Kinetics and Mass Transfer Studies on the Adsorption of Arsenic onto Activated Alumina and Iron Oxide Impregnated Activated Alumina

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The present investigation deals with the uptake of As(III) and As(V) ions from aqueous solution by activated alumina and a new laboratory-prepared sorbent—iron oxide impregnated activated alumina. Iron oxide impregnation onto activated alumina significantly increased the percent arsenic removal and adsorption capacity for As(III) and As(V) ions. The maximum As(III) and As(V) removals were 96.8% and 98.4%, respectively, by iron oxide impregnated activated alumina (IOIAA). Maximum As(III) and As(V) removal of 94.2% and 96.1% was observed over activated alumina. Kinetic studies were performed at different initial sorbate concentrations to determine the mechanism of mass transfer of sorbate onto this sorbent. The maximum removal of As(III) and As(V) by activated alumina and iron oxide impregnated alumina takes place within 6 h and attains equilibrium within 12 h. First-order Lagergren kinetics explained the adsorption of arsenic over activated alumina whereas a pseudo-second order rate equation explained the behaviour of As(III) adsorption over iron oxide impregnated activated alumina. Diffusional effects in solid pellets were also investigated to understand the mechanism of adsorption. These results indicate that the mechanism of arsenic adsorption is complex on both sorbents as both pore diffusion and surface diffusion contribute to the arsenic removal. During the initial period, surface diffusion was predominant but as the adsorption progresses, pore diffusion dominated the rate of adsorption.

Key words: arsenic, diffusion, adsorption, kinetics, iron oxide

Introduction

Contamination of drinking water by arsenic has become a key environmental problem of the 21st century. Arsenic is a ubiquitous element and its presence in water due to natural and anthropogenic sources, leaching and soil erosion, leads to arsenic dissolution into the aquatic environment (Ming 2005; Smedley and Kinniburgh 2002). Arsenic occurs in natural waters mainly as inorganic arsenite and arsenate, it does not often form in its elemental state and is far more common in sulfides and sulfo salts such as arsenopyrite, orpiment, realgar, lollingite and tennantite (Chen et al. 1994; Smedley and Kinniburgh 2002). The most common of the arsenic minerals is arsenopyrite (FeAsS). Arsenic is found associated with many types of mineral deposits, especially those including sulfide mineralization. Arsenic readily substitutes for silicon, ferric, iron and aluminium in crystal lattices of silicate minerals and, therefore, it is possible for it to occur in all geological materials.

Presence of high arsenic concentrations has been reported in drinking water in Taiwan (Chen et al. 1994), India (Chatterjee et al. 1995; Das et al. 1995; Mandal et al. 1996), Bangladesh (Biswas et al. 1998; Karim 2000), Chile (Borgono et al. 1971), North Mexico (Cebrian et al. 1983), Argentina (Astolfi et al. 1981; Nicoll et al. 1989; De Sastre et al. 1992), China, U.S.A. and Nepal (Tendukar and Neku 2002). It has been estimated that 60 to 100 million people in India and Bangladesh are currently at risk as a result of drinking water contaminated by arsenic (Ahmed 1999).

In addition to being a proven carcinogen, inorganic arsenic can lead to gastrointestinal, cardiovascular, dermal and respiratory disorders, hyper-pigmentation and peripheral neuropathy as it gets deposited on or bound to tissues. Taking into consideration its health effects and toxicology, occurrence and human exposure, different regulatory agencies have recommended a maximum contaminant level (MCL) for arsenic in drinking water, e.g., the current WHO guideline value for arsenic in drinking water is 0.01 mg/L and the values in Australia and Germany are 0.007 and 0.01 mg/L, respectively (NHMRC 1996). In 2001, the United States government also reduced its standard from 0.05 to 0.01 mg/L. Many developing countries still have their standards set at 0.05 mg/L.

Numerous technologies such as coagulation, ion exchange, precipitation, membrane processes and adsorption have been adopted for the removal of arsenic from water with varying degrees of success. Adsorption is one of the most common available technologies. Various adsorbents developed for arsenic removal include amorphous iron hydroxide (Wilke and Hering 1996; Reed et al. 2000; Meng et al. 2002; Thirunavukkarasu et al. 2003a), activated carbon (Pokonova 1998; Patanayak
et al. 2000), activated alumina (Rubel and Hathway 1987; Guha and Choudhuri 1990), fly ash (Diamadopoulos et al. 1993), hydrous zirconium oxide (Suzuki et al. 1997), hematite and feldspar (Singh et al. 1996), industrial waste (Low and Lee 1995), lanthanum-loaded silica gel (Wasay et al. 1996), metal-loaded coral limestone (Ohki et al. 1996), pillared clays (Lenoble et al. 2002), rice husk, coconut husk carbon (Manju et al. 1998), soils (Smith et al. 1999) and biological materials such as living or non-living biomass, chitin, chitosan (Elson et al. 1980; Muzzarelli et al. 1984), manganese green sand and iron oxide-coated sand (Thirunavukkarasu et al. 2001; Thirunavukkarasu et al. 2003b).

Successful application of the adsorption technology demands innovation of cheap, nontoxic, easily available adsorbents of known kinetic parameters and sorption characteristics. A prior knowledge of the optimal conditions would herald better design and modelling of the process. Most of the reported studies on arsenic removal focus on the effect of different process parameters such as sorbent and sorbate dose, pH, particle size, etc., and very few studies have concentrated on the mechanism of arsenic uptake. Reaction rate and rate-limiting steps are important parameters for the design of any treatment processes, which can only be determined from a detailed kinetic investigation.

The sorption kinetics describe the solute uptake rate, which in turn governs the residence time of a sorption reaction. It is one of the important characteristics in defining the efficiency of a sorption process. Hence, in the present study, the kinetics of arsenic removal have been carried out to understand the behaviour of these adsorbents.

This work is a methodical investigation of the uptake kinetics of arsenic by activated alumina and iron oxide impregnated activated alumina. Thus, the effect of contact time, amount of adsorbent and concentration of the adsorbate on the uptake of As(III) and As(V) on AA and IOIAA were investigated from a kinetic point of view.

**Material and Method**

All of the chemicals used in the study were of high-purity analytical grade. Double distilled/deionized water was used throughout the study for the preparation and dilution of the stock solutions. All measurements were made in triplicate for the analysis of metal concentration and data were recorded when the variation in two readings was less than ±5%. Before use, all glassware, test tubes and sample bottles used were soaked in hot water and rinsed with laboratory dish soap (Lavolene) for at least 2 h and then rinsed with deionized water.

**Arsenic Stock Solution**

Arsenite [As(III)] and arsenate [As(V)] stock solutions (1000 mg/L) were prepared separately by dissolving dehydrated sodium arsenite (NaAsO$_2$) or sodium arsenate (Na$_2$HAsO$_4$·7H$_2$O) (Merck, Germany) in the deionized water. Dissolution of NaAsO$_2$ or Na$_2$HAsO$_4$·7H$_2$O also includes addition of dilute HCl. Stock solutions were also prepared from standard solutions of arsenate and arsenite (100 mg/L) supplied by Merck (Germany). These stock solutions were then stored in airtight PET bottles at a temperature less than 2°C to avoid any change in concentration of arsenic and the oxidation of solution. Further working solutions were freshly prepared from stock solution for each experimental run. Concentrations of arsenic [As(III) and As(V)] stock solutions were measured periodically to monitor variations in concentration.

Activated alumina (AD-101) used in the study was procured from IPCL, Mumbai, India, whereas iron oxide impregnated activated alumina (IOIAA) was prepared by impregnating ferric salt onto AA pellets. Ferric sulphate [Fe$_2$ (SO$_4$)$_3$·H$_2$O, AR Grade, Merck, Germany] was used for impregnation. The final iron oxide content on the AA pellets was 10% (wt). The detailed procedure for adsorbent preparation (IOIAA) is discussed elsewhere (Kuriakose et al. 2004).

**Kinetic Study**

Kinetic studies were conducted at two different initial sorbate concentrations. AA and IOIAA (1.0 g) were suspended in 100 mL of As(III) and As(V) solutions of initial concentrations of 0.5 and 1.5 mg/L, separately. Solution pH was adjusted with dilute NaOH/HCl. The mixture was stirred continuously at 85 rpm. Preliminary runs were also carried out at different rpm ranging from 30 to 125 to study the mass transfer effect, and final experiments were carried out at 83 rpm where the mass transfer limitations were minimal.

Samples were withdrawn at definite time intervals in the range of 1 to 24 h, filtered and analyzed for residual As(III) and As(V) ion concentration.

**Determination of Arsenic Concentration**

The samples were analyzed for arsenic content by using a graphite furnace atomic absorption spectrophotometer (GF-AAS) with Zeeman background correction (Varian Spectra AA 880, Varian, Australia). Prior to the analysis, the samples were acidified with 0.3% HNO$_3$ (ultra-pure grade, Merck, Germany) and suitably diluted to bring the concentration into the working range of the instrument. All measurements were based on integrated absorbance and performed at 193.7 nm using a hollow cathode lamp (Varian, Australia) with a slit width of 0.5 nm. Argon gas (Sigma gases, India) of ultra-high purity was used to sheath the atomizer and to purge internally. Pretreatment temperature of the furnace was kept at 1400 K and atomization temperature was 2500 K. The calibration range was 20 to 100 μg/L of
arsenic. Analysis was done in triplicate and calibration curves between 10 and 100 µg As/L were prepared. The detection limit of the instrument was 1 µg/L.

**Results and Discussion**

In order to investigate the optimal pH conditions for the removal of arsenic [As(III) and As(V)] species, runs were made at different pH levels ranging from 3 to 12. Maximum As(III) removal was attained over activated alumina (AA) at pH 7.6 (96%) and pH 12 (97%) over IOIAA. For As(V) removal, the corresponding pH values were 5.8 (96.6%) and 7.6 (98.4%) (Singh and Pant 2004; Kuriakose et al. 2004). Although maximum As(III) removal by IOIAA was observed at pH 12.0, the final solution pH was found to be 7.2. The high pH decrease is due to the solubilization of the adsorbent in strongly basic pH (12.0):

\[ FeOOH + OH^- \rightarrow FeO_2^- + H_2O \]  
\[ Al_2O_3 + 2OH^- \rightarrow 2AlO_2^- + H_2O \]

Similar observations were also reported by Zeng (2004). It was also observed that As(III) and As(V) adsorption over AA was exothermic in nature whereas it was endothermic over IOIAA (Singh and Pant 2004; Kuriakose et al. 2004). The physico-chemical properties of both the sorbents are reported in Singh and Pant (2004).

**Effect of Contact Time**

The rate of adsorption is very important for the design of adsorption systems and to investigate the time dependence of metal adsorption, which leads to better understanding of the metal uptake mechanism and mass transfer to the sorbent material. To begin with, the time required for achieving sorption equilibrium was determined. The uptake of both As(III) and As(V) increased with an increasing contact time, however the adsorption rate was rapid in the first four hours. This adsorption rate subsequently decreased and the equilibrium is achieved in 10 h (Fig. 1 and 2). The percent removal was also affected by initial arsenic concentration and decreased on increasing the initial As(III) and As(V) concentrations. At initial As(III) concentrations of 0.5 and 1.5 mg/L at pH 7.6, the percent removals achieved were 93 and 85%, respectively, in the first six hours by AA. The adsorption rate was slowed down as equilibrium was approached. The maximum As(III) and As(V) removals observed were 96.8 and 98.4%, respectively, over IOIAA. These values were 94.2 and 96.1%, respectively, for As(III) and As(V) removal over AA.

In the present study, the maximum adsorption capacity of IOIAA was 378 mg/kg from water having an initial As(III) concentration of 1.4 mg/L. This is significantly higher than the published values for iron oxide-coated sand (18.3 mg/kg) and ferrihydrite (285 mg/kg) for arsenic removal (Thirunavukkarasu et al. 2001). The results obtained from these experiments were used to study the rate-limiting step in the adsorption process.

**Kinetics Study**

The performance and ultimate cost of an adsorption system depends on the effectiveness of the process design and the efficiency of process operation. The efficiency of the process operation requires an understanding of the kinetics of uptake or the time dependence of the concentration distribution of the solute in both bulk solution and solid sorbent and identification of the rate-determining step. Kinetic models available in the literature have been applied to the experimental data obtained to investigate the adsorption mechanism of As(III) and As(V) adsorption on AA and IOIAA and to get the potential rate-controlling step. The models are discussed in the following sections.

![Fig. 1. Effect of contact time on % As(III) and As(V) removal by activated alumina.](http://iwaponline.com/wqrj/article-pdf/41/2/147/230037/wqrjc0410147.pdf)

![Fig. 2. Effect of contact time on % As(III) and As(V) removal by iron oxide impregnated activated alumina (IOIAA).](http://iwaponline.com/wqrj/article-pdf/41/2/147/230037/wqrjc0410147.pdf)
Lagergren Kinetics Model

The first-order rate expression of Lagergren is based on the solid capacity and is given by (Lagergren 1898):

$$\frac{dq}{dt} = k_{ad1} \cdot (q_e - q)$$  \hspace{1cm} (3)

Integrating between \( t = 0 \) and \( t \) and \( q = 0 \) to \( q_t = q \), equation 3 becomes:

$$\log(q_e - q_t) = \log(q_e) - \left( \frac{k_{ad1}}{2.303} \right) t$$  \hspace{1cm} (4)

where \( q_e \) and \( q_t \) (both mg/kg) are the amount of arsenic adsorbed per unit mass of adsorbent at equilibrium and time, \( t \) (h), respectively, and \( k_{ad1} \) is the rate constant (1/h). The values of adsorption rate constants \( k_{ad1} \) for both sorbents at different initial arsenic concentrations were obtained from slopes of the plots (Fig. 3 and 4). A straight line of \( \log(q_e - q_t) \) versus \( t \) suggested the applicability of the first-order rate kinetics model for sorption of As(III) and As(V) over AA and As(V) over IOIAA (Singh and Pant 2004; Kuriakose et al. 2004). The first-order rate constant \( k_{ad1} \) varied between 1.0 to 1.42 per hour as the concentration was increased from 1.6 to 2.3 mg/L for As(III) adsorption over IOIAA (Kuriakose et al. 2004) which indicated that As(III) sorption on IOIAA did not follow first-order rate kinetics at higher sorbate concentration.

Since there was a considerable increase in the first-order rate constant at higher As(III) concentration, this indicates that it is not truly first order. Therefore a pseudo-second order rate equation was attempted for adsorption of As(III) onto IOIAA. The rate equation for second-order chemisorption kinetics is:

$$\left[ \frac{dq}{dt} = k_{ad2} \cdot (q_e - q_t)^2 \right]$$  \hspace{1cm} (5)

where \( k_{ad2} \) is the second-order sorption rate constant (kg/mg h). Integrating equation 5 between boundary conditions \( (t = 0, q_t = 0) \) and \( (t = t, q_t = q_t) \) gives:

$$-\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_{ad2}t$$  \hspace{1cm} (6)

which may be rewritten as:

$$\frac{t}{q_t} = \frac{1}{k_{ad2}q_e} + \frac{t}{q_e}$$  \hspace{1cm} (7)

For the second-order kinetics to be valid, a plot of \( t/q \) versus time must yield a straight line, with slope and intercept in the plot giving the values of \( q_e \) and \( k_{ad2} \) (Fig. 5). As can be seen from Fig. 5, pseudo-second order rate kinetics satisfactorily explain the behaviour of adsorption of As(III) onto IOIAA. \( k_{ad2} \) values as obtained from the plot were 26.35 ± 1.75 g/mg h.

In order to interpret the adsorption mechanism, it is necessary to identify the steps that overall govern the adsorption of arsenic [As(III) and As(V)] onto AA and IOIAA. A foundation for the kinetics has been laid by the mathematical models proposed by Boyd et al. (1947) and Reichenberg (1953) which distinguish between the intra-
particle and mass transfer controlled mechanism. These processes were evaluated in the present investigation.

**Mass Transfer and Diffusional Steps**

The three main steps involved in the uptake of As(III) and As(V) by AA and IOIAA are:

1. Transport of adsorbate [As(III) and As(V)] from bulk solution to the external surface of the sorbent through the film (film diffusion).
2. Transport of sorbate into the pores of AA and IOIAA (pore diffusion).
3. Adsorption of metal on the surface of the sorbent.

It is generally accepted that step 3 is very rapid and does not represent the rate-limiting step in the uptake of As(III) and As(V). Amongst the other two steps, three distinct cases can occur: (i) external resistance can be greater than internal resistance, (ii) external resistance can be smaller than internal resistance, and (iii) internal transport equals external transport. In cases (i) and (ii), the rate will be governed by film and pore diffusion, respectively. In the third case, the transport of ions to the boundary may not be possible at a significant rate, thereby leading to the formation of liquid film with a concentration gradient surrounding the sorbent particle.

Besides adsorption on the outer surface of adsorbent, there is also a possibility of transport of adsorbate ions from the solution into the pores of the sorbent (pore diffusion) due to the rapid stirring in the batch reactor. In the case of strict surface adsorption, a variation in rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial solute concentration and the rate of adsorption will not be linear. The experimental data were used to study the rate-limiting step in the adsorption process.

To understand the mechanism in a simpler way, we assumed that the particles are vigorously agitated during the adsorption. It is reasonable to assume that the mass transfer from the bulk liquid to the particle external surface does not limit the rate. Hence it can be postulated that the rate-limiting step may be surface diffusion or intraparticle diffusion. As these act in series, the slower of the two will be the rate-limiting step. For a spherical shape, the particle diffusion equation may be written as:

\[
\frac{\partial q}{\partial t} = D \left( \frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right)
\]  

where \( q \) is the adsorbed phase concentration. If the uptake of the sorbate by the sorbent is small relative to the total quantity of sorbate introduced into the system, the sorbate concentration will remain essentially constant following the initial step change and the appropriate initial and boundary conditions are:

\[
q(0,0) = 0 \quad q(a_p, t) = q_b, \quad \left( \frac{\partial q}{\partial r} \right)_{r=0} = 0
\]  

where \( a_p \) is the particle radius. An analytical solution equation for the uptake of arsenic may be written as Gupta et al. (2004):

\[
q = 1 - \frac{6}{\pi} \sum \frac{1}{n^2} \exp \left( -n^2 \pi^2 \frac{D_t}{a_p^2} \right)
\]  

The average concentration through the particle is given by:

\[
q = \left( \frac{3}{a_p^2} \right) \int_0^{a_p} qr^2 dr
\]  

For a short time, the equation converges very slowly and gives (Weber and Morris 1963; Gupta et al. 2004):

\[
q = \frac{6}{\sqrt{\pi}} \left( \frac{D_t}{a_p} \right)^{1/2} = K_p \sqrt{t}
\]  

where \( K_p = \frac{6\sqrt{D_t}}{a_p \sqrt{\pi}} \) is the term related to the intraparticle diffusion rate constant. In order to show the existence of intraparticle diffusion in the adsorption process, the amount of As(III) and As(V) sorbed per unit mass of adsorbents at time, \( t \), \( q_t \) was plotted as a function of the square root of time, \( t^{0.5} \). The plots of intraparticle diffusion (\( q \) versus \( \sqrt{t} \)) for different initial As(III) and As(V) concentrations are shown in Fig. 6 and 7 for the two sorbents, respectively.

These curves show an initially curved portion, which indicates the film or boundary layer diffusion effect and the subsequent linear portion are attributed to the intraparticle diffusion effect (Knocke and Hemphill).
It can be seen from Fig. 6 and 7 that the initial straight line is a relatively steeper slope, which depicts a faster sorption while a plateau at the end shows approach towards equilibrium. According to the intraparticle diffusion model, a linear plot indicates that the rate is controlled by intraparticle diffusion. However, the non-linear plots obtained in the present investigation confirm that intraparticle diffusion is not a fully operative mechanism for As(III) and As(V) removal by AA and IOIAA.

The value of $K_p$ for AA as estimated from the slopes of linear portions, were found to be 45 and 129 mg/kg h$^{1/2}$ at As(III) concentrations of 0.5 and 1.5 mg/L, respectively. The values of $K_p$ for other sorbents are given in Table 1. The linear portions of the curves do not pass through the origin (Fig. 7). This indicates that mechanism of arsenite [As(III)] removal on activated alumina is complex and both the mass transfer as well as intraparticle diffusion contribute to the rate-determining step (Gupta et al. 1988).

The dual nature of these plots (Fig. 6 and 7) may be explained as the initial curved portions are attributed to boundary layer diffusion effects while the final linear portions are due to intraparticle diffusion effects. The intraparticle diffusion rate constant, $K_p$, at different initial concentrations were determined from the slope of the final linear portion of the respective plots and are reported in Table 1.

The $R^2$ values are close to unity indicating application of this model. The calculated values of $k_p$ are more for AA (0.37) than for IOIAA (0.25). The values of the intercept give an idea about the boundary layer thickness, i.e., the larger the intercept the greater the boundary layer effect. The boundary layer resistance is affected by the rate of adsorption and increases with contact time, which will reduce the resistance and increase the mobility of sorbate during adsorption. Since the uptake of sorbate [As(III) and As(V)] at the active sites of AA and IOIAA is a rapid process, the rate of adsorption is mainly governed by either liquid phase mass transfer rate or intraparticle mass transfer rate. The divergence in the value of slope from 0.5 indicates the presence of the intra-particle diffusion process as one of the rate-limiting steps, besides many other processes controlling the rate of adsorption, all of which may be operating simultaneously. In order to assess the nature of the diffusion process responsible for adsorption of As(III) and As(V) on AA and IOIAA, attempts were also made to calculate the coefficients of the process.

### Table 1. Kinetics rate constants for adsorption of As(III) and As(V) by activated alumina and iron oxide impregnated activated alumina

<table>
<thead>
<tr>
<th>Initial adsorbate concentration</th>
<th>$k_{ad}$ (1/h)</th>
<th>$R^2$</th>
<th>Intraparticle diffusion coefficient $K_p$ (mg/g h$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Removal of As(III) by AA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.2173</td>
<td>0.985</td>
<td>0.045</td>
</tr>
<tr>
<td>1.5</td>
<td>0.231</td>
<td>0.970</td>
<td>0.129</td>
</tr>
<tr>
<td><strong>Removal of As(V) by AA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.2357</td>
<td>0.9001</td>
<td>0.047</td>
</tr>
<tr>
<td>1.5</td>
<td>0.2553</td>
<td>0.9816</td>
<td>0.131</td>
</tr>
<tr>
<td><strong>Removal of As(III) by IOIAA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>0.6204</td>
<td>0.9348</td>
<td>0.251</td>
</tr>
<tr>
<td>2.1</td>
<td>0.5627</td>
<td>0.9818</td>
<td>0.361</td>
</tr>
<tr>
<td><strong>Removal of As(V) by IOIAA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>0.3188</td>
<td>0.9682</td>
<td>0.285</td>
</tr>
<tr>
<td>2.1</td>
<td>0.3034</td>
<td>0.9888</td>
<td>0.395</td>
</tr>
</tbody>
</table>
Assuming spherical geometry for the sorbent, the overall rate constant of the process can be correlated with the pore diffusion coefficient and film diffusion coefficient independently in accordance with the expressions:

\[ D_f = 0.23 \frac{r_0^2 \delta}{\eta} \]

(12)

\[ D_p = 0.03 \frac{r_0^2}{\eta} \]

(13)

where \( r_0 \) is the radius of the adsorbent (for AA = 0.0325 cm and for IOIAA = 0.04012 cm), \( \delta \) is the film thickness (10\(^{-3}\) cm) and \( c \) is the initial concentration. Employing the appropriate data and the respective overall rate constants, pore and film diffusion coefficients for various concentrations of As(III) and As(V) were calculated for the AA and IOIAA. The pore diffusion process appears to be one of the main rate-limiting steps since the coefficient values are in the range of 10\(^{-10}\) to 10\(^{-11}\) cm\(^2\)/s. In order to understand the mass transfer process, mass transfer analysis was also conducted.

**Mass Transfer Analysis**

In fully mixed agitated absorbers, mixing in the liquid phase is rapid. The concentration of the sorbate, \( C_t \), with respect to time is related to fluid-particle-mass transfer coefficients by the equation:

\[ \frac{\partial C_t}{\partial t} = -K_f S_s \left( C_t - C_s \right) \]

(14)

Assuming spherical particles, the surface area for mass transfer to the particle can be obtained from \( M \), which is defined by:

\[ M = \frac{W}{V} \]

(15)

Thus, the surface area for mass transfer is defined by:

\[ S_s = \frac{6M}{a_f \rho_f \left( 1 - \varepsilon_f \right)} \]

(16)

The incremental mass balance on the sorbent becomes:

\[ M \frac{\partial q_t}{\partial t} = -K_f S_s \left( C_t - C_s \right) \]

(17)

For the differential mass balance of metal ions within the particles, neglecting the effect of intraparticle diffusion, the equation can be written in the form of:

\[ \frac{\partial q_t}{\partial t} = K_{biq} \frac{\partial C_t}{\partial t} \quad \text{For } q_t = 0 \text{ when } t = 0 \]

(18)

Combining equation 17 and 18:

\[ MK_{biq} \frac{\partial C_t}{\partial t} = K_f S_s \left( C_t - C_s \right) \]

(19)

Differentiating equation 14 with respect to time:

\[ \frac{\partial^2 C_t}{\partial t^2} = -K_f S_s \frac{\partial C_t}{\partial t} + K_f S_s \frac{\partial C_s}{\partial t} \]

(20)

Substituting equation 19 and 14 into 20:

\[ \frac{\partial^2 C_t}{\partial t^2} = -K_f S_s \frac{\partial C_t}{\partial t} + K_f S_s \frac{\partial C_s}{\partial t} \left( C_t + \frac{1}{K_f S_s} \frac{\partial C_t}{\partial t} \right) \]

(21)

Integrating equation 21 when \( C_t = C_0 \) at \( t = 0 \):

\[ \frac{C_t}{C_0} = 1 + \frac{MK_{biq}}{1 + MK_{biq}} \exp \left( -\frac{1 + MK_{biq}}{MK_{biq}} K_f S_s t \right) \]

(22)

By rearranging equation 22, it becomes (Mckay et al. 1980; Orumwense 1996):

\[ \ln \left( \frac{C_t}{C_0} \right) = \ln \left( \frac{MK_{biq}}{1 + MK_{biq}} \right) - \frac{1 + MK_{biq}}{MK_{biq}} K_f S_s t \]

(23)

where \( C_0 \) is the initial solute concentration (mg/L), \( C_t \) the solute concentration after time, \( t \) (mg/L), \( K_{biq} \) is the constant obtained by multiplying \( q_m \) and \( b \) (m\(^3\)/kg), \( M \) is the mass of the adsorbent per unit volume of particle free adsorbate solution (kg/m\(^3\)), \( S_s \) is the external surface area of adsorbent per unit volume of particle free slurry (1/m), \( K_f \) is the mass transfer coefficient (m/s). A plot of \( \ln \left( \frac{C_t}{C_0} \right) \) versus \( t \) resulted in a straight straight line with a slope \( \frac{1 + MK_{biq}}{MK_{biq}} K_f S_s \) and the values of mass transfer coefficient, \( K_{biq} \), were calculated from the slope of the plot (Fig. 8). The value of mass transfer coefficients, \( K_{biq} \), obtained were 1.9 \times 10\(^{-3}\) cm/s and 4.0 \times 10\(^{-3}\) cm/s for adsorption of As(III) and As(V) over AA, respectively. Relatively higher values of mass transfer coefficient \( K_f \) [3.2 \times 10\(^{-3}\) cm/s and 6.2 \times 10\(^{-3}\) cm/s for As(III) and As(V)] were observed on IOIAA.

A number of mass transfer coefficients have been reported in the literature for the adsorption of various pollutants onto different adsorbents. The mass transfer values obtained in this study are higher than reported for benzaldehyde carbon (9 \times 10\(^{-3}\) cm/s), phenol and carbon (3.9 \times 10\(^{-3}\) cm/s) (Namasivayam and Yamuna 1995). This can be explained by the fact that larger organic molecules will restrict their mobility in the solution while arsenite anions move easily since these are smaller than organic molecules.
On the basis of the above-mentioned steps, it can be concluded that both pore diffusion and mass transfer contribute toward sorption of arsenite.

Arsenic Removal Mechanism

The mechanism by which arsenic is removed by this procedure probably involves initial formation of a soluble ion pair between the ferrous ion and arsenite. Subsequent oxidation of the iron(II) arsenite complex by ferric arsenate, which would precipitate on AA from solution along with ferric oxyhydroxides, are formed from excess iron. The effectiveness of this method results from the strong interactions between the ferrous and arsenate ion. In addition, surface complexation (formation of As-O-Fe bonds) may also take place, which would increase the association constant.

\[
\begin{align*}
\text{Fe}^{2+} + \text{AsO}_4^{3-} &\rightleftharpoons \text{FeAsO}_4^{3-} + \text{FeO(OH)}_\text{(s)} \\
\end{align*}
\] (24)

The arsenic removal mechanism can also be explained by using the model of a hydroxylated alumina surface subject to protonation and deprotonation. The following ligand exchange reaction can be used to represent arsenic adsorption in acid solution in which *Al represents the alumina surface and an over bar denotes a solid phase.

\[
\begin{align*}
\text{AlOH} + \text{H}^+ + \text{H}_2\text{AsO}_3^- &\rightleftharpoons \text{AlH}_{2}\text{AsO}_3^- + \text{HOH} \\
\end{align*}
\] (25)

The equation for arsenic desorption by hydroxide (alumina regeneration) is:

\[
\begin{align*}
\text{AlH}_{2}\text{AsO}_3^- + \text{OH}^- &\rightleftharpoons \text{AlOH} + \text{H}_2\text{AsO}_3^- \\
\end{align*}
\] (26)

Whereas in the presence of iron oxide, adsorption occurs by:

\[
\begin{align*}
\text{FeOH} + \text{HAsO}_3^{2-} + \text{H}^+ &\rightleftharpoons \text{FeHAsO}_3^{2-} + \text{H}_2\text{O} \\
2(\text{FeOH}) + \text{HAsO}_3^{2-} + 2\text{H}^+ &\rightleftharpoons \text{Fe}_2\text{HAsO}_3^{2-} + 2\text{H}_2\text{O} \\
\end{align*}
\] (27)

All the above reactions may be involved in the arsenic removal.

Conclusions

Activated alumina (AD-101, IPCL, India) has been found to be effective for the treatment of arsenic-contaminated waters. Incorporation of iron oxide onto activated alumina significantly increased the percent arsenic removal and adsorption capacity for As(III) and As(V) removal. The maximum As(III) and As(V) removal strongly depends on initial pH, arsenic concentration and sorbent dose. Depending upon the nature of ions, IOIAA is recommended for the removal of As(III) because of high adsorption affinity. The removal of As(III) and As(V) by activated alumina and iron oxide impregnated alumina takes place within 12 h. The first-order Lagergren kinetics explained the adsorption of arsenic over activated alumina whereas the pseudo-second order rate equation explained the behaviour of As(III) adsorption over iron oxide impregnated activated alumina. These results indicate that the mechanism of arsenic adsorption is complex for both sorbents as both mass transfer and pore diffusion contribute to the arsenic removal. During the initial period, mass transfer was predominant but as the adsorption progresses, pore diffusion dominated kinetics of sorption.

References

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Nomenclature and Abbreviations

C Arsenic concentration in solution (mg/L)
C0 Initial sorbate concentration (mg/L)
Ceq Equilibrium arsenic concentration in solution (mg/L)
Ct Arsenic concentration in solution at time, t (mg/L)
ka Rate constant in BDST model (L/mg h)
kd1 First-order rate constant (1/h)
kd2 Pseudo-second order rate constant (g/mg h)
Koq Constant obtained by multiplied qm and b (L/g)
Kf External mass transfer coefficient (m/s)
kp Intraparticle diffusion coefficient (mg/g h1/2)
m Mass of the adsorbent (g)
Mcq Mass of the adsorbent per unit volume of particle-free adsorbate solution (g)
q Adsorbed phase concentration (mg/g)
qe Amount of solute uptake per unit mass of adsorbent at equilibrium (mg/g)
qm Langmuir isotherm constant (mg/g)
Ss External surface area of adsorbent per unit volume of particle-free slurry (1/cm)
t Time (s)
T Temperature (K)
x Amount of As(III) adsorbed in solid phase (mg)
β Liquid-solid mass transfer coefficient (cm)
ε Bed porosity
εp Particle porosity
ρ Density (kg/m3)
ρs Density of adsorbent (kg/m3)
AA Activated alumina
IOIAA Iron oxide impregnated activated alumina
R2 Correlation coefficient

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