Arsenic removal using novel combined Fe/Mn adsorbent modified with silica
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ABSTRACT
Arsenic pollution has become a dominant environmental concern in recent years. Various techniques for arsenic removal from water have been developed. However, these techniques efficiently remove arsenic from drinking water but require toxic and expensive chemicals and generate a large amount of exhaust sludge, which is not always regenerable. In this study a novel Fe-Mn-Si oxide material was prepared from environmentally friendly and low-cost materials through a co-precipitation process. Batch adsorption experiments were conducted to study adsorption kinetics, adsorption capacity and the effect of temperature and pH on the adsorption of arsenic on Fe-Mn-Si oxide. The maximum adsorption capacity was found to be 9.62, 10.18, and 10.50 mg/g at 25, 35, and 45 °C, respectively. The results compare favorably with those obtained using other adsorbents. The used Fe-Mn-Si oxide could be regenerated using a NaOH solution; 73.4% of the adsorbed arsenic was desorbed by 0.2 N NaOH. Results from this study demonstrate the potential usability of Fe-Mn-Si oxide as a good arsenic-selective adsorbent.

INTRODUCTION
Arsenic pollution has become a dominant environmental concern in recent years because of its adverse effect on human health. Arsenic is a known carcinogen that causes skin, lung, bladder, liver, kidney, and prostate cancers (Boddu et al. 2008). Several studies have reported that chronic health problems related to arsenic primarily stem from the consumption of arsenic-contaminated drinking water. These problems have been widely reported all over the world, for instance, in China (Xia & Liu 2004), India (Roychowdhury et al. 2002), Japan (Kondo et al. 1999) and the USA (Burkel & Stoll 1999), where a majority of groundwater is contaminated with arsenic at levels from 100 to over 2,000 μg/L. Arsenic exists predominantly in inorganic anion forms, AsO$_3^2^-$ (III) and AsO$_4^{3-}$ (V), in natural water and thus in drinking water, its solubility in soil mainly dependent on redox potential and pH conditions. As(V) is the major arsenic species in surface water, whereas As(III) is the dominant arsenic species in groundwater. As(III) is much more toxic, more soluble, and more mobile than As(V) (Ferguson & Gavis 1972). The World Health Organization has set a provisional guideline limit of 10 μg/L for arsenic in drinking water (WHO 1993).

Arsenic contamination or enrichment in natural water can come from both natural processes, such as weathering of arsenic minerals, and anthropogenic activities including mining, smelting of non-ferrous metals, burning of fossil fuel, industrial waste discharge, and application of arsenic herbicides and pesticides. The conventional techniques for removal of arsenic from water include precipitation/co-precipitation, oxidation, reverse osmosis, electrodialysis, ion exchange, membrane filtration, and adsorption (Kartinen & Martin 1995). These techniques are generally less efficiency for removal of As(III) or require toxic and expensive oxidizing agents to oxidize As(III) to As(V) to achieve higher arsenic removal. Adsorption is considered to be one of the most promising of such technologies because an adsorption system can be efficient for removal of As (III) without oxidizing agents.
Various adsorbents for arsenic removal from water have been developed, which include such materials as activated alumina (Singh & Pant 2004), granular ferric hydroxide (Banerjee et al. 2008), iron oxide coated sand (Thirunavukkarasu et al. 2003), iron hydroxide coated alumina (Hlavay & Polyák 2007), granular activated carbon (GAC), Fe(III) oxide impregnated GAC (Mohan & Pittman Jr 2007), and Goethite (Ladeira & Ciminelli 2007). These adsorbents have been reported to efficiently remove arsenic from water; however, most of these adsorbents still involve several problems in terms of efficiency and cost. Thus, there still remains a strong challenge in developing novel adsorbents for arsenic removal with high uptake and regeneration efficiency, low cost, and excellent physical and chemical durability.

Our aim is to find a novel, cost-effective adsorbent for arsenic removal. Iron and manganese oxides are reported as effective adsorbents for arsenic removal. Silica is mainly used for iron oxide modification in order to improve the adsorption performance due to the high surface area and high concentration of reactive surface sites. To the best of our knowledge, no research on Fe-Mn-Si oxide for arsenic removal has been reported in the literature. The main objectives of the present research were to prepare Fe-Mn-Si oxide by coprecipitation from environmentally friendly and low-cost materials for effective arsenic removal and to evaluate its arsenic adsorption capacities.

**METHODS AND MATERIALS**

**Adsorbent preparation**

In the laboratory, Fe-Mn-Si adsorbent was prepared by a coprecipitation process. Ferric chloride (FeCl₃, 7.31 g) was dissolved in 200 mL of distilled water. Ferrous sulfate heptahydrate (FeSO₄·7H₂O, 12.51 g) and anhydrous silicon dioxide (SiO₂, 18 g) were then added to this solution. Potassium permanganate (KMnO₄, 2.37 g) solution was prepared by dissolving KMnO₄ in 200 mL of distilled water. The first solution contained iron and silicon to be added to the potassium permanganate solution with vigorous stirring, and 1 M NaOH solution was added to it to adjust the pH to approximately 4–5. The solution was then stirred continuously for 1 h. After 4 h, a precipitate was formed at room temperature and was separated from the liquid portion. The sedimentation-containing liquor was then dried at 90 °C for 12 h. The dried precipitate, which was dark brown in color, was powdered and stored in desiccators for later use as an adsorbent.

**Arsenic solution**

As(III) stock solution (1,000 mg/L) for batch experiments was prepared by dissolving 1.320 g As₂O₃ (Sigma-Aldrich) in minimum volume (approx. 10 mL) of 5 M NaOH solution. It was neutralized with nitric acid (Ranjan et al. 2009). The working solutions of As(III) of a required concentration were made by diluting the stock solution with deionized water.

**Experimental procedure**

The adsorption experiments were carried out in batch conditions where 0.5 g of adsorbent was added to 100 mL high-density polyethylene (HDPE) bottles containing 50 mL of a working solution of known ion species and concentrations. The effect of different pH values on arsenic adsorption was studied by adjusting the pH of the solution to the required pH range of 2.0–10.0 using either 0.1 M HCl or 0.1 M NaOH solutions. The bottles were settled in an incubator shaker and continuously shaken at 160 rpm for a predetermined time period. The reaction temperature was set in the range of 25–45 °C. After the predetermined adsorption time, solid and liquid phases were separated using a 0.45 μm membrane filter, and arsenic concentrations in the liquid phase were measured. The adsorption capacity, q (mg/g), was calculated using the following mass balance equation:

\[
q = \frac{V(C_0 - C)}{W}
\]

where \(C_0\) and \(C\) are, respectively, the initial and final liquid-phase concentrations of arsenic (mg/L). \(V\) is the volume of solution (L); and \(W\), the dry weight of adsorbent used (g).

For the desorption study, arsenic-loaded Fe-Mn-Si oxide was separated from the solution by filtration after the adsorption experiment, washed with deionized water, and dried at 110 °C. An amount of 0.5 g of dried arsenic-loaded Fe-Mn-Si oxide was added to 50 mL of 0.01–0.2 N NaOH in an HDPE bottle, and the bottle was then shaken at
160 rpm for 4 h at 25 °C. The final concentration of arsenic in the desorption medium separated by filtration was determined. The percentage of desorption was calculated from the amount of arsenic loaded on Fe-Mn-Si oxide and the final concentration of arsenic in the desorption medium.

**Analytical methods**

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was employed to determine the arsenic concentration throughout the experiment. The point of zero charge (pH_{zpc}) was determined from a zeta potential analyzer (Zeta-Meter, USA) under different pH conditions. The background electrolyte of the solutions was 100 mg/L NaCl to maintain constant ionic strength.

**RESULTS AND DISCUSSION**

**Characterization of adsorbent**

The zeta potential of Fe-Mn-Si under different pH conditions decreased with increasing pH. The zero point of charges (pH_{zpc}) of Fe-Mn-Si was 3.3.

The mineral constituents of the adsorbent was investigated through powder X-ray diffraction using an X′Pert Pro XRD system diffractometer with a curved position-sensitive detector configured in vertical geometry with a 2-theta detection range, operated at 40 mA and 40 kV. The results are shown in **Figure 1**. Obvious peaks at 22°, 28°, 32°, 36°, 46°, 57° were observed. Peaks at 22° and 32° are the characteristic peaks of Fe and are assigned to the (110) and (221) planes of Fe, respectively. Peaks at 28° and 57° are the characteristic peaks of Si and are assigned to the (111) and (311) planes of Si, respectively. Peaks at 36° and 46° are the characteristic peaks of Mn and are assigned to the (221) and (400) planes of Mn, respectively.

Scanning electron microscopy (SEM) was used to study the morphology and surface element distribution of the Fe-Mn-Si oxide adsorbent. The image obtained for the Fe-Mn-Si oxide adsorbent is shown in **Figure 2**. The surface of the adsorbent is rough and porous.

**Adsorption kinetics**

Batch experiments were conducted to determine the kinetics of adsorption. An amount of 0.05 g of adsorbent was added to 50 mL HDPE bottles containing 50 mL of arsenic solution with a 10 mg/L concentration. The bottles were shaken for 0.167, 0.334, 0.5, 1, 2, 3, 6, 12, and 24 h at 25 °C. The plot of the arsenic adsorption kinetic data is shown in **Figure 3(a)**. The equilibrium time has been found to be 5 h.

To interpret the experimental data, time-dependent adsorption data have been analyzed using the linear form
of the pseudo-first-order kinetic equation and pseudo-second-order kinetic equation.

The Lagergren pseudo-first-order kinetic model is expressed as (Lagergren 1898):

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  

(2)

where \(q_e\) and \(q_t\) are the amount of adsorbate adsorbed at equilibrium and at time \(t\) (mg/g), respectively, and \(k_1\) is the rate constant of pseudo-first-order adsorption (min\(^{-1}\)). Figure 3(b) shows the plot of the linear form of the pseudo-first-order kinetic model using the adsorption data of Figure 3(a). The values of \(k_1\) and \(q_e\) as well as the evaluated regression coefficients are presented in Table 1. Only the first portion of the adsorption kinetics yields a straight fitting line. Although the \(R^2\) value is reasonably high (\(R^2 = 0.9688\)), the calculated \(q_e\) value obtained from this equation does not give a reasonably high value, too low compared with experimental \(q_e\) values. This indicates that the adsorption process does not follow the pseudo-first-order kinetic model.

The pseudo-second-order kinetic equation is given as (Ho & McKay 1999):

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]  

(3)

where \(k_2\) is the rate constant of pseudo-second-order adsorption (g/mg min). Figure 3(c) shows the linear plot of
the pseudo-second-order equation using the data from Figure 3(a). The plot was found to be linear over the entire sorption period with high regression coefficients \( R^2 = 0.9989 \), confirming the applicability of the pseudo-second-order kinetic model. The pseudo-second-order rate constant \((k_2)\) and equilibrium capacity \((q_e)\) determined from the slope and intercept of the plot (Figure 3(c)) are listed in Table 1. The theoretical \( q_e \) value was also very close to the experimental \( q_e \) value in the case of the pseudo-second-order kinetic equation (Table 1). It is clear from the accuracy of the model that the adsorption of arsenic on Fe-Mn-Si is more appropriately described by the pseudo-second-order kinetic model.

**Adsorption isotherms**

To study the adsorption isotherm of the Fe-Mn-Si oxide for arsenic, 0.5 g of Fe-Mn-Si oxide was added to various 50 mL arsenic solution samples having concentration in the range of 1–100 mg/L at an initial pH of 7. Each sample was shaken for 24 h at 25, 35, and 45 °C under constant shaking of 160 rpm. Figure 4(a) shows the results of arsenic adsorption isotherms on Fe-Mn-Si oxide at different temperatures.

The experimental data obtained were plotted in a linear form of Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) isotherm models as shown below:

\[
\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}
\]

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

where \( C_e \) is the equilibrium concentration (mg/L); \( q_e \) is the amount adsorbed at equilibrium (mg/g); \( q_m \) is the Langmuir constant related to the maximum adsorption capacity (mg/g); and \( b \) is an energy term (L/mg), which varies as a function of surface coverage strictly due to variations in the heat of adsorption. \( K_f \) and \( n \) are the Freundlich constants related to the adsorption capacity of the adsorbent and the magnitude of the adsorption driving force, respectively. The adsorption data of arsenic on Fe-Mn-Si oxide selectively followed Langmuir and/or Freundlich isotherm models at different temperatures, as shown in Figures 4(b) and 4(c). The calculated isotherm parameters along with correlation coefficients are given in Table 2.

It was observed that for data obtained at high temperature, the maximum adsorption capacity \((q_m)\) of the Fe-Mn-Si oxide for arsenic increases. The maximum adsorption capacity \((q_m)\) of the Fe-Mn-Si oxide for arsenic is found to be 9.62, 10.18, and 10.50 mg/g at 25, 35, and 45 °C, respectively. The obtained \( q_m \) values for our Fe-Mn-Si oxide material compare favorably with those obtained using other adsorbents (Table 3). These results suggested that the Fe-Mn-Si oxide adsorbent was effective for As(III) removal.

**Effect of pH on arsenic adsorption**

The pH of the solution is an important factor that has a strong influence on the uptake of the adsorbate. The effect of pH on the adsorption of arsenic on the Fe-Mn-Si oxide was examined at an initial arsenic concentration of 10 mg/L and a constant adsorbent dosage of 0.5 g/50 mL. The pH of the solution was controlled after the adsorption equilibrium to be 2.0–10.0 by adding buffer solutions. Figure 5(a) shows the
results of the adsorption equilibrium of arsenic onto the Fe-Mn-Si oxide as a function of the equilibrium pH of the solution. As shown in Figure 5(a), the adsorption equilibrium of arsenic onto the Fe-Mn-Si decreased with the increase in the pH of the solution. The same trend was also observed with the As(V) species in previous studies (Zhang et al. 2013). This indicates that the amount of adsorption drops in a higher pH region because of the increase in negative-charge sites on the adsorbent surfaces. Many studies suggested that increasing pH decreased As(V) adsorption on iron-containing adsorbents. In pHs between 4 and 7, the predominant As(V) species are $\text{H}_2\text{AsO}_4\text{H}^+$ and $\text{HAsO}_4\text{H}^+$, and these ions are adsorbed on Fe-Mn-Si oxide due to Coulombic interaction (Su & Puls 2007). When the pH is $>9$, the dominant species of As(V) is $\text{HAsO}_4^{2-}$, and this anion may compete with the negative site of the adsorbent surface to reduce the adsorption capability due to electrostatic repulsion (Cheng et al. 2005). The similarity of As(III) adsorption in this study indirectly suggests that the initially added As(III) was oxidized into As(V) and then adsorbed onto Fe-Mn-Si oxide.

Desorption study

To assess the possibility of recycling the sorbent for reuse in a multiple adsorption cycle, arsenic desorption experiments for the used Fe-Mn-Si oxide were conducted using NaOH solutions of 0.01, 0.1, and 0.2 N. An amount of 0.5 g arsenic-loaded Fe-Mn-Si oxide was added to 50 mL fractions of NaOH solution and shaken for 4 h at 25°C. It was found that arsenic desorption was 20.2, 55.2, and 73.4% with 0.01, 0.1, and 0.2 N NaOH, respectively. The results (Figure 5(b))

### Table 2

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Concentration/range</th>
<th>Temperature</th>
<th>Model used to calculate adsorption capacity</th>
<th>$q_m$ mg/g</th>
<th>References</th>
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<tbody>
<tr>
<td>Activated alumina</td>
<td>7.6</td>
<td>1 mg/L</td>
<td>25</td>
<td>Langmuir</td>
<td>0.18</td>
<td>Singh &amp; Pant (2004)</td>
</tr>
<tr>
<td>GAC</td>
<td>7.0</td>
<td>20–23</td>
<td></td>
<td>Langmuir</td>
<td>0.09</td>
<td>Mohan &amp; Pittman Jr (2007)</td>
</tr>
<tr>
<td>Fe(III) oxide impregnated GAC</td>
<td>7.0</td>
<td>1 mg/L</td>
<td>20–23</td>
<td>Langmuir</td>
<td>4.5</td>
<td>Mohan &amp; Pittman Jr (2007)</td>
</tr>
<tr>
<td>Iron oxide-coated sand</td>
<td>7.6</td>
<td>100 μg/L</td>
<td>22</td>
<td>Langmuir</td>
<td>0.041</td>
<td>Thirunavukkarasu et al. (2005)</td>
</tr>
<tr>
<td>Iron hydroxide-coated alumina</td>
<td>6.6</td>
<td>0.1–1.8 mmol/L</td>
<td>25</td>
<td>Langmuir</td>
<td>7.64</td>
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<tr>
<td>Goethite</td>
<td>5.5</td>
<td>10–1,000 mg/L</td>
<td>25</td>
<td>Langmuir</td>
<td>7.5</td>
<td>Ladeira &amp; Ciminelli (2004)</td>
</tr>
<tr>
<td>Present study</td>
<td>7.0</td>
<td>1–100 mg/L</td>
<td>25</td>
<td>Langmuir</td>
<td>9.62</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 5](https://iwaponline.com/ws/article-pdf/13/4/1109/415016/1109.pdf)

**Figure 5** (a) Effect of pH on the adsorption of As(III) on Fe-Mn-Si. (b) Desorption study on Fe-Mn-Si adsorbent using NaOH solution.
show that arsenic-loaded Fe-Mn-Si oxide undergoes effective desorption in the presence of an alkaline-like NaOH.

**CONCLUSION**

A novel adsorbent for effective arsenic removal, Fe-Mn-Si oxide, has been prepared through a coprecipitation method. The adsorbent exhibited high arsenite removal capacity. The equilibrium data fitted the Langmuir isotherm model fairly well, and the maximum adsorption capacity was found to be 9.62, 10.18, and 10.50 mg/g at 25, 35, and 45 °C, respectively. The adsorption process followed the pseudo-second-order kinetic model. The arsenic adsorption capacity of Fe-Mn-Si oxide is highest at low pH and sharply decreased with the increase in the pH of the solution. The used Fe-Mn-Si oxide could be regenerated using a NaOH solution; 73.4% of the increase in the pH of the solution. The used Fe-Mn-Si oxide is highest at low pH and sharply decreased with the increase in the solution.

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