Chapter 6

Removal of Arsenic from Aqueous Solutions Using Iron(III) Adsorption Sites Immobilized by Cation-Exchange Resin

6.1 Introduction

Arsenic is a naturally occurring element in the earth’s crust (20\textsuperscript{th} most abundant element) with an average abundance of 2 ppm (Rau \textit{et al.}, 2003). It is widely distributed in the environment more often as arsenic sulphide (specially arsenopyrite) or as metal arsenates, arsenites and arsenides. Arsenic in natural waters is usually associated with marine sedimentary rocks, weathered volcanic rocks, fossil fuels, geothermal areas, mineral deposits, mining wastes, agrochemical use or irrigation practices. As a compound of underground rock and soil, arsenic finds its way into groundwater and enters food chains through either drinking water or eating plants and cereals that have absorbed the mineral. It enters the environment also from anthropogenic sources, such as petroleum refineries, fossil fuel power plants, non-ferrous smelting activities and from ceramics (Deliyanni \textit{et al.}, 2003). In industry it is used in the manufacture of pesticides and wood preservatives (Dambies \textit{et al.}, 2000). High purity arsenic (>99.9999\%) is used in the manufacture of crystalline gallium arsenide, arsenic conducting material in optoelectronic circuitry, high speed computers and other electronic devices. Increased activity in gold mining also results in arsenic contamination of streams and groundwaters. Other mining activities also generate large amounts of contaminated wastewater since arsenic is present as an admixture in molybdenum,
lead and copper ores. The wastewater generated during the hydrometallurgical
treatment of these minerals usually contains high arsenic levels.

The mechanism and degree of toxicity of arsenic depend on its speciation. The
degree of toxicity of arsenic compounds is as follows: arsenite As(III), arsenate
As(V), methylated arsenicals, and is inversely proportional to the rate of excretion
from the body (Cullen and Reimer, 1989; Korte and Fernando, 1991). Considerable
documentation regarding the health threat of arsenic contamination in groundwater
and drinking water is now available (Kim et al., 2004). Daily consumption of water
with greater than 0.01 mg/L of arsenic, less than 0.2 % of the fatal dose, can lead to
problems with the skin and the circulatory and nervous systems. If arsenic builds
up to higher toxic levels, open lesions, organ damages (such as deafness), black
foot disease and neural disorders, often fatal, can result (Stocker et al., 2003).
Systemic and chronic exposure to arsenic is known to lead to serious disorders,
such as vascular diseases (Blackfoot disease and hypertension) and irritations of
the skin and mucous membranes as well as dermatitis, keratosis, and melanosis.
Inorganic arsenic is a human carcinogen, and ingestion of inorganic arsenic
increases the risk of developing cancer of the bladder, liver, kidney, and skin.

Since 1993, the World Health Organization has recommended a maximum
contaminant level (MCL) for arsenic in drinking water of 10 µg/L (WHO, 1996;
Zouboulis and Katsoyiannis, 2002). In 1998, under European Commission (EC)
directive, 98/83 related to water intended for human consumption, the same value
has been adopted as the MCL to be complied by all European countries within
2003 (Drinking water Directive 98/83/EEC: European Commission Brussels,
drinking water at 10 ppb, replacing the old standard of 50 ppb. The rule became
effective on February 22, 2002. The date by which systems must comply with the
new 10 ppb standard was January 23, 2006 (Schnoor, 1996; EPA, 2002; Stocker et
Therefore the arsenic problem is of primary concern in many countries and further research into the development of cost-competitive technologies for arsenic removal from water sources to meet the MCL value is very much essential.

6.2 Treatment Methods

The main treatment methods used for arsenic removal from contaminated waters fall into the following categories: (1) precipitation–coagulation processes, such as coagulation with iron or aluminium salts or lime softening (2) membrane processes, such as reverse osmosis (RO), nanofiltration or electro dialysis (ED) and (3) adsorption processes, such as adsorption on activated carbon, activated alumina and iron oxides (Zouboulis and Katsoyiannis, 2002).

Even though precipitation with lime, co-precipitation with ferric sulphate, alum precipitation and precipitation as the sulphide using either sodium sulphide or hydrogen sulphide are some common methods, removal of arsenic by coagulation with ferric salts, followed by filtration (co-precipitation), is the best known technique (Ghimire et al., 2003). This technique allows doses of ferric salts below 10 mg/L and achieves residual arsenic concentrations below 10 mg/L. But the iron co-precipitation method also suffers from a post-treatment problem regarding the alkaline sludge produced after the treatment. This sludge, which contains a mixture of gypsum, heavy metal hydroxides and carbonates in addition to a large amount of water, may leak arsenic back to the environment after exposure to water and air. Lime precipitation, which was widely used in the past, is being abandoned as a result of strong evidence showing that calcium arsenate compounds decompose slowly in contact with atmospheric CO$_2$ to form calcium carbonate and soluble arsenic acid.
Membrane processes like RO and ED are more effective in removing As(V) than As(III). An oxidizing agent must be added into the feed water to oxidize As(III) to As(V) to achieve higher arsenic removal (Zeng, 2003). However, the oxidizing agents are normally harmful to most RO and ED membranes. Reverse osmosis and nano-filtration may deliver satisfactory removal efficiencies, but water rejection is very high in these technologies and the discharge of reject water is also a concern. In membrane processes the small pores of the membranes make them more prone to fouling (Katsoyiannis and Zouboulis, 2002). When iron and manganese are present in water, they can promote fouling of membranes, due to precipitation, which might be irreversible. Furthermore, the application of reverse osmosis and nanofiltration for surface water treatment is generally not accomplished without extensive pre-treatment for particle removal. These drawbacks are enhanced by the increased operational costs of membrane processes and by the fact that usually need experienced personnel to run the overall process.

Ion exchange is found to be more effective in removing As(V) than As(III), because As(V) is normally present as an anion in the medium-pH range while As(III) exists as uncharged molecules in water. An additional concern about using ion exchange is that the efficiency of the ion exchange process can be strongly impacted by other competing ions in the water, such as sulphate, selenium, fluoride and nitrate. Disposal of highly concentrated spent regenerant is another major problem. In addition, As(III) is hardly removable by ion exchange method. Incineration is not a good method of safe disposal of arsenic wastes because of the volatilization of arsenic containing compounds. Recovery of arsenic is economically unattractive because of the limited reutilizing possibilities of arsenic. It cannot be thus destroyed, but can only be converted into various forms or converted into soluble compounds in combination with other elements, such as iron.
The requirements for a suitable performance for removal of arsenic from drinking water are:

- high efficiency
- safe technology to ensure the maintainance of the maximum contaminant level
- simple operation
- minimum residual mass

Because of the ease of handling, sludge-free operation, and possibility of regeneration, the adsorption process appears to be the most promising one (Zhang et al., 2003). Many types of adsorbents have been used for the removal of arsenic from aqueous effluents (Rau et al., 2003). They can be classified in to three main groups: those based on aluminium compounds – Alumina or Gibbsite Al(OH)₃ (Manning and Goldberg, 1996; Davis and Misra, 1997; Rau et al., 2003; Shevade and Ford, 2004); those based on lanthanum compounds; and those based on iron compounds (Tokunaga et al., 1997; Zhang et al., 2003). Activated alumina has long been the most often used adsorbent for arsenic removal. However, the problems including the need for pH adjustment, the relatively low adsorption capacity, and aluminum dissolution have prevented activated alumina from wider applications.

Adsorption/co-precipitation with iron oxyhydroxides is the most commonly adopted method for arsenic removal from contaminated water because the method is both effective and cheap compared with other methods, such as ion exchange, membrane separation (RO), bio-reduction and electrolysis (Zhang et al., 2003; Zhang et al., 2004). It is well known that arsenates have a strong adsorption affinity for hydrated iron oxides forming inner-sphere bidentate, binuclear As(V)–Fe(III) complexes. This fact can influence the enrichment with soluble arsenic as both As(III) and As(V) in natural sources (e.g. geothermal springs) (Cullen and...
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Reimer, 1989). On the other hand, it can also be helpful in connection with detoxification of contaminated waters.

Generally two ways of using iron oxyhydroxides for removal of arsenic have been widely investigated. The first is in situ co-precipitation, in which amorphous ferrihydrite is formed (Edwards, 1994; Zhang et al., 2004). The ferrihydrite is more porous and has larger surface area for adsorption than pre-formed material. Iron oxides, especially amorphous iron oxides, have been reported to be effective for arsenic removal (Pierce and Moore, 1982; Cornell and Schwertmann, 1996; Zhang et al., 2003), but the endurance and stability of the adsorbent should be improved. While the crystalline oxides of iron are stable in aquatic environment, the efficiency for arsenic removal is poor. Naturally occurring iron oxides are more attractive for arsenic removal from contaminated water than the synthetic oxides because they are more cost effective (Zhang et al., 2003). However, few studies have been carried out on the feasibility of their use as adsorbents for arsenic removal, particularly on the effects of interfering species, such as silicate and phosphate and interactions between ores and contaminated water. Most iron oxides are available only as fine powders or are generated in aqueous suspension as hydroxide floc or gel (Lai et al., 2000). In such forms, these oxides retain their desirable adsorptive properties for the trace metals, but they are limited to reactor configurations incorporating with large sedimentation basins or filtration unit. Under such conditions, the solid–liquid separation is fairly difficult. Besides, iron oxide alone is not suitable as a filter medium because of low hydraulic conductivity. Vaughan and Reed (2005) reported on the heavy metal removal ability of an iron oxide impregnated granular activated carbon. Min and Hering (1998) used an impregnation technique for the improvement of arsenate sorption on alginate beads.
The alternative method is the agglomeration of the iron oxides or the coating of iron oxides on substrates, such as sand, polymeric materials and activated carbons (Khaodhiaer et al., 2000; Yuan et al., 2002). Iron-coated sands have been tested for removing cations and anions from synthetic and real wastes (Satpathy and Chaudhuri, 1995; Singh et al., 1996; Wilkie and Hering, 1996; Grossl et al., 1997; Gupta et al., 2005) and the results from these studies confirmed that the utilization of iron-coated sand is worth developing for arsenic removal from water.

Various resins, such as Zr-loaded ion-exchange resin (Suzuki et al., 1997; Abrazheev and Zorin 1999), Fe(III)-loaded chelating resin (Chanda et al., 1988; Matsunaga et al., 1996) and Fe(III)-poly(hydroxamic acid) (Haron et al., 1999) have been used for arsenic removal. DeMarco et al. (2003) incorporated hydrated Fe oxide to a macrosorbon cation exchange bead and developed a polymeric/inorganic hybrid sorbent for the removal of As(III) and As(V) ions present in water. The adsorbent particles are essentially spherical macroporous cation exchanger beads within which agglomerates of nanoscale hydrated Fe oxide (HFO) particles are present.

Both amorphous and crystalline hydrated Fe oxides (HFO) show strong sorption affinity towards both As(III) and As(V) oxy acids and oxy anions through ligand exchange in the coordination spheres of structural Fe atoms (Rau et al., 2003). The Duolite bound HFO consists of spherical macroporous polymeric cation exchanger beads with which submission HFO particles have been uniformly and inversibly dispersed. The new sorbent has excellent mechanical strengths and hydraulic properties of spherical polymeric beads with selective As(III) and As(V) removal capacities of HFO microparticles over a specific range of pH.

The objective of this study is to investigate a possible strategy for the removal of arsenic by employing iron(III) loaded macroporous resin as adsorbent by utilizing both the ionic exchange nature of the cation exchanger Duolite C-26 and
the high affinity of Fe towards inorganic As. This work further focused on investigating how various experimental parameters influence arsenic [both As(V) and As(III)] adsorption. These parameters included: pH, adsorbent dose, contact time, temperature and the concentration of As species. The desorption efficiency of the investigated matrices was also tested. This work will provide fundamental data on the potential usefulness of HFOLR in the remediation of As-contaminated water, soils, sediments, and mine wastes.

6.3 Preparation of the Adsorbent

Iron(III) loaded Duolite was prepared by studying the distribution ratio of ferric ion between the Duolite and aqueous phases under various pH conditions. It was found that a maximum attachment of Fe takes place at a pH 2.0–2.5 which would prevent hydrolysis of ferric ions also. Moreover, elution of the ferric ion from the Fe(III)-Duolite resin with 0.5 M sodium hydroxide solution gave a leached solution that contained chloride ions. The Duolite C-26 was first converted into Na⁺ saturated form by washing several times with 0.1 M NaOH and HCl. Loading of Duolite C-26 with Fe was performed by batch equilibrium technique with varying iron(III) solutions (50 – 600 mg/L). Exactly 0.1 g of the resin was shaken in stoppered flasks at pH 2.0 for 3 h using a constant temperature water bath shaker. The initial and final concentrations of iron(III) were determined by AAS.

As seen from Figure 71 there was a significant increase in the amount of iron coated on Duolite beads, when increasing the initial iron(III) concentration from 50 to 600 mg/L. Above that equilibrium amount of iron adsorbed did not show any significant difference, probably because the beads reached the maximum loading capacity under the conditions. The maximum loading capacity for ferric ions calculated using the isotherm data at pH 2.0 was found to be 56.10 mg/g.
The value is comparable with the amount of iron oxides coated on the surface of polystyrene beads (Katsoyiannis and Zouboulis, 2002), and was much higher than the reported amounts when the iron oxide coated sand was used in certain cases where values were between 1 and 2 mg Fe/g sand (Lo et al., 1997) and 20 and 30 mg Fe/g sand (Benjamin et al., 1996).

The amount of iron in iron-loaded Duolite was estimated from the residual concentration of ferric ion and was found to be 45.24 mg/g. Dissociation of ferric ion from the Fe(III)-loaded resin was checked as a function of pH. A considerable amount of ferric ion was released from the resin at a pH higher than 10.0 while only a small amount is liberated from the resin in the wide pH range between 8.5
and 10.0. The iron loaded resin was washed with distilled water until the pH of the residual water was close to 5.0 and when no iron could be detected in the filtrate. The residue was then oven dried at 65 °C for one day. It was then converted to HFOLR by treating with a mixture of NaOH and NaCl solutions. The off white colour of Duolite changes to reddish brown due to the formation of hydrous ferric oxide (HFO). The spheres are fairly mechanically robust and do not break into smaller particles when shaken violently within a glass vial in a simulation of a batch agitator. They can, however, be crushed with an agate mortar and pestle to a fine powder.

Since Duolite is a cation exchanger, under acidic conditions Fe$^{3+}$ will be exchanged with the H$^+$ ions of sulphonic acid groups. When NaCl/NaOH mixture is passed through the Fe loaded Duolite, the Fe(III) will be desorbed and will co-ordinate OH$^-$ and H$_2$O to yield a suspension of hydrous ferric oxide (HFO). After drying, amorphous (or poorly crystalline) FeOOH powder is obtained. The mesoporous character of the resin facilitates encapsulation of HFO. The initially formed FeOOH, through the neutralization of an iron(III) salt solution with alkali, can be gradually transformed to crystalline iron(III) oxides, for example, goethite (α-FeOOH) and/or hematite (α-Fe$_2$O$_3$), mostly depending on the aging time.

### 6.4 Nitrogen Adsorption Experiments

Nitrogen adsorption–desorption isotherm of HFOLR is displayed in Figure 72. The N$_2$ sorption isotherm belongs to Type II according to the IUPAC classification, showing the characteristic hysteresis loop corresponding to the filling of the mesopores (Brunauer et al., 1940). The location of the hysteresis loop in the N$_2$ isotherm can be used to determine whether the material possessed a regular framework pore or interparticle voids, such as a textural pore (Kim et al., 2004).
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The framework porosity at 0.1–0.6 $P/P_0$ in the $N_2$ isotherm indicates that the porosity was contained within the uniform channels of the templated framework, while the textural porosity at 0.7-1.0 $P/P_0$ shows porosity arising from the noncrystalline intra-aggregate voids and spaces formed by interparticle contacts.

The shape obtained for the sample for relative pressure higher than 0.8 suggests the presence of large mesopores. The small hysteresis observed at high relative pressure is consistent with the presence of large mesopores (Wang et al., 2003). A hysteresis loop observed in the $P/P_0$ region between 0.3 and 0.9 was similar to Type H3 hysteresis of the IUPAC classification. This type of hysteresis is contributed by capillary condensation occurring in slit-like mesopores (20–500 Å) present in HFOLR. The adsorption behaviour in the low-$P/P_0$ (< 0.1) region is attributed to monolayer–multilayer condensation. The inflection point (Point B) is close to complete monolayer coverage. This occurs between $P/P_0 = 0.05$ and 0.1.

The value of the constant $C$ of BET equation was found to be 276.6. A large $C$ value is due to the influence of the enhanced adsorption in the low $P/P_0$ region on the BET isotherm and is often associated with microporous materials and is an indication of active sites in internal surfaces (Figure 73). It is also indicative of the sharpness of the knee of the isotherm curve (Gregg, 1982; Kim et al., 2004).

The $t$-plot method, designed by de Boer et al. (1966) was used to evaluate micropore volumes and open surface areas (Figure 74). $V-t$ plot gave +ve intercept equivalent to the micropore volume showing that HFOLR can be considered to be microporous and that high-energy surface adsorption sites are more likely. From the $t$-plot which does not pass through the intersection of the coordinate axes it was proved that adsorption occurred in the micropores. The slope of the line is considered to be related to the external surface area of the adsorbent. Pore size distributions, derived from adsorption isotherms and calculated from BJH (Barret–Joyner–Halenda) method are presented in Figure 75. The obtained curves confirm
that mesopores are rather large. Pore size distributions, range throughout from micropore to mesopore region in such a manner that there is a discontinuous distribution. The nitrogen adsorption data were used to determine the BET surface area (1.51 m$^2$/g), the total pore volume ($2.27 \times 10^{-3}$ mL/g), the average pore radius (60.31 Å) and the micropore volume ($4.44 \times 10^{-4}$ mL/g) of the HFOLR. The observed micropore area, having a value of $1.106 \text{ m}^2/\text{g}$, is much higher than the external surface area ($4.04 \times 10^{-1}$ m$^2$/g). The BET surface area based on nitrogen adsorption isotherms was thus not equal to the external surface area suggesting again that sorption, in this case, occurred mainly in the internal surface.

![Nitrogen adsorption-desorption isotherm of HFOLR](image)

**Figure 72**
Nitrogen adsorption–desorption isotherm of HFOLR
Sample wt.: 0.6920 g
Adsorbate: Nitrogen
Bath Temp: 77.35 K

Figure 73
BET adsorption isotherm plot

Figure 74
de Boer V-t plot
6.5 Effect of pH

Experiments were performed to determine the optimum pH for the maximum removal of As(V) and As(III) and the results are presented in Figure 76. For an initial concentration of 10 mg/L, the adsorption percentage of arsenate on HFOLR reaches a maximum of 99.6 % in the pH range 3.0–4.0 and then decreases to 12.3 % at a pH value of 10.0. When the initial concentration was 25 mg/L, a maximum removal of 86.6 % occurred at a pH of 4.0. At very low pH value, the species of arsenate predominantly exist as H$_3$AsO$_4$. This neutral species is difficult to interact with exchange sites of the sorbent for anion exchange.
As(III) removes less from aqueous solutions than As(V). Furthermore, it can be noticed that the optimum pH value for As(III) removal was around pH 7.0, where 90.8 and 75.5 % removal was possible from an initial As(III) concentration of 10 and 25 mg/L respectively. Arsenic removal was found to be very much decreased for As(V) at higher pH but for As(III), such close dependency was not observed. This observation could be well correlated with the pH$_{pzc}$ of HFO. Pure iron oxides, whether they can be identified as having a particular crystal structure or not, typically have pH$_{pzc}$ in the pH range 7.0–9.0. Over these pH$_{pzc}$ values, iron oxides are present in the monomeric anionic form [Fe(OH)$_4$]$^-$ and hence inappropriate for adsorbing anionic components. Since the pH$_{pzc}$ for the HFOLR was found to be 8.4, the surface of the HFOLR is positively charged when pH < pH$_{pzc}$. The strong adsorption of As(V) and As(III) at pH < pH$_{pzc}$ indicates that the arsenic species are adsorbed on HFOLR through surface complexation, rather than electrostatic
interactions (Bang et al., 2005). It is also seen that the pH_{pzc} value is higher than the naïve Duolite which is an advantage for the removal of arsenic systems. It is well-documented that As(V) tends to be more strongly adsorbed at lower solution pH, because the extent of complex formation between arsenates and iron depends on the ratio of the concentration of arsenates to the concentration of OH⁻ (Zouboulis and Katsoyiannis, 2002).

As(V) was removed from the aqueous solution more efficiently, whereas the removal of trivalent arsenic was not so effective. This difference in removal efficiencies of inorganic arsenic forms could be attributed to the speciation of inorganic arsenic in aqueous solution (Ghimire et al., 2003). This different behaviour of the two arsenic species is due to the different acidity of the respective oxoacids (Rau et al., 2003). Arsenic acid is a relatively strong acid (pK_{a1} = 2.22, pK_{a2} = 6.98 and pK_{a3} = 11.40) and, thus, negative oxoanions of As(V) can be found in solution at relatively acidic pH. Furthermore, the low acidity of arsenous acid (pK_{a1} = 9.22, pK_{a2} = 12.13 and pK_{a3} = 13.30) means that only at neutral to slightly basic conditions do oxoanions of As(III) predominate in solution. The anionic form of H₂AsO₄⁻ can be adsorbed more easily on iron oxides in this pH range as the number of positively charged surface sites available for the adsorption like the cationic monomeric form [Fe(OH)₂⁺] is higher, and adsorption may be facilitated by coulombic interactions, but decreases with increasing pH. The maximum As(V) adsorption is found at lower pH values than expected from the pK_{a1} of arsenic may indicate that immobilization of Fe(III) on this chelating resin produces a remarkable change in the Fe(III)–As(V) chemical interaction in comparison with other adsorbents. Similar results which show the potential acid form with other Fe based adsorbents like ferrihydrite at pH 4–5 (Peng and Di, 1994) and Fe(III)-loaded chelating resin at a pH of 5 (Chanda et al., 1988) have been reported earlier.
On the other hand, these results show the potential of this adsorbent to be used in the removal of As(V) from acidic industrial effluents.

6.6 Effect of Ionic Strength

The effect of ionic strength ($I$) on arsenate and arsenite adsorption by HFOLR was checked by preparing adsorption curves at ionic strengths ranging from 0.001 to 0.1 M NaCl and adding 2 g/L of the adsorbent. It was noted that the arsenate adsorption on HFOLR showed no dependence on $I$. But it was observed at optimum pH, a slight increase in adsorption of As(III) occurred with increase in $I$. McBride (1997) indicates that ions that form outer-sphere surface complexes show decreasing adsorption with increasing ionic strength. Ions that form inner-sphere surface complexes show little ionic strength dependence or show increasing adsorption with increasing ionic strength. Greater ion adsorption with increasing ionic strength is due to the higher activity of the counter ions in solution available to compensate the surface charge generated by specific ion adsorption.

Although more data are required for a firm conclusion, lack of or weak ionic strength dependence suggests that arsenate may be adsorbed on HFOLR by strongly binding chemical bonds, i.e., a largely covalent bond forming inner-sphere complexes with little competitive adsorption of counter anions. The formation of an inner-sphere complex with surface coordination is given by the reaction (Genc et al. 2003).

$$
equiv Fe - OH + L^- + H^+ \leftrightarrow equiv Fe - L + H_2O \quad (6.1)$$

where Fe–OH is a surface hydroxyl group and L is the adsorbed species. The adsorption of arsenite takes place by releasing hydroxyl anion or neutral water molecules from its co-ordination sphere (Ghimire et al., 2003). Adsorption of arsenite can also be regarded to occur via an anion-exchange mechanism. It is thus
tendency of Fe(III) to co-ordinate the anions in preference to OH\textsuperscript{-} or H\textsubscript{2}O that makes Fe(III) loaded materials to be useful for the removal of arsenic.

During this procedure the responsible mechanism for the removal of arsenic was adsorption on iron oxides, which refers to the formation of surface complexes between soluble arsenic species and the solid hydroxide surface sites, as arsenic gets in contact with the deposited iron oxides. Ferric arsenate or ferric arsenite may also be produced, as indicated schematically in the following equations.

\textbf{Arsenate sorption}

\[ M - \text{FeOH} + H\textsubscript{3}AsO\textsubscript{4} \rightarrow M - \text{FeH}_{2}AsO\textsubscript{4} + H\textsubscript{2}O \]  \hspace{1cm} (6.2)

\textbf{Arsenite sorption}

\[ M - \text{FeOH} + H\textsubscript{3}AsO\textsubscript{3} \rightarrow M - \text{FeH}_{2}AsO\textsubscript{3} + H\textsubscript{2}O \]  \hspace{1cm} (6.3)

On the basis of molecular scale, the binding of arsenic species can be described using spectroscopic techniques. Spectroscopic studies of arsenic sorption on goethite and ferrihydride, using EXAFS and XANES have indicated that arsenate is strongly bounded on these surfaces as inner-sphere complexes, which are attached predominantly as binuclear bidentate linkages, whereas at low surface coverage, monodentate linkages can be formed (Manning and Fendorf, 1998; Ladeira \textit{et al.}, 2001). Later studies by Goldberg and Johnston (2001) have suggested that arsenite can also form inner sphere complexes on Fe oxides. However, outer sphere complexes may also occur. Therefore, a more detailed mechanism for arsenate sorption on surface of HFO can be proposed, according to the following equations (Katsoyiannis and Zouboulis, 2002).
The above reactions propose that arsenic is sorbed on iron oxides through specific adsorption (chemisorption), where the adsorbing ion (arsenic) is bounded directly with the surface functional group. In the case of arsenite, where outer sphere complexes are also likely to be formed, water molecules are present between the adsorbing anion and the surface functional group. The values of the affinity constants of surface complexes (log \( K \)) with the surface sorption site have been calculated to be 20.1, 27.9 and 34.5 respectively for monodentate, bidentate and protonated bidentate surface complex formation (Hiemstra and van Riemsdijk, 1996).

6.7 Instrumental Analysis

6.7.1 Thermal analysis

The TG plots for the Duolite and HFOLR are shown in Figures 77 and 78, respectively. The Duolite and HFOLR show a weight loss of 17.5 and 19.0 % respectively, related evolution of water when the temperature rise from 30 to 180 °C for Duolite and from 30 to 180 °C for HFOLR. Above 460 °C, sharp decomposition of Duolite and its decrease in mass begins to occur that eventually becomes less rapid and continues up to 800 °C. But for HFOLR gradual decomposition occurs only after 480 °C, where a decrease in mass starts to occur that eventually becomes quite rapid and culminates in the formation of iron oxide at 700 °C. The DTG
curves are sharp at both the stages. The first step in both the process is due to the loss of adhered water and is sluggish in the case of HFOLR due to the presence of –OH groups. During the latter step, extensive evolution of sulphur dioxide is possible.

Figure 77
The thermogravimetric analysis (TGA) trace for Duolite
6.7.2 FTIR spectral analysis

Positive identification of adsorbed arsenate/arsenite species was provided using the FTIR technique. The infrared spectra of HFOLR containing adsorbed arsenate/arsenite and HFOLR free of arsenic, are given in Figure 79. A strong band at 1122 cm\(^{-1}\), which corresponds to the bending vibration of hydroxyl group (M–OH), was observed for the sample before adsorption (Nakamoto, 1988). After adsorption, the M–OH bending band was slightly shifted to 1126 cm\(^{-1}\) with reduced intensity. But the features assigned to H\(_2\)O remained unchanged. The main absorption bands for Na\(_2\)HAsO\(_4\).7H\(_2\)O were reported at 1636 and 855 cm\(^{-1}\) (Deliyanni et al., 2003). A shift of absorption bands should occur if the symmetry of the ion was lowered by interaction with HFOLR. Arsenate interacts with
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HFOLR surface by chemical bonding, as indicating by the band at 835 cm\(^{-1}\) which was rather weak in the original spectrum of HFOLR and the band at 1633 cm\(^{-1}\) was enhanced in the spectra of HFOLR after arsenate adsorption. These bands shifted slightly from the 1636 and 855 cm\(^{-1}\) peak observed in the spectrum of sodium arsenate due to the fact that the symmetry of arsenate ion was lowered after the adsorption reaction. From these results, it was concluded that specific adsorption should occur at the aqueous arsenate–solid HFOLR interface.

![Figure 79: The IR spectra of HFOLR, HFOLR–As(V) and HFOLR–As(III)](image)

The band at 3445 cm\(^{-1}\) observed in the present study supports the existence of lattice OH\(^{-}\) ions in the particles. It should be noted, however, that the 3400 cm\(^{-1}\) band observed in Figure 79 involves the OH stretching band of adsorbed H\(_2\)O molecules together with the lattice OH band, because a heating temperature of 70 °C would not be high enough to dehydrate the samples completely. The appearance
of a broad band at 3417 cm$^{-1}$ due to O–H stretching vibration and an absorption band at 1625 cm$^{-1}$ arising from the H–O–H bending vibration, are due to water present in the HFOLR. The bands around 625 cm$^{-1}$ and the doublet with maxima around 450 and 410 cm$^{-1}$ are assigned to Fe–O stretching and Fe–OH symmetric and asymmetric stretching vibrations respectively.

After arsenate adsorption the band at 624 cm$^{-1}$ almost vanishes. A band near 835 cm$^{-1}$ observed in an earlier IR study of arsenate sorbed goethite was assigned to the v(As–OH) of As–O–Fe groups. It can be speculated from this result that the As–O groups possibly were involved in surface complexation, and the 835 cm$^{-1}$ assigned to the Fe–O–As groups. The relative intensities of the O–H stretching bands at 3417 and H–O–H bending mode at 1625 cm$^{-1}$ show enhanced intensities as a result of the re-hydration of the sample. The O-H stretching bands and H–O–H bending absorption band positions indicate that the water molecules are coordinated rather than free. Also for free water, a much broader absorption peak is observed for the O-H stretching band. In the case of As(V)/Fe oxide complex, two bands near 835 and 781 cm$^{-1}$ are observed with a separation of about 50 cm$^{-1}$. The “splitting” of the v(As–O) vibration can be explained in two ways. First, the two vibrations correspond to the symmetric and asymmetric stretching modes of a sorbed As complex. The separation between the symmetric and asymmetric vibrations, however, is larger than the splitting in aqueous solution. Furthermore, in aqueous solution the asymmetric v(As–OH) vibration (high-frequency band at 835 cm$^{-1}$) is observed to have more intensity than the symmetric v(As–OH) vibration (at 781 cm$^{-1}$). The IR spectrum of As(V) sorbed-HFOLR is distinct from IR of Fe arsenate salt, which indicates that As(V) is bound as an innersphere complex and not as a precipitated solid phase. In contrast to the spectrum of arsenate sorbed-HFOLR, it was difficult to detect the presence of sorbed arsenite on the surface.
6.7.3 XRD studies

The XRD patterns for the adsorbent (Figure 80) did not yield any crystalline peaks suggesting the amorphous nature (Deliyanni et al., 2003).

![XRD patterns of HFOLR, HFOLR-As(V) and HFOLR-As(III)](image-url)
It can be explained by the fact that the crystallization of iron oxides is strongly retarded by the presence of the anionic resin particles (Zeng, 2003). The XRD analysis also confirmed that the iron(III) oxide prepared in this study was amorphous, presumably due to a short aging time. After arsenic(V) sorption, the loaded sorbent yielded the characteristic bands corresponding to ferric arsenate or ferric arsenite suggesting the formation of specific chemical substances after adsorption (Papassiopi et al., 2003; Dousova et al., 2005).

6.7.4 Scanning electron microscopy/ Energy dispersive analysis of X-ray

SEM micrographs were taken at different magnifications to observe the surface morphology of Duolite, HFOLR and As laden HFOLR (Figures 81–83). The micrographs of HFOLR confirm that the particles are spherical with an average diameter of 170 mm and are porous aggregates of smaller particles. The spheres of HFOLR consist of condensed HFO throughout and are composed of aggregates of nanoparticles that are further fused together to yield the larger spherical particles. The spheres are fairly mechanically robust and do not break into smaller particles when shaken violently within a glass vial in a simulation of a fluidized bed. They can, however, be easily crushed with an agate mortar and pestle to a fine powder.

Duolite had a good surface and cracks, macropores or roughness could be found on the surface. On the contrary, in HFOLR, the pores had been found to be occupied with HFO thus decreasing the mesopores slightly. The pores were apparently occupied by iron oxides, which were formed during the loading process. The pores consist of HFO throughout and are composed of aggregates of nanoparticles that are further fused together to yield the larger spherical particles. No cracks were visible, except for the iron oxides found in the interior (Figure 82). The microstructure of the sample shown by the SEM observation suggests that the
surface was covered with HFO. The As laden HFOLR revealed that the interior pores become more even due to the adsorption (Figure 83).

Energy dispersive analysis of X-ray (EDAX) was used for characterizing the elements associated with the adsorbent before and after adsorption of As(III) and As(V) (Figures 84–86). The EDAX spectra of HFOLR gave signals mainly of Fe and S which are the principal constituents. Within 10 keV three signals were obtained for Fe. It was also tried to verify the distribution Fe on the surface as well as the interior of spherical HFOLR beads. EDAX scanned from the outer surface as well as inner part suggests that slightly higher amount of Fe is present in the mesopores of HFOLR. Since NaCl/NaOH mixture was used for the preparation of HFOLR signals of Na too was seen in the spectra. This indicated that specific adsorption of Na\(^+\) occurred together with Fe\(^{3+}\) onto Duolite. HFOLR causes a change of elemental constitution through adsorption reaction with As(V) and As(III). It can be inferred that iron oxide has already brought about chemical interaction with adsorbate (Figures 85 and 86). Fe–As associations were identified by SEM-EDAX. Prominent signals corresponding to As are observed for HFOLR-As(III) and HFOLR-As(V). Physical adsorption of ions is unable to remain on solid surface through complete elution process. The spectrum of HFOLR-As(III), by using elemental microprobe analysis of SEM/EDAX has only signals corresponding to Fe, S and O indicating that As(III) was adsorbed not through specific adsorption. On the other hand, the signals of As remained as such corresponding to the spectra of HFOLR-As(V) (Figures not shown). This was due to the fact that arsenate ions were chemisorbed on HFOLR and clearly supported the inner-sphere surface complexation mechanism discussed earlier. It can also be seen that Fe continues to be the principal element and the As signals detected in the spectrum are of lesser magnitude ruling out monodendate mode of attachment.
Figure 81
The SEM photographs of Duolite and HFOLR beads
Figure 82
The SEM photographs of HFOLR under various magnifications
Figure 83
The SEM photographs of HFOLR-As(V) and HFOLR-As(III) under various magnifications
Figure 84
The Energy dispersive analysis of X-ray (EDAX) of HFOLR
Figure 85
The Energy dispersive analysis of X-ray (EDAX) of HFOLR–As(V)
6.8 Effect of Initial Concentration and Contact Time

The adsorption was measured as a function of time in order to check whether this adsorption system could be used for the practical operation. Figure 87 shows that it takes at least 8 h to attain the adsorption equilibrium for arsenic(V) under the experimental conditions. On the other hand, the adsorption of arsenic(III) can be equilibrated within 6 h. Since arsenic(III) adsorbs to HFOLR faster than arsenic(V)
this adsorption system is suitable for practical separation of the two valence forms As oxyanions.

The adsorption curves of As(V) on HFOLR for four concentrations shows that for each of these initial concentrations, a relatively rapid adsorption takes place during the first 1 h, followed by a slow sorption which lasts from 4 to 8 h in the case of As(V). The rate of adsorption of arsenate on HFOLR was such that 90% of maximum adsorption after 6 h of stirring at pH 3.5 and ionic strength 0.1 M KNO₃. After 7 h, 99% of the maximum adsorption had taken place, thus 8 h was an adequate realistic time for equilibrium reasons. The adsorption of arsenic in this study was in the order of hours, which may indicate a specific adsorption (Zouboulis and Katsoyiannis, 2002). The amount adsorbed increased from 4.99 to
30.42 mg/g for As(V) and from 4.51 to 22.49 mg/g for As(III) when the initial As concentration was increased from 10 to 100 mg/L respectively. The increase in sorption capacity with increasing residence time indicates that the sorption process is controlled by intraparticle mass transfer, rather than by external mass transfer, thus the critical stage in the arsenic removal kinetics is the diffusion of liquid into the pores.

6.8.1 Sorption mechanism

The kinetics of sorption that describe the solute uptake rate governing the residence time of the sorption reaction is one of the important characteristics that define the efficiency of sorption (Kim et al., 2004). Hence, in the present study, the kinetics of arsenic removal by HFOLR was carried out to understand the adsorption behaviour of the adsorbent. Quantifying the changes in sorption with time requires that an appropriate kinetic model be used, and traditionally, the pseudo-first-order equation and the pseudo-second-order equation for describing the adsorption are applied to understand the sorption kinetics. Good fits were not observed for all concentrations, which in turn indicate that the sorption reaction can not be approximated with either a pseudo-first-order or a pseudo-second-order kinetic model (figures not shown).

The mechanism for the removal of As by adsorption may be assumed to involve the following four steps (Mathews and Weber, 1976).

- Migration of the As species from bulk of the solution to the surface of the adsorbent.
- Diffusion of the As species through the boundary layer to the surface of the adsorbent.
- Adsorption of As species at active sites on the surface of HFOLR.
• Intraparticle diffusion of the As species into the interior pores of the adsorbent.

The boundary layer resistance will be affected by the rate of adsorption and increase in contact time, which will reduce the resistance and increase the mobility of the adsorbate during adsorption. The uptake of As species at the active sites of HFOLR can mainly be governed by either liquid phase mass transfer rate or intraparticle mass transfer rate. For most purposes, the adsorption of the adsorbate at the site on the internal surface occurs almost instantaneously, so it has little effect on the rate of the overall reaction. The transfer of the adsorbate from the bulk of the solution to the surface layer of the solution around a particle can occur rather slowly, but in most treatment systems, this is encouraged by the constant movement of the liquid. On the other hand, the diffusion of the adsorbate through or across the surface of the adsorbent may occur rather slowly, and this diffusion usually limits the rate of the adsorption process (Dogan et al., 2004). The adsorbate species are most probably transported from the bulk of the solution into the solid phase through intraparticle diffusion/transport process, which is often the rate limiting step in many adsorption processes.

6.8.2 Intraparticle diffusion model

The possibility of intraparticle diffusion was explored by using the intraparticle diffusion model.

\[ q_t = k_p t^{1/2} + C \]  

where \( q_t \) is the amount of As adsorbed at time \( t \) (mg/g); \( C \) is the intercept and \( k_p \) is the intraparticle diffusion rate constant (mg s\(^{-1/2}\) g\(^{-1}\)). A plot of \( q_t \) versus \( t^{1/2} \) should be a straight line with a slope \( k_p \) and intercept \( C \) when adsorption mechanism follows the intraparticle diffusion process. Values of intercept give an idea about
the thickness of boundary layer, i.e., the larger the intercept the greater the boundary layer effect (Kannan and Sundaram, 2001). The rate parameters for intraparticle diffusion \( (k_p) \) at different initial concentrations are determined using Equation (1.62).

Such plots may present a multilinearity, indicating that two or more steps take place (Kim et al., 2004). The first, a small sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. The third portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution.

Plots of \( q_t \) versus \( t^{1/2} \) for arsenite and arsenate are shown in Figure 88. The figure consists of an initial steep-sloped portion followed by a slow diffusion period and a final equilibrium period. The initial steep-sloped portion (from 0 to 30 min) is attributed to surface adsorption followed by gradual adsorption, where the intraparticle diffusion is rate-controlled and the plateau to equilibrium. The slow approach to equilibrium is attributed to the resistance offered by the sorbent’s internal structure (McKay, 1996). At this final region, the intraparticle diffusion begins to slow due to the extremely low solute concentration in the solution (Sun and Yang, 2003). The intraparticle diffusion rate was obtained from the slope of the steep-sloped portion corresponding to 30 min to 7 h. The arsenic was initially adsorbed by the exterior surface of the HFOLR. Since the external surface area is small, the adsorption at the exterior surface reaches the saturation level within limited time and the arsenic ions begin to enter the HFOLR via the pores within the adsorbent and are adsorbed by the interior surfaces of the HFOLR. When the arsenic ion diffuses into the pores of the HFOLR, the diffusion resistance is increased, which in turn leads to a decrease in diffusion rate. With the decrease in arsenic concentration in the solution, the diffusion rate becomes constantly lower,
and consequently, the diffusion processes reach equilibrium. In addition, this diffusion rate for As(V) is two times faster than that of As(III), indicating that arsenate ion is more easily diffused and transported into HFOLR pores than arsenite. Arsenic ions are generally present in a hydrated form in aqueous solution (Kim et al., 2004). Arsenite ion has a plane-triangular shape, while arsenate ion has a tetrahedral shape. The radius of an arsenate ion is smaller than that of an arsenite ion: HAsO$_4^{2-}$ - 3.97 Å, H$_2$AsO$_4^{-}$ - 4.16 Å, H$_3$AsO$_4$ - 4.16Å, H$_2$AsO$_3^{-}$ - 4.80Å, and H$_3$AsO$_3$ -4.80Å. Therefore, arsenate ions are able to diffuse into the pores of HFOLR more easily than arsenite ions thus take longer period for attaining equilibrium. The values of $k_p$ were calculated by using correlation analysis (Table 24). The values of $k_p$ increase from 0.0191 to 0.1225 mg/g s$^{1/2}$ for As(V) and from 0.0186 to 0.0942 mg/g s$^{1/2}$ for As(III) with increase in concentration from 10 to 100 mg/L. The high regression coefficient values suggest that the uptake of As(V) varies almost linearly with the half power of time ($t^{1/2}$). This functional relationship corresponds to the characteristic of intraparticle diffusion. It is found that diffusion rate was increased with increase of As concentration (Figure 88).

**Table 25**

Intraparticle diffusion constants of As(V) and As(III) adsorption onto HFOLR at various initial As concentrations

<table>
<thead>
<tr>
<th>Initial Concentration (mg/L)</th>
<th>Intraparticle diffusion constant, $k_p$ (mg/g s$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As(V)</td>
</tr>
<tr>
<td>10</td>
<td>0.0191</td>
</tr>
<tr>
<td>25</td>
<td>0.0563</td>
</tr>
<tr>
<td>50</td>
<td>0.0788</td>
</tr>
<tr>
<td>100</td>
<td>0.1225</td>
</tr>
</tbody>
</table>
Figure 88
Intraparticle diffusion plots for the adsorption of [A] As(V) [B] As(III) at different concentrations
6.9 Equilibrium Isotherms

To establish the most appropriate correlation for the equilibrium curves, isotherm studies have been performed for both As(III) and As(V) using four isotherm equations namely, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The isotherm analyses based on the constants obtained from the linearised plots and $r^2$ error analyses are discussed in the following sections. The experimental data of the amount of sorbate adsorbed on the sorbent are substituted into each equilibrium isotherm model to determine the best-fit model for the sorption system. The traditional approach of determining the isotherm model by linear regression of isotherm equations appears to give very good fits to the experimental data as most of their respective regression correlation coefficients are close to unity (Wong et al., 2004). Even though, the correlation coefficient $r^2$ yields the best-fit isotherm constants based on the linearised isotherm plots it has the disadvantage that it may not provide the best isotherm constants to correlate the original isotherm equation with experimental data points. In addition, since the $r^2$ factor is based on the square of the difference between theoretical and experimental data points, it will result in higher weighting to the higher $C_e$ value data points. Consequently, it will give a better fit correlation to the higher $C_e$ value data points. Thus, a normalization of each parameter is employed in order to have a better comparison between the parameter sets for the single isotherm model. The experimental data of the amount of sorbate adsorbed on the sorbent are substituted into each equilibrium isotherm model to determine the best-fit model for the sorption system. The normalized deviation $\Delta q$ (%) corresponding to Equation (4.30), for the set of values were obtained with respect to each of the models and were used to quantitatively compare the applicability of each model.
Chapter 6

The sorption data were analyzed according to the linear form of the Langmuir isotherm. The plots of specific sorption \((C_e/q_e)\) against the equilibrium concentration \((C_e)\) for As(V) and As(III) adsorption onto HFOLR were found to be linear over the whole concentration range studied at four different temperatures and the linear correlation coefficients were high (figures not shown). The maximum uptake capacities \((Q^0)\) for As(V) and As(III) are 36.2 and 25.8 mg/g, respectively at 30 °C (Table 25). The higher values of \('b'\) for As(V) compared to As(III) at all temperatures suggesting the stronger interaction of As(V) with HFOLR.

Based on the Langmuir isotherm, the values of Gibbs free energy of adsorption for were found to be -22.6, -23.7, -25.0 and -26.6 kJ/mol for As(V) and -21.8, -23.1, -24.4 and -26.0 kJ/mol for As(III) respectively at 30, 40, 50 and 60 °C. The results indicate that As(V) adsorption with a slightly more negative value is more easily adsorbed on HFOLR than As(III).

The Freundlich equation agreed well in regions of low concentration. For most of the cases, the Langmuir equation represents a slightly better fit of the experimental data than the Freundlich equation. The Freundlich equation predicts that the adsorbate concentrations on the adsorbent will increase so long as there is an increase in the As concentration in the liquid. From the logarithmic plots of the Freundlich expression (figures not shown) for the adsorption of As on HFOLR it can be understood that a very good description of data for over the concentration range studied is not possible. Table 25 gives the Freundlich sorption isotherm constants and the linear correlation coefficients. The Freundlich constant, \(n\) indicates the degree of favourability of adsorption. The Freundlich constant, \(n\) have values lying in the range of 1 to 10 for classification as favourable adsorption (Raji and Anirudhan, 1997). A smaller value of \((1/n)\) indicates a stronger bond between adsorbate and adsorbent, while a higher value for \(K_F\) indicates rate of adsorbate removal is high.
The Dubinin-Radushkevich isotherm is generally expressed as given in Equation (1.5) (Dubinin, 1960). Radushkevich (1949) and Dubinin (1965) have reported that the characteristic sorption curve is related to the porous structure of the sorbent. The constant, \( B_D \), is related to the mean free energy of sorption per mole, \( E \) of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution and this energy can be computed using the following relationship (Hasany and Chaudhary, 1996):

\[
E = \frac{1}{\sqrt{2B_D}}.
\]  

(6.8)

The linear Dubinin-Radushkevich isotherm plots for the sorption of the As(V) and As(III) onto HFOLR on examination shows that the isotherm does not provide an accurate description of the data for both the ions over the concentration range studied. The experimental data do not correlate well with the Dubinin-Radushkevich equation and this is confirmed by the low (>0.90) values of correlation coefficients and \( \Delta q \% \) as shown in Table 25. The values of \( E \) calculated using Equation (6.8) are 360.4, 409.8, 532.7 and 735.6 J/mol for As(V) and 237.3, 305.8, 369.5 and 519.5 J/mol of As(III), respectively. This is very much lower than typical range of bonding energy for ion-exchange mechanisms (Ho et al., 2002). The \( q_D \) values are consistent but lesser than the \( Q^o \) values previously determined from the Langmuir isotherm.

Temkin isotherm considers the effects of indirect adsorbate-adsorbate interactions on adsorption isotherms (Rengaraj et al., 2004). The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate-adsorbate interactions. Unlike the Langmuir isotherm, the Temkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. In the Temkin isotherm, the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate
interactions. This model assumes that adsorption is characterized by a uniform
distribution of binding energies, up to some maximum binding energy. The Temkin
isotherm has been used in the form as follows:

\[ q_e = \frac{RT}{b} \ln (AC_e) \]  \hspace{1cm} (6.9)

The Temkin isotherm can be expressed in its linear form as:

\[ q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln (Ce) \]  \hspace{1cm} (6.10)

where

\[ \frac{RT}{b} = B \]  \hspace{1cm} (6.11)

where \( A \) is the equilibrium binding constant corresponding to the maximum
binding energy.

The sorption data can be analyzed according to Equation (6.10). Therefore a
plot of \( q_e \) versus \( \ln C_e \) enables to determine the constants \( A \) and \( b \). The values of the
Temkin constants \( A \) and \( b \) are listed in Table 25 and the theoretical plots of this
isotherm are shown in Figures 89 and 90 for the As–HFOLR systems. The
correlation coefficients are as good as that of Langmuir value and higher than both
Freundlich and Redlich–Peterson values. As shown in Table 25, the value of \( A \) is
larger for As(V)–HFOLR system than that of As(III)–HFOLR interaction. This
means that the adsorbate/adsorbate interaction is larger for the former than that of
the latter. With increase in temperature the values of \( A \) show increasing trend
reiterating stronger interaction of the As species at elevated temperatures.
Figure 89
Comparison of the model fit of various isotherms to the observed isotherm data for the adsorption of As(V) onto HFOLR at different temperatures
Figure 90
Comparison of the model fit of various isotherms to the observed isotherm data for the adsorption of As(III) onto HFOLR at different temperatures
### Table 26

*Langmuir, Freundlich, Dubinin–Radushkevich and Temkin isotherm constants for the adsorption of As(V) and As(III) on HFOLR at different temperatures*

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Parameters</th>
<th>As(V)</th>
<th>Temperature (°C)</th>
<th>As(III)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$Q^0$ (mg/g)</td>
<td>36.2</td>
<td>37.2</td>
<td>38.4</td>
<td>39.9</td>
</tr>
<tr>
<td></td>
<td>$b$ (L/mg)</td>
<td>0.104</td>
<td>0.120</td>
<td>0.148</td>
<td>0.198</td>
</tr>
<tr>
<td></td>
<td>$\Delta q$ (%)</td>
<td>3.5</td>
<td>4.5</td>
<td>4.6</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.996</td>
<td>0.996</td>
<td>0.998</td>
<td>0.996</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>5.8</td>
<td>6.5</td>
<td>7.6</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>0.47</td>
<td>0.46</td>
<td>0.44</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>$\Delta q$ (%)</td>
<td>6.9</td>
<td>7.1</td>
<td>6.8</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.985</td>
<td>0.985</td>
<td>0.987</td>
<td>0.987</td>
</tr>
<tr>
<td>Dubinin–Radushkevich</td>
<td>$q$</td>
<td>25.8</td>
<td>26.9</td>
<td>27.8</td>
<td>29.1</td>
</tr>
<tr>
<td></td>
<td>$B \times 10^6$</td>
<td>3.8</td>
<td>2.9</td>
<td>1.7</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>$\Delta q$ (%)</td>
<td>11.2</td>
<td>11.2</td>
<td>12.0</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.865</td>
<td>0.871</td>
<td>0.855</td>
<td>0.851</td>
</tr>
<tr>
<td>Temkin</td>
<td>$A$ (L/g)</td>
<td>0.96</td>
<td>1.13</td>
<td>1.51</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>$b$</td>
<td>308.9</td>
<td>314.2</td>
<td>324.6</td>
<td>336.3</td>
</tr>
<tr>
<td></td>
<td>$\Delta q$ (%)</td>
<td>4.4</td>
<td>5.6</td>
<td>3.9</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.987</td>
<td>0.984</td>
<td>0.995</td>
<td>0.998</td>
</tr>
</tbody>
</table>
The Freundlich isotherm led to reasonably good results for both As(III) as well as As(V), considering that the error of this equation is randomly distributed in all cases. However, the empirical nature of Freundlich equation makes it difficult to discuss the estimated values of the parameters. The validity of both Langmuir and Freundlich equations for HFOLR may indicate that the apparent monolayer coverage is not reached in the concentration range studied. Another evidence of this behaviour is the comparatively lower adsorption capacity of As(III), compared with As(V), which may be attributed to the different factors discussed in the earlier portions of the study. Considering the pore size distribution of the sorbent from 2 to 500 Å, the steric effect was ruled out as a possible explanation. The D-R equation did not predict experimental data satisfactorily for both the solutes indicating that the same pore volume was not filled by the solutes. The values of correlation coefficients are much lower than the other three isotherms values. In all cases, the D-R equation represents the poorer fit of experimental data than the other isotherm equation. According to the D-R equation, the same saturation capacity should be obtained for HFOLR for liquid concentrations in the vicinity of its solubility provided the density in the adsorbed phase is similar. Therefore, it is deduced that the pore-filling model of the D-R equation is not applicable to this adsorption, which means that the estimated values of the D-R isotherm parameters for HFOLR (Table 25) have no physical meaning. A chemisorption mechanism, which is out of the range of application of Dubinin’s theory, is more plausible in this system.

In order to assess the different isotherms and their validity to correlate experimental results, the theoretical plots for each isotherm have also been shown with the experimental data for the adsorption As(V) and As(III) in Figures 89 and 90 respectively. Based on the proximity of the experimental points with that of the
Removal of Arsenic from .........

theoretically predicted points and correlation coefficient ($r^2$) and $\Delta q$ (%) values (Table 25) it is concluded that Langmuir and Temkin equations give best fit over the entire range of concentrations. The $\Delta q$ (%) values obtained for the other two isotherm equations are higher than that for the Langmuir and Temkin equations in most of the cases.

6.10 Testing with Simulated Groundwater Samples

The present study examined the suitability of HFOLR for treating simulated groundwater sample for the purpose of remediation of arsenic. The sample is based on groundwater of New Jersey, USA, and contained apart from arsenic other metal ions based on Al, Mg, Fe, Ca and Mn as well as anions like fluoride, chloride, sulfate and carbonate (Bang et al., 2005). Two different samples with 1.0 mg/L each of As(V) and As(III) doped were prepared retaining the other reported features. The effect of the mass of HFOLR needed for the removal of As(V) and As(III) from water samples reveals that the removal of As(V) and As(III) was found to increase with increase in mass of adsorbent. Arsenic content could be brought down well below the maximum permissible levels as per WHO norms from 1.0 to 0.01 mg/L, with a HFOLR dose of 2.5 and 3.0 g/L for As(V) and As(III) respectively. The increase in adsorption with increase in mass of HFOLR is due to the increase in adsorbent surface area with increase of mass of adsorbent.
### Table 27

*Chemical composition and characteristics of the New Jersey groundwater and simulated groundwater*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NJ groundwater</th>
<th>Simulated groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td>130 mg CaCO₃/L</td>
<td>–</td>
</tr>
<tr>
<td>Aluminum</td>
<td>&lt;2.0 µg/L</td>
<td>3.0 µg/L</td>
</tr>
<tr>
<td>Arsenic</td>
<td>300 µg /L</td>
<td>1000 µg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>40 mg /L</td>
<td>40 mg/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>8.3 mg /L</td>
<td>15 mg/L</td>
</tr>
<tr>
<td>Fluoride</td>
<td>&lt;0.1 mg/L</td>
<td>&lt;0.1 mg/L</td>
</tr>
<tr>
<td>Hardness, total</td>
<td>140 mg/L</td>
<td>–</td>
</tr>
<tr>
<td>Iron</td>
<td>&lt;0.02 mg/L</td>
<td>&lt;0.02 mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>12 mg/L</td>
<td>17 mg/L</td>
</tr>
<tr>
<td>Manganese</td>
<td>&lt;2.0 µg/L</td>
<td>&lt;2.0 µg/L</td>
</tr>
<tr>
<td>pH</td>
<td>7.92</td>
<td>7.25</td>
</tr>
<tr>
<td>Silica, total</td>
<td>20 mg/L</td>
<td>20 mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>62 mg/L</td>
<td>62 mg/L</td>
</tr>
<tr>
<td>Total dissolved solid</td>
<td>0.26 mg l⁻¹</td>
<td>–</td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.16 NTU</td>
<td>–</td>
</tr>
</tbody>
</table>

*Total concentration after arsenic-spike.*

### 6.11 Regeneration Studies

Regeneration experiments were performed using several eluents, such as hydrochloric acid, citric acid and sodium hydroxide. These eluents are able to
Removal of Arsenic from... desorb As(III) and As(V) efficiently; however, in many cases iron is also released. A simultaneous release of iron and arsenate/arsenite ions does not actually allow the ions to be selectively separated. Moreover, it also restricts the possibility to re-use the sorbent. With a neutral solution the metal-impregnated sorbent is stable, however, the desorption efficiency is very low. Recovery of arsenic compounds from the HFOLR was checked with hydrochloric acid and sodium hydroxide solutions. The quantitative elution of arsenic(V) and arsenic(III) was successfully attained with either 0.1 M hydrochloric acid or 0.1 M sodium hydroxide solution. The best results are obtained with alkaline solutions. Ferric ions are also liberated from the resin with hydrochloric acid solution, but the amount of ferric ion released from the resin with 0.1 M sodium hydroxide solution as regenerant is less than 0.5 % of the total amount of ferric ion retained in the resin. Concentrations of NaOH higher than 0.1 M, however, gave a turbid solution, which is probably due to the generation of ferric hydroxide from the resin.

Desorption tests were thus carried out using sodium hydroxide solution in batch operation. HFOLR was treated with As(III) and As(V) solutions of initial concentration 10 mg/L. HFOLR pre-adsorbed with a known amount of As(V) or As(III) ions, was treated to 0.1 M NaOH solution. The mixture was shaken for 10 h followed by a centrifugation for separation. The desorption efficiency was evaluated by determination of As(V) and As(III) concentration in the supernatant. After desorption, HFOLR was regenerated and loaded with As(V) and As(III) ions again, for four times, under the same conditions as those in the original loading treatment. The result of regeneration data is presented in Table 27. It can be seen that the recovery percentage is higher for As(III). The adsorption capacity of regenerated HFOLR was compared with that of the virgin HFOLR. The adsorption capacity for the HFOLR without regeneration was also investigated for comparison.
The observation that arsenic desorption was completed within 10 h reveals that sorption sites of HFO microparticles are accessible through the network of pores, i.e., obstruction in the pores and subsequent increase in the tortuosity of dissolved solutes did not result from the dispersion of submicron HFO particles within the porous beads. At high alkaline pH, HFO sorption sites are all deprotonated and negatively charged; so are all arsenite and arsenate species. Donnan co-ion exclusion effect is thus very predominant under this condition resulting in efficient desorption (DeMarco et al., 2003).

The increased As solubility at higher pH values may be explained by the limited amount of Fe(III) available in solution after ferric oxyhydroxide precipitation (Twidwell et al., 1994). In fact, the total ferric iron solubility reaches a minimum at a pH of approximately 8.3, and this condition coincides with the location of the point of zero charge for ferric oxyhydroxide. Thus, positively charged iron species dominate at pH values below the point of zero charge. Negatively charged iron compounds are predominant above pH 8.3. As the arsenate species exist in anionic form, the solubility of arsenic should increase with increasing pH above 8.3 because of the repulsion of like charges. It is also important to observe that as the pH is increased, more iron is required for the same amount of arsenic removal, and this is consistent, not with a ferric arsenate precipitation mechanism, but with the co-precipitation of arsenic with the ferric oxyhydroxide solid phase.

It was confirmed that the regenerated resin can be used for the next adsorption–regeneration cycle for an acidic arsenic(V) solution without additional treatment with ferric ions. Preliminary results have shown that arsenate/arsenite can be removed again on the regenerated sorbent.

Following this regeneration procedure the sorptive capacity of the adsorbent remained almost the same, although after four regeneration cycles the adsorptive capacity was decreased very much, due to slowly accumulating quantities of arsenic.
At this point the adsorbent was subjected to complete regeneration by using strongly acidic solutions of HCl. This procedure enabled the recovering of all iron oxides and the described iron impregnation procedure was repeated to yield new samples of HFOLR.

### Table 28

*Regeneration data of As(III) and As(V) (initial concentration 10 mg/L) using 0.1 M NaOH*

<table>
<thead>
<tr>
<th>No. of cycles</th>
<th>Amount adsorbed (mg/g) As(III)</th>
<th>Amount desorbed (mg/g) As(III)</th>
<th>Recovery (%) As(III)</th>
<th>Amount adsorbed (mg/g) As(V)</th>
<th>Amount desorbed (mg/g) As(V)</th>
<th>Recovery (%) As(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.51</td>
<td>4.45</td>
<td>98.67</td>
<td>4.99</td>
<td>4.83</td>
<td>96.69</td>
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<td>2</td>
<td>4.30</td>
<td>4.18</td>
<td>97.09</td>
<td>4.86</td>
<td>4.67</td>
<td>96.09</td>
</tr>
<tr>
<td>3</td>
<td>4.14</td>
<td>3.96</td>
<td>95.65</td>
<td>4.73</td>
<td>4.46</td>
<td>94.28</td>
</tr>
<tr>
<td>4</td>
<td>3.96</td>
<td>3.74</td>
<td>94.44</td>
<td>4.47</td>
<td>4.17</td>
<td>93.29</td>
</tr>
</tbody>
</table>

### 6.12 Advantages of HFOLR

The HFOLR developed in this study has the following advantages over traditionally used iron oxides: (1) big particle size makes it easy to be separated from aqueous system after adsorption activity; (2) the spherical morphology of the adsorbent HFOLR is well suited for "at-the-tap" remediation of arsenic because the spheres would pack together efficiently in a column but still allow a decent water flow rate to be maintained, unlike loose, fine powders; (3) high adsorption capacities contribute to the removal of As from concentrated solutions and the reduction of arsenic levels to below 1 ppm can be achieved with less adsorbent dose; (4) high physical strength, the good mechanical stability exhibited by the sorbent and globular character make it suitable for column use; (5) easy for preparation since all the chemical reactions occur simultaneously in one system;
(6) the process needs no pre-oxidation step since the sorbent is able to remove As(III) as well as As(V) from aqueous medium effectively; (7) the adsorption system is expected to provide low capital and operating cost, and requires minimal monitoring and maintenance, reduces waste generation. The capital cost of the proposed system (based on cost of sorbent) should be at least an order of magnitude lower than that of processes based on ion exchange and other iron based materials.