CHAPTER - V

Result & Discussion
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To determine the effectiveness of iron-oxide-coated sand for the removal of As(V) was conducted to develop a heating process for coating hydrated iron oxide on sand surface to utilize the adsorbent properties of the chemical coating and filtration properties of sand by (Lai et al, 2000). The other study made by coating of ferric and aluminum hydroxide on sand (Axe, 2002; Chakravarty and Dureja, 2002). The coating characteristics of the adsorbents are important in order to evaluate their adsorption capacities. The mechanism of impregnation on the adsorbents such as AdRS-17 by FeCl$_3$ and AdS-24 by FeNO$_3$.nH$_2$O solution used to generate the coating is strongly acidic, due to hydrolysis of the Fe$^{3+}$ ions by reactions of the type-

$$Fe^{3+} + nH_2O \rightarrow Fe(OH)^{3-n} + nH^+$$

During the heating step, water evaporates from the solution, neutralizing and concentrating the residual solution and causing Fe-oxide to precipitate. Most of this precipitate coats the sand grains, although some oxide precipitates in the spaces between the grains (Benjamin, M.M., Sletten, R.S., 1996) Examination of the coating with scanning electron microscopy (SEM) revealed the presence of regular hexagonal crystals, which are characteristic of the iron oxide coated sand (Badruzzaman et al., 2004). Therefore, the coated sand was subjected to more drying cycles, each consisting of 3 h of drying at 110$^\circ$C followed by 21 hours at room temperature. The coating became progressively less hygroscopic during this procedure (Beck, 1993).

The characterization of the adsorbent carried out by FTIR spectroscopy of the hydrous oxides samples revealed the specific sets of peaks as given in Table 3.4 (frequencies in cm$^{-1}$), which play an important role for arsenic removal mechanism by iron coated adsorbents (Singh and Tiwary, 2000) The hydrous oxides of Fe(III) viz. akaganeite, haematite and Mn(IV) viz. amorphous manganese oxide, hausmannite, manganite, hydrous manganese dioxide (todorokite) were prepared using the standard methods (Lenoble, 2002; Lumsodon, 1994). The FTIR spectra of the screened adsorbent such as (AdRS-17, AdS-24, AdS-31 and AdAl-34 are shown in Fig. 3.1-3.8. The FTIR spectra of the short listed adsorbents such as AdRS17, AdS24, AdS31 and AdAl34 and after adsorption with arsenic is illustrated in (Fig 3.1-3.8 and Table 3.3-3.4). Keller (1996)
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reported the positive identification of adsorbed arsenate species using FTIR techniques, the IR spectra of sodium arsenate containing adsorbed arsenate and free arsenate. The main adsorption band observed at 1653 and 849 cm\(^{-1}\) were in close agreement with our observations.

Matis (1999a) reported the XRD patterns for the sorbents after arsenic sorption at pH-7.5 (similar to our pH), the sorbents had the structure of the typical crystalline structure. Two new bands appearing at 22\(^{0}\) and 54\(^{0}\) could attributed to the formation of ferric arsenate. It support that the samples AdRS-17, AdS-24, AdS-31 and AdAl-34 are well crystallized form with strong basal plane reflections at 6.12 A° and 2.78 A° due to bedmate and chloropyrite respectively in all the cases. The chemical analysis of the chemically modified natural adsorbents (AdRS-17, AdS-24, AdS-31 and AdAl-34), which is contains oxides of iron in trace amounts. The significant bands obtained in the infrared spectra of coated sand and red sand along with their possible assignments are given in Table 3.6. Most of the adsorption bands such as those at 3700, 3620, 1100-1000, 770, 690 and 450 cm\(^{-1}\) are attributed to the presence of quartz in the sample The XRD patterns of the two iron coated sand AdRS17 and AdS24 as illustrated in Table 3.5, indicate that the samples are reasonably coated in homogeneous manner and both are of crystalline variety (Manning, 1998; Matis, 1997). The XRD pattern of the arsenic adsorbed AdRS17, AdS24, AdS31 and AdAl34 does not show any significant peak for arsenic because the adsorption is mainly localized in some portion of the adsorbent but not uniformly (Fig. 3.9-3.15 and Table 3.5-3.6). After adsorption of arsenic the band observed at around 625 to 3500 cm\(^{-1}\) range in the case of arsenic becomes very strong and sharp and shifts to higher wave number (Yuan, 2001).

SEM photographs in Fig. 3.16-3.20 were taken at 5000X, 10000X magnifications to observe the surface morphology of the quartz sand and iron-coated sand, respectively. (Edwards and Bonnin, 1997). Quartz sand had a very rough surface and cracks, macropores or roughness could be found on the sand surface (Galer and Delmas, 1997). On the contrary, the iron-coated sand appeared as uniformly coated surface. Quartz sand surfaces were apparently occupied by iron oxides, which were formed during the coating process (Jekel, 1994). No cracks were visible, except for the crystalline iron oxides found on the surface and the microstructure from the sample of polished iron-coated sand. It could be found the sand surface was covered with iron oxide particles by the SEM observation, and the coating thickness of iron oxide was about 4-7. The amount of iron on the sand surface was about 5.7 ± 0.3 mg-Fe/g-sand by acidic digestion analysis (Lai, 1997;
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Lawernce, 1999). The SEM pictures of arsenic adsorbed AdRS17, AdS24, AdS31, AdAl34 are shown in (Fig. 3.16-3.20 and Table 3.7-3.11). The SEM of AdRS17 shows that there may be formation of dehydrated Fe(III) arsenate (scolodite) or Fe$_3$(AsO$_4$)$_2$.8H$_2$O (symplesite) on the surface. But in all the cases it is found that arsenic is deposited in the form of crystal on the surface of the adsorbent non-uniformly i.e. in the localised manner.

Energy dispersive analysis of x-rays (EDX). Li et al. (2000) and Lindberg (1997) were used to analyse the elemental constituents of arsenic adsorbed adsorbents as stated above are shown in Table 3.7-3.11. The spectrum of AdRS17, AdS24, AdS31 and AdAl34 identified the electron-dense material as arsenic along with the other base elements present in the adsorbents. Thus the EDX analysis provides the direct evidence for the specific adsorption of arsenic on the surface of these above mentioned adsorbents. Scanning Electron Micrograph (Chen et al., 1997) of adsorbents showed that coatings of different chemicals are quite well and uniform on sand, alumina and coarse sand particles. Chemical activity and adsorption properties of above sorbents were found to be increased and thus the efficacy of chemically coated natural sorbents enhanced enormously for the removal of chemical pollutants present in the water (McNeill, 1995; Huang, 1997). In the case of chemically coated natural sorbents such as AdRS17, AdS24, AdS31 and AdAl34, SEM photograph showed about their particle size which play an important role to increase the efficacy, because smaller the particle size facilitates more active sites and greater the surface area and different chemical coating activates these active sites towards the metallic pollutants present in the water.

It has been observed from the EPM of AdAl34 adsorbents are usually positive in the pH range 2.5-10. The point at which the EPM is zero is called the isoelectric point. The figures show that the IEP of AdAl34 is 9.9. The IEP of AdS31 is found to be 1.6 by extrapolating the curve to EPM zero. Hiemstra and Van Riemsdijk (1999) reported the surface and pore size distribution for the samples were investigated using BET analysis, the pore size distribution of iron coated sand had been changed after reacting with arsenic, thus parts of pores disappeared through the adsorption process. Similar observation occurs to the uncoated and iron-coated sand surface was obtained by BET surfaces area analyzer for the purpose of observing the surface area of iron-coated sand (Hering, 1997; Hespanhol, 1994).

The reverse of adsorption is known as desorption which is carried out for the regeneration of the adsorbents. The regeneration of adsorbents is one of the most important operations in adsorption technology. The major part involved in lowering the
cost of any adsorption process lies in this regeneration step. The optimum regeneration conditions must be searched to give the greatest adsorbent efficiency and life, with a minimum energy input during regeneration (Hering, 1996; Waltham, 2002). Using arsenic solution for the desorption of the arsenic adsorbed on AdRS-17 have been observed to be 46.0%. Such a behavior is due to an interaction between the surface and added solutes, which may block some of the adsorption active sites for the arsenic molecules. In this way the regenerated adsorbent could be used further to remove the arsenic from the effluent. The regeneration data for the adsorbents could not be obtained in a more accurate way. Cores sand is easily available and cheapest materials.

Matsunaga (1996) and McNeill (1997) studied the uptake of arsenic increases with laps of time and reached the saturation time. The effect of run time on arsenic removal at various initial concentrations, the removal of arsenic from water increases with the lapse of time and attains equilibrium after 125 minutes for different concentrations. It was observed that the process is highly dependent on the initial concentration of the solution. This is because at lower concentration, the ratio of initial number of moles of arsenic to the available surface area is high and subsequently the fractional adsorption becomes independent of initial concentration (Wasay, 1996; Ioannis, 2002). At higher concentration the available sites of adsorption becomes less and hence the percentage removal of arsenic is dependent upon the initial concentration (Bowell, 1994; Hussian et al., 1993)

The progress of adsorption is governed by the kinetics of surface hydroxylation and subsequent acid-base dissociation of aqua-complex of the oxides and the oxide solution interface changes (McNeill, 1995; Goldberg, 2001) in the following manner:

$$M(OH)O^- \leftrightarrow M(OH)_2 \leftrightarrow M^+ (OH)$$

It can be seen from the above equilibrium that the negatively charged ion density lies on the oxygen site of the surface, whereas, the positively charged ion density lies on the metal site of the surface. Similar mechanism was suggested earlier by Zhu (1997) and Wilkie (1996) for double layer model of adsorption of anions at the oxide-solution interface. The above mechanism explains satisfactorily the variation in adsorption with retention period between adsorbent and adsorbate on the basis of surface reaction of adsorbate species with interface, which ultimately reaches the equilibrium condition.

A more appropriate double layer model for explaining the adsorption mechanism at the oxide-solution interface was proposed by (Edwards, 1989; Eilimelech, 1996) According to them, the following equilibria exist, at the surface as well as in the bulk of the solution.

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\begin{align*}
(MOH)_3 & \leftrightarrow (MOH)b \\
(MOH)b + (OH-)b & \leftrightarrow (MO-)b + H_2O \\
(MOH)s + (OH-)b & \leftrightarrow (MO-)s + H_2O
\end{align*}
\]

Where, the subscript s and b refer to the surface and bulk metal hydroxide, respectively. MOH and (MO)\(^-\) denote multivalent metal hydroxides M(OH)\(_n\) and [M(OH)\(_{n+1}\)], respectively. Thus, the above model seems to be more appropriate for explaining the surface reactions involved in such type of oxide-solution systems (Fan, 1997; Elizalde, 2001). The result further indicates that the extent of removal of each as is highly dependent on the concentration. A series of contact experiments were undertaken for varying initial arsenic concentrations, namely 2-10 mg L\(^{-1}\). For low concentrations, there was a rapid uptake of arsenic due to surface mass transfer. Fig. 4.2 shown that the removal of arsenic by AdRS-17 and AdA-24 are 94.05 and 85.23 respectively and Fig. 4.3 shown that for the removal of arsenic from drinking water by AdS-31 and AdAL-34 by increasing the concentration of the arsenic from 2 to 10 mg L\(^{-1}\) at temperature 25±1\(^{0}\)C. The Fig. 4.4 shown that time, the arsenic removal by AdRS-17 and AdS-24 are 93.2 and 81.4% at time of 125 min, after increasing the time removal tends to saturation and all parameters remains constant. The arsenic removal by AdS-31 and AdAl-34 are 74.2 and 68.3% at time of 125 min, after increasing the time removal tends to saturation and all parameters remains constant.

Zhang and Singh (2004) studied the effect of particle size on arsenic adsorption was investigated over the range +125 to -38 um. Such data would be valuable for scaleup and practical application. The experimental results shown in Fig. 4.6 and 4.7 are the plots of the percentage removal of arsenic against particle size are found to increase from 60 to 94% with decrease in particle size of the said adsorbent (AdRS-17, AdS-24, AdS-31 and AdRS-34) from 15 to 40 mesh at temperature 30±1\(^{0}\)C. The data show an increase in the rate of the arsenic uptake as the mean diameter of the sorbents decreases. This can be due to increase in the surface area. Luo and Youn (2001) suggested that internal porosity rather that outer surface area is the major determinant of surface area.

Singh et al. (2002) conclude the removal of arsenic increases in the rate agitation upto 125 minutes and beyond this it is almost constant. The results observed that in Fig. 4.8, the removal of arsenic by AdRS-17, AdS-24 increases from 50 to 88%, 30 to 78% and in Fig. 4.9, the removal of arsenic by AdS-31, AdAl-34 increases from 38 to 82%, 25 to
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65%, at agitation speed starting from 40 to 150 rpm, while the maximum removal occurred at optimum agitation speed at 100 rpm, after increase agitation speed, the removal tends to saturation and decreasement, keeping the all parameters such as concentration, pH, temperature are constant throughout series. Lin and Wu (2001) and Khair (1999) are evident that the rate of adsorption in controlled by the degree of agitation to certain extent as the increasing agitation and reduces the boundary layer resistance to mass transfer and increases the mobility of the system. Lackovic et al. (2000) also reported an increase in the rate of arsenic removal with increasing the degree of agitation for the adsorption at different agitation speeds. This was attributed to the decrease in the diffusion layer thickness surrounding the adsorbent particles. Tokunga and Wasay (1999) also reported an increase in the intraparticle diffusion parameters with an increase in the agitation rate.

The effect on the macro pore was greater than on the micro pore parameter, which remains essentially constant. The increase in external fluid velocity causes a decrease in the external surface film resistance allowing the arsenic to reach the particle surface more rapidly. This in turn, will provide a greater driving force for intraparticle diffusion. Meng and Bang (2000) reported that the rate of arsenic removal from the bulk solution is controlled by the degree of agitation. The effect of increasing the stirring rate is to decrease the boundary layer thickness and hence the film resistance to mass transfer surrounding the adsorbent particles.

It is evident from the Fig. 4.11, the percentage removal of arsenic occurred maximum by AdS-31 and AdAl-34 are 85% and 74% respectively, at initial dose of adsorbents are 0.2 to 1.1 mg/gm, while the maximum removal of arsenic are 93.8% by AdRS-17 and 84% by AdS-24 respectively, at optimum initial concentration 0.8 mg/gm, keeping the other parameter constant such as contact time, temperature, pH, agitation speed. It is further noted that on increases the amount of adsorbent, the curves are continuous and approach towards saturations. Waltham and Ecik (2002) reported the concentration decreased exponentially with an increase in the amount of adsorbent, an adsorbent dose of 5 g/L effectively decreased residual As(V) concentration to below 0.01 mg/L. This may be due to a tendency of the arsenic molecules to escape from the solid phase to the bulk phase (solution) with an increase in temperature of the solution (Khair et al., 1999). Thus, on increasing the temperature of the system from 25 to 45°C, the adsorption of the arsenic on said adsorbents decrease.

The uptake of arsenic have been found to decrease from the range 94 to 78% by such adsorbents (AdRS-17, AdS-24, AdS-31 and AdAl-34) with an increase in
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temperature from 25 to 45ºC. Fig. 4.11 and 4.13 indicating the process is endothermic. Isleyen (1998) reported the variation in the extent of adsorption with temperature may be explained on the basis of the change in chemical potentials which is related to the solubility of the adsorbate species which increases with an increase in temperature, the chemical potential decreases and both the effects i.e. solubility and the temperature effects, work in the same direction (Day, 1998; Das, 1999). This will result in the decrease of adsorption. It is thus concluded that in the removal of the arsenic also depends on the nature of adsorbents in addition the adsorbates. Also, it appears that the behavior of the system containing particular changes when a specific adsorbent is used (Dehyanni et al., 2000). The values of $Q^0$ and $b$ at different temperatures were determined from the slopes and intercepts of the respective plots, are presented in Table 4.3. It is evident from the amount of arsenic adsorbed by various adsorbent such as- AdRS-17, AdS-24, AdS-31 and AdAl-34 are 93.0, 82.9, 88.3 and 76.3% respectively, the $Q^0$ values changes with increase with temperature from 25 to 45ºC. The adsorption capacity of AdRS-17 is greater than these of other adsorbents such as AdS-24, AdS-31 and AdAl-34.

Singh et al. (1998) described using the Langmuir isotherms and confirmed by the linear transformation of the experimental data. The equilibrium parameter, $R_L$ has also been calculated, which indicated that the adsorption of arsenic on coated materials from buffing dust is a favorable process because $R_L$ values lies between 0 and 1 (Singh and Yenkie, 2002). The values of $Q^0$ and $b$ at different temperatures were determined from the Langmuir plots. They obtained $Q^0$ values from 0.64 to 0.75 mg g$^{-1}$ and $b$ from 0.37 to 2.94 L mg$^{-1}$ with the increase of temperature from 25 to 45ºC at an initial concentration of 0.8 mg l$^{-1}$. Sun and Doner (1996) reported the constant $Q^0$ and $b$ related to the capacity and energy of adsorption. The data reveled the applicability of the Freundlich equation in the arsenic removal. The Freundlich equation predicts that the arsenic concentrations on the adsorbents will increase so long as there is an increase in the arsenic concentration in the water. The deviation from linearity of the log plot occurs as the adsorption isotherm a horizontal plate. As before, this suggests a change in the rate and extent of adsorption as new sites are created in the adsorbent surface. The linearised plots of Freundlich isotherm for the adsorption of arsenic on coated adsorbents sand was investigated by Denyanni et al. (2000). The steeper slope of adsorption line for arsenic indicated its greater affinity to coated adsorbents. Nenov and Zouboulis (1994) revealed that the linear plot of $\log \frac{X}{m} v_s$ vs $\log C_e$ indicates the applicability of the Freundlich adsorption isotherm for the present
system exhibiting, thereby, a monolayer coverage of the adsorbate on the outer surface of the adsorbent. Deliyanni et al. (2003) reported that the values of correlation coefficients R², which is a measure of the goodness of fit, confirm the good representation of isotherm data of our study. Singh and Pant (2001) supported that, the logarithmic plot of Qe v/s Ce at various concentration, whereas the values of K and n found these parameters strongly supported to Freundlich isotherm.

To study the effect of pH on arsenic removal from drinking water, pH was adjusted in the range of 3 to 10. The arsenic can be seen from figure, arsenic removal strongly depends on the pH of the solution and maximum removal was obtained in the pH ranging from 6.0 to 7.5. Dutta et al. (1997) were reported that the maximum arsenic removal occurs at a pH ranging from 5 to 8. The effect of pH on As(V) removal can be explained with the help of ionic species diagram which clearly indicates that in the range of highest sorption efficiency, the dominant species are H₃AsO₄ and H₂AsO₄⁻. The reason for less adsorption in the lower pH range is that the only force acting between arsenic specie present and adsorbent is the weak Vander Waal’s attraction. Gregor (2001) supported, the maximum adsorption at pH 7.5 can be attributed to the fact that the difference between the energy released upon adsorption and energy required to dissociate H₃AsO₄ was the maximum. Decrease in removal efficiency at higher pH may be due to presence of high concentration of OH⁻ ions present in the reaction mixture. The mechanism of adsorption may be described as the addition of iron coated sorbents to water at different initial pH is found to have a “buffering” effect, so that resultant pH is around 7-8. This buffering effect can be explained by the amphoteric nature of the iron oxide as given in following equations ([\textit{\Pi}] donates surface groups) (Devila, 1997; Cornel and Schwertmann, 1996):

\[
\begin{align*}
[\textit{\Pi}]\text{FeOH}+2 & = [\textit{\Pi}]\text{FeOH} + \text{H}^+ \\
[\textit{\Pi}]\text{FeOH} & = [\textit{\Pi}]\text{FeO}^- + \text{H}^+
\end{align*}
\]

It is obvious that there no significant change in the amount of As(v) removal in the pH range 2.8-5.0 and thereafter the removal increases abruptly and reaches maximum at pH-7.5 followed by sharp decreases in the extent adsorption upto 10.0 pH. The maximum removal of As(v) at pH 7.5 was also noted by Stenkamp (1994) on iron oxide coated sand using as an adsorbents. The results further show that in highly acidic medium, where the adsorbents surfaces are highly protonated and As(v) mostly exist in the form of neutral H₃AsO₃ species. The degree of protonation of the surfaces reduces gradually and
approaches to zero at pH-7.0, Therefore, the extent of removal starts increasing and reaches maximum at pH-7.5, where the probability of physiosorption can not be ruled out (Peleanu et al., 2000). Effect of pH on adsorption of arsenic per unit mass of the adsorbent for various systems have been studied and is shown in Fig. 4.17. It is observed from the results that the change in pH of the medium has significantly affected the extent of removal of arsenic on AdRS-17, AdS-24, AdS-31, AdAl-34. The adsorption of arsenic increases with the increase of pH of the medium has also been shown graphically for various system (Fig. 4.18). For both the systems the maximum removal was noted at pH 7.5 in the studied pH range. With an increase of pH from 2.5 to 7.5, the uptake of arsenic increases upto 93.05 and 78.4 by AdRS-17 and AdS-24 (Fig. 4.17). Similar observations have also been obtained for the arsenic removal by AdS-31 and AdAl-34 are 89.2 and 76.8 respectively, keeping all parameters through constant. The removal of the arsenic from drinking water by AdRS-17 and AdS-24 with respect to pH variation (pH 2.5 to 7.5) shows that the uptake of arsenic (Fig. 4.17) increases from 62.03 to 94.11% at a temperature 25°C and initial concentration 0.8 mg L⁻¹. It is further noted that in the case of a AdS-31 and AdAl-34, there is no significant change in the amount of arsenic removed in the pH range 2.5 to 4.5 but the removal increases abruptly and reaches maximum at pH 7.5 (Fig. 4.18) followed by a decrease in the extent of adsorption above this pH.

In order to evaluate the ecotoxicological impact (Neff, 1997) of these sorbents, bioassay tests were conducted after the batch and column studies by using standard test fish Poecelia reticulata (Guppy). Physico-chemical characteristics of the filtrate (treated water) were also determined to ensure the quality of the treated water.