Iron oxide impregnated sugarcane bagasse waste material as sorbent for As(III) removal from water: kinetic, equilibrium and thermodynamic studies
Ashish Nashine and Ajay Tembhurkar

ABSTRACT
Adsorption of arsenite (As(III)) from aqueous solutions onto iron oxide impregnated sugarcane bagasse was investigated in this study. The linear regression analysis showed that Langmuir adsorption isotherm fitted well to the experimental data. Langmuir constants ‘a’ related to the adsorption capacity and ‘b’ related to the binding energy of sorption system were found to be 1.55 mg/g and 46.44 L/mg, respectively. A kinetic study revealed that uptake of As(III) was rapid in the first 30 min after which it slowed down and became almost constant after 90 min, indicating that the equilibrium had been reached. Kinetic data correlated well with the pseudo-second order kinetic model, suggesting that the adsorption process might be chemisorption. Estimated pseudo-second order kinetic rate constant was 2.113 g/mg min. Evaluation of thermodynamic parameters (ΔG, ΔH, ΔS) indicated that the adsorption process was feasible and endothermic in nature.
Key words | adsorbent, adsorption, arsenic, isotherm, kinetic

INTRODUCTION
Arsenic in ground water has become a global matter of concern. In recent years, the problem has increased worldwide, including several regions of southeast Asia such as Bangladesh, several states of India, Nepal, Myanmar, Pakistan, Vietnam, Lao People’s Democratic Republic, Cambodia, China (Mukherjee et al. 2006), Chile, Ghana, Hungary, Mongolia, Mexico, New Zealand, Philippines, Taiwan and in the lowlands of Sumatra in Indonesia (Winkel et al. 2008). Arsenic is toxic and has a carcinogenic element and ingestion causes various diseases such as dermatitis, hypertension, respiratory, neurologic and liver disorders (IARC 2004). To reduce arsenic related illness the United State Environmental Protection Agency and many countries have lowered the public drinking-water standard from 50 to 10 μg/L.

Conventionally, coagulation and flocculation, membrane filtration, ion exchange and adsorption processes are used for arsenic removal. Coagulation and flocculation, membrane filtration and ion exchange techniques require relatively high capital and operating costs. Alzheimer’s disease and carcinogenic effects of coagulants alum lime, aluminum sulphate, polyaluminum chloride, polyaluminum silico sulphate, soda ash and synthetic polymers resulting from such treatments are other serious drawbacks of the coagulation and flocculation process (Pushpa et al. 2006). Membranes can be fouled by colloidal matter in the raw water, particularly organic matter. Iron and manganese can also lead to scaling and membrane fouling. It is widely recognized that adsorption is an ideal and appropriate technique compared to other techniques. Adsorption is a cheaper technique, simple in operation and maintenance is usually low. Many adsorbents such as activated carbon (Lorenzen et al. 1995; Wu et al. 2009), activated alumina (Singh & Pant 2004) have been used for arsenic removal, however dissolving of the aluminum is regarded as a human nerve toxin (Zhao et al. 2009). Commercial adsorbents are not suitable for developing countries because they are expensive.

Nowadays, research is devoted towards the study of natural or non-conventional adsorbents as they are cheap,
locally available and environmentally favorable. Regeneration may not be required and they can be disposed of safely. Very little study has been conducted for arsenic removal on adsorbents developed from natural materials. Cupressus female cone (Murugan & Subramanian 2004), shelled Moringa Oleifera Lamarck seed powder (Pushpa et al. 2006), laterite (Maiti et al. 2007), red soil (Nemade et al. 2009) and maize leaves (Kamsonlian et al. 2011) have been studied for arsenic removal from water. Also, various iron(III) oxides such as amorphous hydrous ferric oxide, poorly crystalline hydrous ferric oxide (Wilkie & Hering 1996) and goethite (Gimenez et al. 2007) were found to be effective adsorbent materials for the removal of arsenic from aqueous solutions. Iron oxides have a strong affinity for arsenic in water. However, they are available only as fine powders or are generated in situ as gels, which are difficult to separate from water after adsorption is completed (Guo et al. 2007; Habuda-Stanic et al. 2007). Hence, in the present study natural waste material sugarcane bagasse was identified as the adsorbent material and impregnated with iron oxide for enhanced removal of As(III), which was considered difficult to remove from water. The present study also deals with isotherm, kinetic and thermodynamic analysis for As(III) removal from the water on iron oxide impregnated sugarcane bagasse (IOISB) adsorbent.

MECHANISM OF ADSORPTION

The mechanism of arsenic adsorption on ferric oxide is associated with the formation of surface complexes between soluble arsenic species and the solid hydroxide surface sites. Ferric arsenate or ferric arsenite is produced due to arsenic contact with the deposited ferric oxides as presented in the following reactions (Solozhenkin et al. 2007):

\[
\begin{align*}
M-\text{FeOH} + H_3\text{AsO}_4^- &\rightarrow \underset{\text{Sorption process}}{M-\text{Fe-H}_2\text{AsO}_4 + H_2O} \quad \text{(Arsenate sorption)} \\
M-\text{FeOH} + H_3\text{AsO}_3^- &\rightarrow \underset{\text{Sorption process}}{M-\text{Fe-H}_2\text{AsO}_3 + H_2O} \quad \text{(Arsenite sorption)}
\end{align*}
\]

These equations describe sorption of arsenic on ferric oxides on supports (M).

MATERIALS AND METHODS

Reagents and apparatus

All the chemicals used in the current study were of analytical grade. Stock solutions containing 1,000 mg/L of As(III) was prepared by dissolving As$_2$O$_3$ (SD Fine Chem., India) in distilled water. Working solutions as per the experimental requirements were freshly prepared from the stock solution. Fe(NO$_3$)$_3$·9H$_2$O (Merck) was used for the coating process. Quantitative determination of arsenic was carried out by the silver diethyl dithiocarbamate method using a UV–VIS spectrophotometer (Elico, India, Model no. SL 210) at a wavelength of 535 nm.

Preparation and characterization of adsorbent

Sugarcane bagasse was used for preparing adsorbent. Sugarcane bagasse was air-dried and crushed by a grinder. The biomass was sieved through a 2 mm copper sieve and 40 g of the crushed material was placed in a beaker and mixed with 400 mL of 1 N nitric acid. The mixer was heated on a hot plate maintaining a temperature of 70–80°C for 20 min, cooled and washed with distilled water until the dirty color was removed. The washed biomass was then mixed with 400 mL of 1 N NaOH, heated again at 70–80°C for 20 min and washed thoroughly. This material was air-dried for 3–4 days, grinded and sieved through a 600 micron sieve then the adsorbent was impregnated with iron oxide. A solution was prepared using ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O) and sodium hydroxide. One mL of 10 M sodium hydroxide was mixed with 80 mL 2 M ferric nitrate, then 20 g of adsorbent was placed in a pot and the solution was poured slowly and homogenized by mixing thoroughly. The mixture was kept in an oven at 80°C for 3 h. After 3 h the oven temperature was raised to 110°C for another 24 h. The material was washed with distilled water, dried again in an oven at 80°C for 24 h, sieved through a 600 micron sieve and stored in a capped bottle. The surface area of the adsorbent was measured using a Horiba SA series (Japan) BET (Brunauer–Emmett–Teller) surface area analyzer by nitrogen gas adsorption. The surface morphology of IOISB adsorbent was compared before and after adsorption by scanning electron microscopy (SEM).
Adsorption experiments

Batch adsorption experiments were conducted to obtain the data for the kinetic, equilibrium, and thermodynamic study for As(III) adsorption on IOISB adsorbent at room temperature. The experiment was conducted in glass beakers, containing As(III) solution having 0.380 mg/L initial concentration by varying adsorbent dose (0.5–10 g/L) to study the effect of IOISB adsorbent on As(III) removal. The suspensions were stirred for 60 min. For isotherm study, 10 g/L of the adsorbent was stirred with 250 mL of As(III) solutions having concentrations of 0.2, 0.5, 1.0, 1.5 and 2.0 mg/L. The suspensions were stirred for 90 min, which was the optimum contact time determined earlier, at 30 rpm. The kinetic study was conducted by varying contact time from 5 to 120 min. An adsorbent dose of 10 g/L was stirred with 250 mL of As(III) solutions in a series of beakers having a concentration of 0.395 mg/L at 30 rpm and room temperature. Similar experiments were carried out by varying temperature (283–313 K) at an adsorbent dose of 10 g/L, contact time of 90 min, pH 6, mixing speed of 50 rpm, keeping 0.5 mg/l initial As(III) concentration, which were the optimum values determined earlier. After stirring, suspensions were allowed to settle for 30 min and filtered. The filtrates were analyzed to estimate residual arsenic concentration after adsorption.

RESULTS AND DISCUSSION

Characterization of adsorbent

The BET surface area of the adsorbent was found to be 192.86 m²/g. Figure 1(a) and 1(b) shows the SEM image of IOISB adsorbent before and after adsorption of As(III) ions. From Figure 1(a), it is observed that the adsorbent surface has a highly porous structure. This porous layer contributes to the significantly larger surface area. The adsorbent particles existed in clustered shapes and their actual size could not be determined. After adsorption of As(III), as seen in Figure 1(b), a reduction in the pore area of adsorbent is observed.

Effect of adsorbent dose

The effect of adsorbent dose on As(III) removal at an initial concentration of 0.380 mg/L is shown in Figure 2. The amount of As(III) adsorbed per unit weight of adsorbent ‘q’ (mg/g) decreased with an increase in adsorbent dose, while the percentage As(III) removal increased with an increase in adsorbent dose. There was no appreciable increase in percentage As(III) removal if the adsorbent dose was increased further. This might be due to the availability of more active sites with an increase in the adsorbent dose (Tembhurkar & Dongre 2006). A further increase of adsorbent does not have much affect due to the non-availability of adsorbate around the adsorbent. As(III) removal was 98.90% at 10 g/L adsorbent dose. The As(III) concentration after adsorption at an adsorbent dose of 10 g/L was 0.004 mg/L, which is below the WHO standards of 0.01 mg/L.

Adsorption isotherm

The adsorption isotherms were obtained to determine the capacity of the adsorbent for As(III) removal at room temperature. The adsorbate concentrations were varied from 0.2 to
2.0 mg/L keeping the adsorbent dose at 10 g/L, mixing time 90 min and speed 30 rpm. The pH of the adsorbate was 7.1. The amount of As(III) adsorbed increased linearly from 0.049 to 0.184 mg/g, when the initial concentration increased from 0.5 to 2.0 mg/L, as shown in Figure 3. This was because at a higher solute concentration the adsorption was greater due to increased concentration gradient (Maiti et al. 2007).

The experimental data obtained are applied to the Langmuir and the Freundlich models.

The Freundlich isotherm is expressed as:

\[ q_e = k C_e^{1/n} \]  
\[ \log q_e = \log k + \frac{1}{n} \log C_e \]  

and the Langmuir isotherm as:

\[ \frac{1}{q_e} = \frac{1}{a b C_e} + \frac{1}{a} \]

where \(C_e\) is the equilibrium solute concentration (mg/L), \(q_e\) is the amount of As(III) adsorbed at equilibrium (mg/g), \(k\) and \(n\) are the Freundlich constants representing the adsorption capacity (mg/g) and the adsorption intensity. Larger values of \(k\) mean larger capacity of adsorption. Larger values of \(1/n\) mean that the adsorption bond is weak because the value of \(q_e\) experiences large changes for small changes in \(C_e\). The values of the constants ‘\(n\)’ and ‘\(k\)’ can be determined from the slope and intercept of the plot between \(\log q_e\) and \(\log C_e\).

The experimental data plotted for the Freundlich isotherm and the Langmuir isotherm are shown in Figures 4 and 5. The constants for both models along with regression coefficients (\(R^2\)) are summarized in Table 1. The values of correlation coefficient (\(R^2\)) suggest that both Langmuir and Freundlich isotherms fit the adsorption data adequately.

The results suggest that adsorption of As(III) removal on IOISB is a complex mechanism where the controlling step of arsenic adsorption is by both the surface adsorption and intra-particle pore diffusion. Singh & Pant (2004) and Maiti et al. (2007) have also reported that adsorption of As(III) on activated alumina and natural laterite follows both the isotherm models.

The dimensionless equilibrium parameter \(RL\) is estimated by the following equation to determine if the As(III)
adsorption process by IOISB is favorable or unfavorable for the Langmuir type adsorption process:

\[ R_L = \frac{1}{1 + \frac{b}{C_0}} \]  

(4)

where \( C_0 \) is the initial As(III) concentration and \( b \) is the Langmuir isotherm constant. The value of \( R_L < 1 \) represents the favorable adsorption and \( R_L > 1 \) describes unfavorable adsorption (Singh & Pant 2004).

Values of \( R_L \) at different concentrations as shown in Figure 6 are less than 1 representing the favorable adsorption of As(III) on IOISB adsorbent. Figure 6 also reveals that lower \( R_L \) values are obtained at higher As(III) concentrations, indicating a higher removal efficiency of IOISB adsorbent at higher As(III) concentrations.

### Kinetic study

The kinetic study for As(III) adsorption on IOISB adsorbent was conducted by varying contact time from 5 to 120 min. at 10 g/L adsorbent dose, 0.395 mg/L initial concentration and room temperature (31 °C). It was found that As(III) uptake increased with an increase in contact time. The adsorption of As(III) was rapid in the first 30 min, after which it slowed down and became almost constant after 90 min, indicating that the equilibrium had been reached. Initially the sorbent sites were vacant, hence uptake was increasing with the lapse of time. Later, the number of sites decreased and ultimately the saturation of adsorbent sites occurred after a longer period of operation (Tembhurkar & Dongre 2006). About 99.24% removal of As(III) was achieved at 90 min contact time. Reported equilibrium time for As(III) adsorption are 2 h on iron oxide coated cement (Kundu & Gupta 2006), 2.5 h on natural laterite (Maiti et al. 2007), 20 h on polymeric Al/Fe modified montmorillonite (Ramesh et al. 2007) and 22 h on iron impregnated potato peels (Godboley & Dhoble 2011) adsorbents.

To estimate the uptake rate two kinetic models were analyzed from the data obtained. The pseudo-first order rate model is given by the following expression:

\[
\log \left( \frac{q_e - q_t}{q_e} \right) = \log q_e - \left( \frac{k_1}{2.303} \right)t
\]  

(5)

where \( q_e \) and \( q_t \) (mg/g) are the amounts of arsenic adsorbed at equilibrium and time \( t \) (min), \( k_1 \) is the rate constant of the equation (min\(^{-1}\)). The value of \( k_1 \) is calculated from the slope of the linear plot of \( \log (q_e - q_t) \) versus \( t \), which is shown in Figure 7.

The pseudo-second order rate model is expressed as:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left( \frac{1}{q_e} \right)t
\]  

(6)
where \( h = k_2 q_e^2 \) which denotes the initial sorption rate (mg/g min) and \( k_2 \) (g/mg min) is the rate constant of the pseudo-second order equation. The second order rate constant \( k_2 \) and \( q_e \) are calculated from the intercept and slope of the plot of \( t/q_t \) versus \( t \). The experimental data plotted is shown in Figure 8. The calculated values of \( q_e \), \( k_1 \), \( k_2 \) and \( R^2 \) are presented in Table 2. The experimental \( q_e \) value is in agreement with the calculated \( q_e \) value and the plots show good linearity with an \( R^2 \) value of 0.983. This indicates that the pseudo-second order kinetic model better represents the adsorption kinetics, suggesting that the adsorption process might be chemisorption. Some of the previous researchers also reported that pseudo-second order model correlates well to the experimental data obtained for the adsorption of As(III) on polymeric Al/Fe modified montmorillonite (Ramesh et al. 2007), fly ash agglomerates (Polowczyk et al. 2010) and maize leaves (Kamsonlian et al. 2011).

**Thermodynamic study**

The thermodynamic study for the adsorption of As(III) onto IOISB adsorbent was conducted in the temperature range of 10–40 °C at an initial adsorbate concentration of 0.5 mg/L and adsorbent dose of 10 g/L. It was found that the adsorption capacity increased with increasing temperature. The increase in adsorption capacity at higher temperatures may be due to the enlargement of pore size, i.e. a change in the surface properties of the adsorbent and/or activation of the adsorbent surface (Zeng 2004; Ramesh et al. 2007; Kamsonlian et al. 2011). The increase in adsorption with temperature may also be attributed to the decrease in the thickness of the boundary layer surrounding it, so that the mass transfer resistance of adsorbate in the boundary layer decreases. The possibility of adsorbent diffusion of solute within the pores at higher temperatures may not be ruled out. Since diffusion is an endothermic process, greater adsorption is observed at higher temperature (Wu et al. 2009).

**Table 3** | Estimated thermodynamic parameters (\( \Delta H \), \( \Delta G \) and \( \Delta S \)) for As(III) adsorption onto IOISB adsorbent at different temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( \Delta G ) (kJ/mol)</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>( \Delta S ) (J/mol K)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>–763.305</td>
<td>8,030.49</td>
<td>30.71</td>
<td>0.963</td>
</tr>
<tr>
<td>293</td>
<td>–928.983</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>–1,375.37</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>–1,649.89</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 8** | Second order kinetic model (initial concentration 0.395 mg/L, adsorbent dose 10 g/L, mixing speed 30 rpm).

**Figure 7** | First order kinetic model (adsorbent dose 10 g/L, initial concentration 0.395 mg/L, mixing speed 30 rpm).
The equilibrium partition coefficient ($K_c$) is calculated as:

$$K_c = \frac{C_s}{C_e} \quad (7)$$

The thermodynamic parameters such as change in free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$) are calculated from the following equations and are given in Table 4.

$$\Delta G = -RT \ln K_c \quad (8)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

where $R$ is the gas constant (8.314 J/mol K), $C_s$ and $C_e$ are the equilibrium concentrations of the arsenic in the adsorbent (mg/L) and solution (mg/L) respectively and $T$ is the solution temperature (K). $\Delta H$ and $\Delta S$ are calculated from the slope and intercept of the plot of $\ln K_c$ versus $1/T$ as shown in Figure 9. The estimated values of thermodynamic parameters are shown in Table 3. The negative $\Delta G$ values confirm the feasibility of the adsorption process and the spontaneous nature of As(III) adsorption onto IOISB adsorbent. The more negative values of $\Delta G$ with the rise in temperature imply a greater driving force to the adsorption process and show an increase in feasibility of adsorption at higher temperatures (Ramesh et al. 2007). A positive value of $\Delta H$ indicates endothermic nature of As(III) adsorption on to the adsorbent, whereas the positive value of $\Delta S$ indicates that the randomness increased with temperature during the adsorption of arsenic onto IOISB adsorbent.

The efficiency of IOISB and other adsorbents reported in literature are shown in Table 4.

### CONCLUSIONS

IOISB was found to be a suitable adsorbent for As(III) removal from drinking water. It was found that the maximum adsorption of 98.90% occurs within 90 min of the operation, at an adsorbent dose of 10 g/L, contact time of 90 min, and mixing speed of 50 rpm, when initial adsorbate concentration, pH and room temperature were 0.5 mg/L, 6 and 30°C, respectively. Linear regression analysis showed that both Freundlich and Langmuir isotherms fitted the adsorption data adequately. The adsorption process followed a pseudo-second order kinetic model. The result of the kinetic adsorption model reveals that the adsorption of As(III) onto IOISB adsorbent was because of chemisorptions. The negative $\Delta G$ values obtained from the experimental results confirm the feasibility and spontaneous nature of the adsorption. Positive values of both $\Delta H$ and $\Delta S$ indicate the endothermic nature of
the process with increased randomness at the liquid-solid interface during As(III) ion adsorption in batch studies.

REFERENCES


IARC (International Agency for Research on Cancer) 2004 Some Drinking Water Disinfectants and Contaminants Including Arsenic, monograph 84. IARC, Lyons, France.


Wu, Y. H., Li, B., Feng, S. X., Mi, X. M. & Jiang, J. L. 2009 Adsorption of Cr(VI) and As(III) on coaly activated carbon in single and binary systems. Desalination 249, 1067–1073.


First received 12 June 2016; accepted in revised form 6 October 2016. Available online 14 November 2016