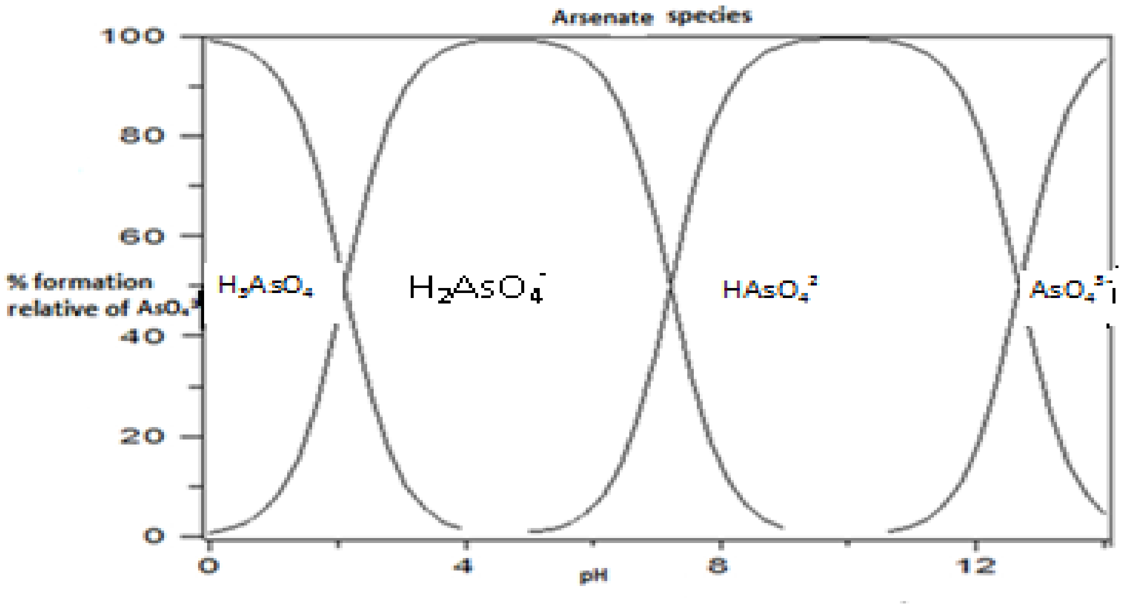


Figure 1.1: Speciation of arsenic as a function of pH (Smedley and Kinnibug, 2002).

The pH diagram for arsenate species is shown in the above figure. Arsenite is thermodynamically stable under reduced conditions, while arsenate is prevalent under oxidized conditions. Arsenic acid and its ionization products are of prime importance for arsenic transport under a wide range of pH.

The pH is an important factor that controls the absorption of arsenate as it exerts influence on speciation and composition of surface functional groups through protonation (Stollenwerk *et al.*, 2007). The pk_a value of arsenate is greater than arsenite, therefore, deprotonation is more difficult for arsenate at neutral pH to form surface complexation and efficiency is highly influenced by the deprotonation ability.

$$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$$

$$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-}$$

$$HAsO_4^{2-} \rightleftharpoons H^+ + ASO_4^{3-}$$

Scheme 1.1: pH diagram for arsenic speciation (Ghimire *et al*., 2002).

Surface complexation will occur if the undissociated arsenic acid donates a proton to the hydroxyl group present. Arsenate deprotonation is greater at a neutral pH (Thirunavukkarasu *et al*., 2003).

Grafe and Spark (2006) noted that, the charge on arsenate is negative and therefore electrostatically attracted to the surface of the positively charged ion. Arsenate adsorption decreases drastically as the pH approaches 7-8 (Richard, 1998). The decrease is caused by a surface charge on the face of any mineral present such that, the negative charge on the surface repulses the negatively charged arsenate ion (Conell *et al*., 2006; Sracek *et al*., 2004). The adsorption maximum for arsenate removal onto chelating ligand is at pH of 4.0 and 7.0 (Sracek *et al*., 2004).

Research has long shown that, arsenic is fatal when ingested at high doses; the effects of low dosages became apparent only in the 1980s (Dinesh *et al*., 2007). The World Health Organization (WHO) guideline value for arsenic in drinking water is 10 µg/L (Dinesh *et al*., 2007). The Environmental Protection Agency (EPA) guideline for arsenic in drinking water is 50 µg/L (Badal *et al*., 2002).

1.1.3 Sources of Arsenic in Wastewater

In wastewater, arsenic occurs both naturally and through anthropogenic activities, that is, human influences. Arsenic can be naturally derived from several parent materials in industrial wastes, including magnetic sulphides and iron ores. The most important arsenic ores are the arsenopyrites, which are often present in sulfide ores. Human influence can result in a build-up of arsenic, which includes the use of arsenical pesticides and the application or disposal of industrial and animal wastes (Xie *et al*., 2006).

1.1.4 General Chemistry and Oxidation of Arsenate

Arsenic is a highly toxic metalloid, it is brittle, crystalline, odourless and tasteless in its elemental form (William and Keneet, 1989). Arsenic rarely occurs in a free state, it is largely found in combination with sulphur, oxygen, and iron (Driehaus *et al*., 1995); Jain and Ali, 2000). In groundwater, arsenic combines with oxygen to form inorganic pentavalent arsenate and trivalent arsenite. Unlike other heavy metalloids and oxyanion-forming elements, arsenic can be mobilized at the pH values typically found in surface and groundwaters (pH 6.5 to 8.5) and under both oxidizing and reducing conditions (Baeyens *et al.*, 2007). While all other oxyanion-forming elements are found within the µg/L range, arsenic can be found within the mg/L range (Smedley and Kinniburg, 2002).

Arsenic is commonly used in glass making and termite control, as a pesticide and herbicide, and in timber preservation, fertilization, wallpaper and ceramics (Toda *et al.*, 2005). As a heavy metal, arsenic is stable in the –lll, 0, +lll and V oxidation states (Toda *et al.*, 2005). It forms several inorganic and organic compounds and it is commonly found in the environment. The most commonly found species in the aqueous environments are arsenite [H_3AsO_4], monomethylasonic acid and dimethylarsonic acid. The most important species with relevance to toxicity in human are arsenite and arsenate. Arsenate species is of most concern to this study (Leermarkers *et al.*, 2006).

In general, inorganic As species are more mobile and toxic than the organic forms to living organisms, including plants, animals and humans. The chemical structures of some common arsenic compounds are listed in Figure 1.2 (Leermakers *et al*; 2006).

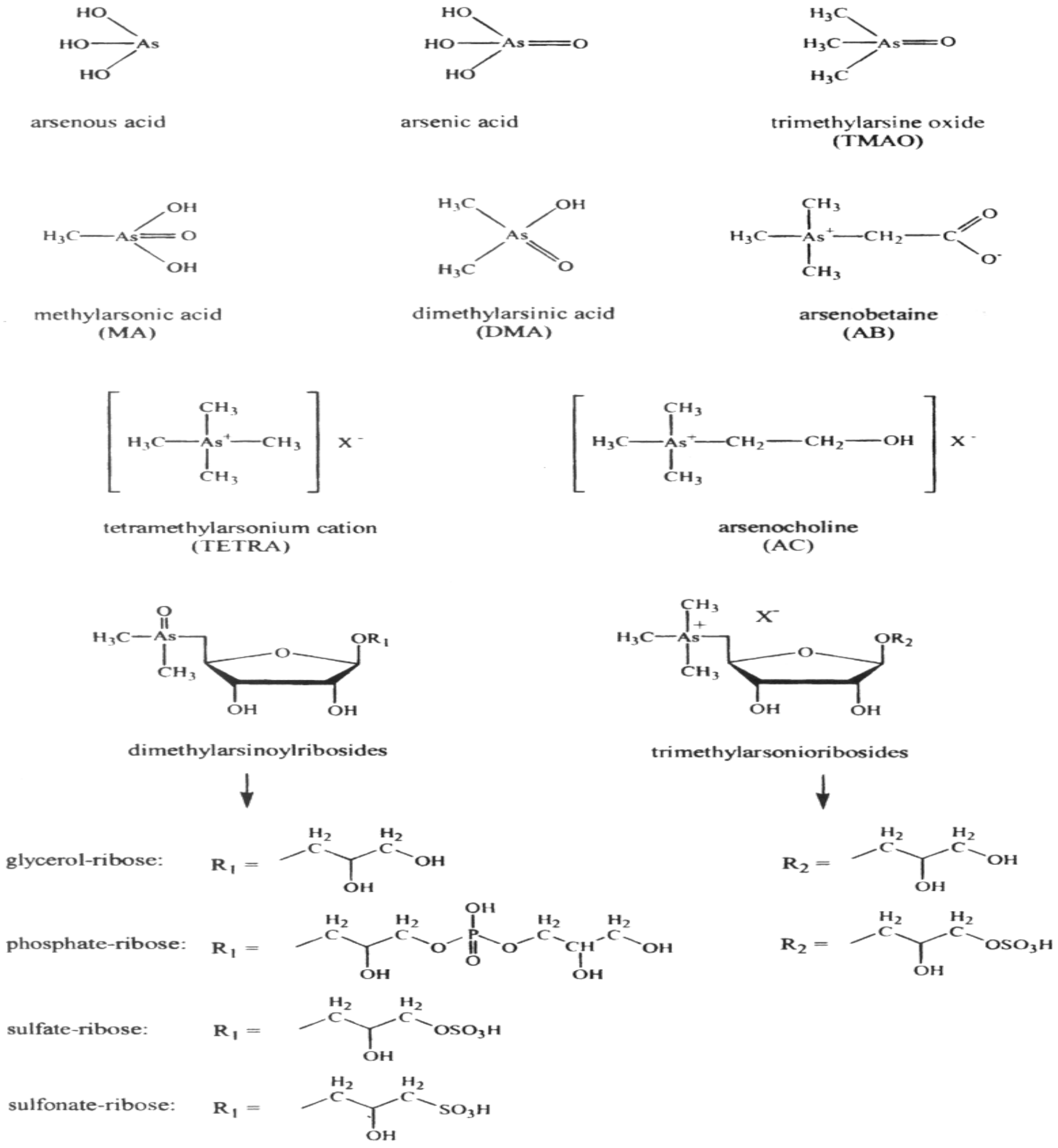


Figure 1.2: Arsenic compounds commonly detected in the environment (Leermakers *et al.*, 2006).

Factors affecting arsenic chemistry as well as its mobility in aqueous solution are pH and redox conditions, solid composition, As-bearing phases, adsorption and desorption, biological transformations, volatilization, and cycling of arsenic in soil (Leermakers *et al.*, 2006). Soil organic matter may alsobe an important factor affecting arsenic chemistry (Dobrah and Zagury, 2006), and specifically, influencing the formation of arsenite in aerobic environments, by mediating the reduction of As(v) to As (III). Organic matter, as an important surface soil component, may impact on the redox transformations of arsenic and its biomethylation, thus affecting arsenic toxicity and its condition in soils (Dobran and Zagury, 2006).

Most of the sorption techniques can hardly remove As(III) because of the presence of uncharged As(III) species in reducing environment over a wide range of pH (0-9) (Smedley *et al.*, 2002). In this regards contaminated water with dominant As(III) species have been treated by oxidizing it to As(v) from its removal from wastewater (Jiang 2001). The most accepted method is simple aeration, however, common oxidizers such as chlorine, permanganate, ozone, chlorine dioxide, monochloramine, solid phase oxidizing media and ultraviolet and solid state (Shailendran *et al.*, 1978).

As(v) is soluble, less toxic and more mobile than As(III) (Ferguson and Gavis, 1972; Shailendran *et al.*, 1978). As^{5+} ($H_2AsO_4^-$ and $HAsO_4^{2-}$) is the predominant form of arsenic in well-oxidized waters, while As^{3+} occurs predominantly as H_3AsO_3 and $H_2AsO_3^-$ in reduced environments (Shailendran *et al.*, 1978).

pH is an important factor that controls the absorption of As^{5+} as it exerts influence on speciation and composition of surface functional groups through protonation (Stollenwerk *et al.*, 2007).

The US Environmental Protection Agency (EPA) conducted a study on oxidation of arsenate, comparing seven oxidizers as shown in Table 1.2 (Ghurye and Clifford, 2001).

Table 1.1: Results of laboratory study of oxidant used to oxidize arsenite to arsenate (Ghurye and Clifford, 2001)

Oxidant	Performance	Interfering Reluctant
Chlorine and permanganate	Rapid oxidation (complete) in less than 1 min in pH range of 6.3 to 8.3	Manganese dissolves iron and sulfide.
Ozone	Rapid oxidation	Sulfide is significant and quenched reaction producing oxidation at high concentration
Chlorine dioxide	Limited oxidation	
Performed monochlororamine	Ineffective	
Filox (Manganese dioxide)	Effective and complete	Performance affected by interfering reductants
Based media	Oxidation	When dissolved oxygen (DO) is reduced
UV	Ineffective when used	Requires sulfite addition to

	alone	perform adequately well.

From the Table 1.2, the study concluded that, ozone, chlorine and permanganate provided effective oxidation of arsenate. However, less than 100% oxidation was obtained with chlorine and permanganate which is due to competition from natural organic matter (NOM).

1.1.5 Toxicities of Arsenate in Water

Arsenate wastewater is very toxic and carcinogenic. Chronic exposure to arsenic at low concentrations is known to increase the risk for developing various forms of cancer such as bladder, lung and skin cancer (Stroud *et al.*, 2011; Marchiset-Ferlay *et al.*, 2012) and the death of aquatic organisms. Exposure to high concentrations may result in various skin ailments such as Blackfoot disease (BFD). The present research has been motivated by the prevalence of health problems due to improper treatment of wastewater before consumed.

1.2 Phosphate

Phosphorous is one of 16 elements that are necessary for plant growth (Mullins, 2009). It is also the key component of acid dezoxiribonucleic (ADN), teeth and bones (Biswas, 2008). In water bodies, it is a main factor limiting the development of aquatic plants (The Everglades hub, 2013). In addition, phosphorous is a principal material of many industries, such as fertilizers, detergents, paints, corrosion inhibitors, beverages, and pharmaceutcals (Biswas *et al*., 2007). However, the over exploitation of phosphorous ores can lead to the fact that, these natural resources can be exhausted in the near future (Aryal and Liakopoulou - Kyriakides, 2011). A large amount of phosphorous in receiving water bodies may come from different sources. Biswas (2008) divided the sources of phosphorous pollution into natural sources (e.g. precipitation, dry fall, decomposition of organic materials, soil erosion) and artificial sources (e.g. use of fertilizers, detergents, human and animal wastes). Wentzel *et al*., 2008 classified them as diffuse sources (e.g. run-off from agricultural fields) and point sources (e.g. wastewater treatment sites). It is estimated that, the amount of phosphorous which enters the aquatic medium through artificial activities is three times larger than that of natural processes, Everglades hub, 2013. An individual discharges 2-3 g of phosphorous to wastewater through feaces and urine every day (Biswas, 2008).

One of the main roles of phosphorus in living organisms is to transfer energy. Organic compounds that contain phosphorus are used to transfer energy from one reaction to drive another reaction within cells. Adequate phosphorus availability for plants stimulates early plant growth and hastens maturity (Lau *et al*., 1997; Corell *et al*., 1998). Although phosphorus is essential for plant growth, mismanagement of soil phosphorus can pose a threat to water quality (Lau *et al*., 1997). The concentration of phosphorus is usually sufficiently low in fresh water so that algae growth is limited. When lakes and rivers are polluted with phosphates, excessive growth of algae often results. High levels of algae reduce water clarity and can lead to decreases in available dissolved oxygen as the algae decays, a condition that can be very detrimental to game fish populations (Lau *et al.*, 1997). Many phosphate compounds are not very soluble in water; therefore, most of the phosphates in natural systems exist in solid form. However, soil water and surface water (rivers and lakes) usually contain relatively low concentrations of dissolved (or soluble) phosphorus. Depending on the types of minerals in the area, bodies of water usually contain about 10 ppb or more of dissolved phosphorus as orthophosphate. Water bodies may also contain organic phosphorus compounds and phosphate attached to small particles or sediments. Total phosphorus in water is the total amount of phosphorus in a solution, regardless of its form, and it is often the form reported in water quality studies (Donnert *et al.*, 1999). Algal growth available or bio-available phosphorus is phosphorus that is estimated to be available to organisms like algae that are present in a lake or river. This is usually estimated by a chemical test that is designed to measure the dissolved phosphorus and the particulate phosphorus that are easily available (Donnert *et al.*, 1999).

Understanding the existence as well as forms of phosphorous is crucial to the selection of treatment technologies (Neethling, 2011). In natural waters, phosphorous can exit in various species as shown in Table 1.3. The orthophosphate presented in the forms of $PO_4^{3-,}$ HPO_4^{2-}, $H_2PO_4^-$ and can accelerate the algae growth.

Table 1.2 Different forms of phosphorous in aqueous solutions (adapted from Wiesmann *et al.*, 2006)

Total phosphorous, P_t			
Particulate phosphorous, Pp (organic and inorganic)	Dissolved phosphorous, P_d		
	Dissolved Polyphosphate, P_{Dp} (inorganic)	Hydrolyzed dissolved phosphorous, PDh	
		Orthophosphate P-PO_4 (inorganic)	Dissolved phosphorous, P_{Ox} (organic)

Condensed inorganic phosphate molecules (with – P-O-P bonds), include both chain-bonded phosphates and cyclic-bonded metaphosphates. Polyphosphates being basic constituents of detergents and water softeners, are the most common inorganic condensed polyphosphates in wastewater (Bashana *et al.*, 2004; Johannessen *et al.*, 2012), and the inorganic orthophosphates PO_4^{3-} ions.

Only about 15% of total phosphorus contained in settled particles may be removed by primary sedimentation with no metal salt addition (Sean *et al.*, 2001).

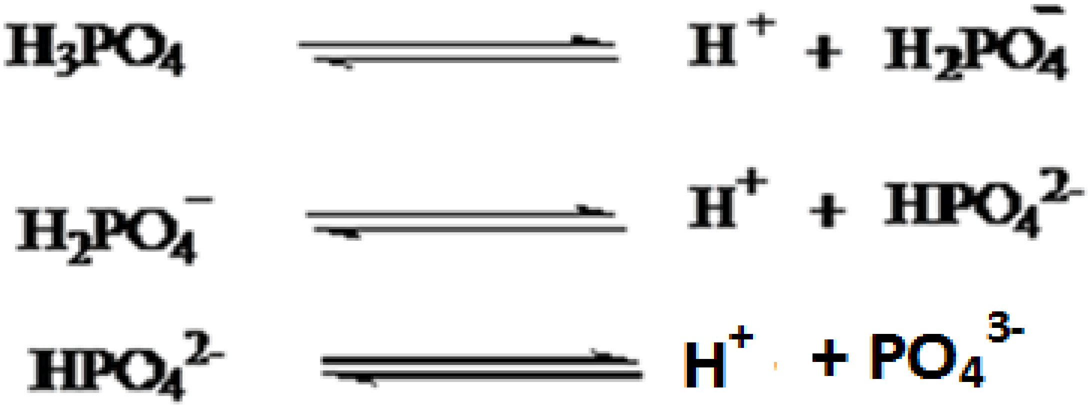
Owing to this fact, traditional removal methods are based on the transfer of soluble phosphorus to a solid phase and are complemented by solid-liquid separation (*Sean et al.*, 2001).

Phosphates are the naturally occurring form of the element,phosphorus and are used almost entirely in form of the compounds, usually in the oxidation states of +3, +5, and −3. Unlike nitrogen and various other members of the family phosphorus tends to exhibit a preference for the +5 state (Grady *et al.*, 2005).

When phosphorus enters wastewater, it can be in either organic or inorganic form. The two forms of phosphorus are as follow:

i. Orthophosphate
ii. Polyphosphate or organic phosphate.

These may be found in the dissolved or particulate state. The dissolved form of orthophosphate is usually mobile with aquatic animals, which leads to eutrophication. The orthophosphate in aqueous solutions are pH dependent as shown into scheme 1.2.



Scheme 1.2: pH diagram for phosphate speciation (Grady *et al.*, 2005).

The various species of phosphate in water exist as a function of pH. At the neutral pH of most waters, the dominant phosphate species according to equilibrium are $H_2PO_4^-$, HPO_4^{2-} and this speciation is based on the following; pKa values: $pK_{a1} = 2.5$, $pK_{a2} = 7.2$ and $pK_{a3} = 12.7$.

The charge on this species will determine the environmental relevant distribution (such as sorption/desorption) that may influence its mobility. Furthermore, the level of protonation of a given chemical species will influence its detection (Grady *et al.*, 2005).

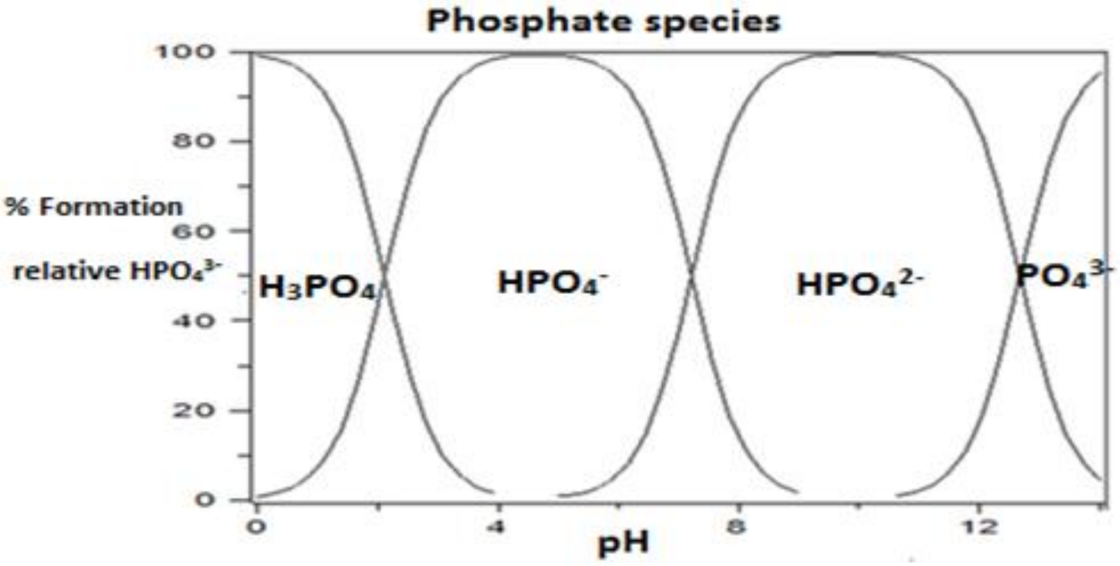


Figure 1.3: Chemical equilibria of phosphates depending on the pH adapted (Grady *et al.*, 2005).

1.2.1 Phosphate Cycle

The phosphorus cycle is similar to several other mineral nutrient cycles as phosphorus exists in soils and minerals, living organisms, and water. Although phosphorus is widely distributed in nature, hardly is it found by itself in elemental form. Elemental phosphorus is extremely reactive and will combine with oxygen when exposed to air. In natural systems like soil and water, phosphorus will exist as phosphate (Corell 1998; Grady *et al.*, 2005).

1.2.2 Sources of Phosphorus in Wastewater

The presence of phosphorous in natural waters in excessive amounts is responsible for eutrophication. De Bashan and Bashan (2004) defined eutrophication as the extraordinary growth of algae as a result of over enrichment of water bodies by nutrients, such as phosphorous and nitrogen. The two common symptoms of eutrophication are algae blooms and oxygen depletion (Everglades hub, 2013). In aquatic solution, high phosphorous concentration accelerates the development of phytoplankton, algae and macro aquatic plants.

When they die, a large amount of oxygen is used for their decomposition, through oxidizing organic carbon and nitrogen into carbon dioxide and nitrate, respectively. Consequently, natural waters become lack of dissolved oxygen, threatening the life of aquatic plants and animals (Benyoucef and Amrani, 2011; Biswas, 2008). There are also many other adverse effects, e.g. decline of sub aquatic plants, the formation of dead zones. These may put the whole ecosystem to a risk of disappearance. It does not only affect aesthetic and ecological values of the ecosystems but also cause severe economic damages. According to Everglades hub (2013), a red tide event occurred near Hong Kong in 1998 affected 90% of Hong's aquaculture farms and caused the estimated economic loss to 40 million USD. People's health may be negatively affected by consuming poisonous fish and shellfish in eutrophication regions. These people may suffer from skin irritation, gastrointestinal illnesses, neurological damage and death. Obviously, as eutrophication has severe impacts on the environment and people's well-being, the USEPA recommends that, the acceptable level of total phosphorous in natural waters should be under 0.05 mgP/L (Mullins, 2009). Thus, this leads to a need to develop cost-effective technologies to achieve this water quality goal.

The phosphorus in wastewater results from non-point sources such as agricultural runoff or erosion and animal husbandry, and from point sources such as, municipal and industrial wastewater discharges. Further diffusive sources were identified which may enter via atmospheric deposition and groundwater (Pidwirny, 2006).

The relative importance of these sources varies widely between countries and regional catchments, depending on the degree of urbanization, the standard of sewage treatment and the nature and intensity of agricultural practices. While industrial sources may be important locally, the two major widespread sources of phosphorus in wastewater are diffused agricultural inputs and municipal wastewater.

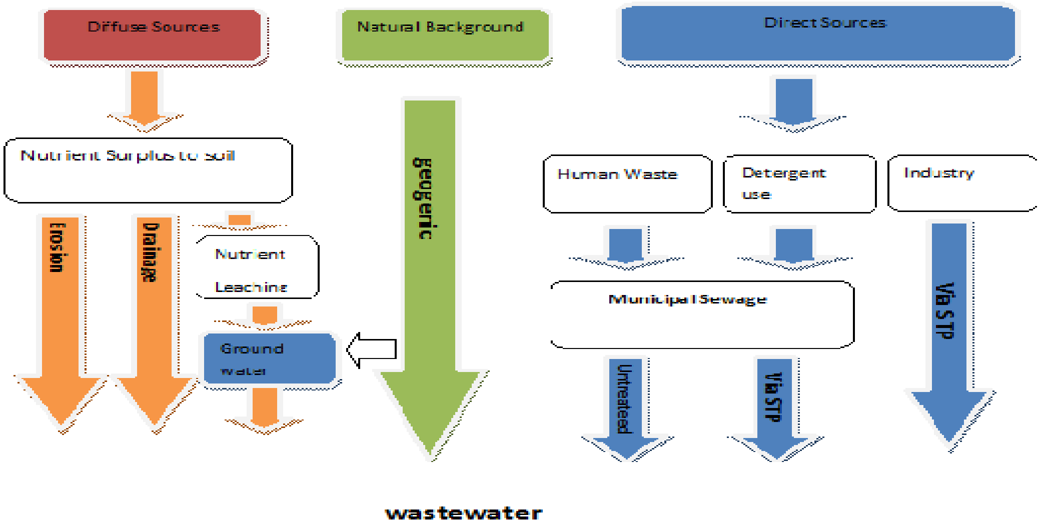


Figure 1.4: Diagram of phosphate source: The main quantified sources are diffusive source, natural background, human waste, phosphorus from detergent use and industrial emission (Behrendt *et al*; 2002).

Organic phosphate molecules (with –P-O-C bonds) are usually constituents of dissolved and suspended compounds of wastewater. Their input to total is estimated at approximately 4%, mostly from plasticizers for plastics or pesticides. In a water environment these compounds are degraded chemically or biologically to orthophosphates (Bashana *et al*; 2004).

1.2.3 Chemistry of Phosphate

The phosphate ion is a polyatomic ion with the empirical formula PO_4^{3-} and a molar mass of 94.97 g/mol (Rasoul *et al*; 2007). It consists of one central phosphorus atom surrounded by four oxygen atoms in a tetrahedral arrangement. The phosphate ion carries a negative three formal charge and is the conjugate base of the hydrogen phosphate ion, HPO_4^{2-}, which is the conjugate base of $H_2PO_4^-$, the dihydrogen phosphate ion, which in turn is the conjugate base of H_3PO_4, phosphoric acid. A phosphate salt forms when a positively charged ion attaches to the negatively charged oxygen atoms of the ion, forming an ionic compound. Many phosphates are not soluble in water at standard temperature and pressure. The sodium, potassium, rubidium, cesium and ammonium phosphates are all water-soluble. Most other phosphates are only slightly soluble or are insoluble in water. As a general rule, the hydrogen and dihydrogen phosphates are slightly more soluble than the corresponding phosphates. The pyrophosphates (anions of pyrophosphoric acid) are mostly water soluble. Aqueous phosphate exists in four forms. In strongly basic conditions, the phosphate ion (PO_4^{3-}) predominates, whereas in weakly basic conditions, the hydrogen phosphate ion (HPO_4^{2}) is prevalent. In weakly acid conditions the dihydrogen phosphate ion ($H_2PO_4^-$) is most common. In strongly acidic conditions, trihydrogen phosphate (H_3PO_4) is the main form (Rasoul *et al.*, 2007; Grady *et al.*, 2005).

1.2.4 The Effects of Phosphates in Water

Phosphorus concentrations in surface waters raise the growth of phosphate-dependent organisms, such as algae and duckweed. These organisms use great amounts of oxygen and prevent sunlight from entering the water. This makes the water fairly unlivable for other organisms. Phosphorus, in receiving waters, leads to extensive algae growth (eutrophication) (Morse *et al.*, 1998).

Phosphates have many effects upon organisms. The effects are mainly consequences of emissions of large quantities of phosphate into the environment due to mining and cultivating activities (Morse *et al.*, 1998). During water purification phosphates are often not removed properly, so that they can spread over large distances when found in surface waters. Due to the constant addition of phosphates by humans and the exceeding natural concentrations, the phosphorus cycle is strongly disrupted. The increasing phosphorus concentrations in surface waters raise the growth of phosphate-dependent organisms, such as algae and duckweed (see Figure 1.6). Reduction of runoff from agricultural usage of land and atmospheric deposition are complex problems better solved by economical and technical means rather than technical alone (Morse *et al.*, 1998).

1.3 Methods of Removing Arsenic and Phosphate from Wastewater

Several arsenic removal technologies have been tested so far for asenic (As) remediation, including ion exchange, activated alumina, reverse osmosis, membrane filtration, modified coagulation/filtration, and enhanced lime softening (Berg *et al.*, 2008). However, for any effective technology to be appropriate for use in affected areas of developing countries like Bangladesh, it should ideally be simple, low cost, also versatile, transferrable, and should be adaptable to both points of use, household units and community-based application (Visoottiviseth *et al.*, 2006). In this regard, Berg et al. (2006) mentioned that, none of the US Environmental Protection Agency (USEPA) recommended technologies are practical in low income regions as they require sophisticated technical systems and hence, these are not currently applied on a broad scale in developing countries. The most common and useful technologies that have been utilized for As removal in developing countries are based on oxidation, co-precipitation and adsorption onto coagulated flocs, and adsorption onto sorptive media (Ahmed 2002). According to Jiang (2001), these technologies could be cost-effective for removing As for the developing world.

Phosphorous removal is necessary for controlling eutrophication in natural waters and phosphorous recovery. This process was first studied in 1950s (Biswas, 2008). To date, a wide variety of phosphorous removal technologies are available to meet more strict regulations. According to Strom (2006), phosphorous removal technologies can be grouped into physical treatments (filtration of particulate phosphate, membrane technologies, magnetic separation); chemical treatments (precipitation, crystallization, anion exchanger, adsorption); and biological treatments (assimilation, enhanced biological phosphorous removal – EBPR, constructed wetlands). However, there is a general operation principle for all these methods. The phosphorous ions are initially changed into insoluble compounds, in the forms of salt precipitates or phosphorous built-in in microorganisms (in activated sludge) and plant (constructed wetlands). The insoluble compounds are then separated from wastewater (Rybicki). De Bashan and Bashan (2004) argued that, all these methods were not sustainable. The reason is that, the phosphorous is usually simultaneously removed with other pollutants, including poisonous substances, leading to the fact that, phosphorous cannot be recycled.

Regarding the development trend of phosphorous removal technologies, Biswas (2008) claimed that, currently chemical precipitation is widely applied for its high efficiency and space saving. However, such problems as high as chemical expenditure, additional sludge production, effluent neutralization requirement have limited its use in phosphorous decontamination (Strom, 2006). Besides, it is difficult to recycle phosphorous in this method as it is unintentionally precipitated with other pollutants (de-Bashan and Bashan, 2004). There is an increasing trend in using EBPR for phosphorous elimination.

Phosphate removal can be enhanced by human activities. These include:

i. The reduction of emission from the primary source points e.g. wastewater treatment plant and the diffusion into agriculture.
ii. The decrease of phosphate input to the material flow and as a result to the sewage e.g. replacement of phosphates detergents.
iii. The removal of phosphate at the wastewater treatment plant by introducing additional removal capacity.

There moval of phosphate is considered a major challenge in wastewater treatment, particularly for small-scale wastewater treatment systems. Phosphorus removal from wastewater may also occur by precipitation, although this is believed to be quantitatively less significant than removal by sorption. In more acidic conditions, precipitation of phosphate with Fe and Al may become more important (McNeil *et al*; 1997).

Arvin 1985 noted that, systems for chemical P-treatment are generally classified into three general categories:

i. Primary treatment (i.e. primary sedimentation if present), for which the term pre-precipitation may be used (Zhao *et al*., 1998).
ii. Secondary treatment (typically an activated sludge or buffer system) for which the term "Simultaneous precipitate" may be used (Johannessen *et al*., 2012). Normally, secondary treatment can only remove 1-2 mg/l, so a large excess of

phosphorous is discharged in the final effluent, causing eutrophication in surface waters. New legislation requires a maximum concentration of P discharges into sensitive water of 2 mg/l.

iii. Tertiary treatment (chemical flocculation followed by sedimentation of flotation, sometimes followed by filtration for which the term “post-precipitation” may be used (Zhao *et al*., 1998).

1.3.1 Ion Exchange

Ion exchange is identified as a good method for the removal of arsenate by the United States Environmental Protection Agency (Ann *et al*., 2005).

Ion exchange is a physical or chemical process in which ions held electrostatically on the surface of a solid phase are exchanged for ions of similar charge in a solution. It is a reversible interchange where there is no permanent change in structure of the solid. The solid is typically a synthetic anion exchange resin, which is used to remove particular contaminants of concern. Ion exchange is commonly used in drinking water treatment for softening (that is removal of calcium, magnesium etc. in exchange of sodium) as well as removing nitrate, arsenate, selenate etc. from municipal water (Clifford, 1999). For arsenic removal, an ion exchange resin, usually loaded with chloride ions at the “exchange sites”, is placed in vessels. The arsenic containing water is passed through the vessels and the arsenic “exchanges” for the chloride ions. The water exiting in the vessel is lower in arsenic but higher in chloride than the water entering the vessel. Eventually, the resin becomes “exhausted”; that is, all or most of the “exchange sites” that were loaded with chloride ions become loaded with arsenic or other anions. The chloride ions that used to be on the resin were exchanged for the arsenic and other anions that were in the treated water. The effect of the presence of sulphate in competition with other anions, is an important factor to ion exchanger treatment of the arsenic. Sulphate levers can limit the applicability of ion exchanger as arsenic treatment. However, sulphate, selenium, fluoride, and nitrate compete with arsenic and can affect the removal process. So, the low selectivity in the presence of other competing anions (Tsuji, 2002) has made this process less attractive. Other factors affecting the use of the ion exchange process included contact time and spent regenerant disposal.

1.3.2 Coagulation or Flocculation

Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles. Rapid mixing is required to disperse the coagulant throughout the liquid. Flocculation is the action of polymers to form bridges between the larger mass particles or flocs and bind the particles into large agglomerates or clumps. Bridging occurs when segments of the polymer chain adsorb on different particles and help particles aggregate. An anionic flocculant will react against a positively charged suspension, adsorbing on the particles and causing destabilization either by bridging or charged neutralization. Apart from arsenic removal, this treatment can effectively remove many suspended and dissolved constituents from water: turbidity, iron, manganese, phosphate and fluoride are few to mention. This technology removal is highly dependent upon initial arsenic concentration, dosage of coagulant, pH and the valence of the arsenic species. Ferric salts are common in the uses of coagulant. Of all the coagulants studied, ferric chloride and ferric sulphate have been most successful. Yuan *et al*. (2003) studied a combination system of ferric sulphate coagulation and filtration in arsenic removal. The method is economic and effective. Zouboulis and Katsoyiannis (2002) studied arsenic removal by applying a modification of a conventional coagulation and flocculation process.

The coagulants were found to be efficient, regarding arsenic removal which had achieved up to 99% of arsenic removal. (Karcher *et al*., 1999; Guo *et al*., 2000) also reported the uses of ferric chloride and lime-polyferricsulphate as the coagulants. Han *et al*., 2002 used ferric chloride and ferric sulphate as flocculants in arsenic removal. The results have shown a significant arsenic removal through adsorption mechanism onto the ferric complexes present. Wickramasinghe *et al*., 2005 also studied the application of ferric based coagulants in treating the city groundwater which have been contaminated by arsenic. The results of the bench-scale experiments conducted indicate that, coagulation with ferric ions followed by filtration is effective in reducing arsenic concentration in the water tested. However, the actual efficiency of removal is highly dependent on the raw water quality. However, problems with this technique are the safe separation, filtration, and the handling and disposal of the contaminated coagulant sludge. Moreover, in many instances, it seemed to be difficult to lower the arsenic concentration to the acceptable level by this technique.

The coagulation process has traditionally been used to remove solids from drinking water supplies. However, the process is not restricted to the removal of particles. Coagulants render some dissolved species e.g. natural organic matter - (NOM), inorganics, and hydrophobic synthetic organic compounds (SOCs)] insoluble and the metal hydroxide particles produced by the addition of metal salt coagulants (typically aluminum sulfate, ferric chloride, or ferric sulfate) can absorb other dissolved species. Major components of a basic coagulation/filtration facility include chemical feed systems, mixing equipment, basins for rapid mix, flocculation, settling, filter media, sludge handling equipment, and filter backwash facilities (Biswas, 2008; De-Bashan and Bashan 2004). High cost of chemicals; Chemical sludge; Neutralization of effluent; Do not recycle arsenate and phosphate (Biswas 2008; De-Bashan and Bashan 2004; Strom 2006; Tanyi 2010). Coagulation is used particularly in situations where dissolved iron (Ferrous) is not present in the raw water source. The addition of ferric salts promotes the formation of iron hydroxides that have a high adsorption capacity for arsenate (Vaishya *et al*., 2006). The coagulant itself is also a significant factor for the efficiency and extent of arsenate removal in the treatment system. Studies have shown that, ferric salt coagulants ($FeCl_3$) perform more effectively than alum in the removal of an equal weight dosage basis (Nimal *et al*., 2012). Despite some of the positive results obtained using the coagulation method or coagulants for larger potable water treatment plants, the handling of excess sludge can make this process challenging for smaller communities (Nimal *et al*., 2012). Typically, coagulation or precipitation techniques are costly and not considered suitable for the removal of arsenic.

The removal of phosphate with the aid of coagulation is a widely used process. However, the use of fresh coagulants may not be so admirable, because of the chemical costs and the treatment and disposal of a large amount of chemical sludge (Tanyi, 2010). Therefore, it is necessary to find other costs effective treatment methods and materials. Chemical sludge is an inevitable byproduct from the wastewater treatment when a metal salt is added as a coagulant. Huge amounts of chemical sludge are produced from water and wastewater treatment plants (Bashan, 2004; Strom 2006).

1.3.3 Co-precipitation

Co-precipitation involves removal of two or more constituents by a precipitation reaction. This method can typically reduce the concentration of arsenic in aqueous solutions. During the flocculation process, all kinds of micro-particles and negatively charged ions are attached to the flocs by electrostatic attachment. Arsenic occurs in non-ionized form and is not subjected to significant removal. This can be achieved by the addition of bleaching powder (Chlorine) or potassium permanganate or ozone (Arvin, 1985). On the other hand, precipitation of phosphate with calcium, results in the formation of apatites (e.g $CaHPO_4$: $Ca_4H(PO_4)$: $Ca_3(PO_4)_2$ or hydroxyl apatite ($Ca_5(PO_4)_3$). However, precipitation with lime or calcium salts is probably not as cost effective as the use of iron or aluminum salts (Arvin, 1985). The precipitation of phosphorus occurs at a high pH using lime.

1.3.4 Membrane Separation

Membrane separation is a selective barrier process which allows some constituents to pass while blocking the passage of others. Because of their selective permeability for different compounds, such membranes can act as a molecular filter to remove dissolved arsenic, along with many other dissolved and particulate compounds. High pressures are required to cause water to pass across the membrane from a concentrated to dilute solution. For this reason, membrane separation is addressed as a pressure driven process. Pressure driven processes are commonly divided into four overlapping categories of increasing selectivity: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and hyperfiltration (HP) or reverse osmosis (RO). Microfiltration can be used to remove bacteria and suspended solids with pore sizes of 0.1 to micron. Ultrafiltration will remove colloids, viruses and certain proteins with pore size of 0.0003 to 0.1 microns. Nanofiltration relies on physical rejection, based on molecular size and charge. Pore sizes are in the range of 0.001 to 0.003 microns. Reverse osmosis has a pore size of about 0.0005 microns and can be used for desalination. High pressures are required to cause water to pass across the membrane from a concentrated to dilute solution. In general, driving pressure increases as selectivity increases. It is clearly desirable to achieve the required degree of separation (rejection) at the maximum specific flux (membrane flux/driving pressure). Separation is accomplished by microfiltration membranes and ultrafiltration membranes via mechanical sieving, while capillary flow or solution diffusion is responsible for separation in nanofiltration membranes and reverse osmosis membranes (Choong et al., 2007). Lately, advancement of membrane technology has taken place in the name of electro-ultrafiltration (Weng *et al.*, 2005), which is found to possess good potential in treating arsenic from water. Shih (2005) had showed an overview of arsenic removal on pressure driven membrane process and explored the parameters that may influence the arsenic removal efficiency by membrane technologies such as source water parameters, membrane material, membrane types and membrane process.

Table 1.3: Typical Pressure Range for Membrane Processes (Strom 2006)

Membrane process	**Pressure range**
MF	5 – 45 psi
UF	7-100 psi
NF	50-150 psi
RO	100-150 psi

Microfiltration: Microfiltration removes contaminants from the fluid micro porous membrane. The normal microfiltration porous range is 0.1 - 10 (µm). Micro filtration is different from nanofiltration and reverse osmosis because microfiltration alone cannot remove the dissolved arsenate and arsenite species from arsenic wastewater. Removal of arsenic by microfiltration membrane can only be achievable by increasing particle size of arsenic bearing species. Coagulation (Ghurye *et al.*, 2001; Han *et al.*, 2002; Meng *et al.*, 2000) and flocculation processes prior to microfiltration could increase the particle size of arsenic bearing species effectively and were found to remove arsenic species from arsenic wastewater.

Water passes through the membrane with low pressure to high pressure in two systems. Microfiltration is normally used for drinking water treatment. It effectively removes major pathogens and contaminants such as Giardia lamblia cysts, cryptosporidium and large bacteria.

Ultrafilteration: Ultrafiltration processes are generally capable of removing some colloidal and particulate constituents in wastewater. Considering this, ultrafiltration alone, like microfiltration, may not be a viable technique for arsenic removal for wastewater. However, ultrafiltration may be appropriate for surface waters with high colloidal and particulate arsenic concentrations. However, this process can be used to remove arsenic from ground water.

Polyelectrolyte-enhanced ultrafiltration (PEUF) is a separation process that can remove low-concentration ionic species from aqueous solution and it is particularly effective for multivalent ions. This process includes the addition of water-soluble polymer, followed by the ultrafiltration operation. The polymer is a polyelectrolyte of opposite charge to the target ions, causing the pollutant ions to bind to the polymer due to electrostatic attraction to form macromolecular complexes. These complexes are retained by the membrane in the retentive stream, while the uncomplexed ions pass through the membrane to permeate the stream. In previous studies, PEUF has been applied to the separation of cationic metal ions like Cu^{2+}or $Cd^{2+}$with anionic polymer

(Sasaki et al., 1989; Tabatabai et al., 1995), or anionic ions like chromate (CrO_4^{2-}) with cationic polymer (Tangvijitsri *et al.*, 2002).

Potential advantages of this method are low energy requirements involved and the fact that the process can be operated in a steady-state mode.

The PEUF process for arsenic removal involves addition of cationic polyelectrolyte, poly(diallyldimethyl ammonium chloride) to bind anionic arsenate species to form polyelectrolyte – arsenate complexes, which are separated by a subsequent ultrafiltration process. Figure 1.5 shows a systematic diagram of PEUF to remove anionic arsenic species from water.

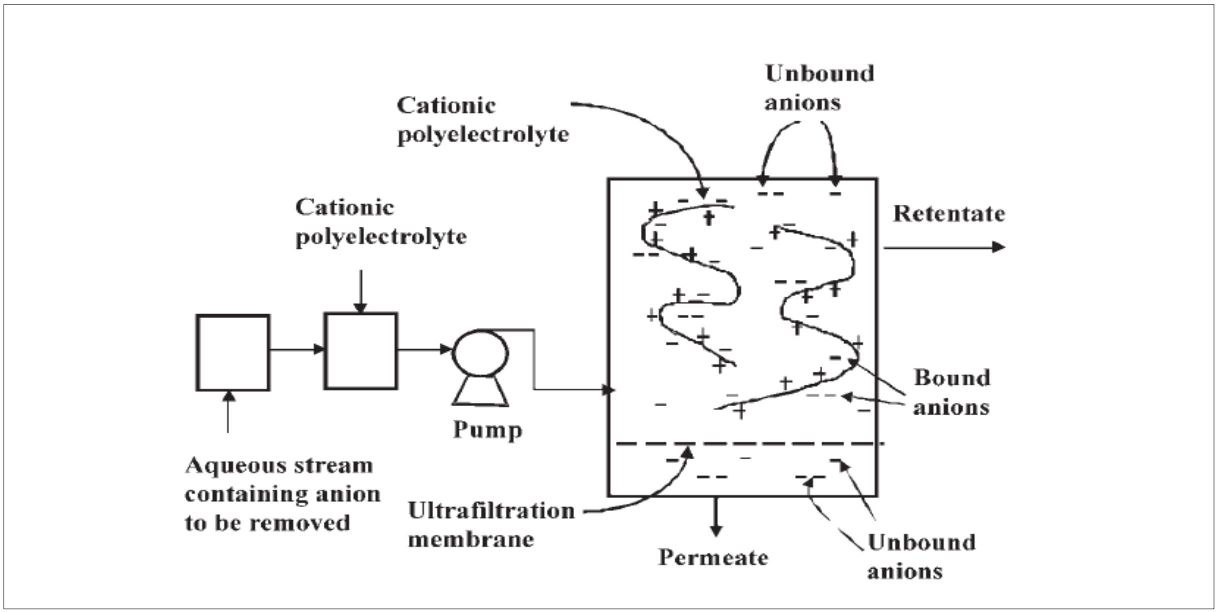


Figure 1.5: Diagram of Polyelectrolyte- Enhanced Ultrafiltration (PEUF) to Remove Anionic Arsenic Species from Water (Tabatabai *et al.*, 1995).

Ultrafilteration removes viruses and certain protein with pore size of 0.003 to 0.1 microns. (Edward et al., 2001) reported that, electric repulsion of ultrafilteration plays an important role in arsenic rejection beyond the achievable with only pore-size dependent sieving.

Nanofilteration: Nanofiltration membranes can remove different valence ions and different molecular weight organic molecules from water, depending on membrane charge and pore size. Nanofiltration is used for purification, biochemical substance separation, wastewater reclamation and water softening (Ji *et al.*, 2011). Nanofiltration membranes are charged both positively and negatively and are also made from polyamids, sulfonated polysulfone and sulfonated polyphenyleneoxides. The positively charge membrane is more effective in removing multi-valent cations and anions, also remove amino acids below their isoelectric point. Positively charged Nanofiltration has been developed in recent years (Ji *et al.*, 2011).

Reverse osmosis: This method can be used as a stand-alone arsenic treatment under most water quality conditions and capable of achieving over 90% removal of As(V) in a single pass (Garud *et al.*, 2011). Figure 1.6 shows a flow diagram for a typical reverse osmosis membrane process. The lines represent optimal stream and processes. As an added advantage, the reverse osmosis also removes several other constituents from water, such as organic salts, dissolved minerals and colour. This treatment process is relatively insensitive to pH. In order to drive water across the membrane surface against natural osmotic pressure, feed water must be sufficiently pressurized with a booster pump. For drinking water treatment, typical operating pressure is between 100

– 350 psi. Water recovery is typically 60 – 80%, depending on the desired purity of treated water. Reverse osmosis and nanofiltration foul quickly in the treatment of wastewater, making them prohibitively expensive (Strom, 2006).

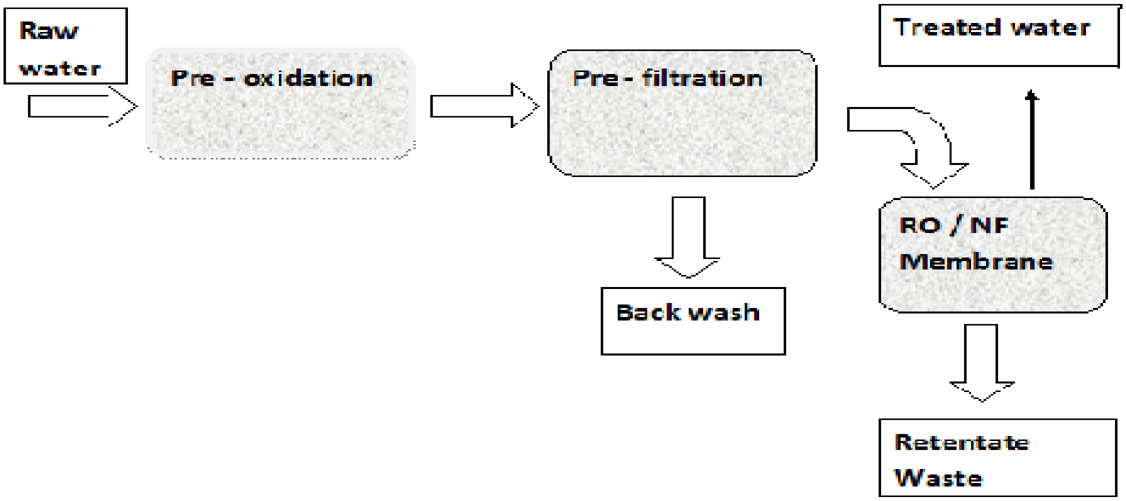


Figure 1.6: Flow diagram for reverse osmosis membrane process (Garud *et al.*, 2011).

1.3.5 Oxidation

This method is used for the removal of soluble form of iron and manganese by conversion to their insoluble form (Oscarson *et al.*, 1982). Mangenese dioxide is capable of oxidizing arsenate which has been successfully used for removal of arsenate by chemical oxidation and sorption into manganese oxide.

The efficiency of sorptive media depends on the use of oxidizing agent as an aid to the sorption of arsenic in wastewater. The saturation of media by different contaminants and components of water takes place at different times of operation depending on the specific sorption affinity of the medium to the given component. Various works have been done on surface adsorption for removal of arsenate from wastewater (Saha *et al.*, 2001). These include: wood charcoal, banana pith, coal fly ash, tea leaf, rice husk, saw dust activated carbon, bauxite, hematite, iron oxide, anhydrous granular ferric oxide (Vaisha *et al.*, 2004; Saha *et al.*, 2001). The results obtained from experiments conducted using batch adsorption studies with an arsenate solution of concentration 1 mg/L for a 6 hour contact time in the laboratory as shown in Table 1.4 (Saha *et al.*, 2001).

Table 1.4 Removal Efficiency of Arsenic in Different Media (Saha *et al.*, 2001)

Adsorbent	Dose (g)	% Removal of As(V)
Coal fly ash	10	28
Sand	10	22
Rice husk ash	10	12
Saw dust	10	36
Mushroom	10	35
Spent tea leaf	10	42
Banana pith	10	18
Wood charcoal	10	37
Water hyacinth	10	70
Kimberlite tailing	10	40
Activated carbon	10	65
Bauxite	10	80
Hematite	10	60
Laterite	10	70
Iron-oxide coated sand	10	85
Activated alumina	10	86
Hydrous granular ferric oxide	10	89
Calcined waste egg shell	10	91

Air oxidation: Atmospheric oxygen is a readily available oxidizing agent, however, the kinetics of air oxidation of arsenic are very slow, taking weeks (Pierce and Moore, 1982). Pierce and Moore, (1982) have shown that, when distilled water spiked with arsenite, (pH 7) is saturated with oxygen, arsenic speciation stays relatively unchanged for days (Pierce and Moore, 1982). When water is saturated with air instead of pure oxygen, the dissolved oxygen levels are much lower, so oxidation rates are even slower. Hering et al., 1997reported half-lives of arsenite in water saturated with oxygen and air as 2-5 and 4-9 days, respectively (Hering *et al*; 1997). Air oxidation of arsenite can be catalyzed by bacteria, strong acidic or alkali solutions, copper, powdered activated carbon, and higher temperature (Hering *et al*., 1997).

Solar Oxidation**:** This is a simple method of oxidation of arsenic in transparent bottles to reduce arsenic content of drinking water at a neutral pH (Stephen *et al*., 2001). Ultraviolet radiation can catalyze the process of oxidation of arsenite in presence of other oxidants like oxygen.

Chemical oxidation: Arsenite can also be directly oxidized by a number of other chemicals, including gaseous chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide, and Fenton's reagent (H_2O_2/Fe^{2+}).

Ultraviolet radiation can catalyze the oxidization of arsenite in the presence of other oxidants, such as oxygen. Direct UV oxidation of arsenite is slow, but may be catalyzed by the presence of sulfite (Ghurye and Clifford, 2000) and ferric iron (Emett and Khoe, 2001). Chlorine also affects oxidation of phosphates. Chlorine is a rapid and effective oxidant, which leads to side reactions with organic matter, producing toxic trihalomethanes as a by-product. The amount of chlorine added will depend on composition of the water and it is widely available globally, though if improperly stored can lose its potency rapidly (Emett and Khoe, 2001).

1.3.6 Biological Treatment

Phosphorus removal from wastewater has long been achieved through biological assimilation – incorporation of the phosphorus as an essential element in biomass, particularly through growth of photosynthetic organisms (plants, algae, and some bacteria, such as cyanobacteria). Traditionally, this was achieved through treating ponds containing planktonic or attached algae, rooted plants, or even floating plants (e.g water hyacinths, duckweed) (Awuah *et al*., 2004). Land application of effluent during the growing season has also been used to treat phosphorus. Constructed wetlands are now an established practice as well. In all of these cases however, it is necessary to remove the net biomass growth in order to prevent eventual decay of the biomass and the re-release of the phosphorus (Strom, 2006).

Sludges and side stream destroy the organic material (such as digestion) which has the potential to release the particulate organic phosphorus present as soluble organic or inorganic phosphate. In particular, anaerobic condition are likely to release soluble phosphorus from sludges and iron precipitate (ferrous phosphate is much more soluble than ferric phosphate) (Liao *et al*., 2003). In some case, these problems, particularly with anaerobic digestion, have not been as severe as originally anticipated (Liao *et al*., 2003). Britton et al. (2005) reported that, a demonstrative treatment of “anaerobic” digester supernatant in pilot (using a fluidized bed rector) can remove phosphorous in wastewater by addition of magnesium chloride and pH.

Microalgea: Microalgae *Chlorella vulgaris* and *Scenedesmus dimorphus* had been shown to be capable of removing up to 55% of the phosphates from dairy industry and pig farming wastewaters (Marques *et al.*, 2001).

Another strain of *Scenedesmus*, grown in artificial wastewater, also removed more than 50% of the phosphates (Kim *et al.*, 2007). Production of starch yielded wastewater with a unique C:N:P ratio of 24:0.14:1. This effluent supported good growth of *Spirulinaplatensis* in wastewater. Their application is severely limited by the difficulties of harvesting the enormous microalgal population developed in the water after treatment. Therefore, the idea of entrapping microalgae for easy removal by sedimentation with spherical gels gained some momentum. The *C. vulgaris,* immobilized in two natural polysaccharide gels (carrageenan and alginate), was used to treat primary domestic wastewater. Algal uptake of nutrients and adsorption on alginate gels were the major mechanisms involved in the removal of ammonium and phosphates (Tam and Wong, 2000).

Wetland: The removal capacity of phosphorus by a wetland can be substantial. Several types of plants used in wetland and their capacity to remove phosphorus are listed in the Table 1.5:

Table 1.5: Shows the Report on Removal of Phosphorus from Wastewater in Wetland (Korner and Vermaat, 1998).

Plant type	Type of wastewater	Phosphorus removal	References
Eichhorinia crassipes (water hyacinth)	Untreated and partially treated domestic sewage	8 mg / g dw	Mohan and Hosetti, 1998
Gracilaria chilerisis (macroalgea)	Effluent from fish, oyster and sea, urchin cultivation	Small	Perdomo *et al*., 2001
Typha latifolia (emergent macrophyte)	Septic tank liquid	96.6%	Marques *et al*., 2001
Zizancopsis bonariesnsis *Typhasubulata* (emergent macrophyte)	Anaerobically treated municipal wastewater	Small	Ayaz and Akca, 2000
Cyperus sp	Domestic sewage		Nyakang'o and Van Bruggen, 1999
Cyperus papyrus	Municipal sewage		
		39%	

Phragmites mauritianus	Irrigation drainage	0.05g / m^2 / d	Headley *et al*.,
mix of *Typha sp*,	from nurseries or		2000
Cyperus,	a synthetic	58%	
Hydrocotylesp.Hydroclesis	sewage		Drizo *et al*.,
sp. And *Pontederia sp.*			1997.;
			Kurniadie and
Phargmites australis	Domestic sewage	65 – 90%	Kunze, 2000
(reads)	Synthetic sewage	(irrigation)	
			Coleman *et al*.,
Phargmites	Primary reated		2001
karkaschoenoplectus	domestic sewage		
volidus	Artificial sewage	69%	Abe and Ozaki
		98%	1999
Junceiseffuses,scrpus			
validus			
C. papyrus, African		50 – 60%	
marigold peppermint			
		90%	

Assessment of the contribution of duckweed *Lemna gibba*, a marcrophyte, and its associatedmicro-organisms (algae and bacteria forming an attached biofilm) to remove nutrients showed that, the biological floating mat complex (plants and microbes) is responsible for removing up to 75% of the nutrients in the wastewater. The macrophyte contributed up to 52% of phosphorus removal by its own growth; the associated organisms and micro-organisms removed the rest (Drizo *et al.*, 1997).

1.3.7 Adsorption

Adsorption phenomena are operative in most natural, physical, biological, and chemical systems. Adsorption operations employing solids such as activated carbon, metal hydrides and synthetic resins are used widely in industrial applications for purification of waters and wastewaters. Activated carbon is also commonly used as the material in arsenic treatment (Wang, 2010; Huang and Fu, 1984; Gimbel and Hobby, 2000). The process of adsorption involves separation of a substance from one phase, accompanied by its accumulation or concentration at the surface of another. Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Adsorption capacity depends on activated carbon properties, adsorbate chemical properties, temperature, pH etc. Many activated carbons are available, but few are selective. These are expensive as well. Therefore, the research of this work is to find improved and tailor-made materials, which will meet several requirements such as; regeneration capability, easy availability, cost effectiveness and others. Consequently, low-cost adsorbents have drawn attention to many researchers and characteristics as well as application of many such adsorbents are reported. However, low-cost adsorbents are discussed herein after.

Recently, adsorption of arsenic, using natural materials or the waste products from industrial or agricultural operations have emerged as an option for developing economic and eco-friendly wastewater treatment processes. Numerous low-cost adsorbents have so far been studied for the removal of arsenic from water and wastewater. Dry plants, red mud, fly ash, zeolites, blast furnace slags, hydrotalcites, hydroxides, functionalized nanofibres and various bioadsorbents are few to mention.

Red mud is a ferric hydroxide material, the by-product of smelting and refining of ores containing gold, cobalt, silver, copper and iron. It has been used to develop effective adsorbents to remove arsenic from aqueous solutions. Arsenic adsorption on red mud is pH dependent and an acidic solution having pH range of 1.1 to 3.2 favored As(v) removal, while alkaline aqueous medium (pH $\approx$ 9.5) was effective for As(III) removal (Altundogan *et al.*, 2000). Heat and acid treated red mud has also been reported to have better adsorption capacity for arsenic removal (Altundogan *et al.*, 2002).

Fly ash is one of the residues generated in the combustion of coal. It is generally captured from the chimneys of power generation facilities. The availability of fly ash is so high that, at many places, its disposal is a problem. As such, a number of workers have attempted to use it as an adsorbent in pollution control. Removal of arsenate at pH 4 was reported higher than that at pH 7 or 10 by using fly ash collected from coal power stations (Diamaddopoulos *et al.*, 1993).

1.4 Scope of the Thesis

The aim of this study was to develop electrospun nanofiber sorbents that has tunable characteristics for uptake of anions from wastewater samples and releasing them into solutions, upon adjustment of pH, for quantification. The study focused on optimizing parameters for electrospinning two different polymers into nanofibers and characterizing the sorbents developed from the nanofibers in terms of their tunabililty for uptake and release of arsenate and phosphate from aqueous environments, reusability and loading capacities.

Electrospinning conditions were optimized for two different polymers, that were synthesized from 2-amino-4,6-dihydroxylpyrimidine, polyvinylmethylketone and polyvinylbenzylchloride. The nanofibers were fully characterized in terms of their average diameters, morphologies and surface area. The nanofiber mat were then stamped out into optimized masses and applied as adsorbents for uptake of toxic anions, using batch contact and solid phase extraction. Parameters affecting adsorption such as initial concentration, contact time and pH were also investigated. The capacity of the functionalized electrospun fibers to anions from spiked water and wastewater was determined. The loaded sorbents were then desorbed and their efficiencies of adsorptions/desorption as well as cycles of usage determined.

1.5 Purpose of Study

In the past years, many (small scale) and community based arsenic and phosphate removal technologies have been developed. Field tests (e.g. probes) are used in various countries. However, some questions remain unanswered on the efficiency and applicability/appropriateness of the technologies, particularly because of low arsenic concentration in some source water composition. Some removal techniques are quite simple, but the main disadvantage associated with them is because of large amounts of toxic sludge they produce which need further treatment before disposal into the environment. Besides, these systems must be economically viable and socially acceptable. This work is to synthesized an improved tailor-made material, which will meet several requirements such as; regeneration capability, easy availability, cost effectiveness, optimized masses and applied as adsorbents for uptake of toxic anions.

1.6 Research Hypotheses

i. 2-amino-4,6-dihydroxylpyrimidine can be synthesized with polyvinylmethylketone to produce a functionalized polymer.
ii. Polyvinylbenzylchloride can be electrospun into nanofibers, also post functionalized with ethylenediamine and finally quaternized with three different alkyl groups (methyl, ethyl and propyl) to give quaternized nanofibers.
iii. Nanofibre will be a good nanomaterial to remove arsenate and phosphate from wastewaters.

1.7 Research Approach

The primary objective of this work was to develop cost-effective nanofiber materials for the removal of arsenic(v) and phosphate from wastewater by the following:

i. synthezed polyvinylmethylketone with 2-amino-4,6-dihydroxylpyrimidine, electrospun into a nanofiber.
ii. Electrospin polyvinylbenzylchloride into nanofibers, post functionalized with ethylenediamine and then quaternized, using three different alkyl groups to produce different nanofibers for arsenic and phosphate.
iii. Characterization of the sorbent materials.
iv. Application of the sorbent materials.

An introduction to background information for arsenic, scope of study and review of current remedial strategies has been presented in this chapter. The review starts with electrospinning in general, different methods of functionalizing electrospun nanofibers, different characterization methods used for electrospun nanofibers, followed by the toxic effect of arsenic (v) and phosphate in various contaminants. Such as; soil, sewage, water, their treatments and disposal will be discussed in chapter two.

Instrumentation, Surface characterization techniques, preparation of solutions are presented in Chapter 3. Treatment of wastewater by the super-cleaned and surface functionalized electrospun nanofibers was also examined and results are presented in Chapter 4. The advancement, novel ideas, conclusions, and future recommendations are discussed in Chapter 5.

1.8 Problem Statement

Anions in wastewater are global environmental and health problems due to the potential of chronic or acute toxic effect (Dermatas, *et al.*, 2004; Hudson-Edwards *et al.*, 2004).

Arsenic(v), (As^{5+}) is one of the most widely known toxic elements, it is fairly widespread globally, often very mobile, may be acutely toxic in small doses, and it has a number of exposure pathways that may lead to serious health problems and deaths. Argentina, Bangladesh, Canada, Chile, China, Germany, Hungary, India, Japan, Mexico, New Zealand, Poland, Romania, Taiwan, Thailand, the USA, Vietnam, and West Bengal are some notable locations with arsenic contamination problems in soils and water (Anawar *et al.*, 2002; Roychowdhury *et al.*, 2002; Mitra *et al.*, 2002; Pandey *et al.*, 2002; Chakraborti *et al.*, 2001; Smith *et al.*, 2001; Mudur 2000; Chowdhury *et al.*, 2000; Tchounwou *et al.*, 1999). Variations in As concentration and speciation is becoming increasingly important to understand in ensuring attainment of water quality standards, especially for drinking water (Smedley and Kinniburg, 2002). Saha *et al.* (1999) and Weng-Ping (2007) reported that, one of the least regulated and studied anions, is an emerging contaminant that affects the internal body. For example, cancers in bladder, liver, kidney and lung due to arsenic exposure through drinking water.

Current treatment of anions in wastewater approaches focus on stabilization by speciation change, adsorption, and precipitation into low solubility complexes, but when applied in remedial technologies, they often do not result in successful stabilization of toxic anions in wastewater. Changes in environmental conditions, such as pH, can result in the re-introduction of previously stabilized anions back into the dissolved phase.

The need of cost-effective treatment technology that can permanently remove arsenic and other anions in their various forms in contaminated wastewater has been of major concern. One of the possible methods of arsenic (v) removal from solution could be the use of electrospun nanofibers with high specific surface areas and porosities that impart on them very high adsorption capacities (Huang *et al*., 2003). Electrospun nanofibers affinity for sorption of arsenic may be low, but with surface functionalization, using ligands on the electrospun nanofibers is known to improve the removal efficiency of these anions from wastewater.

CHAPTER 2

2.0 LITERATURE REVIEW

In this chapter, an extensive review of the literature is presented in order to outline the current state of research and understanding of synthesis of the polymer, electrospinning of polymer into nanofiber and post functionalization of electrospun nanofiber for the removal of arsenic(v) from water. The literature survey covers a range of topics related to the potential impact in the design and synthesis of 2-amino-4,6-dihydroxylpyrimidine and polyvinylbenzylchloride.

The review starts with the description of electrospinning in general, different methods of functionalizing electrospun nanofibers, different characterization methods used for electrospun nanofibers, followed by the review of toxic effect of arsenic(v) and phosphate in various contaminants such as; soil, sewage, water, their treatments and disposal (Yeung *et al*., 2012; Mitra *et al*., 2002; Pandey *et al*., 2002; Zhang *et al*., 2005; Chen *et al*., 2007; Cheung *et al*., 2000; Pengthamkeerati et al., 2008; Oguz *et al*., 2009; Yang *et al*., 2009).

2.0 Electrospinning

This is a process whereby fibres are generated by the application of electrostatic forces to a jetting polymer solution. The incorporation of nanofillers into electrospun fibers enhances the fiber properties relevant to a number of applications, particularly mechanically reinforced composites (Megelski *et al*., 2002). Electrospinning is allowed for the creation of nanofibres (fibres with a diameter well in the realm of nano dimensions), that can be collected to form a non-woven fabric. The resulting material can be applied to create many products including medical devices, tissue engineering scaffolds, clothing and filtration media (Megelski *et al*., 2002).

There is significant interest in electrospun tissue engineered scaffolds, due to their great potential to pattern the native extra-cellular matrix. During the past two decades, significant advances have been made in the development of biodegradable polymer, so biodegradability is one of the most important properties, as the scaffold should degrade with time andso replaced with newly regenerated tissues.

Nair and Laurencin (2007) reported the most applicable Polyesters' polymers, especially lactic acids, glycolic acids and their copolymers with 3-caprolactone, are the most commonly known and used among all biodegradable polymers for fabrication of novel materials for medical use and for tissue engineering applications. Among natural polymers; collagen, chitin as well as its N-acetyled derivative, chitosan, fibronectin and gelatin, are the most popular polymers for biomedical application. Various synthetic and natural biopolymers have been electrospun to satisfy different clinical requirements.

Electrospinning supplies great flexibility in selecting materials for drug delivery applications, using either bio-degradable or non-degradable materials that can be used for control. Whether drug release occurs via diffusion alone or via diffusion and scaffold degradation. Electrospun fibres can be oriented or arranged randomly, giving control over both the bulk mechanical properties and the biological response to the scaffold. Nowadays, all kinds of drugs such as antibiotics, anticancer agents and proteins, DNA, and RNA can be incorporated into electrospun scaffolds.Using the various electrospinning techniques, the applications of electrospinning in tissue engineering and drug delivery are almost unlimited. There are a number of different drug loading methods like coatings, embedded drug, and encapsulated drug (coaxial and emulsion electrospinning). These techniques can be used to give a good control over drug release kinetics (Sill and Recum, 2008).

2.1 Description of the Electrospinning Process

In the electrospinning system, a polymer solution is held by its surface tension at the end of a capillary tube which is subjected to an electric field and an electric charge is induced on the liquid surface due to this electric field. When the electric field applied reaches a critical value, the repulsive electrical forces overcome the surface tension forces. Eventually, a charged jet of the solution is ejected from the tip of the needle and an unstable and rapid whipping of the jet occurs in the space between the capillary tip and collector which leads to evaporation of the solvent, leaving a polymer behind (Theron *et al.*, 2004). The jet is only stable at the tip of the spinneret and afterwards instability starts. Thus, the electrospinning process offers a simplified technique for fibre formation.

2.2: Types of Electrospinning

2.2.1: Mono Nozzle

The polymer solvent solution emerges from the nozzle and forms a droplet. The nozzle is charged and this transfers its electrical energy to the droplet. When this happens, a jet, made of the liquid polymer is ejected from the tip of the cone. As the jet enters, the field formed between the nozzle and the collecting wheel, it stretches and loops. The lengthening of the polymer fibre is due to simultaneous but separate events the solvent evaporating from the polymer, which solidifies as a fibre, and the charges within the polymer repelling each other (Raneker *et al.*, 2007).

2.2.2: Multiple Nozzle

Coaxial electrospinning expands the versatility of electrospinning by enabling the formation of core-sheath structured micro/nanofibres. Using the coaxial electrospinning method, different characteristics from each polymer can be combined into one fibre. This process consist of the multiple solution feed system, which allows for the injection of one solution into another at the tip of the spinneret. The fluid is believed to act as a carrier that draws in the inner fluid at the tip of the needle of the electrospinning jet (Bazilevsky *et al.*, 2007). If the solutions are immiscible, then a core shell structure is usually observed. Miscible solutions however can result in porosity or a fibre with distinct phases due to phase separation during solidification of the fibre.

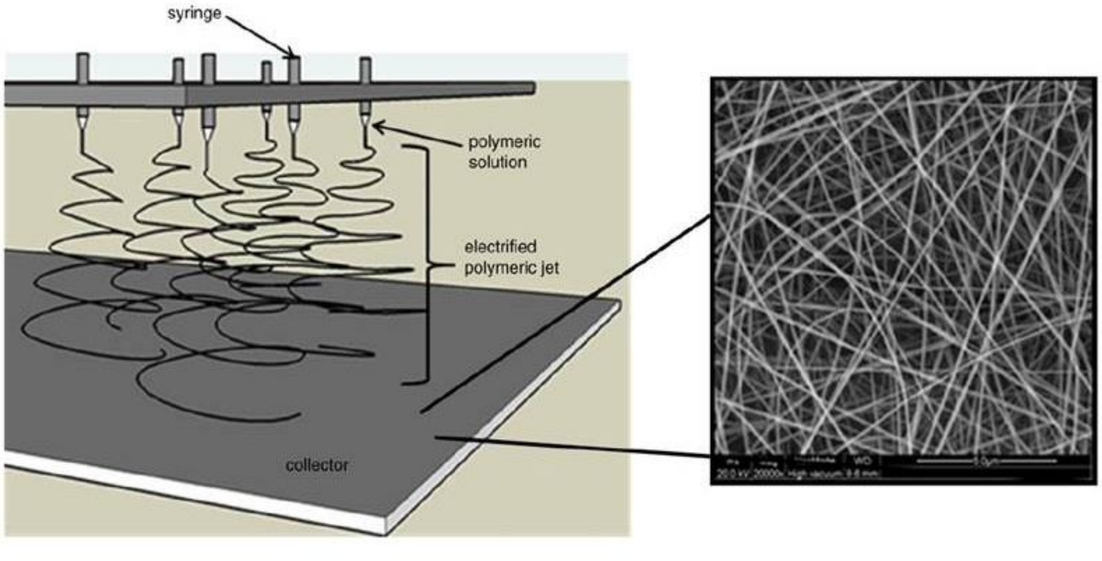


Figure 2.0: Shows a multi-jet electrospinning setup (Theron *et al.*, 2004).

2.2.3: Needleless Electrospinning

Needleless electrospinning method is an alternative electrospinning technology with the aim of producing nanofibres on a large scale from a compact space. Needleless electrospinning is featured as electrospinning of nanofibres directly from an open liquid surface. Numerous jets are formed simultaneously from the needleless fibre generator without the influence of apparatus

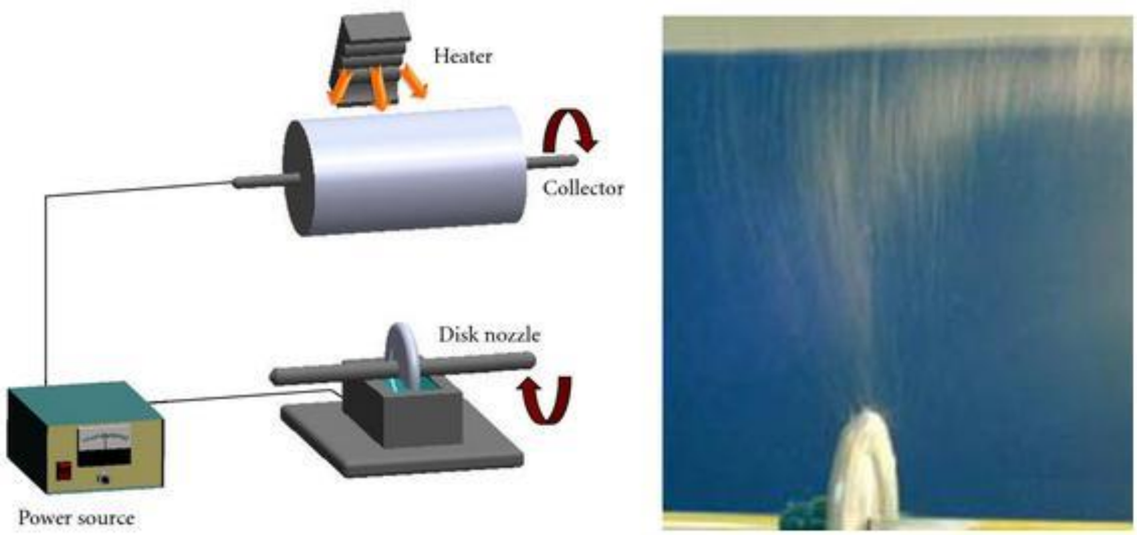


Figure 2.1: Apparatus for needleless electrospinning (Yarin and Zussman, 2004).

for needleless electrospinning setup and a picture of the electrospinning process of thecapillary effect that is normally associated with needle-like nozzles which is hundred times more efficient than the conventional electrospinning methods (Yarin and

Zussman, 2004). A needleless setup uses a rotary spinneret to upward-electrospin nanofibres which has considerable improvement in the nanofibre production rate (Jirsak *et al.*, 2005). The earliest rotating electrospinning can be dated back to the 1970s when Jirsak *et al.*, 2005 filed a patent on using rings to electrostatically spin fibres. In 2005, Jirsak et al., patented a roller electrospinning device, which has been commercialized by Elmarco with the brand name Nanospider TM. As a development to the work, Jirsak *et al.* (2005) Niu *et al.* (2009) used cylinder and disc as fibre generators to perform needleless electrospinning and showed the effect of the spinneret shape.

2.3: Electrospinning Parameters

Many parameters can influence the transformation of polymer solutions into nanofibres through electrospinning. These parameters include the following:

i. The solution properties such as viscosity, elasticity, conductivity and surface tension.
ii. Governing variables such as; hydrostatic pressure in the capillary tube, electric potential at the capillary tip, and the gap (distance between the tip and the collecting screen).
iii. Ambient parameters such as solution temperature, humidity, and air velocity in the electrospinning chamber (Ramakrishna *et al.*, 2005). Each of these parameters affects the fibre morphology obtained from electrospinning, and by proper manipulation of these parameters, we can get nanofibres of desired morphology and diameters (Ramakrishna *et al.*, 2005).

2.3.1: Solution Parameters

Concentration: The concentration of polymer solution is a very important technique during fibre formation via electrospinning. At lower polymeric concentrations, due to the effect of the applied voltage and surface tension of the polymeric solution, the charged jet fragments into discrete droplets before reaching the collector (Venugopal *et al*., 2005; Greiner *et al*., 2007). At an increased polymeric concentration, as the viscosity increases the chain entanglement between polymeric chains improves and nanofibres are formed. The concentration of polymer in the solution to be electrospun thus has an effect on both the viscosity and surface tension of the liquid, which ultimately decides the electrospinnability of the solution into nanofibre with increased diameters as the polymer concentration increases. However, at concentrations beyond a certain limit, the viscosity of the solution becomes exceedingly high, disrupting the flow of the polymer solution through the capillary (Venugopal *et al*., 2005; Greiner *et al*., 2007).

Fong (1999) reported that, with an increase in solution viscosity, the bead diameter increased while the density of beads decreased. At greater viscosities, the bead shape became less spherical and more spindle-like, resulting in bead defects nanofibres. A high surface tension of the solution at lower levels of polymer concentration caused the fibre jet to fragment into droplets. When the concentration is suitable, smooth nanofibers can be obtained (Fong, 1999).

Molecular weight: This is also important in the solution parameter that affects the morphology of electrospun fibre. Generally, high molecular weight polymer solutions have been used in electrospinning as they provide the desired viscosity for the fibre generation. Huang *et al*; 2003 reported that, when the molecular weight solution is too low, this tends to form beads rather than fibres, and a high molecular weight solution produces fibres with larger average diameters. Molecular weight of the polymer reflects the number of entanglements of polymer chains in a solution, hence solution viscosity (Huang *et al.*, 2003). The entanglement plays an important role in the processing of electrospinning. Consequently, even when polymer concentration is low, high molecular weight poly-L-lactic acid (HM-PLLA) can maintain enough number of entanglements of the polymer chains, thus ensuring a sufficient level of solution viscosity to produce a uniform jet during electrospinning and restrain effects of surface tension, which plays a significant role in beads formation on electrospun nanofibers (Tam *et al.*, 2000). Huang *et al.* (2003) investigated the effect of molecular weight of the polymer, and found that, as the molecular weight increased, the number of beads and droplets decreased.

Effect of solvent: The choice of solvent is important for polymer to solubilize and be transformed into nanofibres during electrospinning. When selecting a solvent, the solubility of the polymer in the solvent and the boiling point of the solvent as indicative of its volatility are important. Volatile solvents are preferred as they facilitate dehydration of the nanofibres, the capillary tip to the collector surface owing to their lower boiling point and hence rapid evaporation rate. However, highly volatile solvents with very low boiling points should be avoided as they may evaporate at the capillary tip and thereby result in clogging and obstructing the flow-rate of the polymer solution (Fong *et al.*, 1999; Greiner *et al.*, 2007; Haghi *et al.*, 2002; Sill and Recum, 2008; Theron *et al.*, 2004; Zong *et al.*, 2002). The separation phase occurs at the liquid-air interface when the jet is travelling through the atmosphere towards the collector, which is a result of the volatility of the solvent and influences the porosity of the nanofibres that are formed (Sill and Recum, 2008).

Table 2.1: Shows the Solvent Properties and the Resulting Fibres

Solvent	Boiling point °C	Other properties	Fibre morphologies	References
DCM	39.8	Low electric constant and high surface tension	Beaded large diameter	Jaruswannapoom *et al*., 2005
Chloroform	61.2	High intrinsic viscosity Beaded at very low polymer concentration	Beaded with low concentration	Son *et al*., 2004
Methanol	64.7	High dielectric constant Small fibre diameter with in concentration	increase methanol Concentration until 50% then increase fiber diameter	Jaruswannapoom *et al*., 2005
THF	66	High dipole moment, good conductivity ribbon- like, high pore density	Smooth and beaded	Zong *et al*., 2005; Jaruswannapoom *et al*., 2005
Ethyl acetate	77.1	High surface tension	Smooth and beaded	Jaruswannapoom *et al*., 2005

[DCM: dichloromethane; THF: Tetrahydrofuran; MEK: methyl ethyl ketone; DMF: dimethylformamide].

Megelski *et al*. (2002) demonstrated the influence of solvents on the porosity of electrospun polystyrene nanofibres. The two solvents used were tetrahydrofuran (THF) (highly volatile) and dimethylformamide (DMF) (less volatile), with different boiling points and vapour pressures to electrospin polymer nanofibres. Jarusuwannapoom *et al*., 2005 confirms that, nanofibres that were electrospun from THF had very high surface pore densities whereas nanofibres from DMF displayed almost completely smooth surface morphology. Eighteen different solvents were tested and it was found that, only five (DMF, THF, ethyl acetate, 1,2-dichloroethane, and MEK) were optimal for electrospinning of polystyrene to give a smooth surface morphology.

Surface tension: Surface tension has also been identified as important parameters in the electrospinning process. A larger surface tension value signifies increased difficulty in extending the surface of a liquid from the interior molecules. The surface tension is thought to be the force acting against the stretching of the charged jet; therefore, higher surface tension leads to larger diameters (Jarusuwamapoom *et al*., 2005).

When the concentration of the polymer solution is fixed, it reduces the surface tension of the solution and thereby converts beaded fibres into a smooth fiber (Haghi and Akbari, 2007; Zhang *et al*., 2005). Zhang *et al*. (2005) reported that, when surface tension and solution viscosity are adjusted by changing the mass ratio of the solvent mixture this change will have an effect on the fibre morphology.

Viscosity: The smooth fibres could not be obtained with a very low or high viscosity because of the concentration of the polymer solution, molecular mass of the polymer and the density of the solvents used. If the polymer solution is high, it results in hard ejection and if low, it spatters and forms a beaded fibre. When polymer solution (viscosity) is optimized by adjusting the concentration, then a bead free fiber can be obtained (Jarusuwamapoom *et al.*, 2005; Koski *et al.*, 2004; Ki *et al.*, 2005).

Addition of low concentrations of polyelectrolytes as demonstrated by Koski *et al.*, 2004; Ki *et al.*, 2005 and vibrating the solution at low frequencies during electro spinning He *et al.*, 2004; Wan *et al.*, 2007 are the two known methods for changing solution viscosity without an appreciable changing concentration. Vibrations facilitate temporary disentanglement of polymer chains by disrupting the van der Waal's interactions between them and therefore reducing the solution viscosity. By merely vibrating the capillary tip (at 400 kHz) Wan *et al.*, 2007, generated thinner nanofibers of poly(butylene succinate) compared to when vibrations were not used. The vibration technique might also be used in electrospinning gels and coagulated materials that are difficult to electrospin.

2.3.2 Spinning Parameters

Electric field: The electrical field is defined as the applied voltage divided by the distance between the tip and collector. Higher electric field values are obtained either through decreasing the distance between the tip and collector or by applying higher voltages (Buchko *et al.*, 1999). In electrospinning, the electric current associated with the process can typically be measured in a microampere. The droplets or fibres transport charge across the gap between the charged needle and the electrically grounded target. High voltages and high electric field strengths are also associated with higher productivity (Buchko *et al.*, 1999; Mo *et al.*, 2004), which is mainly considered to be due to increase in electrical current and electrostatic stresses, which in turn draw more material out of nozzle (Theron *et al.*, 2004). In most cases, a higher voltage causes greater stretching of the solution due to the greater columbic forces in the jet as well as a stronger electric field and these effects lead to reduction in the fibre diameter and also rapid evaporation of solvent from the fibre results. At a higher voltage, there is also greater probability of beads formation (Buchko *et al.*, 1999; Deitzel *et al.*, 2001; Megelski *et al.*, 2002; Lee *et al.*, 2004; Mo *et al.* 2004). Wannatong *et al.*, 2004 suggested that, dielectric constants of the solvents are important in electrospinning because solutions with higher dielectric constants tend to disperse the surface charge density on the jet, more evenly and this leads to the production of fibers with uniform morphologies and smaller diameters.

Collector: This is an important aspect of the electrospinning process where the collector usually acts as the conductive substrate to collect the charged fibres during electrospinning. Different types of collectors have been developed. These including aluminum foil which is used as a collector. Other collectors are as follow; conductive paper, conductive cloth, wire mesh (Wang *et al.*, 2005), grids, parallel or gridded bar (Li *et al.*, 2004), rotating rods or wheel (Xu *et al.*, 2004), liquid bath (Ki *et al.*, 2007).

When the conductive area is less, it generates beaded fibres, because of the reduced surface area. Wire screen with aluminium foil and wire screen without aluminium foil were compared in the same conductive area and it was found that, the pure wire screen is a better fibre collector, because with the use of a wire screen the transfer of fibres to other substrates becomes easy. Fiber alignment is determined by the type of collector and its rotation speed (Wang *et al*., 2005; Doshi and Reneker, 1995).

Flow rate: The flow rate of the polymer solution in the syringe is another technique used in spinning parameters. When the flow rate is very high, bead fibres are formed with a thick diameter, rather than a smooth fibre with a thin diameter, owing to the short drying time prior to reaching the collector and low stretching forces. At lower flow rates, more of the recommended polymer solution will get enough time for polarization (Deitzel *et al*., 2001).

Distance between tip and collector: Varying the distance between the tip and the collector has been examined as another approach to controlling the fibre diameters and morphology. It has been found that, a minimum distance is required to allow the fibres sufficient time to dry before reaching the collector. The effect of tip and the collector distance on fibre morphology is not as significant as other parameters and this has been observed with electrospinning of PVA (Zhang *et al*., 2005), gelatin (Ki *et al*., 2005). The spinning of silk-like polymer with fibronect in functionality fiber at closer distances produced flatter fibres, while further distances gave rounder fibres (Buchko *et al*., 1999).

2.3.3 Ambient Parameters

The ambient parameter includes temperature and humidity that influence the morphology of the electrospun fibre. The effect of temperature on the electrospinning of polyamide-6 fibres ranging from 25 to 60°C which was found that with increase in temperature, there is a yield of fibres with decreased fibre diameter. They attributed this decline in diameter to the decrease in the viscosity of the polymer solutions at increased temperatures. It has been found that, at very low humidity, a volatile solvent may dry rapidly, as the evaporation of the solvent is faster. Sometimes, the evaporation rate is much fast, when compared to the removal of the solvent from the tip of the needle, this creates a problem with electrospinning. As a result, electrospinning process may be carried out only for a few minutes before the needle tip is clogged (Li *et al.*, 2005). It has also been suggested that, the high humidity can help the discharge of the electrospun fibre (Li and Xia, 2004; Li *et al.*, 2005).

2.4 Functionalization of Electrospun Nanofibres

The surface of the electrospun nanofibre can be functionalized with a ligand in order to create reactive sites that are specific to the desired binding molecules or analyte of interest (Ramakrishna, 2005) and also, to enhance their absorption properties (chemicalsensors and biosensors) (Lewis, 1997) and also extend their shelf life. The modern trends in the functionalization of nanofibers such as treatment by blending, coating, radiation with electromagnetic wave, electron beam, iron beam and corona or plasma treatment have also been found useful for the synthesis of electrospun nanofibers (Dunaway *et al.*, 1998).

Chemical modification involves the introduction of one or more chemical species to a given surface to produce a surface that can enhance chemical and physical properties. Chemical modifiers by reactions (e.g., crosslinking or grafting, etc.) could also be carried out prior to, during electrospinning or by post-spin treatments. Chemical modification has been shown to be the most versatile route to nanofibers characterised by new functionalities (Majee and Ray, 1988).

Liu and Hseish (2003) have successfully introduced double-bond units into cellulose fibers via deacetylation, followed by reaction with methacrylate chloride. Immobilization of the ligand containing the desired functional group on the nanofibers by alkylation as with Merrifield resins which also provides a potential route. The chemical reactions can be carried out at sites that can undergo a neuclophilic or electrophilic attack. Examples of this are polyvinylmethyl ketone, polyvinylbenzylchloride which can be treated with amino compounds that introduce the groups through a Schiff base condensation or neuclophilic reaction (Yuang *et al.*, 2004).

2.5 Characterization of Electrospun Nanofibres

The process of characterization of the electrospun nanofibre produced remains one of the most difficult tasks of getting a single fibre. In order to empirically understand the electrospinning process, an assessment of the entire process from polymer selection to mechanical testing needs to be carried out accurately. Generally in electrospinning, the polymers used are characterized into three distinct categories: physical and structural, mechanical, and chemical (Reneker *et al.*, 1996). Nanofibres have attracted such attention due to their remarkable micro and nano structural characteristics, high surface area, small pore size, and the possibility of their producing three dimensional structures that enable the development of advanced materials with sophisticated applications (Theron *et al*., 2004). Uniform and bead-free nanofibers are formed only when all the electrospinning parameters are optimized. However, it is difficult to check case-by-case whether all the parameters are optimized prior to electrospinnning. Optimization of the electrospinning parameters could be checked during electrospinning using the stability and shape of the Taylor cone or the pattern of nanofiber deposition.

2.6 Application of Electrospun Nanofibres

The applications of electrospun fibre have provided several advantages such as; high surface to volume ratio, very high porosity and enhanced physico-mechanical properties. This is because in this process, manipulation of the solution and process parameters can be done easily to get the desired fibre morphology and mechanical strength. The electrospun fibres are required in a small amount and the electrospinning process itself is a versatile process as fibres can be spun into any shape using a wide range of polymers (Lee *et al*., 2004). Electrospun nanofibres are broadly applied in biomedical applications, as tissue engineering scaffolds, in wound healing, drug delivery, filtration, affinity membrane, in immobilization of enzymes, small diameter vascular graft implants, healthcare, biotechnology, environmental engineering, defense and security, and energy storage (Zhang *et al*., 2005). The diagram below provides the use of some applications of electrospun nanofibres in various fields.

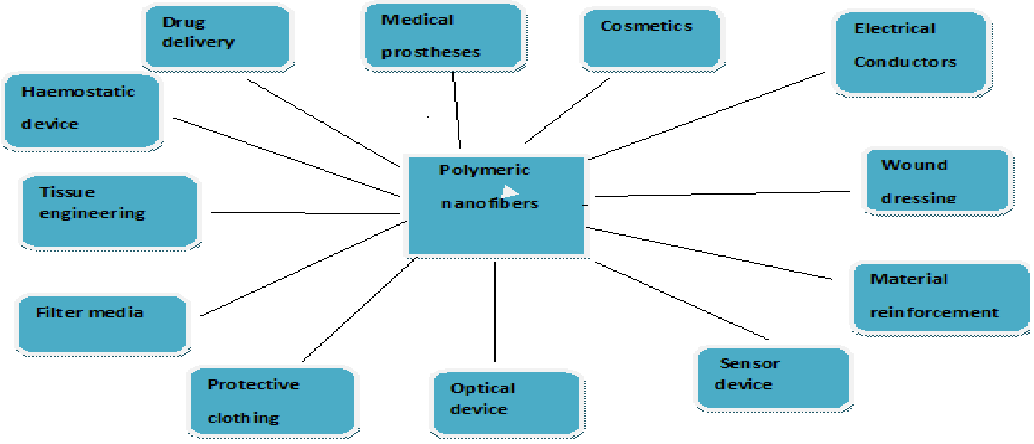


Figure 2.2: Shows the application of electrospun nanofibre (Huang and Vane, 2003).

The surface of the electrospun nanofibres can be functionalized with adsorbing ligands (cationic) and this can be applied towards anion in wastewater due to its affinity. Functionalized electrospun nanofibre permits the purification of wastewater based on their properties (Bhardwaj and Kundu, 2010). The high porous structure and the high surface area with the functionalities present on the electrospun nanofibre makes it useful for the selective uptake of anions in wastewater (Zussman *et al*., 2002). Electrospun nanofibres are increasingly being used for wastewater filtration and purification (Tsai *et al*., 2002).

2.6.1 Electrospun Nanofibers used in Filtration

Filtration efficiency of electrospun membranes is related to the thinness of the fibers in air and water filtration, the removal of tiny particles in the submicron range is required (Greiner and wendoff, 2007; Greiner and wendoff, 2008; Tsai *et al.*, 2002). Filtration channels and structural elements of a filter must be matched to the scale of the particles or droplets that are to be captured in the filter. Thus, we can take advantage of the unique properties of electrospun membranes consisting of very small diameter fibres. It has been realized that, electrospinning is rising to the challenge of providing solutions for the removal of unfriendly particles in such submicron ranges. Generally, due to the very high surface area to volume ratio and the resulting high surface cohesion, tiny particles of the order of <0.5 mm can be easily trapped in the electrospun nanofibrous structured filters and this improves the filtration efficiency (Tsai *et al.*, 2002).

2.7 Origin of Arsenic in Soils, air and water

Arsenic (As) can be present in soils, air and water as a metalloid and as chemical compounds of both inorganic and organic forms (Matschullat, 2000; Miteva *et al.*, 2005). Arsenic ranks twentieth in abundance of elements in the earth's crust, fourteenth in seawater and is the twelfth most abundant element in the human body (Mandal and Suzuki, 2002). Despite its abundance, it is one of the most toxic elements encountered in the environment (Cullen and Reimer, 1989; Dermatas *et al.*, 2004; Hudson-Edwards *et al.*, 2004). Arsenic can enter terrestrial and aquatic environments through both natural geologic processes (geogenic) and human (anthropogenic) activities. The natural pool of As in surface soils arose from the net of geological, hydrological and soil-forming biogeochemical processes. Under typical soil-forming conditions, the nature of soil As is controlled by the lithology of the parent rock materials, volcanic activity, weathering history, transport, sorption, biological activity and precipitation (Kabata-Pendias and Adriano, 1995).

Arsenic concentrations in surface water and groundwater depend on daily and seasonal variations in raw water input (McNeill *et al.*, 2002). For example, Fuller, et al., 1991 reported diurnal variations in As of 39 – 50 and 57 – 83 µgL^{-1} in a stream. One possible reason for seasonal As concentration variations is uptake and release of As by aquatic plants. These plants may absorb As in the spring and summer, causing a slight decrease in As concentrations in the water (Shibata *et al.*, 1996). Some concentration variations are 11 – 21 and 16 – 63 µgL^{-1} in surface waters (McLaren and Kim, 1995) and 10 – 220 µgL^{-1} in groundwater (Gibbs and Scanlan, 1994). Variations in As concentration and speciation is becoming increasingly important to understand in ensuring attainment of water quality standards, especially for drinking water (Smedley and Kinniburg, 2002).

2.8 Arsenic Concentration in Soils and water around the World

Arsenic is a significant contaminant of soils and groundwater in many regions of the world. Depending on the country, exposure to As has come from natural sources, from industrial sources or from food and beverages. High concentrations of As in drinking water (above 50 µg L^{-1}) have been reported in several countries; including Argentina, Chile, China, Japan, Mexico, Poland, Mongolia, Nepal,Taiwan, Vietnam, and some parts of the United States. The world's largest As health issues are the contamination of drinking water aquifers in Bangladesh and West Bengal, India, potentially affecting millions of people (Anawar *et al*., 2002; Roychowdhury, *et al*., 2002; Mitra *et al*., 2002; Pandey *et al*., 2002; Chakraborti *et al*., 2001; Smith *et al*., 2001; Mudur 2000; Chowdhury *et al*., 2000; Tchounwou *et al*., 1999). Localized groundwater As problems are being reported by some countries and new cases are continuing to be discovered. Many countries, particularly developing ones, still use the50 μgL^{-1} of As standard, in part because of lack of adequate testing facilities for lower As concentrations (Narcise *et al*., 2005). Groundwater is an important source of drinking water there because the region is arid. The groundwater environment is predominantly oxidizing, with neutral-to-high pH (6.3-8.9). The main form of arsenic present in the region is As(V), and total arsenic concentrations are 8 to 624 µg/L (mean = 100 µg/L) with 50% of the groundwater samples investigated having arsenic concentrations >50 µg/L. The exposed population was estimated at more than 400,000 in the Lagunera Region (Smedley and Kinniburg, 2002). Mining activities can also cause release of arsenic into groundwater. About 1,000 peoplewere diagnosed with arsenic-related skin disorders in the Ron Phibun District in Nakhon SiThammarat Province of southern Thailand in the late 1990s (Pandey, *et al*., 2002). Arsenic concentrations up to 5000 µg/L were found in shallow groundwater, induced or exacerbated by mine workings. Another important mining area is the Ashanti Region of central Ghana, but arsenic was found at surprisingly low concentrations in the region. Some mining areas in the USA also are seriously contaminated by arsenic, such as the Fairbanks, Alaska, gold-mining district, the Leviathan Minein California, and Kelly Creek Valley, Nevada (Smedley and Kinniburg, 2002).

2.9: Health Effect of Arsenic

Arsenic (As) is a Class “A” human carcinogen as classified by the USEPA and its presence in the environment at specific concentrations, either as a dissolved contaminant in water, food web bioaccumulation, or as an inhaled particulates in the atmosphere, is of great concern to the well being and health security of humans, with the situation being at its worst in Asia (Stroud *et al.*, 2011; Marchiset-Ferlay *et al.*, 2012). The ingestion of As into the human body takes place either by direct intake of arsenic rich water (via drinking or cooking foods) or by indirect intake through crops grown using arsenic-contaminated water.

Organic arsenic is considered to be less toxic than inorganic arsenic and the toxicity decreases in order of AsH_3> As(III) > As(V) organic arsenic compounds (Conell *et al.*, 2006). Chronic exposure to low concentrations of arsenate can cause dermal changes like skin pigmentation; hyperkeratosis, cancer, melanosis, and ulceration (see Figure 2.3). Other chronic non - dermal effects of arsenic reported are diabetes (Weng-Ping, 2007), damage to the cardiovascular system (Hussam *et al.*, 1991), hypertension, respiratory effects (Ann *et al.*, 1996), adverse pregnancy out come (Ann *et al.*, 2005) and increased carcinogenic rates in humans at exposure to high concentrations of arsenic (World Health Organization, 2000). However, discussion is still on going about the threshold limit of carcinogenic action of arsenate, since both US and non US based studies showed only a positive correlation between exposure to arsenic and the occurrence of cancer on arsenic concentrations above 100 µg/g. Exposure to arsenic can also occur through food, water and air (Gorby *et al*., 1994). However, attention has been given to it since more than 90 % of arsenic in food is in form of organic arsenic. Water is the second major route of exposure to total arsenic and as it is mainly present in inorganic arsenic in natural water (Shakya *et al*., 1996).

Figure 2.3: Skin lesions on feet and palm from chronic arsenic poisoning from drinking water (Saha, 2003; Weng-Ping, 2007).

The first study related to exposure of arsenic through drinking water and prevalence of skin cancer was conducted by the WHO with the subsequent lowering of the maximum permissible level from 50 µg/L to 10 µg/L. However, many developing countries are still complying with a limit of 50 µg/L (Berg *et al*., 2006; Gu *et al*., 2010). Some other studies also reported, shows the prevalence of internal body cancers of parts like bladder, liver, kidney and lung due to arsenic exposure through drinking water (Saha *et al*., 1999; Weng-Ping, 2007).

The high level of arsenic in drinking water may result in an increase in childhood liver cancer mortality rate (Saha *et al*., 1999). In her study, Saha and his partners reported that the prostate was a target for inorganic arsenic carcinogenesis.

The noncancerous effects of ingesting arsenic include: cardiovascular diseases (Weng-Ping, 1997), as well as pulmonary, immunological, neuro-logical and endocrine (e.g. diabetes) disorders (Basu *et al*., 2001). Studies carried out in southwestern Taiwan showed that, chronic exposure to arsenic from drinking water leads to the occurrence of pterygium, a fibrovascular growth of the bulbar conjunctival and underlying sub conjunctival tissue that may cause blindness (Lin and Wu, 2001). Arsenic exposure is said to be responsible for a decrease in the IQ scores in children (Rasoul *et al*., 2007), and to children's cognitive development (Rosado *et al*.; 2007).

Arsenic is a major risk factor for Blackfoot disease, a unique peripheral vascular disease that was endemic to the southwestern coast of Taiwan (Saha, 2003). Arsenic induced neuro-toxicity, like many other neuro degenerative diseases, causes changes in cytoskeletal protein composition and in hyperphosphorylation. These changes may lead to disorganization of the cytoskeletal frame work, which is a potential mechanism of arsenic induced neurotoxicity (Vahidnia *et al.*, 2007). The arsenic toxicity causes respiratory complications and induces changes in the humoral as well as mucosal immune responses (Ismail *et al.*, 2008).

2.9.1 Treatments of Arsenic Using Different Adsorbents

In the adsorption process, activated carbon is most popular and widely used adsorbent in wastewater treatment throughout the world, but the high prices and regeneration cost of activated carbon limits their large scale use for the removal of inorganic and organic pollutants, and has encouraged researchers to look forlow cost adsorbing materials (Bailey *et al.*, 1999).

Recently, adsorption of arsenic, using natural materials or the wastes products from industrial or agricultural operations has emerged as an option for developing economic and eco-friendly wastewater treatment processes. Numerous low-cost adsorbents have so farbeen studied for the removal of arsenic from water andwastewater. Dry plants, red mud, fly ash, zeolites, blast furnace slags, hydrotalcites, hydroxides and various bioadsorbents are few to mention. Removal of heavy metals by these materials might be attributed to their protein, carbohydrates and phenolic compound contents, which have metal-binding functional groups such as carboxyl, hydroxyl, sulfate, arsenate and amino groups. Mohan and Pittman, 2007 reported that, the loss of metal ions from their solutions in the presence of natural materials may be due to the adsorption on surface and pores, and to complexation by these materials.

Below shows several of natural materials that have been used as adsorbents for arsenic removal Chitosan, one of the common bioadsorbents, is produced from chitin, which is the structural element in the exoskeleton of crustaceans (shrimp, crabs, shellfish) (Amit and Mika, 2009). Chitin, a long-chainpolysaccharide, is the most widely occurring natural carbohydrate polymer next to cellulose. Various researches on chitosan have been done in recent years and it can be concluded that, chitosan is a good adsorbent for all heavy metals. Dambies *et al.*, (2000) tested the adsorption of As(V) onto molybdate impregnated chitosan gel bead and reported that the sorption capacity increased with the impregnation and optimum pH was 3. Powdered chitosan, obtained from shrimp shell, was converted into bead form (Chen and Chung, 2006) and used to remove arsenic from water in both batch and continuous process.

Zeolites are basically hydrated alumino-silicates having micro-porous structure that can accommodate a wide variety of cations without any change in structure. It has been received increasing attention for pollution control in wastewater treatment. However, most of zeolites havebeen made synthetically; some of them are made for commercial use, while others are created by scientists to study their chemistry. Zeolites have been receiving increasing attention for pollution control as standard components in wastewater treatment (Kesraoui-Ouki and Kavannagh, 1997). Wang and Peng 2010 reported that, natural zeolite utilization in water and wastewater treatment. Xu et al., 2002 reported adsorption and removal of As(v) from drinking water by aluminum-loaded shirasu-zeolite and found its effectiveness over a wide range of pH (3 to 10).

Common competing anions such as chloride, nitrate, sulphate and others had little effect on As(v) adsorption but arsenate greatly interfered with their adsorption.

Fly ash is one of the residues generated in the combustion of coal. It is generally captured from the chimneys of power generation facilities. The availability of fly ash is so high that, at many places its disposal is a problem (Diamaddopoulos *et al.*, 1993). Clay and peat (AI-Jlil and Alsewailem, 2009).

2.9.2 Organic-inorganic Hybrid Polymers as Adsorbents for Removal of Heavy Metal Ions from Solutions

Wang *et al*. (2012), Gao *et al*. (2010), Zaitseva *et al*. (2013), Simsek *et al*. (2012) reported that, the promising organic-inorganic hybrid polymers have been used for the removal of toxic species from wastewater. In the compounds, the functional variation of organic materials is combined with the advantages of a thermally stable and robust inorganic substrate, resulting in strong binding affinities toward selected metal ions and relatively high metal ion adsorption capacities. Functionalized ionalized hybrid polymeric materials as adsorbent are regarded as one of the most effective techniques because metal ions can be chemically bonded by the organic-inorganic polymer hybrids. These kinds of materials often present the best properties of each of its components in a synergic way and have high performances of physical, chemical and mechanical properties (Simsek *et al.*, 2012).

Organic-inorganic hybrid polymeric materials are currently intensely studied (Sanchez *et al.*, 2005), for their efficient applications. The intrinsic multi functional character of these materials makes them potentially useful in multiple fields. Walcarius *et al*., 2001 reported that different forms of organic-inorganic hybrids were studied due to their interesting properties resulting in a number of applications such as electro analytical applications (Walcarius *et al*., 2001). These materials are divided into two classes on the basis of interactions between organic and inorganic components. In class I, organic and inorganic are embedded and there are weak interactions, such as hydrogen bonding, van derWaals, п–п or weak electrostatic interactions between them and in class II, these two components are bonded together through strong covalent or coordinative bonds (Sanchez *et al*., 2005). The functional variation of organic materials combines with the benefits of thermally stable inorganic substrate. These materials have strong binding affinities toward selected metal ions (as cations or oxyanions) and relatively high metal ion adsorption capacities and can be used for wastewater treatment and solid-state separation of heavy metals.

The electrospun nanofibers have high specific surface areas and porosities that impart on them very high adsorption capacities (Huang *et al*., 2003). The electrospinning process offers the flexibility for surface functionalizing the nanofibers with moieties that have high affinities for the anions. For example, anions are known to interact strongly with ligands such as the diazoles (Aguado *et al*., 2009; Yoshitake 2003). Kang *et al*. (2007) reported that the binding abilities of the electrospun nanofibers for anions are dramatically enhanced when they are surface functionalized with ligands. Functionalized electrospun nanofibers could therefore, make an excellent adsorbent for the removal of anions from aqueous enviromnents. The anions adsorbed could easily be leached back into solutions by pH adjustments in order to avail the anions of quantification without affecting the integrity of the sorbent. These remarkable features of synthesised polyvinylmethylketone with 2-amino-4,6-dihydroxylpyrimidine and polyvinylbenzylchloride electrospun nanofibers make them to be the preferred sorbent materials for the removal of arsenic(v) and phosphate from wastewater.

2.9.3: Disposal of Arsenic

Waste disposal is an important consideration in the treatment selection process (Adel and Farakka, 2003). Arsenic removal technologies can produce several different types of liquid and solid wastes, including the following:

i. Sorption processes with disposable media, such as granular ferric hydroxide: backwash water, regeneration liquid, neutralization fluid, rinse water, sludge, and spent media.

ii. Sorption processes with reusable media, such as ion exchange: backwash water,

ii. regeneration liquid, neutralization fluid, rinse water, sludge, and spent media.

i. Membrane processes, such as reverse osmosis: spent membranes, reject brines, and backwash water.

ii. Iron/manganese removal and green sand filtration: filter backwash fluid, sludge, and spent media.

However, the removal technologies frequently remove other contaminants in addition to arsenic, the residual may also have concentrated levels of co-occurring contaminants, such as lead, barium, or radio nuclides. The removal of co-occurring contaminants may pose disposal problems even when the arsenic levels in process residuals are not high enough to lead to a hazardous waste classification or interfere with local limits set by publicly owned treatment works. Water systems should thoroughly test their wastes prior to making disposal decisions.

2.9.4 Removal of Phosphate Using Different Adsorbents

The phosphorus removal treatments if in effective, results in phosphorus and nitrogen in the water supplies in areas surrounding industry and manufacturing plants to be in excess than normal (Lau *et al*., 1997). Large amounts of phosphorus in water can lead to pH changes and changes in water oxygen levels that can be detrimental to aquatic life. Phosphorus is also a nutrient that is responsible for eutrophication (Trepanier *et al*., 2000). Eutrophication is the rapid growth of algae due to excess nutrients in water, which covers the top of water and prevents sunlight from reaching aquatic plants. This causes their death and a decline in water oxygen levels. There are a variety of methods currently available for the removal of phosphorus during wastewater treatment. The current major treatment methods lie in adsorption, chemical precipitation, enhanced biological phosphorus removal, and constructed wetlands. Several advancements have been made in the last ten years, including a growing basis for establishing treatment methods that are more environmentally friendly and inexpensive.

2.9.5 Toxic Effect of Phosphate

Many water bodies cannot be used for drinking, fishing, recreation, irrigation or industrial purposes (Lau *et al.*, 1997). Because of eutrophication which shows the scale of the problem and its importance. Figure 2.4 is a picture of a eutrophied body of water followed by its ecological consequences.

Figure 2.4 Algal and water weeds growing widely algal bloom (Lau *et al.*, 1997).

i. Loss of biodiversity.
ii. Water plants die causing propagation of bacterial decomposers.
iii. The proliferation of bloom-forming species that could be toxic.
iv. Decreasing of water quality (e.g. colour, taste and water treatment problems, transparency, odour).

v. Bacteria consume more oxygen causing its shortage in water body and thus killing aquatic animals; e.g. fish.

Humans have changed the natural phosphate supply radically by addition of phosphate-rich manures to the soil and by the use of phosphate-containing detergents. Phosphates are also added to a number of foodstuffs, such as cheese, sausages and hams.

Considering the fact that 3 to 20% of phosphorus used as a fertilizer globally is washed back to water bodies, there is an estimated resultant of 12 to 80 million tones of phosphates in wastewater worldwide (Zhang *et al*., 2005).

Phosphate is a dietary requirement and the recommended intake is 800 mg/day and; a normal diet provides between 1000 and 2000 mg/day, depending on the extent to which phosphate rich foods are consumed. Too much phosphate intake can cause health problems, such as kidney damage and osteoporosis. Phosphate shortages can also occur and these are caused by extensive use of medicine. Too little phosphate can cause health problems. White phosphorus attacks the skin and, when ingested, causes a necrosis of the jawbone, called “phossy jaw.” Certain organic esters of phosphoric acid, used as lubricating-oil additives, have been found to cause permanent paralysis when accidentally ingested. Phosphine is extremely toxic, as are its organic derivatives. Some of the most toxic substances known to man, collectively termed nerve gas, are organic derivatives of phosphorus (Morse *et al*., 1998).

In view of high toxicities of arsenate and phosphate to water-bodies and the environment, efforts ought to be made to reduce their concentrations in water to the lowest possible levels or to remove them completely.

2.9.6 Adsorption of Phosphorus from Wastewater

Adsorption of phosphorus, leaves open the possibility of phosphorus desorption from the material and regeneration of there covered phosphate from wastewater. A wide range of materials can be used as asorbent forth is adsorption process, including, but not limited to, metal oxides and hydroxides, furnace slag, fly ash, and chemically modified clays (Chen *et al*., 2007; Cheung *et al*., 2000; Pengthamkeerati *et al*., 2008; Oguz *et al*., 2009; Yang *et al*., 2009; Bowden *et al*., 2009).

The cost-effective on the sorbent material was also noted and efficient material that can be used for the removal of phosphorus from wastewater. Also, to note, a subfield of phosphorus adsorption that has been developing involves the synthesis of sorbent materials from waste in an effort to lower the cost of production.

2.9.7 Chemically Modified Clay Adsorption

The use of clay in phosphorus adsorption seems to be a very promising approach to wastewater treatment due to the high availability and natural origins of clay (Wu *et al*., 2006; Rao *et al*., 2005; Mishra *et al*., 2004; Bhor *et al*., 2008; Roulia, 2005; Ooka *et al*., 2003; Ning *et al*., 2008; Ma and Zhu, 2006; Zhu *et al*., 2009; Kasama *et al*., 2004). Clays are normally a layered alumina – silicate material. In current research of phosphorus adsorption by clay, the main types of clays used are vesuvianite (Rao et al., 2005), montmorillonite (Rao *et al.*, 2005; Mishra *et al.*, 2004; Bhor *et al.*, 2008; Ooka *et al.*, 2003) and bentonite. These materials have a high negative surface charge that is balanced by the presence of alkali earth cations such as sodium and calcium ions. These cations determinethe inter layer spacing in clay materials. By replacing these cations with larger inorganic hydroxyl-metalpoly cations, the interlayer spacing can be increased inclay. Montmorillonite is one of the most abundant clays on earth and is useful in adsorbent materials. Naturally, montmorillonite has a negative surface charge and shows low uptake of anions due to repulsion. However, by exchanging the interlayered cations with pillaring agents, such asoligomeric polycations, the ability of montmorillonite to attract anions greatly increases.

Lanthanum had shown to be highly efficient in the adsorption of phosphate and is also environmentally friendly, so it was chosen to be studied in this context. Through a measured increase in interlayer spacing, it was determined that montmorillonite was successfully pillared with La/Al inter layer cations. This material exhibited over three times the adsorption capacity than Al-pillared montmorilloniteina 7-hour time period. Equilibrium is rapidly attained within the first 5 hours of there action, as several other articles has suggested, is a characteristic of phosphate-clay adsorption reactions. Similar to the previous study, the montmorillonite material was seen to reach maximum sorption capacity at around pH 4 due to less electrostatic repulsion and hydroxide anion competition. The presence of competing anions does have an effecton the sorption capacity of pillared clays. This experiment tested the adsorption capacity of phosphorus in the presence of other anions commonly found in fresh water (HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^-). As suggested by the ion exchange mechanism, which is generally thought to be the mechanism behind this type of reaction, the presence of these anions lowers the adsorption capacity of phosphorus. This is a result of the competition between the phosphate ion and other ions for the exchange site. Most other adsorbents are heavy and regeneration of phosphorus becomes difficult due to the sinking of the adsorbent to the bottom of the body of water.

2.9.8 Fly ash adsorption

Zeolites synthesized from fly ash were experimented with to determine its efficiency in phosphorus removal (Chen *et al.*, 2007; Cheung *et al.*, 2000; Pengthamkeerati *et al.*, 2008). These materials have a high cation exchange capacity and theoretically have a potential for use in phosphorus removal. In comparison with raw fly ash, zeolite synthesized from fly ash has a higher phosphate immobilization capacity. Raw fly ash had a high sorption capacity for phosphorus where as the zeolite synthesized from fly ash had higher removal efficiency for ammonium. Several salts were added to the zeolite to create aluminium and iron containing zeolites. These materials showed maximum sorption capacity in solutions containing less than 25 mg P/L and showed a decline in removal efficiency in solutions containing over 200 mg P/L removal through the ligand exchange mechanism.

2.9.9 Phosphorus Precipitation Using Iron

Iron salts are also used in the chemical precipitation of phosphorus from wastewater. They are not the most efficient salts to be used by this method, however they are relatively cheap and form a settled precipitate in a short amount of time. While iron comes in the form of Fe(II) and Fe(III), Fe(II) has cost benefits that make it the more appealing form to use. In environments that are highly oxygenated, Fe(II) can be converted into Fe(III) which forms a strong complex with phosphate. The ratio of total phosphorus to iron in the sample that allowed for sufficient removal came out to be 1:1.30 with 90.6% removal of the phosphorus in effluent containing 0.48 mg P/L. It shows that a low and economical ration of iron to phosphorus can allow for sufficient removal.

CHAPTER 3

3.0 MATERIALS, EXPERIMENTAL TECHNIQUES AND METHODS

Introduction

This chapter presents and explains the study areas, chemicals used, sampling, experimental and analytical techniques used in this study. The descriptions of the sampling areas where the samples were collected are presented in Section 3.1 and Section 3.2 with the sampling details. Section 3.3 presents instrumentation. Section 3.3.1 surface characterization, 3.4 the chemicals and their preparations and Section 3.4 presents the standard analytical techniques and experimental procedures used in the study.

3.1 Study Area

The wastewater samples were collected from the Makana Municipality, a relatively large municipality located in the Cacadu District in the Grahamstown situated in the Eastern Cape province of South Africa. It has a semi-urban environment with its tributaries leading into the Bloukrans River and out to sea at Port Alfred. The growing population has a major impact on the river: due to the wastewater and storm water infrastructure that are not being able to retain the increased capacity of the waste. Wastewater infrastructure is continually leaking into the stream which together with a lack of enforcement with regards to loitering, dumping of waste, farming, agricultural activities, which has resulted the stream to becoming highly polluted with major impacts occurring downstream. The choice of the study area used was based on the convenience and economic reasons; close proximity and easy access to each sample location were considered. The map of the sample collection locations is presented in Figure 3.1.

s

Figure 3.1.: Map of locations where wastewater effluent samples for AsO_4^{3-} and PO_4^{3-} were collected in Grahamstown, Eastern Cape Province.

3.2 Materials

3.2.1 Sampling

The wastewater samples were collected along Bloukrans River to the South of Grahamstown. The sample were collected 500 m above the sea level close to a walk away over the stream just below the parking lot from Shoprite manually using an air tight plastic container to prevent ingress of air. The wastewater sample was filtered with 0.45 µm pore size membrane filter paper using a vacuum pump device. The filtered sample was analyzed using physical and chemical methods. The physical methods include pH determination using Hanna pH meter while the chemical methods involved the determination of anions using inductively coupled plasma, optical emission spectroscopy (ICP-OES). The filtered samples were preserved by adding 3 drops of concentrated nitric acid (HNO_3) for approximately 100 ml sample and preserved at 4 °C until the time of analysis. The analytical technique used for anions analysis was inductively coupled plasma optical emission spectroscopy (ICP-OES).

Table 3.1: Shows a list of chemicals and reagents used for the experiments

Chemicals	**Purity/ Concentration**	**Supplier**
Sodium nitrate	99 %	Sigma – Aldrich
Sodium nitrite	99%	Sigma – Aldrich
Arsenic(lll) oxide	99%	Sigma – Aldrich
2-amino-4,6-dihydroxylpyrimidine	99%	Sigma – Aldrich
Polyvinylmethylketone	99%	Sigma – Aldrich
2,6 Lutidine	99%	Sigma – Aldrich
Methyl iodide	99%	Sigma – Aldrich
N,N-Dimethylformamide	99%	Merck Chemicals
Diethyl ether	99%	Merck Chemicals
Ethanol	99%	Sigma – Aldrich
Hydrochloric acid	0.0364 g/mL	Sigma – Aldrich
Ferric(lll) chloride	99%	Merck Chemicals
Sodium metabisulphite	97%	Merck Chemical
Dipotassiumhydrogen phosphate	99%	Merck Chemical

All other chemicals were of analytical grade and were used without any further purification. Standard solutions were freshly prepared using ultrapure water generated from milliQ system (Massachusetts, USA). All glassware was washed, rinsed and soaked overnight in 4M HNO_3 and then oven dry before use.

3.3: Experimental

3.3.1: Preparation of Reagents

This section presents and described the methods of preparation of reagents used for the synthesis of APPMKNFs and PVBC. The methods of preparing these reagents are described below:

Preparation of 0.02M NaOH

A mass of about 8.0 g of sodium hydroxide pellets was weighed in a 1000 mL beaker and dissolved with 200 mL millipore water. After complete dissolution, the solution was transferred into a 1 L volumetric flask for adequate dissolution and filled it to mark with millipore water. The solution was used in the section was 3.3, 3.61.

Preparation of 1M H_2SO_4

1 M sulfuric acid solution was prepared by adding 12.75 mL of conc. H_2SO_4 and made up to 250 mL with millipore water after 2 min in a 250 mL standard volumetric flask. The solution was used in section 3.4, 3.6.

Preparation of 5M HCl

5 M HCl solution was prepared by adding 107.4 mL of conc. HCl and made up of volume to 250 mL with millipore water after 5 min in a 250 mL standard volumetric flask. The solution was used in section 3.5, 3.5.

Preparation of 0.1 M Nitric Acid

0.1 M nitric acid solution was prepared by adding 1.55 mL ofconc. HNO_3 and made up of volume to 250 mL with Milli pore water after 2 min in 250 mL standard volumetric flask.

Preparation of 0.1 M $FeCl_3$ in 6 M HCl

A mass of about 3.24 g of $FeCl_3$ was weighed into a 100 mL beaker and dissolved in 100 mL of 6M HCl solution. After complete dissolution, the solution was transferred int a 200 mL stardard volumetric flask for adequate dissolution and filled to mark, with 6 M HCl. The solution was used in section in 3.5.

Preparation of 0.05 M $Na_2S_2O_5$

A mass of about 2.375 g of $Na_2S_2O_5$ was weighed into a 100 mL beaker and dissolved with 100 mL of Millipore water. After complete dissolution, the solution was transferred into a 250 mL volumetric standard flask and was filled to mark with Millipure water. The solution was used in section in 3.5.

Preparation of 1000ppm AsO_4^{3-} Stock Solution

Arsenic stock solution 1000 ppm arsenic(v) was prepared by dissolving 1.320 g of arsenic trioxide (As_2O_3) in a minimumamount of 0.02 M sodium hydroxide (NaOH) solution. The solution was acidified topH 3.5 with dilute hydrochloric acid (HCl) and diluted to 100 mL with milliporewater at 60°C, the solution was cooled to room temperature. The solution was stored at 4°C for one month. Working solutions of the desired arsenic(v) concentrations were prepared from the stock solution daily. The following concentrations of (5, 10, 15, 20, 25 and 30) ppm was each prepared from the 1000 ppm stock. The solution was used in sections of 3.6, 3.7.

Preparation of 1 L Phosphate Stock Solution

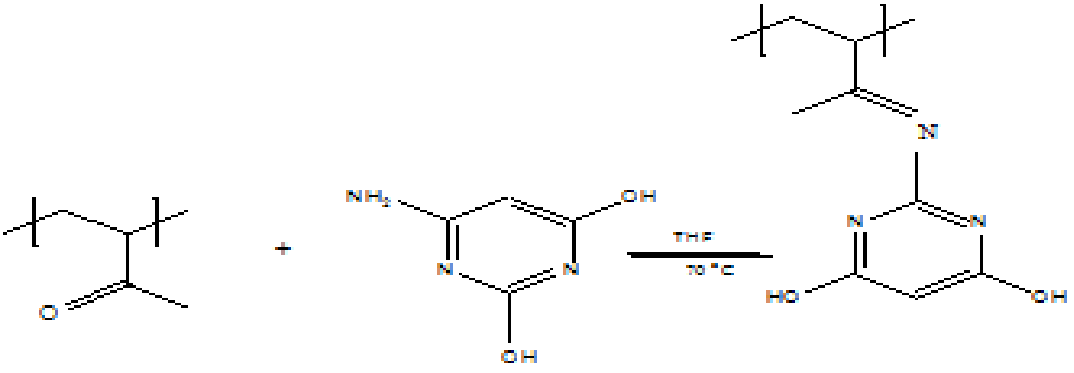
A mass of about 1.7425 g of dipotassium hydrogen phosphate was weighed in 500 mL beaker; 250 mL of Millipore water was added. After dissolution of the salt, it was carefully transferred into 1 L standard volumetric flask, 10 mL of 2 M H_2SO_4 was added to the solution and filled to mark, using Millipore water after shaking for adequate mixing. The solution was used in the sections of 5.1.1, 5.1.2.

Preparation ofStock 60.0 mg/L Phosphate Standard Solution

A mass of about 1.716 g of KH_2PO_4 was dissolved in 250 mL flask of Millipore water at 60°C. Cool the solution to room temperature and the volume down to 250 mL. 1 mL of obtained solution contained 10 mg. The solution was used in the Sections of 5.1, 5.2.

3.4: Preparation of 2-amino-4, 6-dihydroxylpyrimidine Functionalized Polyvinylmethylketone (APPMKNFs) and Functionalized Polyvinylbenzylchloride (PVBC)

A mass of about 0.33 g of 2-amino-4,6-dihydroxylpyrimidine was weighed in 15 mL of prepared 0.02 M NaOH solution, and was reflux for 2 hrs at 70°C after complete dissolution. 0.035 g of polyvinylmethylketone was dissolved in 10 mL of DMSO in a beaker and was added drop wise with continuous stirring for 12 hrs to the solution via a Schiff base condensation reaction as shown in scheme 3.1. On cooling, the solution was slowly poured, while stirring vigorously into a 250 ml beaker containing ethanol to precipitate the synthesized polymer, which was filtered under vacuum suction, washed extensively with diethyl ether and dried in a desiccator.



Scheme 3.1: Synthesis of 2-amino-4,6-dihydroxylpyrimidine functionalized polyvinylmethylketone polymer

After electrospinning, the fibers surface of the produced materials that can be provided with functional groups, such as the hydroxylgroups (OH) and the imine (NH) are sites of various possible reactions.

As mentioned previously, electrospun nonwoven fabrics made of polymer nanofibers offer properties of major interest for many applications, through their high surface to volume ratio, their high porosity, but also through the possibility of functionalizing the fibers surface. Functionalized electrospun membranes that can remove several contaminats from drinking water by adsorption and filtration have been explored. The advantages of functionalized nanofibers over other sorbent materials are their high density of functional groups which are of particular interest as various reactions are carried out on these sites. Surface functionalization is a common field of application of functional groups on nanofibers which enables the surface to obtain functional nanomaterials (Huang *et al.*, 2007). Electrospun nanofibers are suitable to be used as filtering media in water filtration applications due to their unique properties. More specified, they can be used in low pressure filtration due to the surface area of the sorbent material (Bjorge *et al.*, 2009).

3.5 Fabrication of APPMKNFs and PVBC

There are many solutions and process parameters that govern the outcome of morphology of nanofibers (Son *et al.*, 2004; Li and Xia 2004]. Polymer solution parameters mainly include viscosity, conductivity and surface tension (Liang *et al.*, 2007; Pillay *et al.*, 2013; Li and Xia, 2004). One of the principal parameters that impact the process of electrospinning is viscosity of the polymer solution, which depends on polymer concentration and polymer type. The process of electrospinning is also based on the stretching of a charged jet of polymer solution (Greiner and Wendorff, 2007). The low viscosity results in low surface tension, which cannot counter-balance the electrostatic forces (Duan *et al.*, 2004; Hogan and Biswas, 2008). Table 3.2 shows different concentrations of polymers that was electrospun into nanofibers for APPMKNFs and PVBC.

Table 3.2: Shows the different concentrations of APPMKNFs and PVBC used for electrospinning

	APPMKNFs					**PVBC**					
Wt of polymer	5 % (w/v)	7.5 % (w/v)	10 % (w/v)	15 % (w/v)	20 % w/v)	20 % (w/v)	25 % (w/v)	30 % (w/v)	35 % (w/v)	40 % (w/v)	45 %(w/v)
Solvent	DMF: THF	DMF: THF	DMF: THF	DMF: THF	DMF: THF	DMF: THF	DMF: THF	DMF: THF	DMF: THF	DMF: THF	DMF: THF
Ratio	3:7	3:7	3:7	3:7	3:7	1:1	1:1	1:1	1:1	1:1	1:1
Flow rate	0.5 ml/h	0.5 ml/h	0.5 ml/h	0.5 ml/h	0.5 ml/h	0.2 ml/h	0.2 ml/h	0.2 ml/h	0.2 ml/h	0.2 ml/h	0.2 ml/h
Distance	13 cm	13cm	13 cm	13 cm	13 cm	15 cm	15cm	15cm	15cm	15Cm	15 Cm
Voltage	12kv	12 kv	12kv	12kv	12kv	15kv	15kv	15kv	15kv	15kv	15kv

Several solutions of various concentrations were prepared, based on (Tan *et al.*, 2005). Two sets of solutions were prepared: (i) functionalized polyvinylmethylketone (ii) polyvinylbenzylchloride, at different polyer concentrations as shown in the table above in an Erlenmeyer flask. The composition of the electrospinning solutions is detailed in Table 3.2 Magnetic stirrer was inserted as well as a weighted quantity of polymer into the flask and the flask was fitted with a stopper to avoid evaporation of the solvent and the stirring step were done to get approximately 10mL of the solution. Under magnetic stirring and at room temperature, the powder dissolved in three hours for the lowest concentrations to 24 hrs for the highest ones. After total dissolution, the mixture was homogeneous and transparent. It was then transferred into a syringe as shown in Figure 3.2.

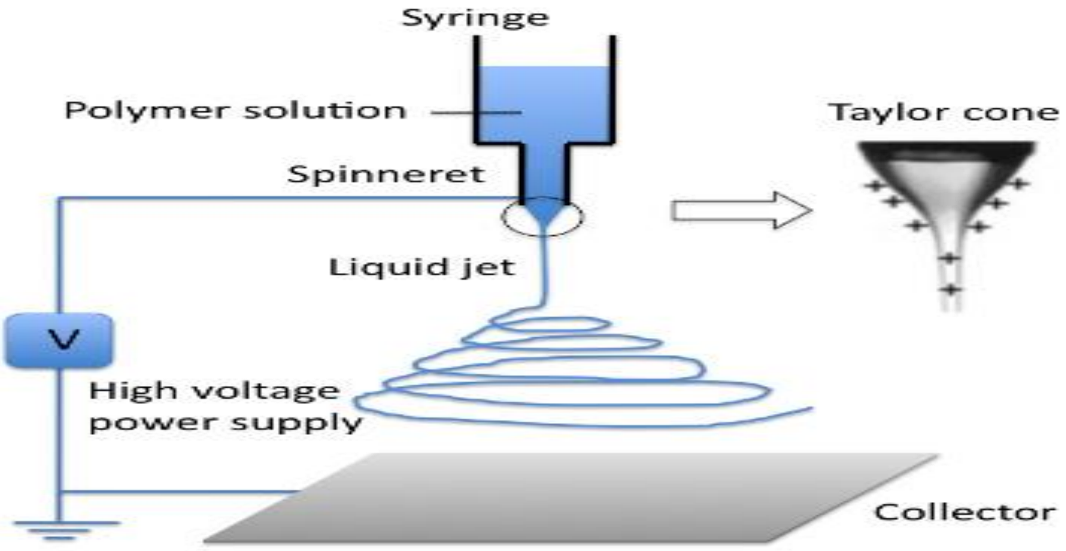


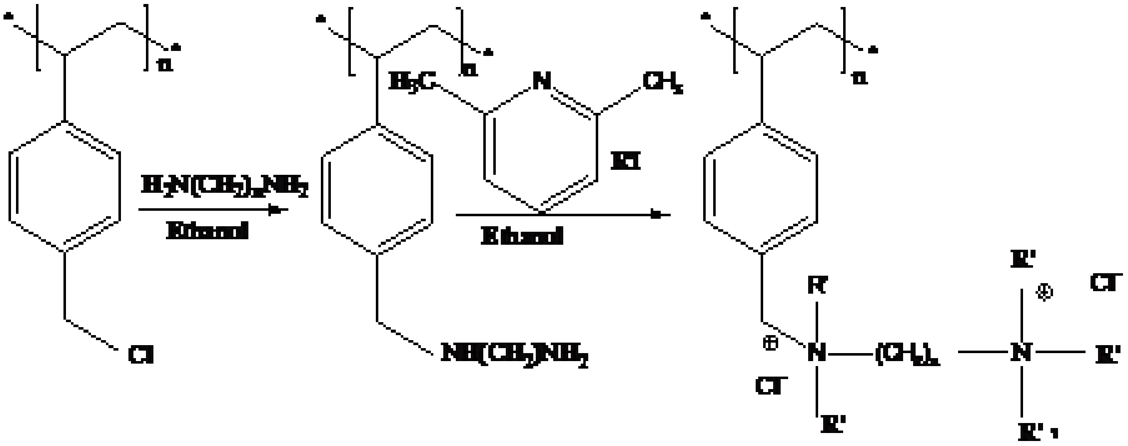
Figure 3.2: Schematic of a typical electrospinning system (Li *et. al.*, 2010)

The electrospinning setup above utilized in this study consists of a 20 mL polypropylene syringes, and were utilized to load the electrospinning solution. An electrically grounded, detachable, flat metal screen that is adjustable to a desired height as shown in figure 3.2 and flat metal screen was used to collect electrospun nanofibers.

3.6 Functionalization/Quatenization of Polyvinylbenzylchloride (PVBC)

A mass of about 2.15 g of PVBC nanofiber presented in Figure 4.5.6 was cut out in circular portions of (1.5cm) of the nanofiber sheet soaked in 8.0 g of ethylenediamine (EDA) in 15 mL of ethanol and shaken on a mechanical shaker for five days (Scheme 3.2) and the reaction in the vessel was allowed to proceed at 80 - 100°C for 36 hrs for the amination reaction. After the reaction, the modified fibers were removed from the solution and the fibers washed with methanol, Soxhlet extracted with methanol, and then air dried.

A mass of about 2.0 g each of the functionalized polyvinylbenzylchloride were prepared in different 100 mL reaction vessel. A 50mL of ethylenediamine was introduced into the 100 mL vessel containing 7 .0 g of methyl iodide. 4.0 g of lutidine and ethanol was added into 100 mL reaction vessel with a stirrer and was shaken on a mechanical shaker at 50°C to 60°C for 24 hrs. The quaternized fibre was filtered under vacuum and, washed extensively with water. The iodine was removed by washing the quaternized fibers with 100 mL of 0.1 M $FeCl_3$ in 6 M HCl, followed by using a hot 100 mL of 0.05 M $Na_2S_2O_5$ solution and finally 50 mL of conc. HCl was used to protonate the sites and the fiber was dried in a desiccator for 24 hrs.



Scheme 3.2: The functionalization of polyvinylbenzylchloride-based diquaternary ammonium nanofibres PVBC (R′= CH_3, C_2H_5 and C_3H_7)

3.7 Adsorption Experiment of Arsenate from Wastewater (Batch Studies) Using APPMKNFs and PVBC

This section presents batch sorption experiments that were conducted to examine the adsorption isotherms, the kinetics and the effect of solution pH and competitive anions on the adsorption behavior using the functionalized APPMKNFs and PVBC on arsenate removal.

The batch adsorption studies were carried out in 100 mL flask, each containing 100 mL of As (v) solution prepared with As_2O_3. A mass of 12 mg of the beeded free nanofibers in Figure 4.6.(b) for (APPMKNFs) were cut out in circular portions from the aluminum foil of (1.5 cm) adsorbents in the flask and agitated at 250 rpm in a thermostart shaker at 25°C for 2hrs. The desorption kinetics experiments were carried out at an initial As (v) concentration of 10 – 50 µg/l and the solutions pH were controlled in the range of 3.5 – 10. The effect of co-exisiting anions on arsenate sorption were conducted in 10 µg/l of arsenate solution. After the addition of competiting anions into the arsenate solution, the solution pH was adjusted to 3.5 – 6.5 and kept constant during the sorption process. The equilibrium concentrations of the competing anions were quantified after the sorption. After the sorption, the fibers were separated from the solution, using 0.45 µm membrane filter briefly rinsed with Millipore water to remove the residual solutions trapped among the fibers and then prepared for other analysis. The initial and final As (v) concentrations in the solutions in each of the flasks were quantified using inductively coupled plasma optical emission spectrometry (ICPOES).

The percent removal can be calculated using the formula below:

$$Qe = \frac{V(Co - Ce)}{W}$$

where C_o, C_e, W and V are the initial anion concentration, equilibrium anion concentration, dry weight of adsorbent and solution volume respectively.

3.7.1 Desorption Experiment of Arsenate from APPMKNFs using Batch Studies

The sorption studies were carried out in 0.1 M NaOH in batch experiments, in order to find a suitable solvent system for desorption of arsenate and recovery from

APPMKNFs. The desorption was possible due to the stripping ability of OH^- at a higher concentration and proved effective in eluting adsorbed arsenate.

Desorbability was calculated by the following equation:

$$\%\, Desorbability = \frac{C_a}{C_f} \times 100$$

C_a = Quantity of ion desorbed to the elution

C_f = Amount of ion adsorbed on the adsorbent

3.8. Adsorption of Arsenate Using Solid Phase Extraction (SPE)

This section presents the study of electrospun nanofibre in SPE disk fabrication as the sorbent material was packed in a simple home made device connected to a vacuum manifold.

SPE can be defined as a physical extraction process involving a liquid phase and a solid phase (which can be packed or free-flowing sorbent), the increased use of packed sorbent formats seems to have led to a bias towards packed-sorbent SPE devices (Lokhnauth, 2005). Braus *et al*. (1951) was the first to report the applications of packed sorbent, using the SPE method he packed 1.2–1.5 kg of granular activated carbon into an iron cylinder for the isolation of organic compounds. Xu *et al*. (2009), was the first to report the fabrication of SPE devices that relied on relatively, mechanically strong electrospun nanofibers as the sorbent bed. There have been several other reports on the use of nanofibers packed in the same format (Xu *et al.*, 2010; Shu-Yan *et al.*, 2010; Xu *et al.*, 2010; Xu *et al.*, 2011; Xu *et al.*, 2010)

Since then, there has been significant progress in SPE technology, as evidenced by the development of new format and sorbents of a wide range of morphologies and chemistries on Surface area materials used for SPE (Braus and Middleton, 1951).

To optimize extraction, it is important to be aware of the nature of the sorbent used with respect to physicochemical characteristics. The most important physicochemical characteristics for optimal extraction are porosity and specific surface area. This research was focused on demonstrating the feasibility of using the quaternized CH_3, C_2H_5 and C_3H_6 electrospun nanofibers as an SPE-sorbent material for the extraction of arsenate and phosphate from wastewater. The nanofiber-sorbent beds in Figures 4.6(g) and 4.6(h) were "packed" by cutting out circular portions (1.5 cm) of the nanofibers sheets from the aluminum foil into the SPE disk for extraction procedure for a flow through the process as shown in Figure 3.3.

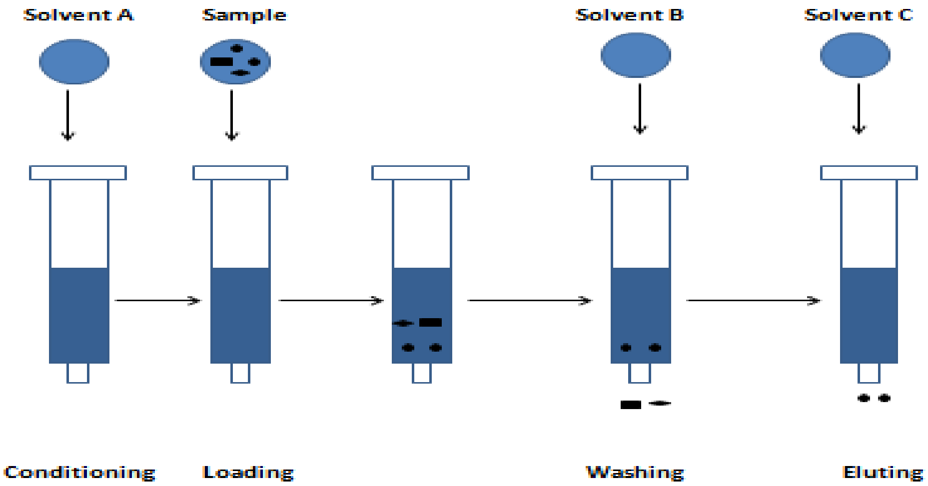


Figure 3.3: Shows the removal of arsenate using solid phase extraction (SPE)

SPE method was conducted to examine the adsorption isotherm effect of pH and the competitive anions on the adsorption of arsenaic(v) and phosphate from wastewater, using three different quaternized nanofibers (R′: CH_3, C_2H_5 and C_3H_7). 5 mg each adsorbent material was chopped in a circular portions (1.5 cm) in the SPE disk. 100 mL of arsenate and phosphate solutions were prepared in 250 mL flask, each of which contained 100 mL of phosphate.

In the sorption experiments, the phosphate concentration varied from 0.1- 150 mg/L and the solution pH was adjusted to 2.5 - 6.5 and was controlled throughout the filtration experiment. The effects of co-existing anions were conducted in 5 mg/L of phosphate solution. The solution pH was adjusted to 2.5 - 6.5 and kept constant during the sorption process and the equilibrium concentrations of the competing anions were measured after sorption. After the sorption of arsenate and phosphate, the fiber in the

SPE disk was rinsed with Millipore water to remove the solution trapped in the disk and prepared it for other analysis.

The initial and final phosphate concentrations in the solution from each of the collected flasks were determined using (ICP-OES).

3.8.1 Adsorption/Desorption Studies for Arsenate Removal Using Quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) Nanofibers

The effect of the functionalized (adsorbent) was observed in Figure 4.6 on the uptake of arsenate present in the contaminated water sample. About 5 mg of the circular portions (1.5 cm) of the quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) nanofibres were added to 25 ml of arsenate solutions in and stirred for 30 min. The loaded nanofibre materials were filtered off, washed with Millipore ultra pure water and dried in the desiccators using vacuum. The used dried firre was placed in 25 ml of 0.1 M NaOH solution and stirred for 30 min. in order to desorb the arsenate adsorbed on the nanofibers. The extent to which arsenates were enriched was determined using the ICP-OES anaytical technique.

3.9. Instrumentation

3.9.1. Surface Characterization Techniques

3.9.2 Scanning Electron Microscope

The fibres were prepared for Scanning Electron Microscope (SEM) in the Electron Microbiology unit of the Rhodes University. The prepared samples were mounted on the

SEM, using a double-sided graphite tape and then sputter coated with gold using a Balzers' union sputter device (Balzer, 1998). The samples were viewed, using TESCAN Vega Ts 5136 LM typically at 20Kv at a working distance of 20 min.

A scanning electron microscope was used for producing images of a sample by scanning it with a beam of electrons in form of laser scan patterns. The electrons were made to interact with atoms of the samples thereby producing a signal that contained information, about the sample's surface topography as well as its composition (Cross, 2001). An electron beam possesses energy ranging from 0.2 Kev to 40 Kev and focused by one or two condenser lenses to a spot of about 0.4 nm to 5 nm in diameter. As the beam of electron passes through pans of scanning coils or pans of deflector plates in the electron column of the final lens, the beam is deflected so that it scans in a roster fashion over a rectangular area of the sample surface. As the primary beam interacts with the sample, the electron loses energy by repeated random and absorbing within a few drop shaped volume of the specimen, known as the interaction volume, which extends from less than 100 nm to around 5 µm to the surface. The electrons and landing energy as well as the atomic number of the specimen density, are determining factors of the size of the interaction volume. The energy exchange between the electron beam and sample results in the reflection of electrons can be detected by specified detectors. The specimen absorbs the beam of current which is detected and used to create images of the distribution of specimen (Balzer, 1998). The SEM micrograph is known to have magnification of a range of six order of magnitude starting from 10 to 500,000 µm (Cross, 2001).

3.9.3 Energy Dispersive X-Ray Spectroscopy (EDS)

The EDS system is typically integrated into a SEM instrument. An EDS system includes a sensitive X- ray detector, a liquid nitrogen Dewar for cooling and software to collect and analyze energy spectra. The detector is mounted in the sample chamber of the main instrument at the end of a long arm, which is cooled by liquid nitrogen. The most common detectors are made of Si (Li) crystals that operate at low voltages to improve sensitivity.

An EDS detector contains a crystal that absorbs the energy of the incoming X-ray by ionization, yielding free electrons in the crystal that becomes conductive and produce an electrical charge bias. The X-ray absorption thus converts the energy of individual X-rays into electrical voltages of proportional size and the electrical pulses correspond to the particular X-ray.

An advantage of EDS is the spot mode; users can acquire a full elemental spectrum in only a few seconds. The support software makes it possible to readily identify peaks; this makes EDS a useful survey tool to quickly identify unknown phases prior to quantitative analysis. It can also be used in the semi-quantitative mode to determine chemical composition by peak-height ratio relative to a standard.

3.9.4 Brunauer, Emmett, Teller (BET) Analysis

Brunauer, Emmett, Teller (BET) analysis involves carbon dioxide adsorption isotherms which were measured at 77K, using Micrometrics ASAP 2020 surface area and porosity analyzer. Prior to each measurement, the samples were degassed for a minimum of two weeks to ensure complete removal of adsorbed impurities. Degassing was performed at 70°C for the liner polymers and at 150°C for cross linked polymers. The BET theory (Brunauer *et al.*, 1938) explains the physical adsorption of gas molecules on solid surfaces and provides the basis for measurement of the specific surface area of a material. The basic concept of the theory is an expansion of Langmuir theory, which deals with monolayer molecular adsorption and a multilayer adsorption built on the hypothesis that, gas molecules are adsorbed on solid layers and that, there is no interaction between each adsorption layer (Pagnanelli *et al.*, 2005).

$$\left[\frac{1}{V}\right](\frac{P_0}{P-1}) = \frac{C-1}{V_{mc}}\left[\frac{P}{P_0}\right] + \frac{1}{V_{mc}} \text{eq (1)}$$

where P and P_o are the equilibrium and the saturation pressure of adsorbent at the temperature of adsorption.

V is the adsorbed gas quantity [in volume unit].

V_{mc} is the monolayer adsorbed gas quantity.

C is the BET constant, which is expressed by the equation below:

$$C = \exp.\left[\frac{E_1 - E_2}{RT}\right] \text{eq (2)}$$

The equation 1 is an adsorption isotherm and can be plotted as a straight line with $\frac{1}{V}$ $[\frac{Po}{P-1}]$ on the Y axis and Q = $\frac{P}{Po}$ on the X axis according to experimental results, this plot is known as a BET plot.

The BET method is usually used in surface science for the calculation of surface areas of solids by physical adsorption gas molecules. Total surface area [S_{total}] and a specific surface area S are evaluated by the following Equations in (3) and (4)

$S_{BET,\ total} = \frac{V_m N_s}{V}$eq. (3)

where V_{mc} represents the volume and the unit of molar volume of the adsorbate gas.

$S_{BET} = \frac{S_{total}}{\alpha}$ eq. (4)

Where N is the Avogadro's number,

S is the adsorption cross section of the adsorbing species

V is the molar volume of adsorbate gas

A is the mass of adsorbent (g)

3.9.5 X-Ray Diffraction (XRD)

This section presents and describes X-ray diffraction analysis operation and the set-up conditions used. This technique is used to identify mineral phase of a sample and its particle size.

Table 3.3 Operating conditions of X-ray diffraction analysis

Parameter	**Settings**
X-ray detector	Vantec 1

Generator voltage	40 Kv
Generator current	40 Ma
Scanning range angle (Θ)	10^o-80^o
Scanning type	Locked couple
Scan speed per step	2θ/min and step size of 0.02^o Theta
Scan time	0.5 sec per step
Scan size	0.03^o
Synchronous rotation	Copper Kα (alpha) at 1.540598

3.9.6 Langmuir Isotherm

The Langmuir sorption isotherm describes how uptake occurs on a homogeneous surface by a monolayer sorption without interaction (Langmuir, 1916; Singh et al.; 2004). The linear form of the Langmuir isothermal may be represented as

$\frac{\mathrm{Ce}}{Qe} = \frac{Ce}{Qm} + \frac{1}{(kaQm)}$ (Langmuir isothermal) eq. (5)

where C_e [mg/L] and Q_e [mg/L] are concentration of anions and adsorption equilibrium, Q_m [mg/g] and K_a are the theoretical maximum adsorption capacity and Langmuir equilibrium constant related to the theoretical maximum adsorption capacity.

3.9.6.1 Freundlich Isotherm

The Freundlich sorbtion isotherm describes the equilibrium on heterogeneous surfaces and the linear form of the isotherm, which can be represented by

$\log Q_e = \log_F + \frac{1}{n} \log Ce$ (Freundlich isotherm) eq. (6)

3.9.7. Inductively Coupled Plasma (ICP) Spectrometry

The Thermo Electron iCAP 6000 series-optical emission spectrometer (Cheshire, United Kingdom) was operated with the following parameters below. When the elements (atoms or ions) are excited and subsequently return to a low energy status, emission rays are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined, based on the element emission line at a specific wavelength and the content of each element is determined, based on the position of the photon rays by the intensity rays.

To generate plasma, first, argon gas is supplied to the coil (torch) and a high frequency electric current is applied to the work coil at the tip of the torch tube, using the electromagnetic field created in the torch tube by the high frequency current. The argon gas is ionized and plasma is generated. The plasma has a high electron density and temperature (10000K) and this energy is used in the excitation–emission of the sample. The solution samples are introduced into the plasma in an atomized state tube through the narrow tube in the centre of the torch or coil.

Table 3.4: Shows the ICP-OES operating parameters

Parameter	Setting
Applied radio frequency (RF) power	1150W
Plasma (Ar) gas flow	5.0 L/min
Auxiliary gas flow	0.5 L/min
Nebulizer (Ar) gas flow rate	1.5 L/min
Sampling dept	8.5 mm
Sampling pump rate	50 rpm
Time scan acquisition	50 ms / point
Cooled spraying chamber temperature	4 °C
Camera temperature	46.63 °C
Generator	24 °C
Optics temperature	36.9 °C
Total integration	30 s per analyte
Sample flush time	30 s
Number of replicates	3

3.9.9. Fourier Transform Infrared (FTIR)

The FTIR spectra (400 – 4000 cm^{-1}) were recorded with a Perkin Elmer FT 100 Spectrometer (Masschusetts, USA) equipped with a germanium (Ge) universal ATR sampling accessory. The FTIR were used for the characterization of the polymers and starting reagents.

3.9.9.1 Elemental Analysis

A vario Elemental ELIII Micro cube was used for elemental analysis is also called CHNS elemental analyzer. The calibration of the instrument was done with the use of sulfanilamide and acetanilide standards. The basic principle of quantitative CHNS analysis is high temperature combustion of organic and many inorganic solid or liquid samples. The gaseous combination products were purified, separated into various components and analyzed with a suitable detector such as a thermal conductivity detector (TCD) and optional infrared detector (IR) for sulphur.

CHAPTER 4

4.0. Results and Discussions

4.1. Characterization of APPMKNFs and Quaternized PBVC

4.2.1 FTIR Studies

4.2.2 APPLICATION OF APPMKNFs ON ARSENIC(V) REMOVAL

The FTIR results of the Schiff base ligand, 2–amino–4,6-dihydroxylpyrimidine, was synthesized with polyvinylmethylketone through a condensation reaction is presented in Figure 4.1 below.

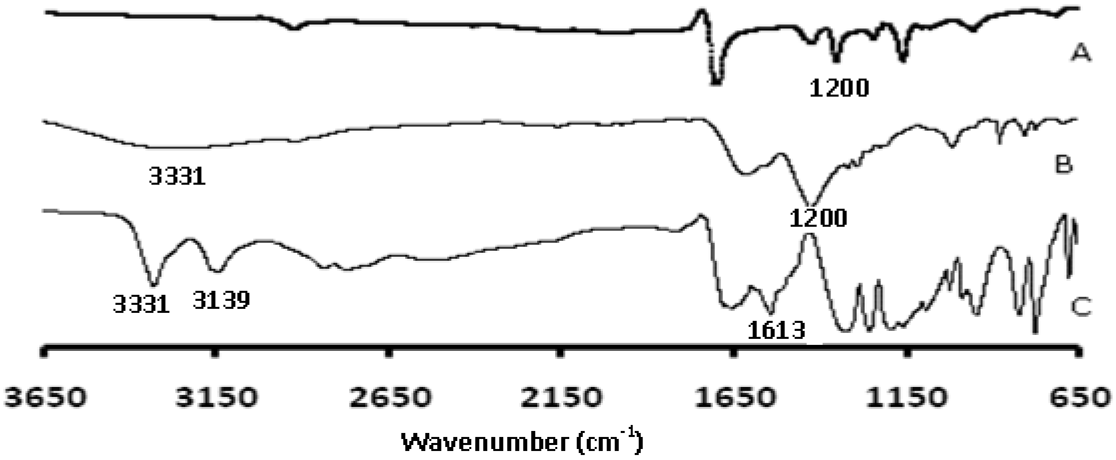


Figure 4.1: FTIR absorption spectra of polyvinylmethylketone, 2-amino-4,6-dihydroxylpyrimidine and the functionalized polymer nanofibres (APPMKNFs)

In the polymer spectrum (A) in Figure 4.1, the characteristic band at 1696 cm^{-1} corresponded to the stretching vibration of the C=O groups. The broadband of the ligand, spectrum (B) ranging from 3139.24 cm^{-1} and 333.64 cm^{-1} correspond to the combination of the stretching vibration bands of both OH and NH groups. Looking at the polymer and the ligand spectra new set of bands were found at 1613, 1200 and 2921 cm^{-1}. The band at 1613cm^{-1} can be assigned to the C=N stretching vibrations of the imine group, confirming the formation of Schiff bases between the spectrum (A) and spectrum (B). The bands at 1200 and 2928 cm^{-1} were assigned to the stretching vibrations of the C-N and C-H bonds.

4.2.2 FTIR Studies of Unfunctionalized and Functionalized PVBC

The characteristic peaks in the spectrum (A) of the PVBC can be assigned as follows: 670 cm^{-1} $_v$(C-Cl), 2976 cm^{-1} corresponds to the CH (CH_3, C_2H_5 and C_3H_7), while 1451 cm^{-1} spectrum represents the CH bending vibration of the same CH group in the alkyl groups. After the functionalization, the spectrum shows some significant changes. The $_v$(C-Cl) at 670 cm^{-1} disappeared completely to form a new band at peaks 1562 cm^{-1} which can be assigned to N-H group of the amine group, while the peaks at between 1610 and 799 cm^{-1} are due to C=O and C=N stretching groups. The presence of band at 3336 $cm^{-1}$is due to bonded OH groups, which indicates the presence of water of crystallization. According to the FTIR spectra, the location where the chemical reaction took place during the preparation of PVBC may be proposed in Figure 4.2.

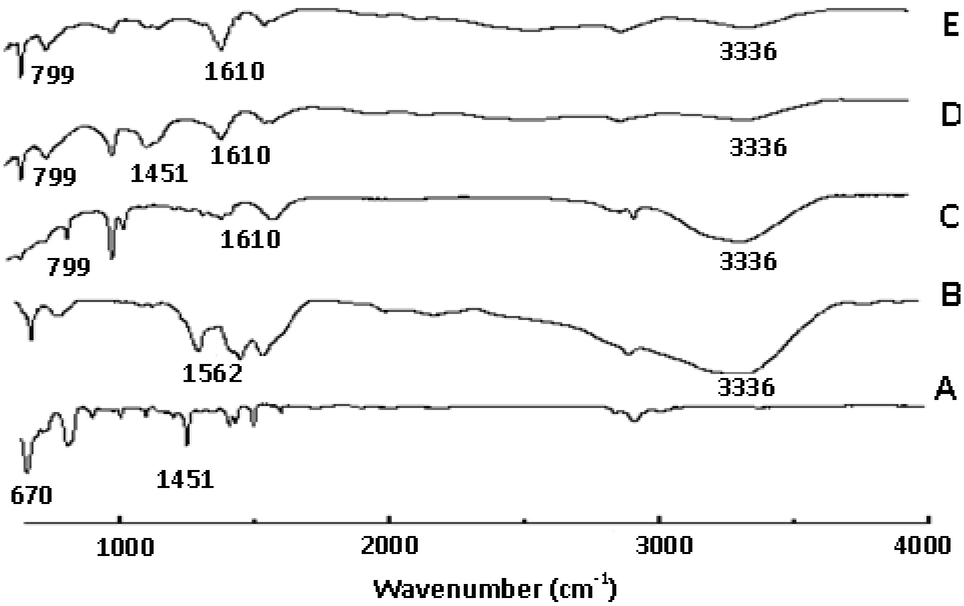


Figure 4.2: FTIR absorption spectra for the unfunctionalized polyvinylbenzylchloride (A), functionalized PVBC (B) and the quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) (C, D and E) nanofibres.

4.2.3 FTIR showing the desorption Studies of Functionalized PVBC (R′ = C_2H_5 and C_3H_7) nanofibers using 0.1 M NaOH.

The FTIR studies after desorption using 0.1 M NaOH in figure 4.3 shows some significant changes. The band at peak 1562 cm^{-1} which can be assigned to N-H group of the amine disappeared completely in the FTIR spectra after desorption as shown in figure 4.3

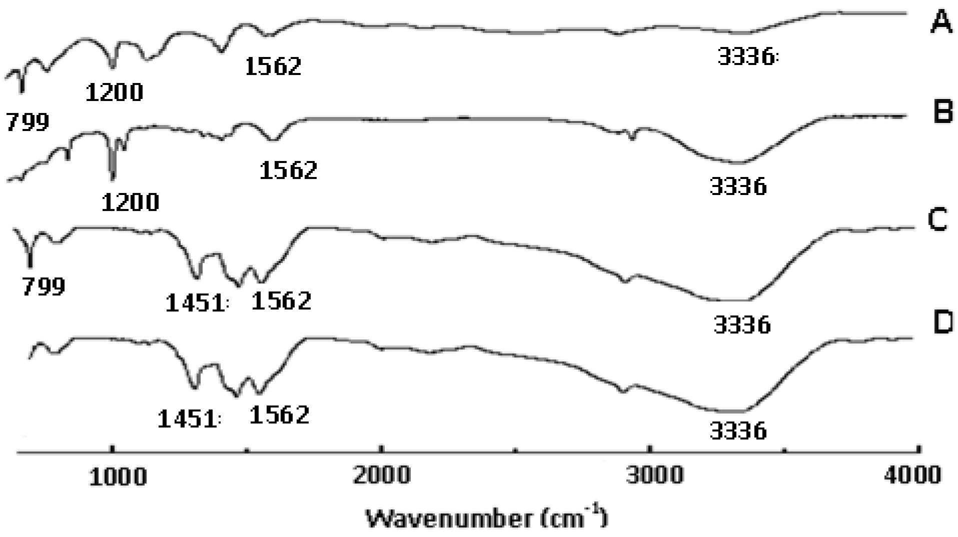


Figure 4.3: FTIR spectra for (A) and (B) shows before desorption studies, (C and D) after desorption using 0.1 M NaOH for the functionalized polyvinylbenzylchloride PVBC (R′ = C_2H_5 and C_3H_7) nanofibres.

4.3. CHNS Microanalysis of APPMKNFs

The results of the CHNS microanalysis are listed in Table 4.1 for the unfunctionalized and the functionalized APPMKNFs. It was evident that, the nitrogen content in the unfunctionalized polymer was absent, and the nitrogen present after functionalization of the polymer with 2, amino-4,6dihydroxylpyrimidine is shown in the Table 4.1.

Table 4.1: CHNS Microanalysis

APPMKNFs	C (%)	H (%)	N (%)
Unfunctionalized polymer	90.91	6.45	
Functionalized polymer	54.42	6.81	38.49

4.4 Energy Dispersive X-ray Spectrometer (EDS) Used for PVBC

The EDS is coupled to a Scanning Electron Microscope (SEM). The obvious advantage of EDS elemental analysis over conventional chemical analysis is that, elemental composition of selected phase can be analysed in a bulk sample.

In order to get more structural information and understanding on the adsorption mechanism of the unfunctionalized and the functionalized PVBC, an energy dispersive x-ray spectrometer (EDS) was used to investigate the elemental composition of the fibers as shown in Figures 4.4 and 4.5. The EDS detects X-rays from the sample when excited by the highly focused, high-energy, primary electron beam, penetrating into the sample. Comparing EDS images of unfunctionalized and functionalized PVBC, Fig. 4.4 shows the removal of Chlorine and this confirms that the fibers were functionalized with the presence of Nitrogen as clearly observed in the EDS spectra and this was in corroboration with FT-IR results.

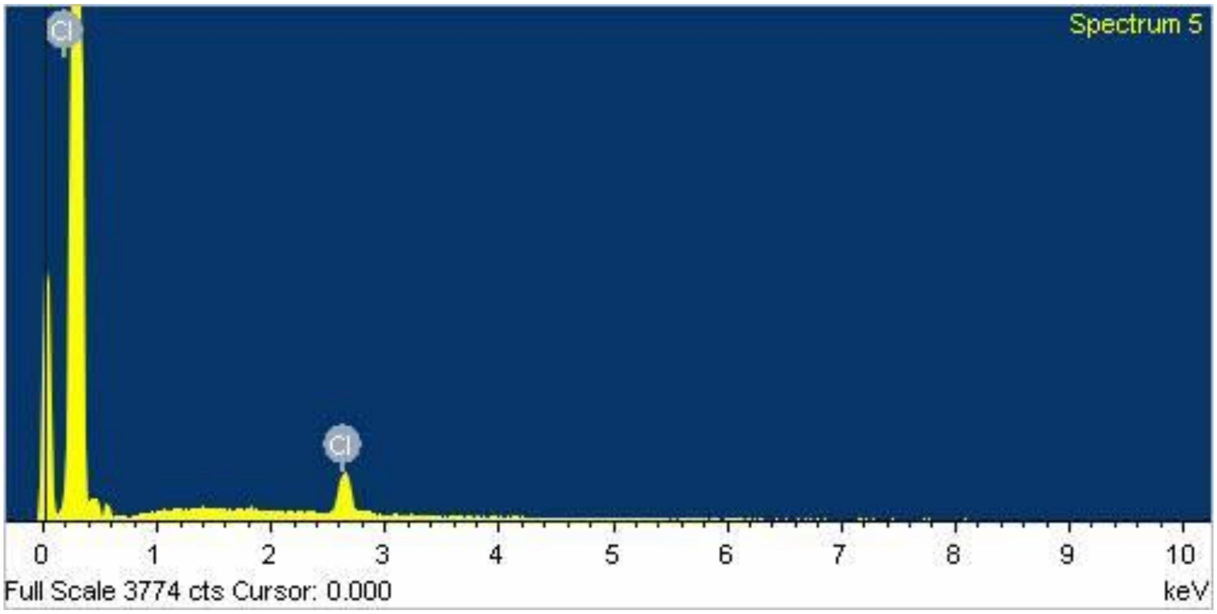
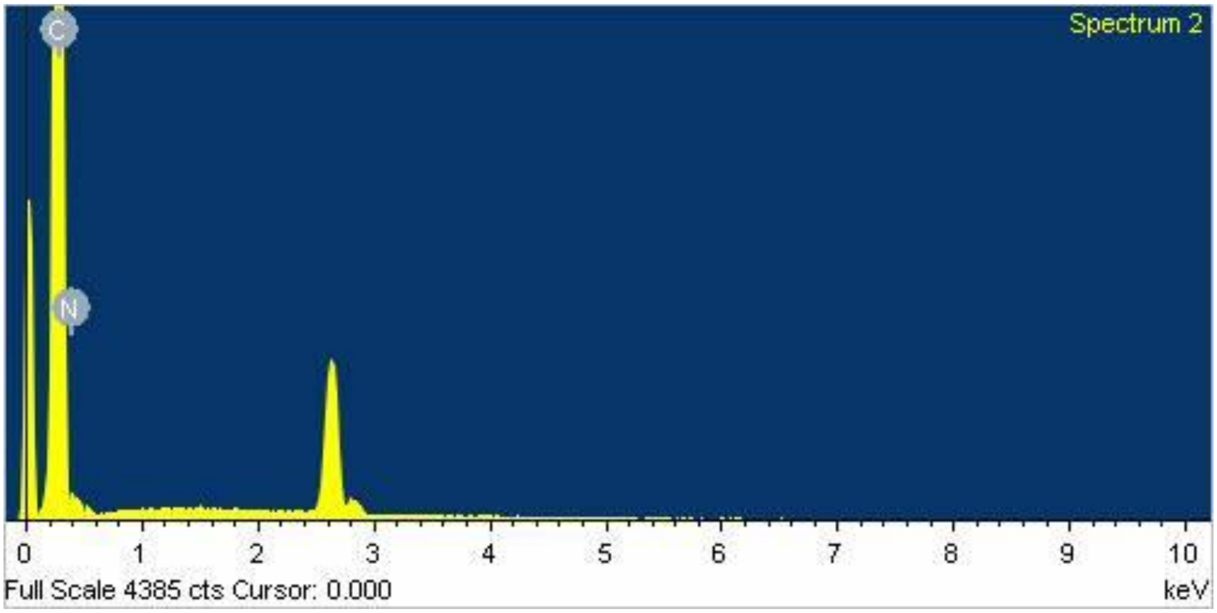


Figure 4.4: EDX spectra of unfunctionalized PVBC nanofibre



Figures 4.5: EDX spectra of quaternized PVBC nanofibers.

4.5 Scanning Electron Microscopy (SEM)

Electrospinning is a technique that utilizes the electric force to drive polymer fluid and to produce polymer nanofibers. The shear viscosity, electric conductivity and surface tension of the polymer solution are the most important properties affecting the formation of nanofibers (Bhuvanesh *et al.*, 2007).

The increase in polymer concentration could adversely affect the cohesiveness of the liquid, thus leading to reduction in the surface tension of the polymer in solution.

The SEM images of the electrospun nanofibers (APPMKNFs and PVBC) are shown in figure 4.6 For the solution less than 10 %(w/v) for APPMKNFs and 25 %(w/v) PVBC, a droplet spray occurred and a continuous jet of polymer particles was formed. The jet from low viscosity solutions breaks up into droplets due to the lower amount of polymer. At solution concentration of 10 % (w/v) APPMKNFs and 25 and 30 %(w/v) PVBC, the presence of beads were observed, but the beads were completely disappeared and the formation of fibers were observed when the concentration of the solution was increased to 20 %(w/v) APPMKNFs and 30, 40 and 45 %(PVBC). It is believed that, the relatively high viscosity of the solution, voltage and distance made the morphology of the fiber to improve. The best optimum condition for the morphology used for APPMKNFs was 20 %(w/v) with diameter 127-200 nm, and the morphology for PVBC was observed with 45 %(w/v) solution, with diameter ranging from 650 – 680 nm.

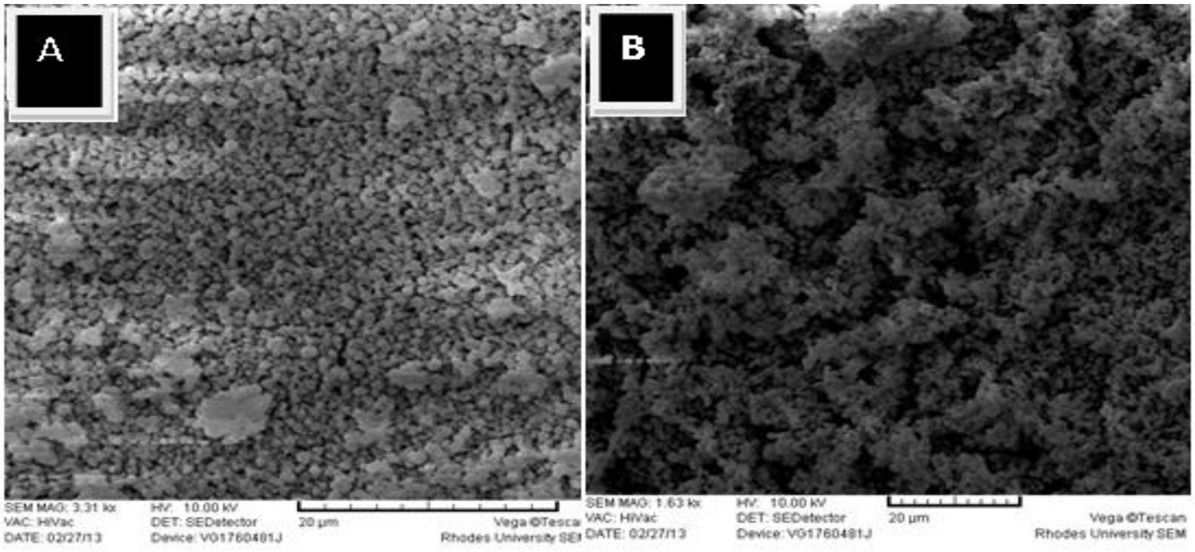


Figure 4.6 SEM images (scale bar = 20 µm) showing the morphology (particles) of electrospun nanofibers from APPMKNFs at concentration of (A) 5 % w/v (B) 7.5 % w/v (voltage of 12 Kv and at a constant spinning distance of 13 cm).

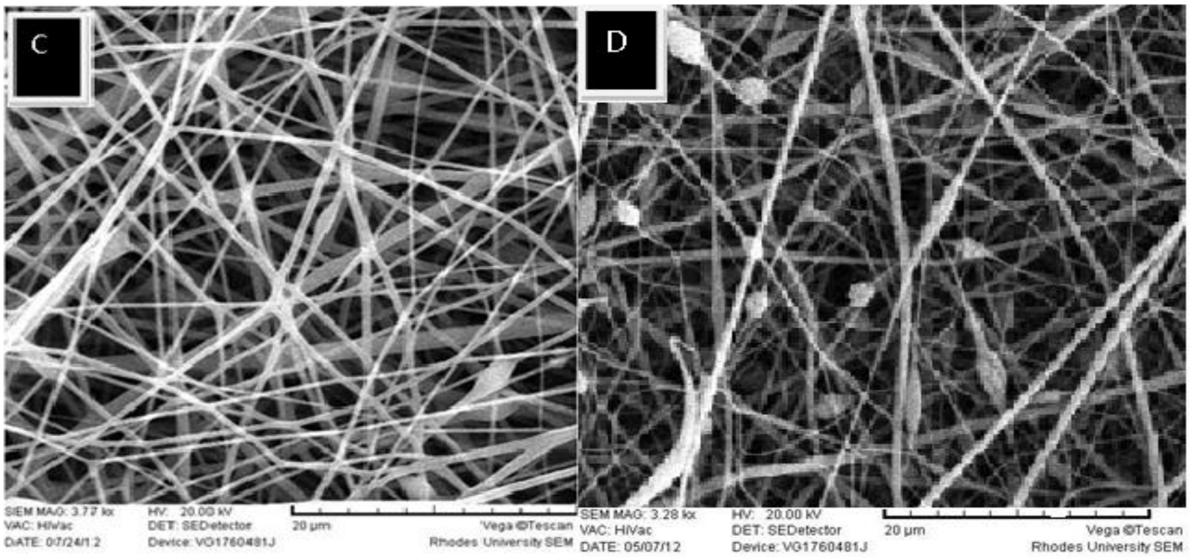


Figure 4.6.(a) SEM images (scale bar = 20 μm) showing the morphology of (beeded) electrospun nanofibers from APPMKNFs at concentration of (C) 10 % w/v (D) 15 % w/v voltage of 12 Kv and at a constant spinning distance of 13 cm).

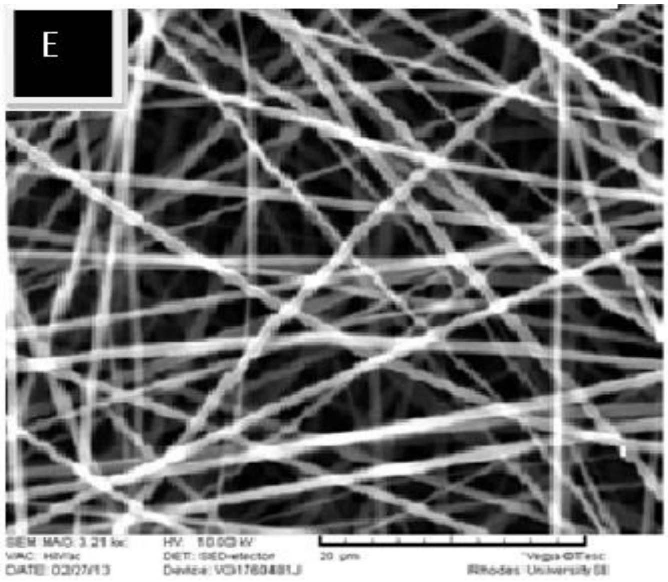


Figure 4.6.(b) SEM images (scale bar = 20 μm) showing the morphology of (beed free) electrospun nanofibers from APPMKNFs at concentration of (E) 20 % w/v. (voltage of 12 Kv and at a constant spinning distance of 13 cm).

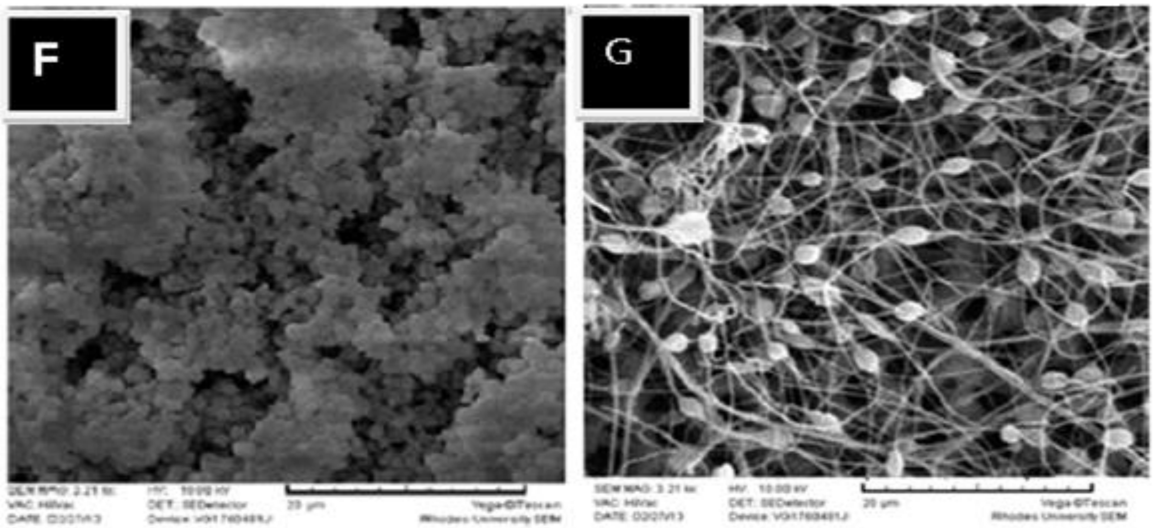


Figure 4.6.(c) SEM images (scale bar = 20 μm) showing the morphology of fibers electrospun from PVBC solutions at concentration of (F) (particles) 20 % w/v (G) (beeded) 25 % w/v. (voltage of 15 Kv and at a constant spinning distance of 15 cm).

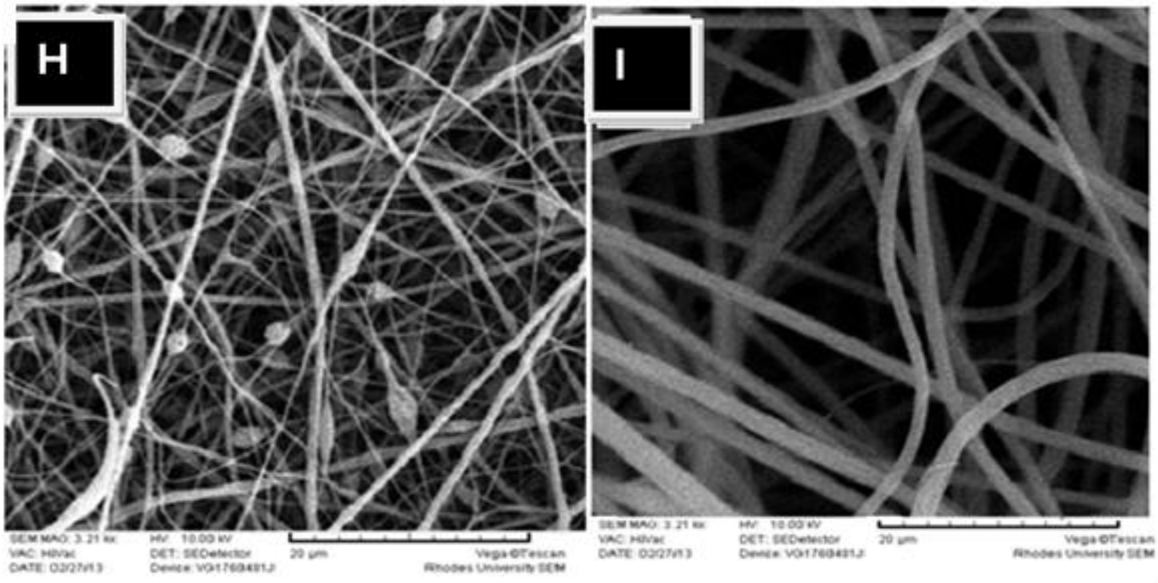


Figure 4.6.(d) SEM images (scale bar = 20 µm) showing the morphology of fibers electrospun from PVBC solutions at concentration of (H) (beeded) 30 % w/v (I) (beed free) 35 % w/v. (voltage of 15 Kv and at a constant spinning distance of 15 cm).

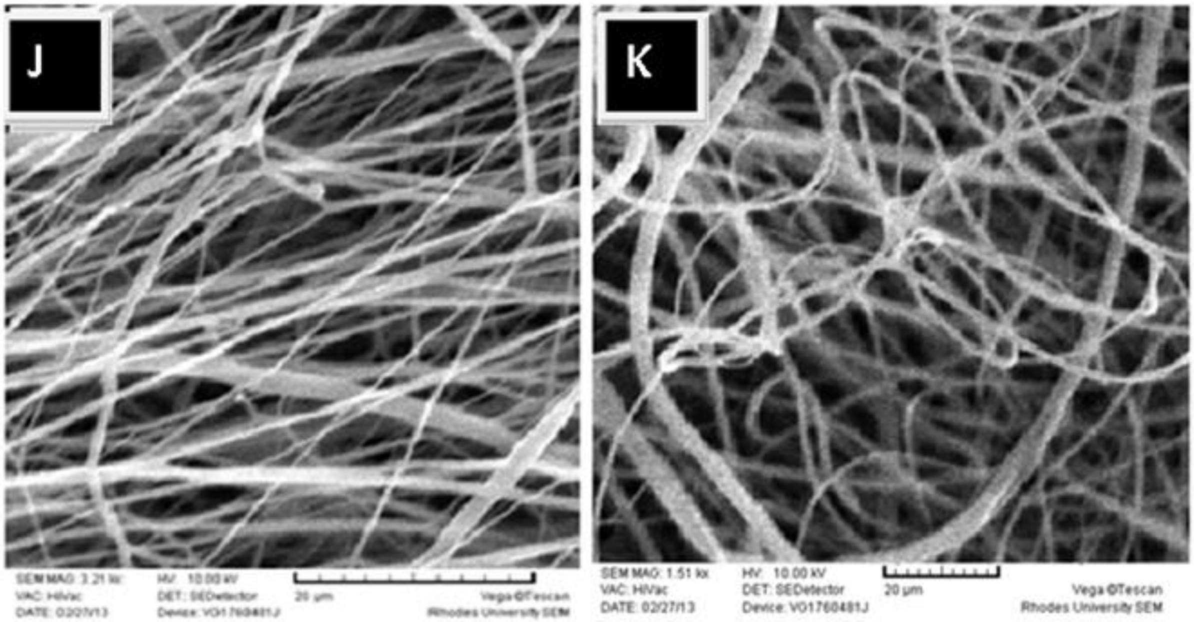


Figure 4.6.(e) SEM images (scale bar = 20 µm) showing the morphology of fibers electrospun from PVBC solutions at concentration of (J) 35 % w/v (K) 40 % w/v. (voltage of 15 Kv and at a constant spinning distance of 15 cm).

The morphology of the functionalized PVBC nanofibers is shown by the SEM images presented in Figure 4.6.(e).K

The functionalized PVBC nanofiber materials containing the amine (EDA) groups shows a slight difference with a change in morphology during functionalization and the fibers were not damaged. The fiber diameter range was 665-769 nm. This shows a slight increase in the fiber diameter after the functionalization with EDA.

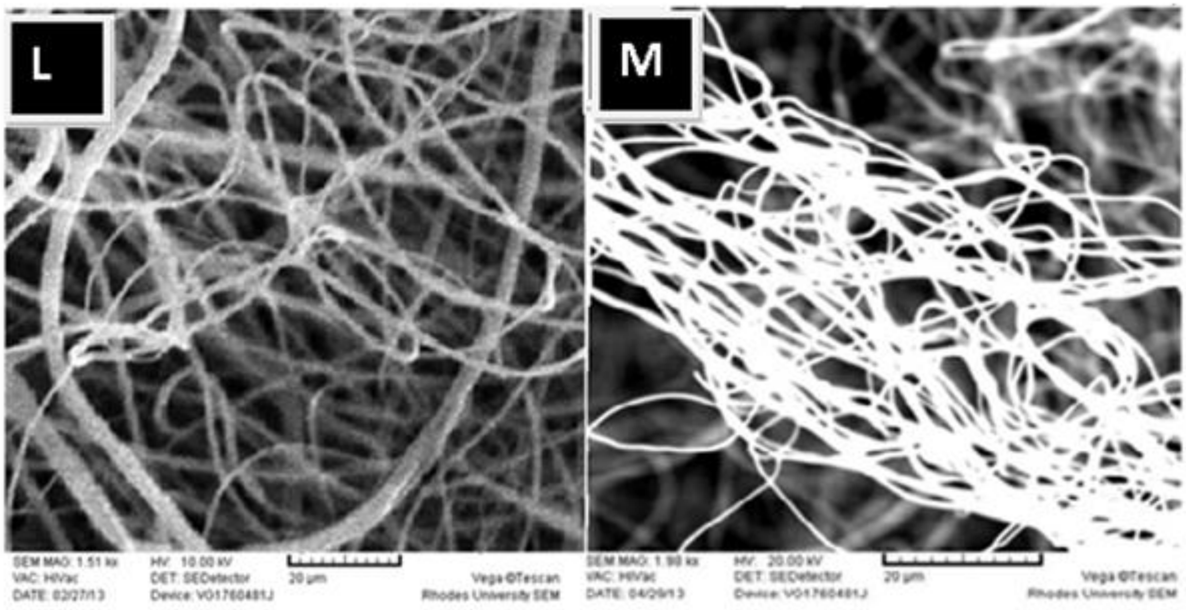


Figure 4.6.(f) SEM images (scale bar = 20 μm) showing the morphology of of nanofibers (L) unfunctionalized fiber and (M) functionalized fiber with EDA,

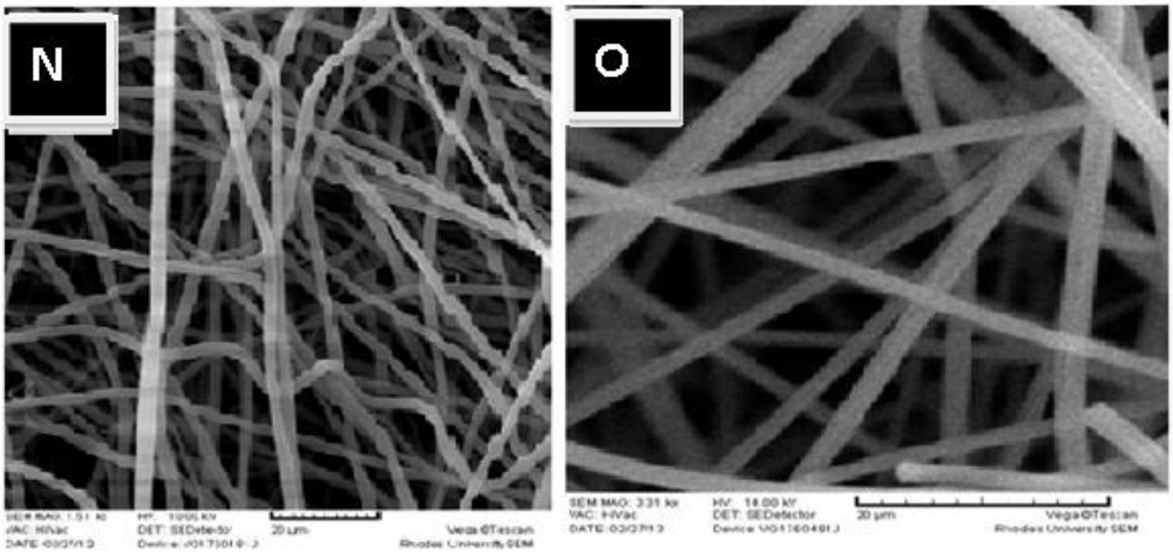


Figure 4.6.(g) SEM images (scale bar = 20 μm) showing the morphology of nanofibers (N) quaternized fiber with CH_3 and (O) quaternized fiber with C_2H_5

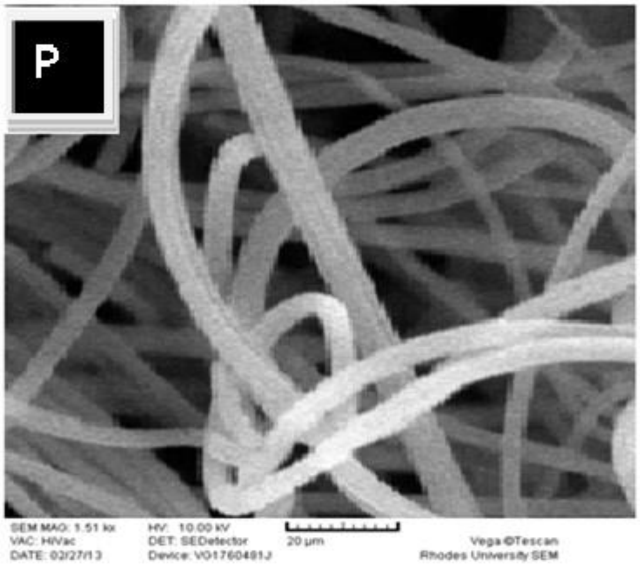


Figure 4.6.(h) SEM images (scale bar = 20 μm) showing the morphology of of nanofibers (P) quaternized fiber with C_3H_7.

4.6 X-ray Defraction Analysis (XRD)

Figure 4.7(a) shows the spectrum of the PVBC with a broad peak at 20 in 2θ degree axis which indicate the absence of Nitrogen. The sharp peak on Figure 4.7(b) at 40 in 2θ degree axis is assigned to the N in the NH_3^+ groups on the surface of the functionalized PVBC (Pel et al. 1995; Li *et al.,* 2007), verifing that, the enhanced nitrogen content on the fiber surface was from amine groups.

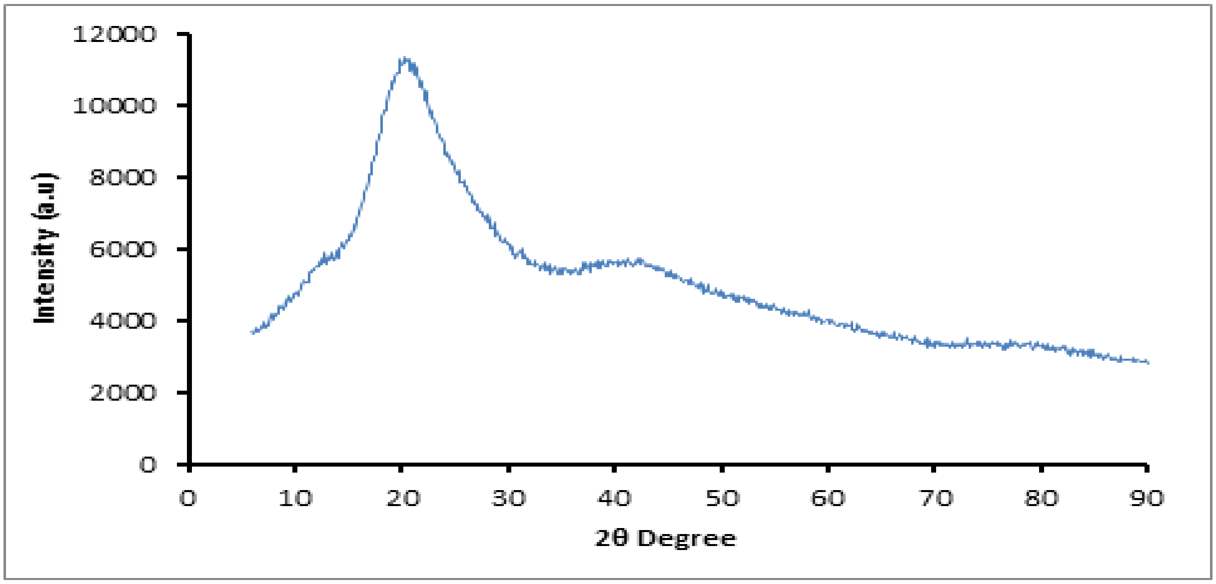


Figure 4.7 (a): shows the XRD pattern of the unfunctionalized PVBC

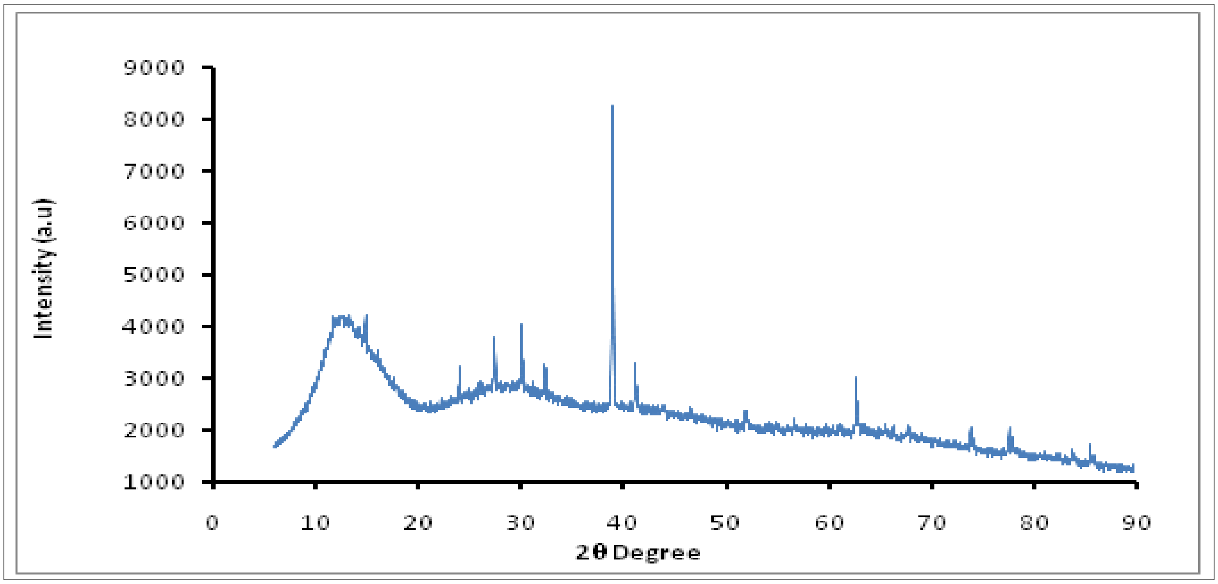


Figure 4.7 (b): Shows the XRD pattern of functionalized PVBC with EDA

4.7 BET Surface Area

The specific surface area of the sorbent defines its efficiency for adsorption. The surface area of APPMKNFs, unfunctionalized and the functionalized PVBC nanofiber materials were measured, using the BET method and the results are presented in Table 4.2.

Table 4.2: BET single point surface area measurements for APPMKNFs, unfunctionalized and functionalized PVBC sorbent materials.

MATERIALS	APPMKNFs	UNFUNCTIONALIZED PVBC	FUNCTIONALIZED PVBC
m^2/g	114.2 m^2/g	341.1 m^2/g	243.3 m^2/g

It was observed that, the surface area of the sorbent materials (PVBC) changed after the functionalization with amine. When quaternized after the functionalization with the alkyl groups (CH_3, C_2H_5 and C_3H_7) it can be concluded that the surface area of the sorbent materials was reduced as shown in Table 4.2.

4.8 The Effect of Initial Solution pH on the Removal of Arsenate using APPMKNFs and Quaternized PVBC Nanofibers from Wastewater. Operation Performed Thrice, N = 3.

4.8.1. The Effect of Solution pH on the Removal of Arsenate using APPMKNFs

The removal rate of arsenic was affected by the pH as shown in Figure 4.8 a, using 10.0 µg/l As(V). The pH of the medium is one of the most critical parameter in the adsorption process of arsenic from aqueous solutions. The pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature of the physic chemical interaction of the species in solution and the adsorptive sites of adsorbents (Chiban *et al.*, 2011d).

The solution pH is an important factor for all water and wastewater treatment processes. Therefore, experiments were performed in order to investigate the effect of pH of solution on the removal of arsenic(v) from wastewater. Figure 4.8 a shows the percentage removal of As(v) as a function of effect of pH between 3 and 12. This shows that, arsenate species are ionic in this pH range. The As(v) at the pH value of 3.0 is present in anionic form and therefore, it can be effectively removed by APPMKNFs adsorbent which has a high specific surface area and abundant surface hydroxyls. The test results exhibited that the functionalized (APPMKNFs) has a high removal capacity towards As(v) via hydrogen bonding. The highest removal efficiency being at pH 3.0 (99.27%) was chosen as an optimum pH condition for further experiments. Above pH 8.0 As(v) removal was found to be decreased due to the negative charge on the sorbent material leading to electrostatic repulsion on ions that surrounded the surface of the adsorbent by hindering the approach of As(v) to the adsorption sites present on the surface of the adsorbent.

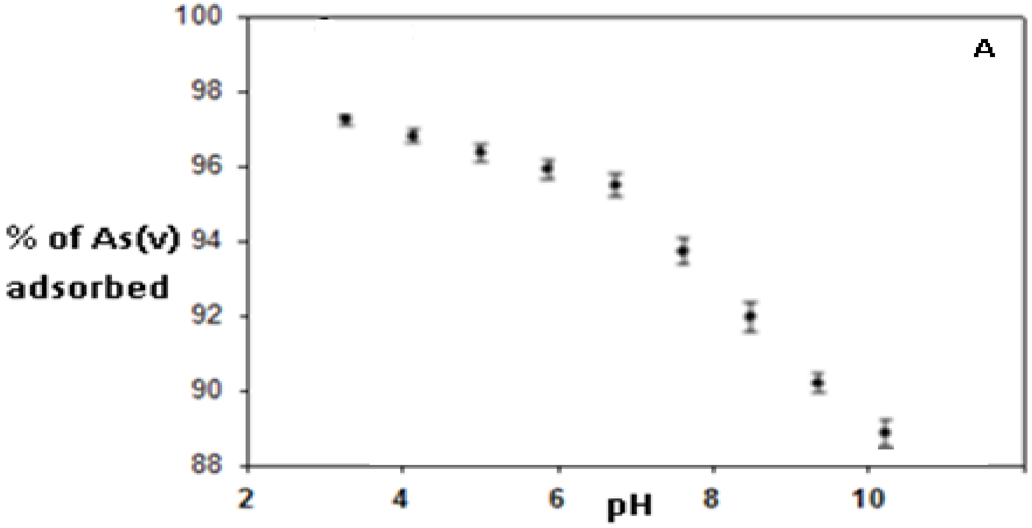


Figure 4.8(a): Effect of initial (A) solution pH on the adsorption of As(V) onto APPMKNFs. (Experiment conditions employed: initial As(v) concentration 10

µg/L, adsorbent dosage 12.0 mg/L, adsorption time 30 min, agitation speed 150 r/min). n = 3

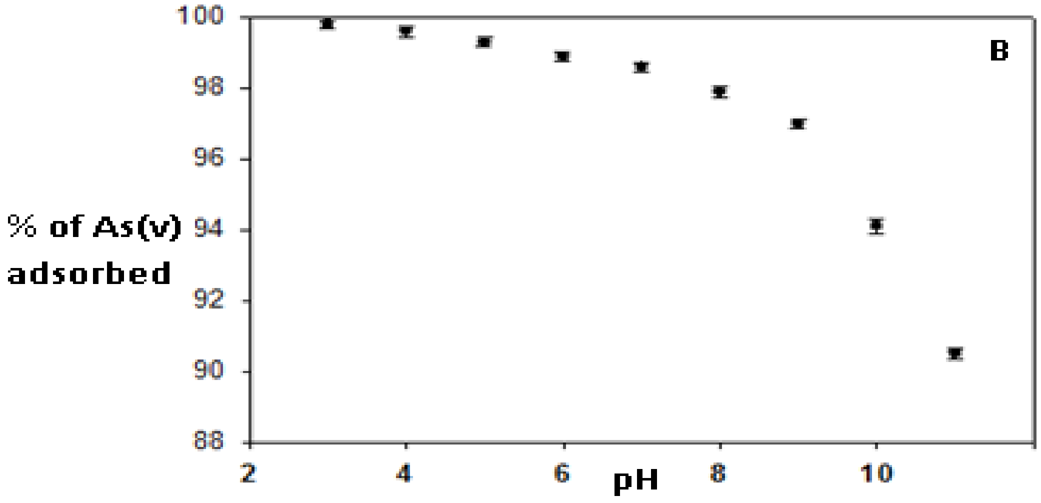


Figure 4.8.(a): Effect of final (B) solution pH on the adsorption of As(V) onto APPMKNFs. (Experiment conditions employed: initial As(v) concentration 10 µg/L, adsorbent dosage 12.0 mg/L, adsorption time 30 min, agitation speed 150 r/min). n = 3

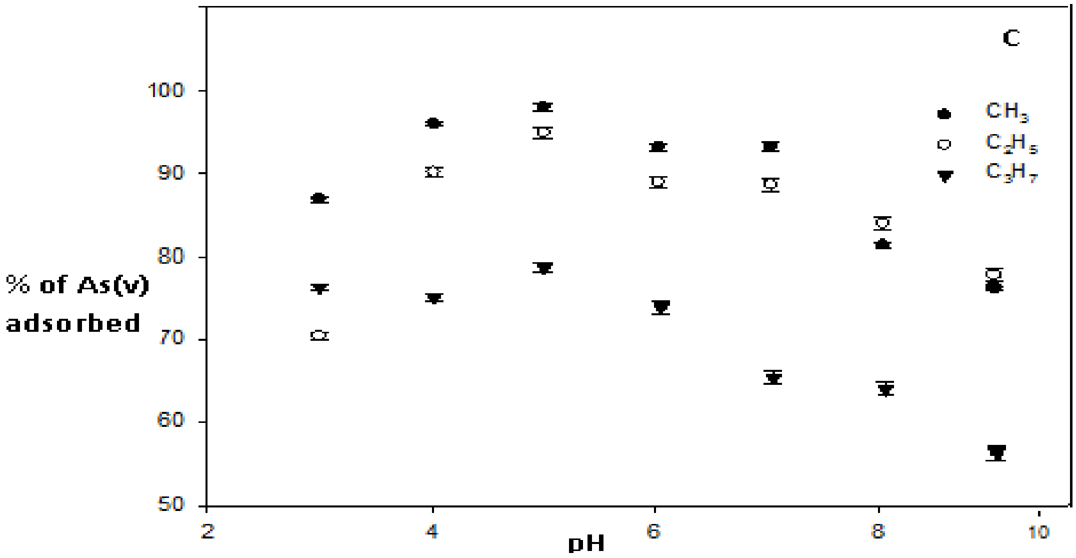


Figure 4.8 (b): Effect of initial(C) solution pH on arsenate removal onto quaternary PVBC (R′ = CH_3, C_2H_5 and C_3H_7) nanofibres (n = 3). (Experiment conditions employed: initial As(v) concentration 10 µg/L, adsorbent dosage 5.0 mg/L, adsorption time 30 min, agitation speed 150 r/min).

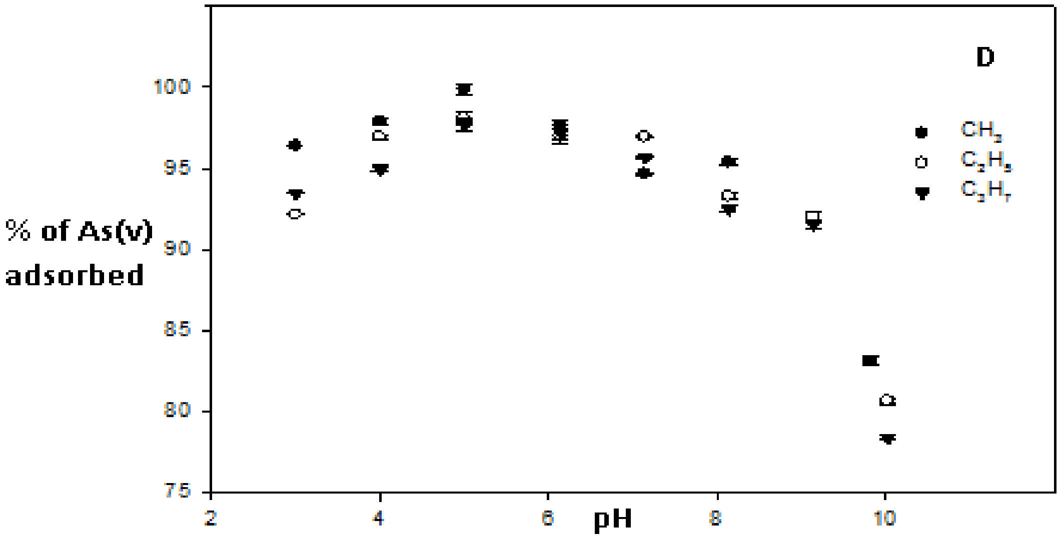


Figure 4.8 b: Effect of final (D) solution pH on arsenate removal onto quaternary PVBC (R′ = CH_3, C_2H_5 and C_3H_7) nanofibres (n = 3). (Experiment conditions employed: initial As(v) concentration 10 µg/L, adsorbent dosage 5.0 mg/L, adsorption time 30 min, agitation speed 150 r/min).

Figures 4.8 (a) and 4.8 (b): Show the optimum pH for arsenate removal was 5.0 for the three quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) nanofibres. The solutes interact with mineral surfaces due to their electrical surface charge and because of the ionic interactions involving the functional groups (NH_4^+, H^+ and OH^-) on the surface of nanofibres (R′ = CH_3, C_2H_5 and C_3H_7 quaternized PVBC) as well as ions in the solution. The adsorption amount for arsenate was 99.7 %, 97.31 % and 95.47 % respectively for the quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) were obtained. The solution pH does not only affect the charge property on the quaternized PVBC surface through the protonation of the amine groups, but also influenced arsenate speciation in solution. Arsenate exists in the surface of water as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} in aqueous solution. $H_2AsO_4^-$ is the main species in solution at pH 3 to 6, while $HAsO_4^{2-}$ and AsO_4^{3-} becomes the major species at the pH range studied. The electrostatic attraction plays an important role in the sorption process. The amine groups were first protonated in the acidic mediun of the solution and thus, adsorbed more of negative arsenate which means that more of the arsenate groups were found at lower pH. When the solution pH was increased, the number of protonated amine groups on sorbent materials appeared to have been de-quarernized due to N-H group of the amine group on the sorbent material at a higher pH. As a consequence, the sorption amount on the quaternized PVBC sorbent material for arsenate decreased as the pH increases (Shubo *et al.*, 2008; Ismail, 2012).

4.8.2 Treatment Technology of Arsenate using APPMKNFs and Quaternized PVBC Nanofibers

The treatment was conducted by adsorption method to assess the efficiency and effectiveness of the synthesized nanofibres.

4.8.3: Effect of Adsorbent Dosage of Arsenate Removal onto APPMKNFs

The effect of adsorbent dosage on percentage adsorption of As(v) was shown in Figure 4.8 (c) and the removal efficiency of As(v) considerably increased with the increase of adsorbent dosage. The increase in adsorbent dosage from 2.0 to 12 mg/L resulted inan increase from 558 to 98.7% in adsorption of As(v). This may be due to the greater availability of the exchange able sites or surface area at higher concentrations of the adsorbent. On the other hand, the increase inthe efficiency of removal may be attributed to the fact that with an increase in the adsorbent dosage, more adsorbent surface or more adsorption spots were available for the solute to be adsorbed (Kord Mostafapour *et al.*, 2013; Bazrafshan *et al.*, 2013; Pandey *et al.*, 2009). A further increase in adsorbent dosage (> 12 mg/L) did not cause significant improvement in As(v) adsorption. This may be due to the adsorption of almost all As(v) to the adsorbent and the establishment of equilibrium between the As(v) adsorbed to the adsorbent and those remaining unadsorbed inthe solution. The results of this study are in accordance with obtained findings by other researchers (Li *et al.*, 2012; Kord Mostafapour *et al.*, 2013; Bazrafshan *et al.*, 2012).

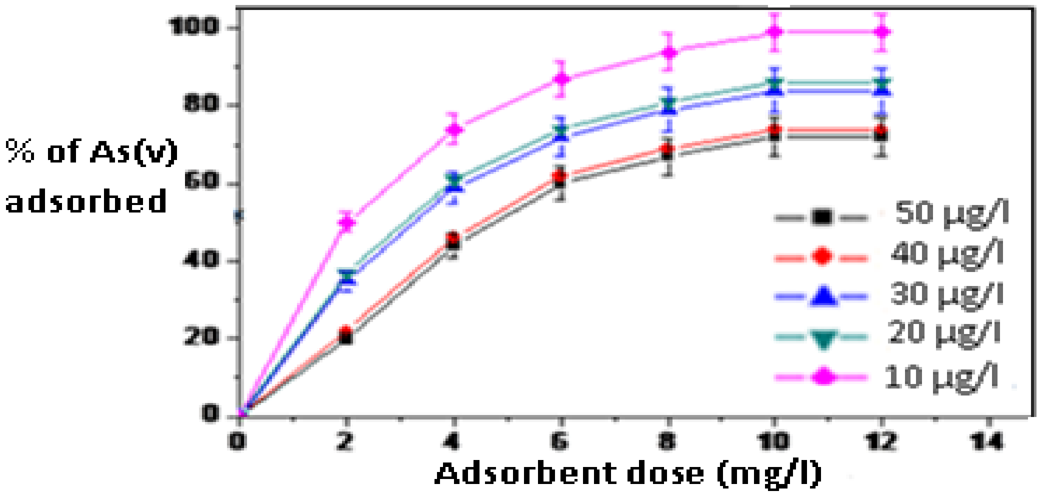


Figure 4.8 (c): Effect of arsenate concentration and adsorbent dosage on arsenate removal onto APPMKNFs (n = 3). (Experiment conditions employed: initial As(v) concentration10 µg/L, solution pH 3.0, adsorption time 30 min, agitation speed 150 r/min).

4.8.4 Effect of Adsorbent Dose on Arsenate Removal onto PVBC Nanofibers

The criteria for selection of suitable adsorbent materials include: the cost of the medium, the ease of operation or handling the cost of operation, the useful service life per cycle the adsorptioncapacity of the adsorbent, the potential of reuse and the possibilities of regeneration of adsorbent.

Figures 4.8 (d), 4.8 (e) and 4.8 (f) shows the effect of adsorbent dose on percentage removal of As(v). The figure reveals that, uptake of As(v) increases rapidly from 2 to 5 g/l, and marginally thereafter due to more surface area, with increase in adsorbent dose (Gupta *et al.*, 2005). The sorption curve is a typical sigmoidial curve that indicates an increase in sorption as the sorbent dose is increased. The curve beveled off, indicating exhaustion of sorption reaction through a good amount of sorbent surfaces available to the sorbate – solvent interaction.

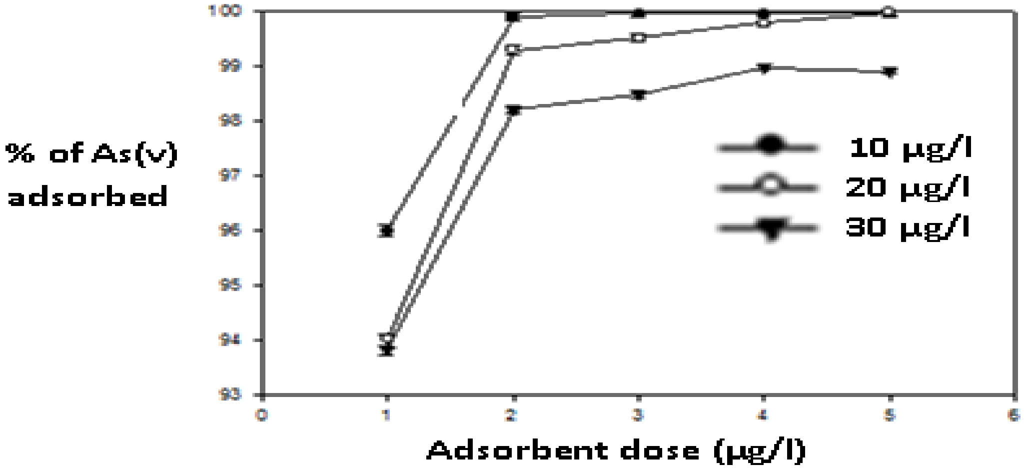


Figure 4.8 (d): Effect of arsenate concentration and adsorbent dosage on arsenate removal onto quaternary PVBC R′ CH_3 (n = 3). (Experiment conditions employed: initial As(v) concentration10 µg/L, solution pH 5.0, adsorption time 30 min, agitation speed 150 r/min).

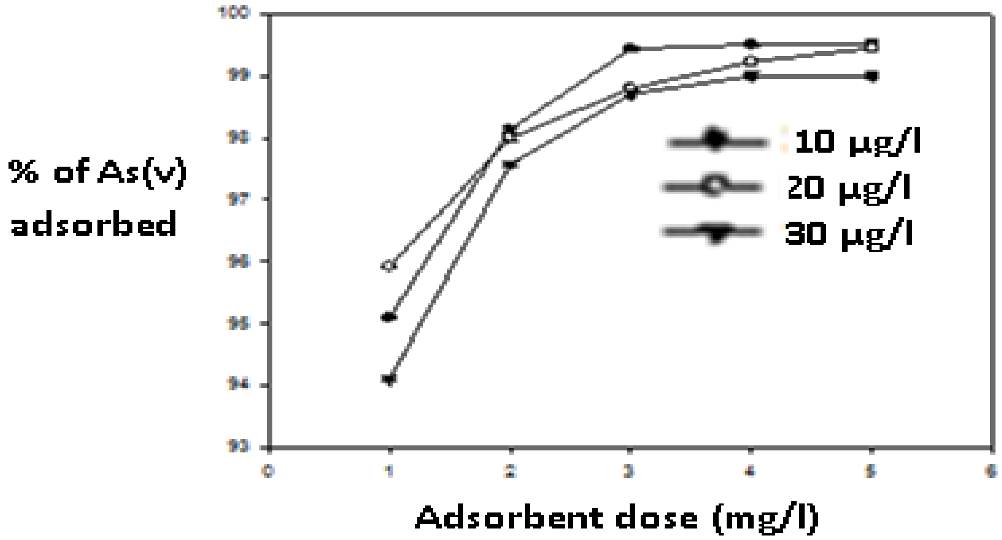


Figure 4.8 (e): Effect of arsenate concentration and adsorbent dosage on arsenate removal onto quaternized PVBC (R′ = C_2H_5) (n = 3). (Experiment conditions employed: initial As(v) concentration10 µg/L, solution pH 5.0, adsorption time 30 min, agitation speed 150 r/min).

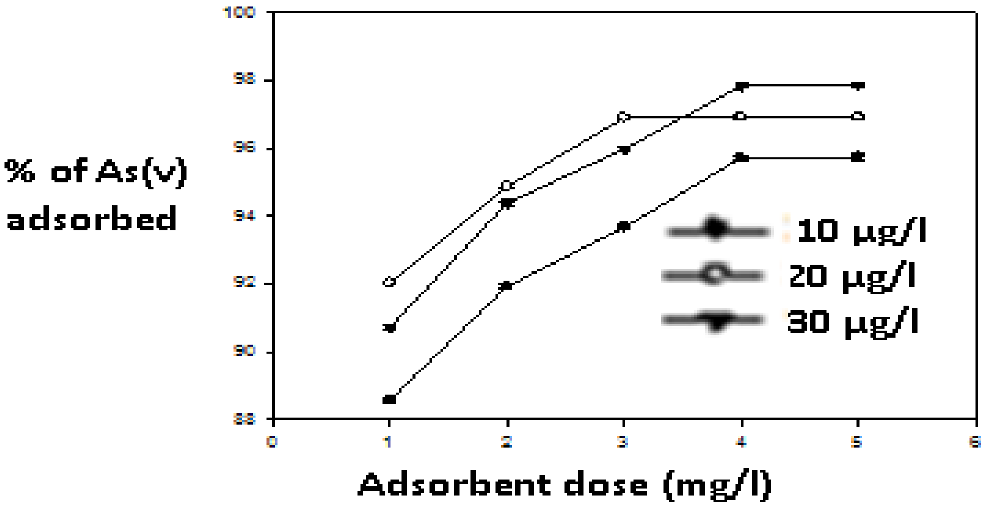


Figure 4.8 (f): Effect of adsorbent dosage on the adsorption of As (V) removal onto quaternary PVBC R′ C_3H_7 (n = 3). (Experiment conditions employed: initial As(v) concentration 10 µg/L, solution pH 5.0, adsorption time 30 min, agitation speed 150 r/min).

4.8.5 Adsorption Isotherms

Adsorption of anions on adsorbent for an adsorbate is an important factor to investigate (Yang *et al.*, 2007). The adsorption capacity values were calculated, using Langmuir isotherm [Eq. (1) and Freundlich equation Eq. (2)]

$$\frac{Ce}{Qe} = \frac{Ce}{Qm} + \frac{1}{(kaQm)} \qquad \text{Langmuir isotherm} \quad (1)$$

$$\log Q_e = \log_F + \frac{1}{n} logCe \qquad \text{Freundlich isotherm} \quad (2)$$

Where C_e [mg/L] is arsenate concentration

Q_e [mg/g] is adsorption equilibrium

Q_m [mg/g] is the theoretical saturation adsorption capacity of the monolayer

K_a [L/mg] is the theoretical maximum adsorption capacity and Langmuir equilibrium constant related to the theoretical maximum adsorption capacity.

K_f and n are the Freundlich constants, which are indicators of adsorption capacity and adsorption intensity.

Equilibrium data, commonly known as adsorption isotherm are basic requirements for desigining of adsorption system. In this work, the equilibrium data for As(v) onto APPMKNFs was evaluated with Langmuir and Freundlich models.

The adsorption data fitted the Langmuir more than the Freundlich isotherm. The Langmuir equation is used to describe a monolayer adsorption without adsorbate interaction. The values of correlation coefficient for the Langmuir model (R^2 = 0.9968) were higher than those of the Freundlich mode (R^2 = 0.8313), showing that the adsorption in the experiment better fits the Langmuir model.

Table 4.3: Parameters of Langmuir adsorption equation and Freundlich isotherms equation for adsorption experimental data for APPMKNFs

Isotherm	Values	Unit
Langmuir	145.1	Q_m (mg/g)
	1.05	K_a (mg/L)
	0.9968	R^2
Freundlich	0.563	K_F
	2.686	n
	0.8313	R^2

4.8.6: Adsorption Kinetics of Arsenate onto APPMKNFs and Quaternized PVBC

4.8.6.1 Adsorption Kinetics of Arsenate onto APPMKNFs

The effect of contact time on the As(v) removal efficiency was also investigated. The main purpose of the study was to establish the ideal conditions of the adsorbent capacity, by considering the contact time of the solution at the solid/liquid interface. Contact time is one of the effective factors in batch adsorption process. The effect of contact time on As(v) adsorption efficiency was shown in Figure 4.8(e) as it is shown that, the removal efficiency of As(v) onto the APPMKNFs composite adsorbent significantly increase during the initial adsorption stage (0–15 min) and then continued to increase at a relatively slow speed with contact time until a state of equilibrium was attained after 30 min. There was no significant change in As(v) removal rates after 15 min up to 30 min. Based on these results, 30 min was taken as the time of adsorption experiments. Generally, the removal rate of sorbate was rapid initially, but it gradually decreased with time until it reached equilibrium. This phenomenon can be attributed to the fact that, a large number of vacant surface site were available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Similar findings were reported by Kord Mostafapour *et al.*; 2013; Gulnaz et al., 2011.

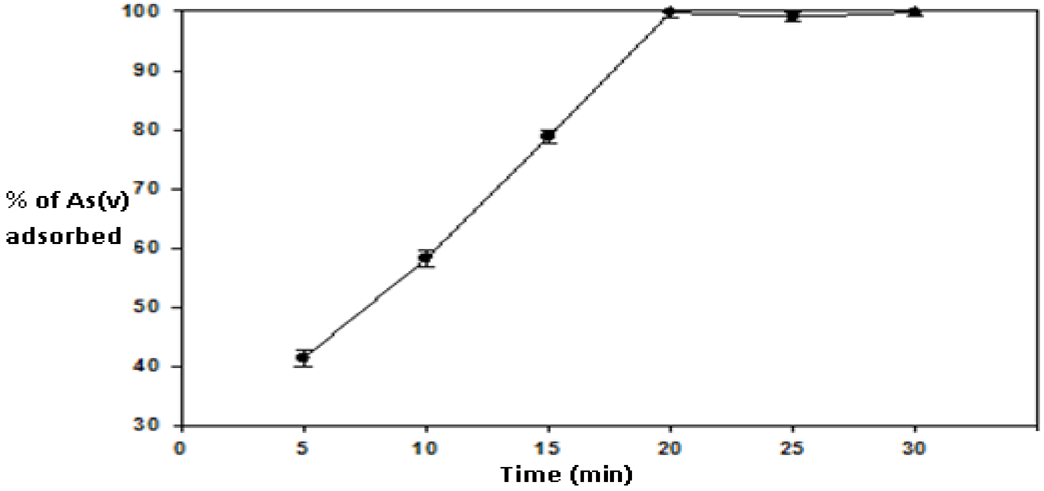


Figure 4.8(g): Adsorption kinetics for the removal of arsenate onto APPMKNFs (n = 3). (Experiment conditions employed: initial As(v) concentration 10 µg/L,adsorbent dosage 12.0 mg/L, solution pH 3.0, agitation speed 150 r/min).

4.8.6.2: Adsorption Kinetics of Arsenate Removals onto Quaternized PVBC (R' = CH_3, C_2H_5 and C_3H_7) (n = 3)

As noted above, the adsorption kinetics plays an important role in the efficiency of arsenate removal from a solution. The sorptive uptake of arsenate by quaternized ammonium nanofibre from water at a solution pH of 5.0 shows a graphic representation of percent of arsenate removal with contact time. In Figure 4.8 (f) below, the nanofibre quaternized with methyl group is the highest at 99.2 %, followed by ethyl and propyl groups at 97.92 % and 97.01 % respectively. Almost 100% removal occurred within 15 min for the methyl group and between 93% and 97 % was removed in 40 min for ethyl and propyl groups respectively. The percent sorption of sorbate as a function of contact time indicates a triphasic pattern, with an initial step portion, indicating a high rate of uptake. The rate of uptake was constant, which is represented by Figure 4.8(f). The high uptake of arsenate was due to the diffusion of arsenate from the bulk of the solution onto the surface of the sorbent, which is described as instantaneous sorption.

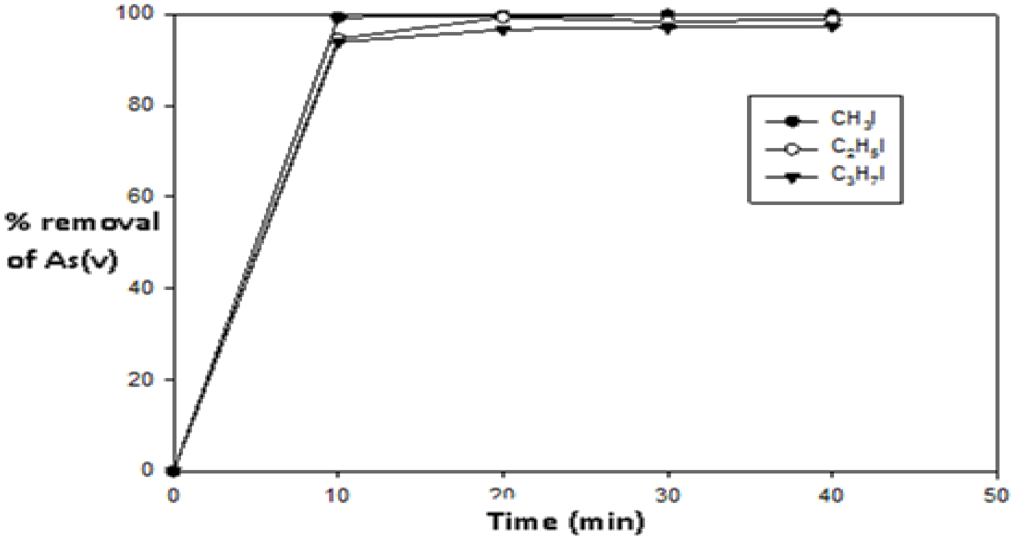


Figure 4.8(h): Adsorption kinetics of arsenate removals onto quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) (n = 3). (Experiment conditions employed: initial As(V) concentration 10 µg/L, adsorbent dosage 5.0 mg/L, solution pH 5.0, agitation speed 150 r/min).

4.9.7 Effect of Co-existing Anions of As(v) Removal onto APPMKNFs

In wastewater sources, several anionic components might exist, which could compete with arsenic for the available adsorption sites. Among the major co-existing anionic components, arsenate As(v), sulfate (SO_4^{2-}), chloride (Cl^-), are usually present in wastewater possibly inhibiting arsenic removal. In order to investigate the effect of co-existing ions on As(V) removal, standard arsenic solutions were spiked with SO_4^{2-} and Cl^- and also a blank were prepared respectively and the removal of arsenic was determined. At fixed pH of 3.0, the effects of different anions Table 4.4 showed that, sulfate and chloride caused the greatest percentage decrease in As(v) removal among the anions. Under the experimental conditions, chloride resulted in a bigger decrease in As(v) removal than sulfate. The effect of sulfate was minimal under the experimental conditions. It is well known that sulfate and chloride strongly adsorb to metal oxide surfaces via inner-sphere complexation similar to the interaction mode of arsenate with metal oxides (Bailey *et al*., 1999). In the blank sample, the significant reduction of As(v) adsorption capacity was due to SO_4^{2-} and Cl^- competing with As(v) for the hydroxyl group adsorption sites on APPMKNFs on the spiked sample as shown in the graph below (Table 4.4). Hence, the removal of As(v) is most significantly affected by sulfate and chloride.

Table 4.4: Effect of co-existing anions on adsorption of As(v) onto APPMKNFs using wastewater samples (n = 3). (Experimental conditions employed: initial As(v) and co-exisiting anions concentration 10 µg/L 30 µg/L, adsorbent dosage 12 mg/L, solution pH 3.0, agitation speed 150 r/min).

Sorbent material	**Anions**	**% of As(v) adsorbed**
APPMKNFs	Blank, $AsO_4$3-, SO_4^{2-} and Cl^-	99.79, 98.14, 72.35 and 63.21

The effect of co-existing anions on the removal of arsenate, using quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) was studied with spiked and standard solutions. The competitive sorption of the coexisting anions including; sulfate, chloride, nitrite and nitrate were studied in the spiked solution of arsenate containing 10 µg/L of the co-existing anions. There was no significant difference for the adsorption of arsenate in the presence of the co-existing anions. In light of these observations, we can say that the quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) are suitable materials for arsenate removal in the presence of the co-existing anion as shown in the Table 4.5.

Table 4.5: Effect of co-existing anions on the removal of arsenate onto quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7). (Experimental condition10 μg/L of arsenate and 30 μg/l of co-exisiting anions dosage 12 mg/L agitation speed 150 r/min) (n = 3).

Sorbent material	**Anions**	**% of As(v) adsorbed**
quaternized PVBC	Blank, AsO_4^{3-}, SO_4^{2-}, Cl^-	99.97, 97.95, 92.21
(R′ = CH_3)	and NO_2^-	89.89, 80.19 and 78.42
quaternized PVBC	Blank, AsO_4^{3-}, SO_4^{2-}, Cl^-	97.69, 95.01, 86.71
(R′ = C_2H_5)	and NO_2^-	86.10, 76.88 and 74.95
quaternized PVBC	Blank, AsO_4^{3-}, SO_4^{2-}, Cl^-	80.44, 79.00, 66.99
(R′ = C_3H_7)	and NO_2^-	61.22, 60.63 and 57.47

4.9.8 Desorption Studies of Arsenate onto APPMKNFs and Quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) Nanofibes (n = 3)

Desorption experiments were carried out to investigate the feasibility of regeneration of the used APPMKNFs and quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) adsorbent, after As(v) adsorption. Figures 4.9, 4.9.(a), 4.9.(b) and 4.9.(c) show the desorption efficiency of As(v) with 30 min and 40 min desorption time. The recovery efficiencies of As(v), using the four different sorbent materials.

The arsenate sorption capacity of the sorbent material in Figure 4.9 (APPMKNFs) shows that, there was a slight decrease, after the fifth cycles and this shows that the sorbent material was good and could be reused several times without loss of binding ability for arsenate, compared to the quaternized PVBC (R' = CH_3, C_2H_5 and C_3H_7) nanofibers which can be used four times. These results agree with the work of Gillman, 2006 and Chiban et al., 2009 that NaOH solution could be used as solvent to regenerate As(v) from the adsorbent materials.

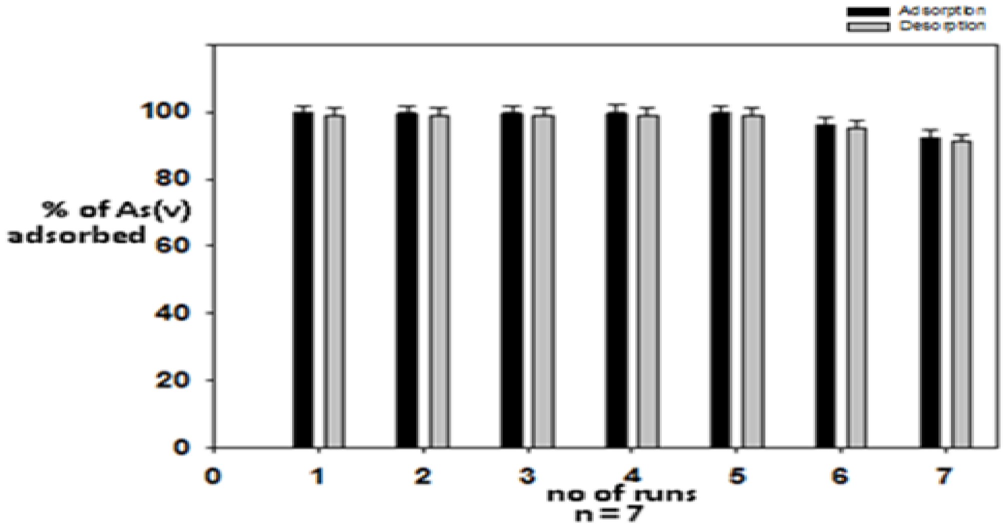


Figure 4.9 Reusability cycles on arsenate removal onto APPMKNFs pH = 3.0. (Experimental condition10 µg/L adsorbent dosage 12 mg/L agitation speed 150 r/min) (n = 6).

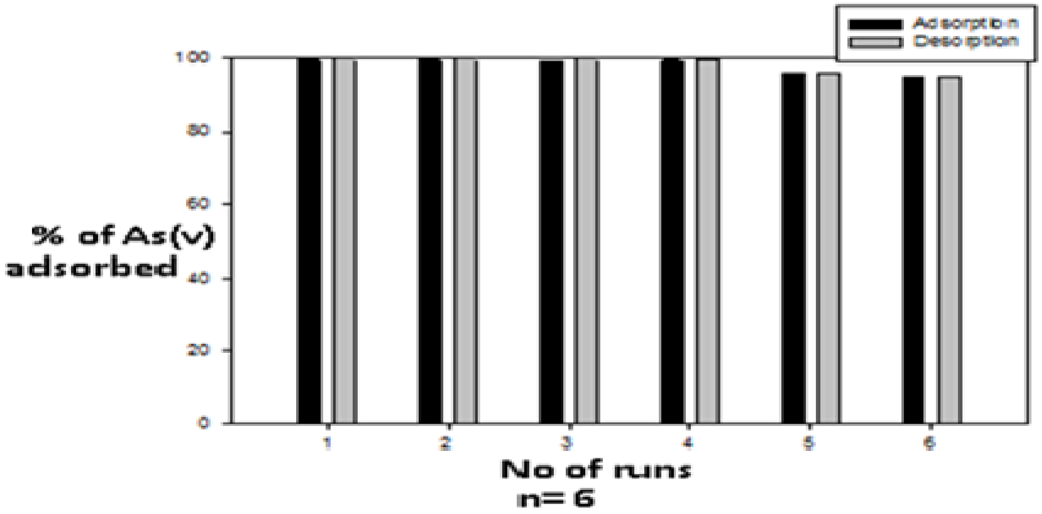


Figure 4.9.(a) Reusability cycles for arsenate onto quaternized PVBC (R′= CH_3) nanofibres pH = 5.0 (Experimental condition10 μg/L of arsenate adsorbent dosage 5 mg/L agitation speed 150 r/min) (n = 6).

Figures 49 (b and c) below are largely determined by the efficiencies of their recovery and the extent to which the adsorbed arsenate are desorbed. There was no significant change in the efficiencies of adsorption and desorption up to the 4th time of use. The decline in efficiencies after the 4th usage of the quaternized PVBC (R′ C_2H_5 and R′ C_3H_7) nanofibers could be attributed to the losses of amount of the sorbent during usage.

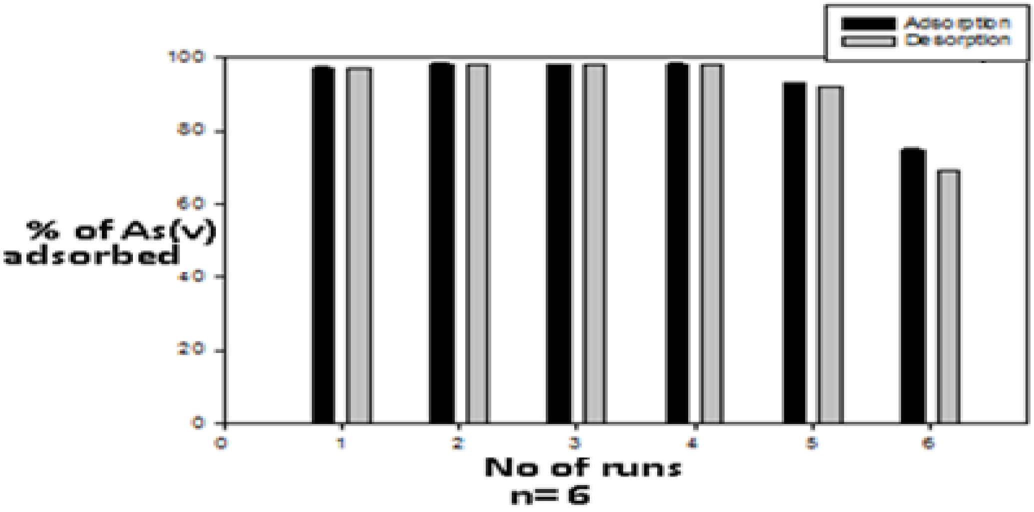


Figure 49.(b) Reusability cycles for arsenate removal onto quaternized PVBC (R′ C_2H_5) pH = 5.0 (Experimental condition10 μg/L of arsenate adsorbent dosage 5 mg/L agitation speed 150 r/min) (n = 6).

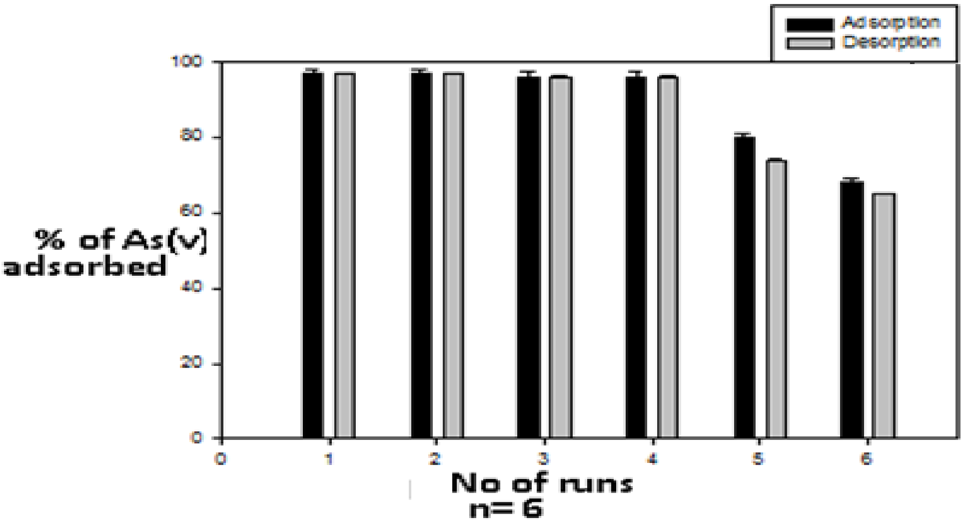


Figure 4.9.(c) Reusability cycles of arsenate removal onto quaternized PVBC R′ (C_3H_7) pH = 5.0. (Experimental condition10 μg/L of arsenate adsorbent dosage 5 mg/L agitation speed 150 r/min) (n = 6).

Kang *et al.*, (2007) reported that the binding abilities of the electrospun nanofibers for anions are dramatically enhanced when they are surface functionalized with ligands than the unfunctionalized electrospun nanofibers. From this study, functionalized electrospun nanofibers therefore used was found to exhibit excellent adsorbent for the removal of As(v) and PO_4^{3-} from wastewater. The anions adsorbed was easily leached back into solutions by pH adjustments in order to avail the As(v) and PO_4^{3-} for quantification. These remarkable features of synthesised polyvinylmethylketone with 2-amino-4,6-dihydroxylpyrimidine and polyvinylbenzylchloride electrospun nanofibers make them the preferred sorbent materials for the removal of arsenic(v) and PO_4^{3-} from wastewater.

CHAPTER 5

5.1 Treatment Technologies for Phosphate Removal onto Quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7)

This section presents and discusses the adsorption for the removal of phosphates from wastewater sample, the effect of pH, time and co-exisiting anions onto quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) nanofibers.

5.2 The Effect of Solution pH on Phosphate Removal onto Quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7)

Initial pH is usually considered to influence the adsorption of anions at the solid-liquid interfaces in aqueous systems. The adsorption of phosphate onto quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) nanofibres was investigated at pH values ranging from 3.0 to 10.0 starting with an initial phosphate concentration of 10mg/L, adsorbent dose of 1.00 mg/L. Figure 5.1 shows that phosphate adsorption onto PVBC (R′ = $CH_{3,}$ C_2H_5 and C_3H_7) nanofibres are strongly pH dependent. There are three prominent points in the measured adsorption at pH 3.0 and 6.0, 3 and 5.5 and 3 and 6 for (R′ = CH_3, C_2H_5 and C_3H_7). The adsorption of phosphate remained high within this pH range, and decreased dramatically beyond this pH range. A similar result was also observedby other researchers investigating phosphate adsorption onto aminated fibers (Namasivayam and Sangeetha, 2004). The observed trend is related to phosphate.

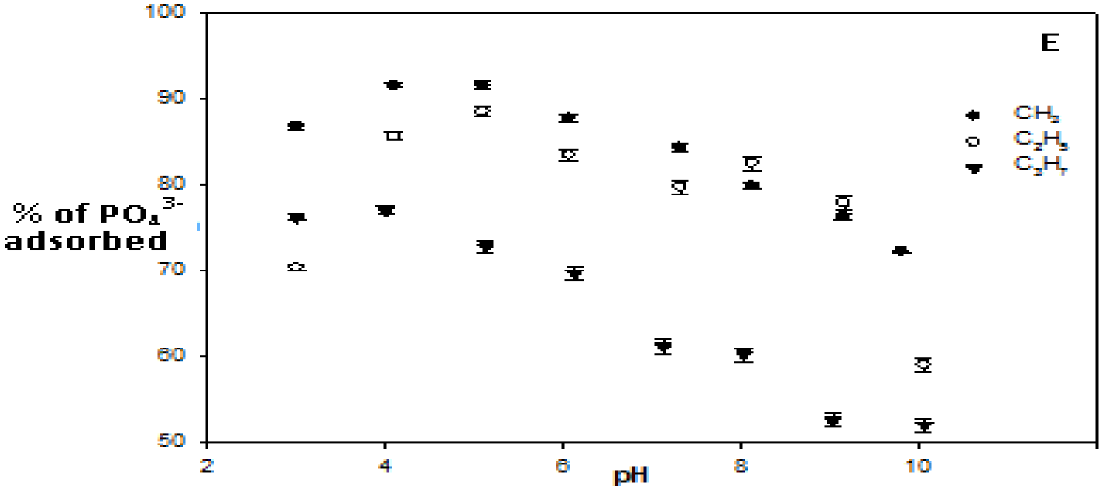


Figure 5.1: The effect of initial solution pH on phosphate removal onto quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7). (Experimental condition: concentration of phosphate 30 µg/l, adsorbent dose 5 mg/l pH 5.0, time 20 min agitation speed 120 r/min) (n = 3).

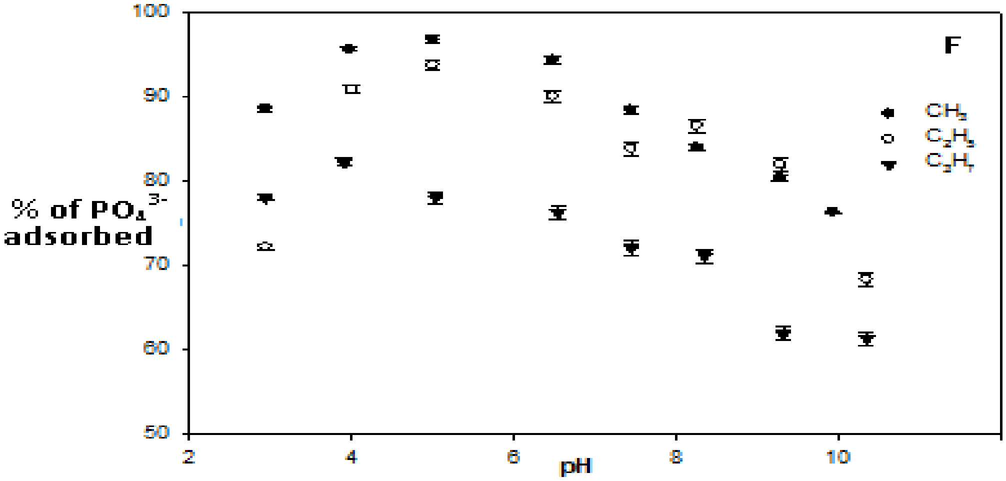


Figure 5.2: The effect of final solution pH on phosphate removal onto quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7). (Experimental condition:

concentration of phosphate 30 µg/l, adsorbent dose 5 mg/l pH 5.0, time 20 min agitation speed 120 r/min) (n = 3).

Proton dissociation equilibria, phosphate can exist as H_3PO_4, H_2PO^-, HPO_4^{2-} and PO_4^{3-}, depending on the solution pH value. Below pH 3.0, the predominant specieis H_3PO_4, which is weakly, bound to adsorbent sites. With the increase in solution pH, the dominant species are $H_2PO_4^-$ and HPO_4^{2-} which are readily adsorbed by the PVBC (R′ = CH_3, C_2H_5 and C_3H_7) sites on the adsorbent.

The R′ = CH_3, C_2H_5 and C_3H_7 on the quaternary PVBC prevents the functional group on the nanofibers to have affinity towards phosphate in solution at a high pH due to the sterric hinderance on the surface of the adsorbent and the analyte in solution. (Cumbal and Sengupta, 2005).

5.3 Effect of Adsorbent Dosage and of Phosphate onto Quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7)

Phosphorous removal increased with increasing adsorbent dose up to a specific level, and then it remained unchanged. The removal efficiency of phosphate increased substantially from 58.40 to 99.07 %, 50.95 to 94.51 % and 66.17 to 78.51%, using quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) nanofibres as the dosage rose from 1.0 to 5mg/L (Xu *et al*., 2009). Also, the % removal of phosphate decreased when the phosphate concentration increased from 10 mg/L to 50 mg/L and this agree with the work of Mezenner and Bensmaili (2009). In general, the adsorption capacity of phosphate ions increased while their % removal decreased with increasing initial concentration of phosphate species, as shown in Figures 5.3a, 5.3b and 5.3c.

There were more binding sites available for phosphorous adsorption when higher adsorbent dose was used. However, further increase of adsorbent dose did not accelerate further the % removal of phosphorous. By that time, though there were additional adsorption sites, there was no more phosphate ions left in the solution as most ofthem were adsorbed. These results suit findings quoted by Ismail 2012; Kumar *et al.*, 2010; Mezenner and Bensmaili 2009; Yue *et al.*, 2010.

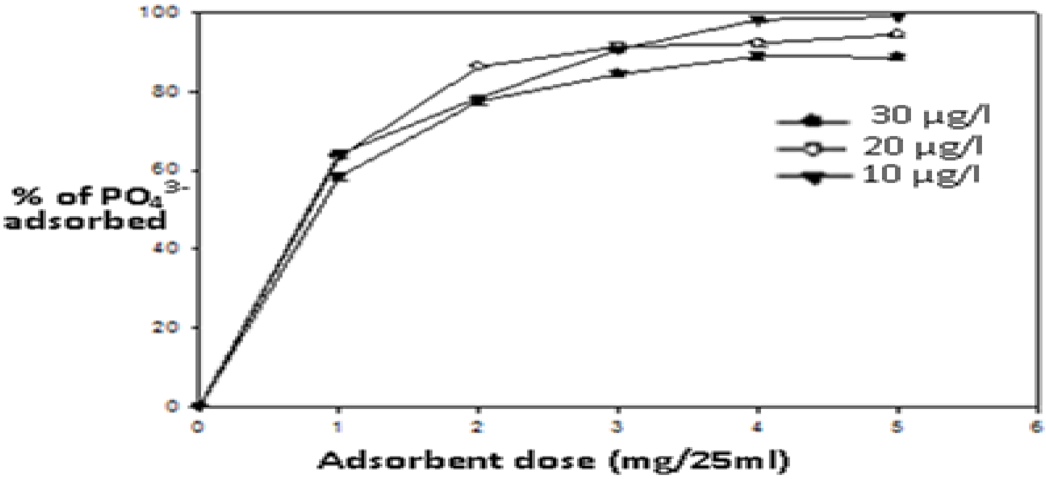


Figure 5.2: Effect of phosphate removal onto quaternized PVBC (R′ = CH$_3$) nanofibres (Experimental condition: concentration of phosphate 30 µg/l, adsorbent dose 5 mg/l pH 5.0, agitation speed 120 r/20 min) (n = 3).

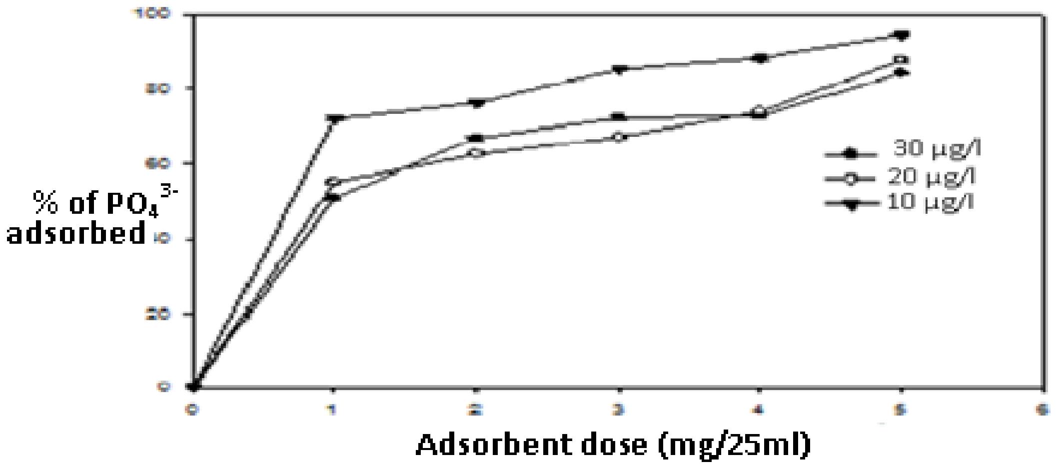


Figure 5.3. Effect of phosphate removal onto quaternized PVBC (R′ = C_2H_5) nanofibres.(Experimental condition: concentration of phosphate 30 μg/l, adsorbent dose 5 mg/l pH 5.0, agitation speed 120 r/20 min) (n = 3).

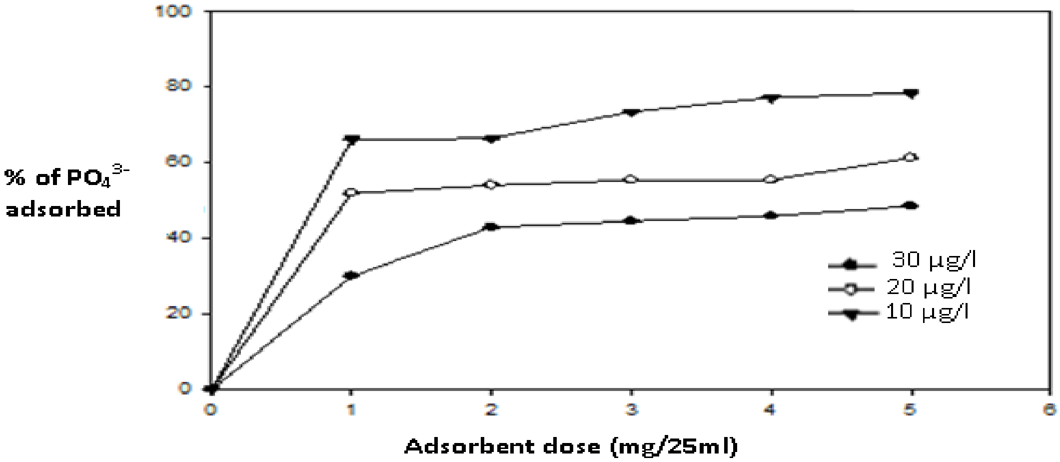


Figure 5.4: Effect of phosphate removal onto quaternized PVBC (R′ = C_3H_7) nanofibres. (Experimental condition: concentration of phosphate 30 μg/l, adsorbent dose 5 mg/l pH 5.0, agitation speed 120 r/20 min) (n = 3).

5.4 Effect of Time on Phosphate Removal onto Quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7).

Adsorption kinetic experiments were conducted to determine the rate of phosphate adsorption on quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) using initial phosphate concentrations of 10 mg/l. Figure 5.4 illustrates the adsorption of phosphate against contact time, and all the three curves for quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7) exhibit the same trend. The adsorption of phosphate increased with increase in time and after 10 min the rate of removal is very fast, as shown in Figure 5.4 below. Within 10 - 20 min, the adsorption of phosphate increases as expected over the time course of the experiment and reached saturation after 20 min. The optimum time to attain the equilibrium is 20 min. Xu *et al.* (2009) observed that the removal of phosphate by modified wheat residue reached equilibrium in 10 - 15 min.

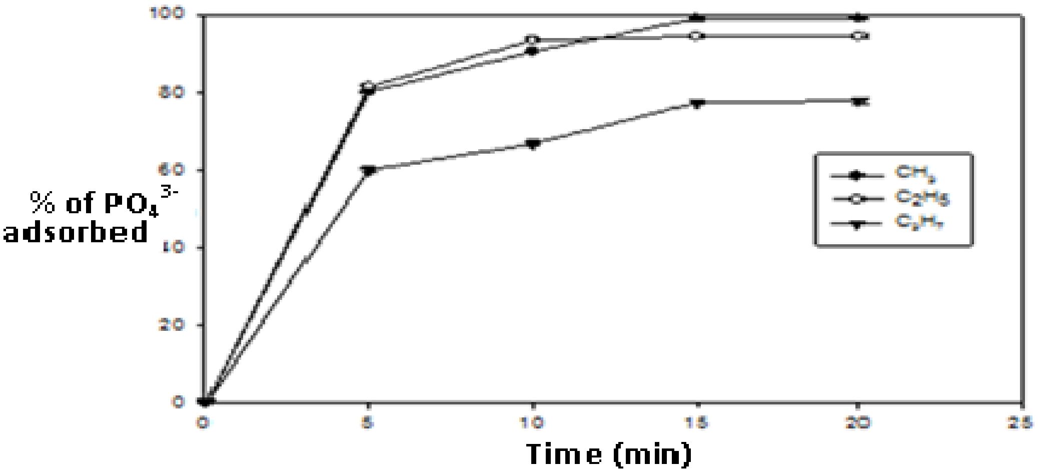


Figure 5.5: Adsorption kinetics of phosphate removal onto quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7).(Experimental condition: concentration of

phosphate 30 µg/l, adsorbent dose 5 mg/l pH 4.0, agitation speed 120 rs/20 min) (n = 3).

5.5: Effect of Co-existing Anions onto Quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7)

The efficiency of the adsorbent in the removal of phosphate for the treatment of wastewaters is affected by the selectivity between various common chemical species. The adsorption in multi-component systems is complicated because ion–ion competition and ion–surface interactions are involved. Multi-component interactions take place at the active adsorption sites where the solid–liquid phase and equilibrium will emerge.

Coexisting ions such as; chloride, sulfate, and bicarbonate are generally present in wastewater, and could interfere in the uptake of phosphate by adsorbent through competitive adsorption. To assess the effects of these anions, the tests were conducted in the presence of 5 mg/L phosphate, and 30 mg/L sulfate, bicarbonate, and chloride concentrations, onto quaternized PVBC(R′ = CH_3, C_2H_5 and C_3H_7) at initial pH of 4.5. The adsorption superiority order of anions was in the following order: CO_3^{2-}> SO_4^{2-} > Cl^- were also shown in Table 5.5.1. The higher uptake with R′ = CH_3 might be due to higher ratio of initial number of phosphate moles to the available surface area at of the quaternized sorbent material; hence adsorption was dependent on the alkyl groups present on the sorbent material.

Table 5.1: Effect of co-existing anions onto quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7).(Experimental condition: concentration of phosphate 30 µg/l and 50 µg/l of co-existing anions, adsorbent dose 5 mg/l pH 4.0, agitation speed 120 r/20 min) (n = 3).

Sorbent material	**Anions**	**% of phosphate adsorbed**
quaternized PVBC (R′ = CH_3)	Blank, SO_4^{2-} , Cl^-, and CO_3^{2--}	98.95, 97.40, 94.61 and 98.91
quaternized PVBC (R′ = C_2H_5)	Blank, SO_4^{2-}, Cl^-, and CO_3^{2-}	93.56, 93.03, 90.02 and 94.78
quaternized PVBC (R′ = C_3H_7)	SO_4^{2-} , Cl^-, and CO_3^{2-}	77.42, 77.14, 66.98 and 77.19

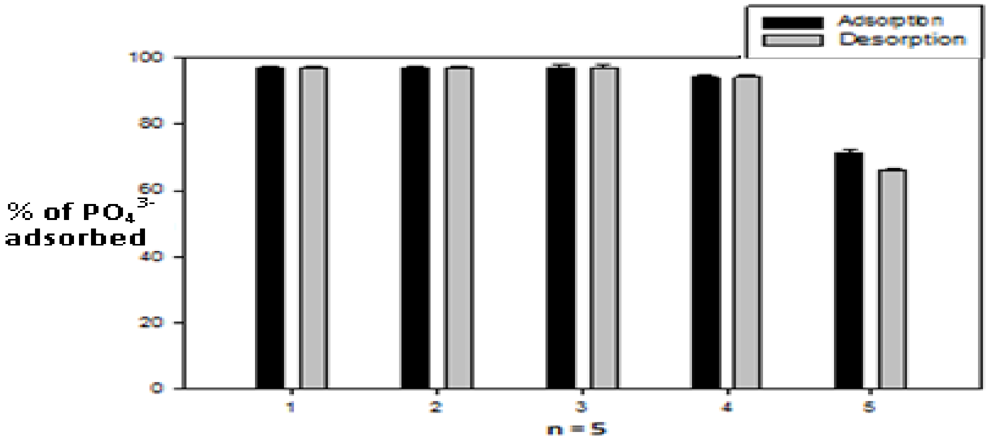


Figure 5.6: Reusability of phosphate removal onto quaternized PVBC (R′ = CH_3) nanofibre. (Experimental condition: concentration of phosphate 30 µg/l, adsorbent dose 5 mg/l pH 5.0, agitation speed 120 r/20 min) (n = 3).

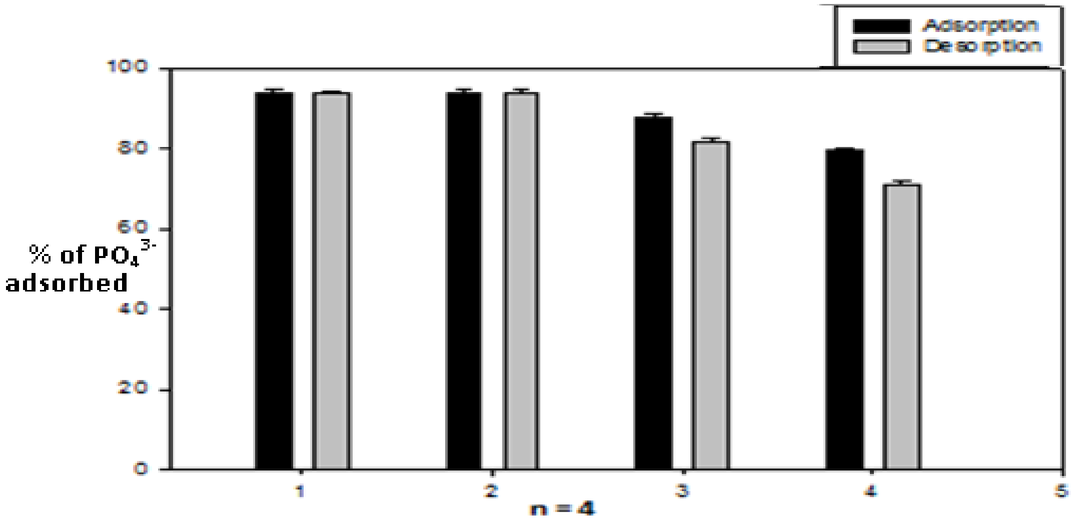


Figure 5.7: Reusability of phosphate removal onto quaternized PVBC (R′ = C_2H_5) nanofibre. (Experimental condition: concentration of phosphate 30 µg/l, adsorbent dose 5 mg/l pH 5.0, agitation speed 120 r/20 min) (n = 3).

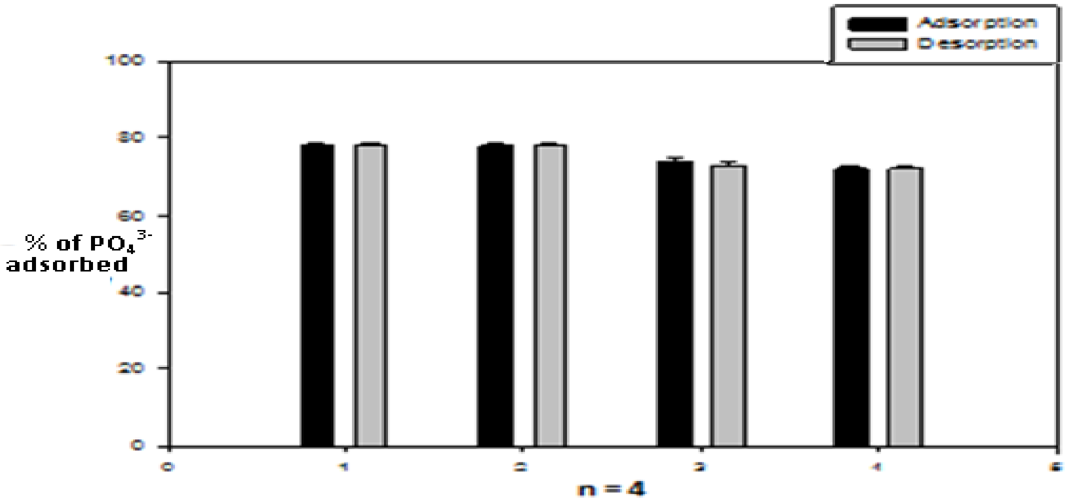


Figure 5.8: Reusability of phosphate removal onto quaternized PVBC (R′ = C_3H_7) nanofibre. (Experimental condition: concentration of phosphate 30 μg/l, adsorbent dose 5 mg/l pH 5.0, agitation speed 120 r/20 min) (n = 3).

To recover the adsorbed phosphate, 0.1 M NaOH was used for the desorption of quaternized PVBC (R′ = CH_3, C_2H_5 and C_3H_7). The surface of the adsorbent material for quaternized PVBC CH_3 was very efficient because the nanofibre became active and its sites were regenerated four times, while a decrease occurred at the fifth reuse. The adsorption capacity of regenerated quaternized PVBC (C_2H_5 and C_3H_7) decreases after the second run with the same concentration of NaOH used and this indicates that, it is too strong for desorption because the quaternized PVBC (C_2H_5 and C_3H_7) sorbent materials appeared to have been de-quarernized due to the N-H group of the amine group in the presence of strong NaOH as shown in figure 6.0. This agree with the work done by Ismail, (2012) who found that the desorbabilities of phosphorous uptake after the second run for granular date stones and palm surface fibers were 10-11.2% and 12.1-13%, respectively.

Thus, these may be significant challenges for the reuse of quaternized PVBC (C_2H_5 and C_3H_7) sorbent material for phosphorous removal.

CONCLUSION AND FURTHER RESEARCH

Arsenic and phosphate in wastewater are major problems that people are facing worldwide. Arsenic removal from drinking water has become mandatory for many wastewater systems after the U.S. EPA promulgation of the 10 µg/L final arsenic rule in 2006. This rule was designed to save human lives by reducing the degree of prolonged arsenic exposure, there by reducing the risk of both internal and skin cancers. The phosphate water bodies cannot be used for drinking, fishing, recreation, irrigation or industrial purposes because of eutrophication, which shows the scale of the problem. Several techniques such as coagulation / precipitation, reverse osmosis, ion exchange, and adsorption effectively lower the concentrations of arsenic in aqueous solutions. Coagulation and softening with metal ions such as aluminum and ferric salts require the use of large-scale facilities for implementing water treatment. Reverse osmosis requires the use of membranes, which are expensive to maintain and replace, and ion exchange uses costly resins. Coagulation, reverse osmosis, and ion exchange require the treatment of reject stream for the ultimate disposal of arsenic contaminants. Despite these disadvantages, adsorption is a highly efficient method for removing arsenate and phosphate from aqueous medium because of its simplicity, ease of separation and handling and regeneration capacity.

There has been considerable interest in the use of novel low-cost functionalized electrospun nanofibers adsorbents for the removal of arsenate and phosphate from wastewater that is often consumed without further purification there for leading to toxic effect of human health, as it is done in this research. Electrospinning is a simple, versatile, and cost-effective technology which generates non-wovenfibers with high surface area to volume ratio. Solution and processing parameters such as viscosity, molecular weight, concentration of the polymer, applied voltage, tip to collector distance, and others. Significantly affect the fiber morphology and by the manipulation of these parameters to get desired properties for specific application of the uptake of arsenic(v) and phosphate from wastewater.

The arsenic and phosphate adsorption capacities of low cost adsorbents presented vary, depending on the characteristics of the individual adsorbent, concentration of arsenic and phosphate, pH, contact time effect of co-exisiting anions and reuseability.

In this study, four different novel fibers were prepared through the modification of fiber surface, using multi nitrogen containing aminating reagents for APPMKNFs and PVBC R′ = CH_3, C_2H_5 and C_3H_7. The adsorbent with the highest sorption capacity was obtained when APPMKNFs and PVBC R′ = CH_3 was used than PVBC R′ = C_2H_5 and C_3H_7, due to the more amine groups, and positive hydrogen bonded for APPMKNFs, and the the less carbon groups on the PVBC R′ = CH_3 than PVBC R′C_2H_5 and C_3H_7 because of the sterric hinderance on the surface of the nanofibers and de-quarernized N-H group of the amine group at a high pH on the sorbent material. The batch and solid phase extraction (SPE) experimental results show that, the sorption of arsenate and SPE for phosphate on APPMKNFs and PVBC R′ = CH_3 was very fast as well as pH- dependent. The sorption amount of APPMKNFs as well as PVBC R′ = CH_3 for the equilibrium of arsenate concentration was reduced from 50 µg/l to 10 µg/l within 30 min because of the protonated functional groups on the surface of APPMKNFs and PVBC R′ = CH_3, which had proved to be better than other conventional adsorbents used for the removal of this toxic anions from wastewater.

Unresolved issue

Characterization of developed sorbent materials using the same instruments (such as CHNs micro analysis, Scanning Electron Microscopy (SEM), X-ray Diffractions (XRD), Energy Dispersive X-ray Spectrometer (EDS), BET Surface Area) as were used for APPMKNFs, PVBC and functionalized PVBC ought to have been carried out but assumptions were made based on the work of previous workers on the same materials in our group of researchers, this may further be looked into.

Recommendations (Further work)

The project can get into the next phase of research which is to study arsenic(III) removal in wastewater using functionalized APPMKNFs and quaternized PVBC R′ = CH_3, C_2H_5 and C_3H_7 electrospun nanofibers as a sorbent materials. There are many parameters that can be studied such as the characterization of the sorbent materials using the same instrument (such as CHNs micro analysis, Scanning Electron Microscopy (SEM), X-ray Diffractions (XRD), Energy Dispersive X-ray Spectrometer (EDS), BET

Surface Area), initial concentration of arsenic(III) in the solution, the pH of the solution, the temperature, contact time of the adsorption process, coexisting anions and the reusability of the sorbent materials. During this study, the time required for the adsorption process to reach equilibrium can also be determined. Adsorption equilibrium is achieved when the rate of adsorption is equal to the rate of desorption, thus making any further adsorption highly unlikely (maximum amount of adsorbate bind on the reactive sites of the adsorbent). It is preferred that the adsorption equilibrium should be achieved as fast as possible while maintaining high percentage of anion removal.

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