Hydrous Iron(III)-Tin(IV) Binary Mixed Oxide: Arsenic Adsorption Behaviour from Aqueous Solution

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Groundwater in the Bengal delta plain is primarily in an anoxic environment and As(III)/As(total) ratios reported are in the range of 0.60 to 0.90. Most of the studied adsorbents showed greater adsorption affinity for less toxic As(V) than for more toxic As(III). The synthesis and physicochemical characterizations of iron(III)-tin(IV) binary mixed oxide composite with systematic arsenic adsorption behaviour are reported here. The parameters studied are the effect of pH, adsorption capacity with varying arsenic loads, contact time for kinetics and isotherm modelling by batch method. In the pH range of 3.0 to 9.0, the adsorption of As(III) is found to be nearly the same while that of As(V) decreases with increasing pH for the studied arsenic concentrations (5.0 to 20.0 mg L⁻¹). The adsorption data were analyzed using various kinetic and isotherm model equations. The rate of adsorption of As(III) was faster than that of As(V) at equilibrium pH ~7.0 and temperature 30(± 2)ºC. The adsorption kinetic data for arsenic fitted best with the Ho’s pseudo-second order (R² = 0.99–1.00 for As(III) and ~0.97–0.98 for As(V)) and parabolic diffusion (R² = 0.98–0.99) equations. The present kinetic data fitted the power function and simple Elovich kinetic equations well (R² = 0.97–1.00), except the data obtained for As(III) from the 20.0 mg L⁻¹ solution. The analyses of adsorption data for As(III) and As(V), respectively, at equilibrium pH 6.8(±0.1) and 7.3(±0.1) with three different two-parameter isotherm model equations show the fitting order: Langmuir > Freundlich > Temkin. The monolayer adsorption capacity (θ₀, mg g⁻¹) values evaluated from the Langmuir isotherm for As(III) and As(V) are 43.86 and 27.55, respectively.

Key words: arsenic, adsorption, hydrous iron(III)-tin(IV) mixed oxide, isotherm, kinetics, pH

Introduction

Naturally occurring high arsenic levels in groundwater of the Bengal delta plain pose health risks to the public in India and Bangladesh, because people in both countries are dependent upon groundwater as the main drinking water source. Many other countries worldwide have also faced similar problems (Smedley and Knniburgh 2002). Among the various arsenic species, As(III) is reported to be the most toxic (Ferguson and Davis 1972; Cullen and Reimer 1989; Korte and Fernando 1991), because As(III) is soft in nature, and combines readily with the soft thiol (-SH) group of the cystein residue in protein. Underground aquifers at a depth of 30 to 40 m in the Bengal delta plain are in a strong reducing (anoxic) environment, and As(III) to As(total) ratios are 0.6 to 0.9 (Harvey et al. 2002). Thus, As(III) is the major species in Bengal delta plain groundwater, and direct As(III) extraction from water into the solid phase is thought to be important in light of present-day concepts of “green chemistry” and public health.

Numerous methods have been reported for removing arsenic from water. Among them, adsorption onto a solid surface has been found to be the most convenient in the field for third world countries where people are unable to deal properly with toxic sludge. Adsorbents studied to date are amorphous aluminium oxide (Anderson et al. 1976; Gulledge and O’Conor 1973), activated alumina (Rosenblum and Clifford 1984; Singh et al. 2001), activated carbon (Huang and Fu 1984), amorphous iron hydroxide (Pierce and Moore 1982), hydrous iron oxide (Hsia et al. 1994; Wilkie and Hering 1996), granular ferric hydroxide (Driehaus et al. 1998; Thirunavukkarasu et al. 2003a), ferricydrte (Fuller et al. 1993; Raven et al. 1998; Jain and Loepert 2000), goethite (Sun and Doner 1998), crystalline hydrous ferric oxide (Manna et al. 2003), red mud (Altundogan et al. 2002), hydrated zirconium oxide (Manna et al. 1999), crystalline hydrated titanium oxide (Manna et al. 2004), iron oxide-coated sand and ferrihydrite (Thirunavukkarasu et al. 2001, 2003b), Fe(III)-Si binary oxide (Zeng 2004) and iron oxide impregnated activated alumina (Kuriakose et al. 2004). Many of the adsorbents are shown to be more efficient in removing As(V) than As(III). Crystalline hydrous ferric oxide can adsorb both arsenic species with nearly equal efficiency (Manna et al. 2003) and hydrous stannic oxide showed higher efficiency for As(III) (Manna 2005) when contamination levels in aqueous solutions were low.

The underground aquifers of the Bengal delta plain at a depth of 30 to 40 m contain 60 to 90% As(III) of total

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arsenic (Harvey et al. 2002), so adsorbents with greater As(III) scavenging power are required for contaminated water treatment. It was assumed that the hydroxide oxide of metal ions with eighteen valence electrons (ns²np⁶nd¹⁰) might have greater affinity for softer As(III) than harder As(V) due to the soft-soft interaction. Tin(IV) oxide, a 4s²4p⁶4d¹⁰ species, if incorporated into the lattice of the most abundant ferric oxide, may enhance As(III) sorption efficiency of the latter compound. Thus, an attempt was made to synthesize mixed oxide of iron(III) and tin(IV), and use it for arsenic adsorption study. The synthesis, physicochemical characterization and systematic arsenic adsorption behaviour of iron(III)-tin(IV) binary mixed oxide composite are reported.

Experimental

Chemicals

Standard stock As(III) and As(V) solutions (1000 mg L⁻¹) were prepared by dissolving arsenic oxide, As₂O₃ (AR, BDH), and disodium hydrogen arsenate, Na₂HAsO₄, (Baker Analyzed Reagent) in 10 mL of 4% (w/v) NaOH and distilled water, respectively. The former solution was then acidified by adding 20 mL of concentrated HCl (AR, BDH) per litre of solution before volume make-up, and it was then frozen. The working solutions of required concentrations were prepared by diluting the stock solution with distilled water, and standardized by spectrophotometric (Hitachi model U-3210) measurement using silver diethyldithiocarbamate (SDDC) (AR, BDH) reagent. The pH levels of the working solutions were adjusted to a required value just before performing the experiments. HCl (1%) and NaOH (4%) were used as required for adjusting the pH of the arsenic solutions.

Synthesis of Adsorbent

Binary iron(III)-tin(IV) mixed oxide was synthesized by hydrolyzing 0.1 M FeCl₃ in 0.1 M HCl with 0.1 M Na₂SnO₃ in 0.1 M NaOH at 60°C with constant stirring followed by the addition of 0.1 M sodium hydroxide solution until the pH of the supernatant liquid was between 4.0 and 5.0. The precipitate was aged for 24 h, filtered, washed with deionized water and then dried at ~60°C in an air oven. Finally, the dried product was ground to the required particle size (0.14–0.29 mm) for experimental study.

Characterization of the Synthetic Oxide

The empirical composition of iron(III)-tin(IV) oxide was determined by classical chemical analysis. Here, a definite amount of the mixed oxide was treated with HNO₃ (1:1), where iron(III) oxide goes to solution leaving tin(IV) oxide as residue. The tin(IV) oxide residue was filtered using a sintered glass crucible of known weight, and determined gravimetrically. Iron(III) in solution was estimated by titration with standard EDTA solution using sulfoalicylic acid as an indicator. Thermal data, thermogravimetric analysis (TGA) and differential thermal analysis (DTA), were recorded using a Setaram analyzer in an argon gas atmosphere at a heating rate of 20°C min⁻¹ over a temperature range of 30 to 900°C. X-ray diffraction (XRD) analysis of the mixed oxide was carried out using a Phillips x-ray diffractometer. Surface area was determined by BET nitrogen gas adsorption technique using a micromerities surface analyzer. The pHₚₑₚ was reported on the basis of our experimental findings from electrophoretic mobility measurement of solid suspensions containing 0.02% solid in 0.01% NaCl at various pH levels. The Fourier transform infrared (FTIR) spectrum was recorded using a Perkin Elmer-RXIFT spectrophotometer.

Batch Experiment

Batch adsorption tests of arsenic onto the binary mixed oxide were carried out by mechanical agitation (agitation speed: 150–160 rpm) at a temperature of 30(±2)°C. Here, 50-mL aliquots of varying initial arsenic concentrations (5.0–500.0 mg L⁻¹) were each treated with 0.1 g of mixed binary oxide (particle size: 0.14–0.29 mm) in a 100-mL polythene container. The agitated solutions were filtered through 0.45-µm membrane filter, and the filtrate was analyzed for arsenic. The quantity of arsenic adsorbed was calculated by the difference of initial and residual amounts of arsenic in the solution divided by the amount of the adsorbent used. To check the reproducibility of the experimental data, each experiment was conducted three times.

Batch sorption kinetics experiments were conducted by adding 2.0 g of mixed oxide per litre of arsenic solution taken into a 2.0-L of polythene container and agitated (150–160 rpm) at 30(±2)°C. The pH of the equilibrated solution was monitored and adjusted to ~7.0 as practicable using dilute HCl or NaOH solution as required. A definite volume of solution (5.0 or 10.0 mL) was sampled at a definite time interval for arsenic analysis.

Analytical Method

Arsenic analysis in solution was conducted using a spectrophotometer (Hitachi, model-3210) and hydride generator-atomic absorption spectrophotometer (Perkin Elmer, Analyst-100) having a detection limit of approximately 10.0 and 1.0 µg L⁻¹, respectively. The methods used for the determinations were as depicted in standard methods of water and wastewater analysis (AWWA 1998).
Results and Discussion

Physicochemical Characteristics of the Adsorbent

Some physicochemical parameters of the mixed oxide are shown in Table 1. The x-ray diffraction pattern (Fig. 1) showed no clean characteristic peaks with good intensity except two at 2θ angle values ~9.50º and 34.22º with d-spacing (Å) 9.31 and 2.62. Thus, it could be suggested that the iron(III)-tin(IV) mixed oxide synthesized is amorphous in nature. The Fourier transform infrared (FTIR) spectrum (Fig. 2) of the synthetic mixed oxide showed the absorption peaks for water (υ [cm⁻¹] = 3401.9, 3754.4 and 1626.0 [bending]), bridging hydroxyl group (υ [cm⁻¹] = 969.8 [bending]), Fe-O (υ [cm⁻¹] = ~670) and Sn-O (υ [cm⁻¹] = ~528). An additional peak at ~2370 cm⁻¹ is for CO₂, which is presumably absorbed from air. As the υ_{Sn-O} (cm⁻¹) shifts to a slightly lower frequency value from that of synthetic Sn(IV) oxide (υ_{Sn-O} = 562.1 cm⁻¹) and Fe(III) oxide (υ_{Fe-O} = 670 cm⁻¹), the possible presence of some interactions between iron(III) and tin(IV) via oxygen were revealed. Thus, the synthetic mixed oxide is basically a hydrous binary composite mixture. TGA thermogram showed 21.10 and 1.32% loss of weight in the range of drying temperature of 30 to 130°C and 130 to 900°C, respectively. The weight loss of 6.73% obtained at a temperature of 110°C is attributed to the irreversible loss of physically adsorbed water molecules, and is the moisture content of mixed oxide. The remaining ~14.4% loss of weight in the drying temperature range of 110 to 130°C is presumably due to dehydroxylation of metal hydroxides. The DTA thermogram showed no exoergic peak. This indicates that polymerization or crystallization does not occur while drying up to 900°C. The determined surface area of the mixed oxide composite was found to be less than either of the pure oxides, which is presumably due to the diffusion of stannic oxide into the lattice structure of ferric oxide. The mole ratio of Fe to Sn metal content in the oxide composite was obtained as 1:1. The determined pH_{ZPC} of the binary oxide, an important property of adsorbent, was found (6.2–6.9) nearly intermediate of the

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fe(III)-Sn(IV) mixed oxide</th>
<th>CHFOᵃ</th>
<th>HSOᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Particle form</td>
<td>Amorphous</td>
<td>Crystalline</td>
<td>Amorphous</td>
</tr>
<tr>
<td>2. Metal content (%)</td>
<td>1:1</td>
<td>55.85</td>
<td>61.60</td>
</tr>
<tr>
<td>3. Colour</td>
<td>Brown</td>
<td>Black</td>
<td>White</td>
</tr>
<tr>
<td>4. Particle size (mm)</td>
<td>0.14–0.29</td>
<td>0.14–0.29</td>
<td>0.14–0.29</td>
</tr>
<tr>
<td>5. Surface area (m²g⁻¹)</td>
<td>127.0</td>
<td>165.6</td>
<td>140.8</td>
</tr>
<tr>
<td>6. Bulk density</td>
<td>n.d.ᵃ³</td>
<td>1.25</td>
<td>1.38</td>
</tr>
<tr>
<td>7. pH ZPC</td>
<td>6.2–6.9</td>
<td>6.8–7.7</td>
<td>4.6–6.4</td>
</tr>
<tr>
<td>8. Moisture content (%)</td>
<td>6.73</td>
<td>18.21</td>
<td>4.22</td>
</tr>
</tbody>
</table>

ᵃCrystalline hydrous ferric oxide (Manna et al. 2003).
ᵇHydrous stannic oxide (Manna 2005).
ᶜn.d.; Not determined.
pure oxides. This \( \text{pH}_{ZPC} \) value indicates that the surface of the mixed oxide is neutral or heterogeneous in the pH range 6.2 to 6.9 and is positive and negative at pH below 6.2 and above 6.9, respectively.

**Adsorption Capacity**

The adsorption capacity of an adsorbent is a significant parameter in understanding the efficiency of that adsorbent. The higher the adsorption capacity value, the more efficient the adsorbent is. It is defined as the amount of adsorbate adsorbed per unit weight of the adsorbent; however, it depends on the solution chemistry and experimental conditions.

The determined adsorption capacities (mg g\(^{-1}\)) of As(III) and As(V) as a function of arsenic concentration used at an initial temperature of 30(±2)ºC and pH 7.0 are shown in Table 2. Results show that the adsorption capacity (mg g\(^{-1}\)) for As(III) is greater than As(V) at any initial arsenic concentration ranging from 5.0 to 500 mg L\(^{-1}\). The adsorption capacities (mg g\(^{-1}\)) obtained for As(III) were 2.46(±0.03) and 44.67(±1.50) while that for As(V) were 1.17(±0.02) and 23.35(±1.15) for lowest used (5.0 mg L\(^{-1}\)) and highest used (500 mg L\(^{-1}\)) arsenic concentrations, respectively. The results indicate that As(III) is retained in larger amounts than As(V) on Fe(III)-Sn(IV) binary metal oxide composite in the studied arsenic concentration range at an initial pH 7.0. This observation closely resembles the observation of Raven et al. (1998). They found that arsenite adsorbed on ferrihydrite was in larger amounts than arsenate at the initial concentration >0.267 mole As kg\(^{-1}\) ferrihydrite and at pH >7.5.

**Distribution Coefficient (K\(_d\))**

The K\(_d\) values are calculated using the working formula:

\[
K_d = \frac{\text{Total amount of arsenic present in solid phase (mg)}}{\text{Total amount of arsenic present in solution (mg)} \times \frac{\text{volume of solution (mL)}}{\text{weight of adsorbent (g)}}}
\]

Results (Table 2) show that the calculated K\(_d\) values for both As(III) and As(V) sorption decrease with increasing arsenic load in solution. This is due to the greater amount of residual arsenic in solution with increasing arsenic load. However, the K\(_d\) value of As(III) at a given initial load of arsenic is found to be greater than As(V) at an initial working pH of 7.0. This indicates clearly [evident from separation factor \( \alpha = K_d \text{As(III)}/K_d \text{As(V)} \)] that the synthetic binary oxide composite can be used as an adsorbent for separating As(III) and As(V) from their mixture which has importance in light of arsenic speciation from the contaminated groundwater.

**Effect of Contact Time**

The time-dependent arsenic adsorption data obtained at 30(±2)ºC and at equilibrium pH 6.8(±0.1) for As(III) and 7.3(±0.1) for As(V) are shown in Fig. 3 and 4. Results show that the adsorption capacity for As(III) on binary oxide increases with increasing contact time, and equilibrium was reached in ~2 h. The adsorption capacity for As(V) increased also with increasing contact time, but the time required to reach equilibrium was ~9 h. The rate of As(III) sorption was found to be much faster than

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**Fig. 2.** FTIR spectrum of synthetic iron(III)-tin(IV) mixed oxide.
As(V) onto the mixed oxide under the present experimental conditions indicating the differences in adsorptive behaviour of these two arsenic species. After an hour of contact, the adsorption percentages for As(III) and As(V) were ~85.0 to 95.0% and ~33.0 to 43.0%, respectively, than those obtained at their respective equilibrium times. Our findings agree well with the results reported by Raven et al. (1998) using ferrihydrite at high initial arsenic load (1000 mg As g⁻¹ ferrihydrite). Similar results were also reported using iron(III)-Si binary mixed oxide by Zeng (2004), but contact time required (3 h) in approaching equilibrium was higher than the present study. Another group of workers (Kuriakose et al. 2004) observed that the required contact time was 10 h in reaching As(III) sorption equilibrium onto iron oxide impregnated activated alumina with rapid sorption in 4 h. Thus, iron(III)-tin(IV) binary oxide composite adsors As(III) requiring much less contact time compared to As(V). This faster adsorption of As(III) than As(V) onto the adsorbent is presumably due to the presence of tin(IV) with iron(III) in the mixed binary oxide.

Effect of pH
The results shown in Fig. 5 and 6 are the arsenic adsorption capacities (mg As g⁻¹ adsorbent) of the synthetic binary mixed oxide at different final equilibrium pH values ranging between 1.0 to 9.0 and solution arsenic concentrations (5.0, 10.0 and 20.0 mg L⁻¹), respectively. Results show that As(V) adsorption capacities were higher than As(III) in an equilibrium pH range of 1.0 to ~3.5, when arsenic concentrations used were 10.0 and 20.0 mg L⁻¹. When arsenic concentration in solution was low (5.0 mg As L⁻¹), the adsorption capacities for both arsenic species were found to be nearly equal in an equilibrium pH range of 1.0 to ~5.2. In contrast, Manna et al. (2003) found nearly equal adsorption percentages for both arsenic species onto the crystalline hydrous ferric oxide.

<table>
<thead>
<tr>
<th>Initial arsenic load (mg L⁻¹)</th>
<th>Adsorption capacity (mg g⁻¹)</th>
<th>Distribution coefficient (Kₐ, mL g⁻¹) 10⁻³</th>
<th>Separation factor (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As(III)</td>
<td>As(V)</td>
<td>As(III)</td>
</tr>
<tr>
<td>5.0</td>
<td>2.46 (±0.03)</td>
<td>1.17 (±0.02)</td>
<td>30.75</td>
</tr>
<tr>
<td>10.0</td>
<td>4.58 (±0.06)</td>
<td>2.35 (±0.08)</td>
<td>5.45</td>
</tr>
<tr>
<td>20.0</td>
<td>8.67 (±0.14)</td>
<td>3.34 (±0.15)</td>
<td>3.26</td>
</tr>
<tr>
<td>50.0</td>
<td>20.08 (±0.60)</td>
<td>6.84 (±0.56)</td>
<td>2.04</td>
</tr>
<tr>
<td>100.0</td>
<td>27.50 (±1.01)</td>
<td>13.19 (±0.80)</td>
<td>0.61</td>
</tr>
<tr>
<td>200.0</td>
<td>32.50 (±1.10)</td>
<td>17.95 (±1.05)</td>
<td>0.26</td>
</tr>
<tr>
<td>300.0</td>
<td>37.26 (±0.95)</td>
<td>21.30 (±0.95)</td>
<td>0.17</td>
</tr>
<tr>
<td>400.0</td>
<td>41.49 (±1.05)</td>
<td>22.62 (±1.02)</td>
<td>0.13</td>
</tr>
<tr>
<td>500.0</td>
<td>44.67 (±1.50)</td>
<td>23.35 (±1.04)</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Fig. 3. Effect of contact time on adsorption of As(III) by iron(III)-tin(IV) binary mixed oxide at 30(±2)°C and at equilibrium solution pH 6.8(±0.1). Arsenic concentration (mg/L): ◆ 10.0, ■ 20.0.

Fig. 4. Effect of contact time on adsorption of As(V) by iron(III)-tin(IV) binary mixed oxide at 30(±2)°C and at equilibrium solution pH 7.3(±0.1). Arsenic concentration (mg/L): ◆ 10.0, ■ 20.0.
oxide in pH values up to 6.0, when initial arsenic concentration used was 10.0 mg L\(^{-1}\). Thus, the difference obtained in pH values is presumably due to the presence of tin(IV) oxide (pH\(_{ZPC}\) = 4.6–6.4) with iron(III) oxide, which changed the surface nature (charge) of the mixed oxide composite from the pure ferric oxide.

Clearly, less adsorption of As(III) than As(V) onto the synthetic iron(III)-tin(IV) binary mixed oxide at pH 1.0 to ~3.5 obtained from the high arsenic loaded solutions used is due to the electrostatic repulsion of like charges faced between the H\(^{+}\) centre of the O-H bond in As(OH)\(_3\) (pK\(_1\) = 9.2) and surface positive charge of the adsorbent (pH\(_{ZPC}\) = 6.2–6.9) at the solid-liquid interface. When the concentration of arsenic solution used was 5.0 mg L\(^{-1}\), the decrease in As(III) adsorption compared to As(V) was not reflected clearly up to equilibrium solution pH ~3.5. This is obviously due to low solute load per gram of adsorbent compared to the surface adsorption sites available. The adsorption capacity for As(III) of the studied adsorbent was found to be much greater than As(V) at equilibrium pH >5.5, though some workers reported reverse results. In contrast, Yoshida et al. (1976) found maximum sorption of both arsenic species occurring at pH 6.0 onto ferric hydroxide impregnated silica gel. Altundogan et al. (2002) reported an alkaline pH range for maximum adsorption of arsenic onto red mud. The present observed effect of pH on arsenic adsorption is almost similar to the report of Zeng (2004). Additionally, it was found that the adsorption of As(III) was almost independent of pH, while that of As(V) was highly pH dependent. It was noted that As(V) sorption onto the present mixed oxide showed the increase in pH of the final solution. This was less significant at initial pH values of 1.0 and 2.0 where final pH of solutions were 1.05 to 1.15 and 2.15 to 2.20, and more significant increase was noted for the initial pH of 3.0 and 4.0 where the final pH values were of 3.3 to 3.5 and 4.5 to 4.7. However, this pH rise also increases with increasing initial As(V) loading in solution, and the pH change was found to be insignificant for the equilibrated solution for initial pH 7.0. Again, As(V) sorption at initial pH ≥8.0 was found to take place with decreasing final solution pH. In contrast, As(III) sorption took place at identical initial pH conditions with no noticeable change of final solution pH.

The mechanisms for As(III) and As(V) sorption onto the present mixed oxide may be depicted differently. The As(III) adsorption in the studied pH range is thought to take place via electrostatic interaction resulting in outer sphere surface complex formation. In addition, As(OH)\(_3\) has an unshared electron pair on the central atom which may be donated to the metal ion present in the solid mixed oxide-forming inner sphere complex. The surface adsorption via a complex formation model is somewhat similar to the mechanisms as depicted by others (Raven et al. 1998; Hsia et al. 1994). This leads to chemical stabilization. Apart from As(III), As(V) sorption takes place via an electrostatic or ligand (anion) exchange phenomenon because pentavalent species exist as neutral H\(_2\)AsO\(_4\) and anions (H\(_2\)AsO\(_4\)\(^-\) and HAsO\(_4\)\(^2-\)) in the studied pH range (pK\(_1\), pK\(_2\) and pK\(_3\) values for H\(_2\)AsO\(_4\) are 2.18, 6.50 and 11.50, respectively) of 1.0 to 9.0. The decrease in As(V) adsorption capacity compared to As(III) obtained at a final solution pH ~7.0 than the pH ~6.0 was found to be ~45%. Zeng (2004) also reported similar observations using iron(III)-Si binary oxide where As(V) adsorption at pH 9.6 was nearly negligible compared to that at pH 6.5. This decrease agreed well with the pH\(_{ZPC}\) (6.2–6.9) of the adsorbent which can be well explained using the ion-exchange property (Amphlet 1964) of synthetic oxide, because the synthetic material shows cation-exchange properties above isoelectric pH (6.9) values. At pH >6.9, As(V) sorption takes place via the cation (available in solution, here Na\(^+\)) adsorption in the first adsorption sphere and, thereon As(V) sorption
takes place. The As(V) species is at the second adsorption sphere, and adsorption capacity, therefore, reduced remarkably. Moreover, the electrostatic repulsion between the negatively charged surface sites and anionic As(V) species further reduces the As(V) adsorption. Again, As(III) sorption capacity at pH between 6.5 to 9.0 was found to be much greater than As(V) at any level of initial arsenic load due to the presence of comparatively soft tin(IV) (4d^10) with borderline iron(III) (3d^5) in the mixed oxide, which prefers to bind softer nonionic As(III) than harder ionic As(V) (Pearson 1988), and nonionic As(OH)_3 is not to be repelled electrostatically by the negative surface charge of the adsorbent.

**Adsorption Isotherm**

The following linear form of the isotherm equations is used for analyzing arsenic adsorption data obtained (Fig. 7) at 30(±2)°C and at equilibrium solution pH 6.8(±0.1) for As(III) and pH 7.3(±0.1) for As(V):

- **Langmuir isotherm:**
  \[ \frac{C_e}{q_e} = \frac{1}{\theta_0 b} + \frac{C_e}{\theta_0} \]  
  (1)

- **Freundlich isotherm:**
  \[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  
  (2)

- **Temkin equation:**
  \[ q_e = a + b \log C_e \]  
  (3)

where \( q_e \) is the amount of arsenic adsorbed at equilibrium (mg g\(^{-1}\)) and \( C_e \) is equilibrium concentration (mg L\(^{-1}\)) in solution. The other parameters are different isotherm constants, which can be determined by regression of experimental data.

From graphical plots (best fit plots shown only) of the experimental data, isotherm parameters along with correlation coefficients are estimated (Table 3). The results indicate that the present isotherm adsorption data for both arsenic species could be described best by the Langmuir model (Fig. 8), which is evident from the highest correlation coefficients (R\(^2\) ~0.99). However, the adsorption data for both arsenic species also fitted well with the Freundlich (R\(^2\) ~0.97–0.98) model. Although the present isotherm sorption data fit was found to be poorest with the Temkin (R\(^2\) ~0.94–0.95) model, the chemisorptions, at least partially, are indicated. The present adsorption data describe the two-parameter isotherm models as indicated in order: Langmuir > Freundlich > Temkin for both arsenic species. From the trends in fitting of the adsorption data with the two-parameter isotherm models, similar mechanisms can be envisaged for As(III) and As(V) sorption onto the mixed oxide. The evaluated adsorption capacity (\( \theta_0, \text{mg g}^{-1} \)) due to monolayer surface coverage for As(III) is much greater (43.86 mg g\(^{-1}\)) than for As(V) (27.55 mg g\(^{-1}\)). The value of \( \theta_0 \) for lower valent species onto mixed oxide was found to be greater than pure iron(III) oxide (\( \theta_0 = 33.33 \text{ mg g}^{-1} \)) and pure tin(IV) oxide (\( \theta_0 = 15.85 \text{ mg g}^{-1} \)). The \( \theta_0 \) value (43.85 mg g\(^{-1}\)) for As(III) of this binary metal oxide composite is greater than that of iron(III)-Si binary oxide (\( \theta_0 = 21.10 \text{ mg g}^{-1} \)) (Zeng 2004) which suggests the greater adsorption affinity for As(III) of iron(III)-tin(IV) oxide. This indicates the prospective use of mixed oxide in direct As(III) extraction from the groundwater.

The essential characteristic of the Langmuir isotherm can be expressed in terms of the dimensionless separation

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**TABLE 3.** Estimated isotherm parameters for arsenic sorption at 30(±2)°C onto iron(III)-tin(IV) binary mixed oxide at final pH 6.8(±0.1) for As(III) and pH 7.3(±0.1) for As(V)

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>As(III)</th>
<th>As(V)</th>
<th>As(III)</th>
<th>As(V)</th>
<th>As(III)</th>
<th>As(V)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \theta_0 ) (mg g(^{-1}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Langmuir</td>
<td>0.9872</td>
<td>0.9904</td>
<td>43.86</td>
<td>0.0573</td>
<td>0.0124</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>0.9681</td>
<td>0.9794</td>
<td>6.1009</td>
<td>0.7878</td>
<td>2.9206</td>
<td>1.6969</td>
</tr>
<tr>
<td>Temkin</td>
<td>0.9433</td>
<td>0.9486</td>
<td>8.9879</td>
<td>10.9310</td>
<td>5.2249</td>
<td>-2.7845</td>
</tr>
</tbody>
</table>
factor (RL), which is indicative of the isotherm shape that predicts whether an adsorption system is favorable or unfavorable. The separation factor (RL) is defined by Weber and Chakravorty (1974) as:

$$RL = \frac{1}{1 + bC_0}$$  \hspace{1cm} (4)

where b is the Langmuir equilibrium constant (L mg\(^{-1}\)) and C\(_0\) is the initial concentration (mg L\(^{-1}\)) of sorbate. The values of RL, which lie between 0 and 1 suggest more favorable sorption of As(III) than As(V) onto the mixed oxide. Comparative data for Langmuir constants and RL values of arsenic sorption onto the mixed oxide with pure metal oxides are shown in Table 4. The θ\(_0\) value, a Langmuir constant which determines the monolayer adsorption capacity (mg g\(^{-1}\)), shows that the mixed oxide can be a better adsorbent for As(III) than for As(V) removal. This is due to the presence of more acidic and relatively soft tin(IV) oxide with iron(III) oxide.

### Adsorption Kinetics

The equilibrium kinetics sorption data, obtained at 30(±2)\(^\circ\)C and equilibrium solution pH 6.8(±0.1) for As(III) and 7.3(±0.1) for As(V) at 30(±2)\(^\circ\)C by the mixed oxide, and 7.3(±0.1) for As(V) at varying contact times (Fig. 3 and 4), indicate that the adsorption of As(III) onto the binary mixed oxide was found to be much more rapid than that of As(V) when solution concentrations (mg L\(^{-1}\)) of arsenic used were 10.0 and 20.0. This agreed well with the observation made earlier (Manna et al. 2003) using crystalline hydrous ferric oxide when arsenic concentrations in solution were higher (25.0 and 50.0 mg L\(^{-1}\)) than in the present study. The present kinetic results show that the time required for approaching equilibrium was ~2 h for As(III) and ~9 h for As(V). Thus, the iron(III)-tin(IV) mixed oxide adsorbent would require less contact time for As(III) removal than that for As(V). The dissimilarities of adsorption kinetics between the binary oxide adsorbent and single iron(III) oxide are most likely attributed to the fact that the active components in the present binary oxide adsorbent are both hydrous ferric oxide and stannic oxide for arsenic adsorption which differs from the conclusion made by Zeng (2004) using iron(III)-Si binary mixed oxide for arsenic adsorption study.

The model equations used for analyzing kinetics data for arsenic adsorption were pseudo-first order (Lagergren 1898), pseudo-second order (Ho 2004), power function, simple Elovich and parabolic diffusion (Sparks 1989). The linear mathematical forms of kinetics equations used are shown below:

**Lagergren pseudo-first order:**

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$  \hspace{1cm} (5)

**Ho’s pseudo-second order:**

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (6)

**Power function:**

$$\log q_t = \log a_1 + b_1 \log t$$  \hspace{1cm} (7)

**Simple Elovich:**

$$q_t = a_2 + b_2 \log t$$  \hspace{1cm} (8)

**Parabolic diffusion:**

$$q_t/t = a_3 + (b_3/t^{1/2})$$  \hspace{1cm} (9)

where k\(_1\) (time\(^{-1}\)) and k\(_2\) (g mg\(^{-1}\) time\(^{-1}\)) are the rate constants of the pseudo-first order and pseudo-second order adsorption rate process, respectively; and q\(_e\) and q\(_t\)

### Adsorption Kinetics

- **Fig. 8.** Langmuir isotherm plot for arsenic sorption at equilibrium solution pH 6.8(±0.1) for As(III) and pH 7.3(±0.1) for As(V) at 30(±2)\(^\circ\)C by the mixed oxide.

### Table 4. Comparison of Langmuir constants and RL values on arsenic(III) and arsenic(V) sorption on iron(III)-tin(IV) binary mixed oxide with pure oxides at 30(±2)\(^\circ\)C

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate species</th>
<th>θ(_0) (mg g(^{-1}))</th>
<th>b (L mg(^{-1}))</th>
<th>Reference</th>
<th>C(_0) (mg L(^{-1}))</th>
<th>RL-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed oxide</td>
<td>As(III)</td>
<td>43.859</td>
<td>0.0573</td>
<td>Present work</td>
<td>12.5</td>
<td>0.583</td>
</tr>
<tr>
<td></td>
<td>As(V)</td>
<td>27.548</td>
<td>0.0124</td>
<td></td>
<td></td>
<td>0.866</td>
</tr>
<tr>
<td>CHFO(^a)</td>
<td>As(III)</td>
<td>33.33</td>
<td>0.396</td>
<td>Manna et al. (2003)</td>
<td>12.5</td>
<td>0.168</td>
</tr>
<tr>
<td></td>
<td>As(V)</td>
<td>25.00</td>
<td>0.017</td>
<td></td>
<td></td>
<td>0.824</td>
</tr>
<tr>
<td>HSO(^b)</td>
<td>As(III)</td>
<td>15.85</td>
<td>1.45</td>
<td>Manna (2005)</td>
<td>12.5</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>As(V)</td>
<td>—</td>
<td>—</td>
<td></td>
<td></td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\)Crystalline hydrous ferric oxide.

\(^b\)Hydrous stannic oxide.
are the amount of arsenic adsorbed per unit mass of adsorbent (mg g⁻¹) at equilibrium and at time, t, respectively. The other parameters present in equations 7 to 9 are the respective kinetic equation constants.

The widely used equations for kinetics modelling of adsorption data are the Lagergren (equation 5) and Ho (equation 6). The linear plots (equations 5–9) for determining the nature of kinetics obtained for the sorption data of As(III) and As(V) at temperature 30(±2)°C and, at equilibrium pH values 6.8(±0.1) and 7.3(±0.1), respectively, for 10.0 and 20.0 mg L⁻¹ arsenic solutions are shown in Fig. 9 to 16 (only best fit plots shown). The kinetics parameters evaluated from the plots are given in Table 5. The results show that, in general, both the pseudo-second order and parabolic diffusion plots (Fig. 9–12) gave good correlation coefficient values (0.97 < R² < 1.0) for the kinetics data for both arsenic species over the studied concentration range. However, the As(III) sorption kinetic data describe the pseudo-second order equation given by Ho (2004) better (R² = 0.9938 and 0.9964) than the parabolic diffusion equation (R² = 0.9956 and 0.9810); but the As(V) sorption kinetics data describe the latter equation (equation 9) better (R² = 0.9848 and 0.9930) than the former equation (equation 6) (R² = 0.9718 and 0.9807). Apart from that, the power function (equation 7) and simple Elovich (equation 8) equations describe the arsenic sorption kinetics data well (−0.97 ≥ R² < 1.0), except the data obtained from 20.0 mg L⁻¹ of As(III) solution (R² = −0.91). The Lagergren pseudo-first order equation (equation 5) describes arsenic sorption kinetics data obtained from 10.0 mg As L⁻¹ fairly well with linear correlation coefficient (R²) values of 0.9556 for As(III) and 0.9886 for As(V), but that describes the data obtained from 20.0 mg As L⁻¹ poorly. Kuriakose et al. (2004) found similar results for As(III) adsorption onto iron oxide impregnated activated alumina.

Fig. 9. Pseudo-second order kinetic plot for As(III) sorption at equilibrium pH 6.8(±0.1) and at 30(±2)°C by the mixed oxide. Arsenic concentration (mg/L): ◆ 10.0, ■ 20.0.

Fig. 10. Pseudo-second order kinetic plot for As(V) sorption at equilibrium pH 7.3(±0.1) and at 30(±2)°C by the mixed oxide. Arsenic concentration (mg/L): ◆ 10.0, ■ 20.0.

Fig. 11. Parabolic diffusion kinetic plot for As(III) sorption at final pH 6.8(±0.1) and at 30(±2)°C by the mixed oxide. Arsenic concentration (mg/L): ◆ 10.0, ■ 20.0.

Fig. 12. Parabolic diffusion kinetic plot for As(V) sorption at final pH 7.3(±0.1) and at 30(±2)°C by the mixed oxide. Arsenic concentration (mg/L): ◆ 10.0, ■ 20.0.
Thus, it could be generalized that the Lagergren pseudo-first order equation describes the sorption kinetics data the poorest. The pseudo-second order rate constant \((k_2)\) values for As(III) increases and those for As(V) decreases with increasing initial loading concentration of adsorbates while the pseudo-first order constant \((k_1)\) values show the reverse trend.

**Conclusion**

1. The synthetic iron(III)-tin(IV) mixed oxide composite was amorphous and hydrated in nature. The iron and tin mole ratio is 1:1.
2. This adsorbent possesses a strong affinity for As(III) in comparison to As(V) in the drinking water pH range and at 30(±2)°C.
3. The adsorption of As(III) was found to be almost pH independent while that of As(V) was highly pH dependent.
4. The rate of As(III) adsorption is much faster in comparison to As(V) by iron(III)-tin(IV) mixed oxide adsorbent at pH ~7.0.
5. Both As(III) and As(V) adsorption data fitted well with the Langmuir and Freundlich isotherm models.
6. Adsorption kinetic data for As(III) could be best described by both the Ho’s pseudo-second order and parabolic diffusion equations, while that for As(V) could be explained best also by both the power function and parabolic diffusion equations.
7. The arsenic adsorption behaviour of this binary mixed oxide adsorbent was dependent on the components present in the mixed oxide.
8. Monolayer adsorption capacity\((\theta_0, \text{mg g}^{-1})\) of this binary mixed oxide showed good potential for removing arsenic from contaminated groundwater in the Bengal delta plain, where As(III) to As(total) is in the range of 0.6 to 0.9.
TABLE 5. Kinetic models and other statistical parameters at 30(±2)°C, and final solution pH 6.8 (±0.1) for As(III) and pH 7.3 (±0.1) for As(V) sorption on the mixed oxide

<table>
<thead>
<tr>
<th>Kinetic model equations</th>
<th>Parameters</th>
<th>As(III) concentration (mg/L)</th>
<th>As(V) concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.9918</td>
<td>0.9100</td>
</tr>
<tr>
<td></td>
<td>a1</td>
<td>0.455</td>
<td>5.033</td>
</tr>
<tr>
<td></td>
<td>b1</td>
<td>0.4504</td>
<td>0.877</td>
</tr>
<tr>
<td>Power function</td>
<td></td>
<td>0.9100</td>
<td>0.9891</td>
</tr>
<tr>
<td></td>
<td>a2</td>
<td>-1.1366</td>
<td>4.6486</td>
</tr>
<tr>
<td></td>
<td>b2</td>
<td>2.3025</td>
<td>1.4588</td>
</tr>
<tr>
<td>Simple Elovich</td>
<td></td>
<td>0.9075</td>
<td>0.9686</td>
</tr>
<tr>
<td></td>
<td>a2</td>
<td>-1.1366</td>
<td>4.6486</td>
</tr>
<tr>
<td></td>
<td>b2</td>
<td>2.3025</td>
<td>1.4588</td>
</tr>
<tr>
<td>Parabolic diffusion</td>
<td></td>
<td>0.9686</td>
<td>0.9768</td>
</tr>
<tr>
<td></td>
<td>a3</td>
<td>-0.0089</td>
<td>-0.1846</td>
</tr>
<tr>
<td></td>
<td>b3</td>
<td>0.4430</td>
<td>2.4579</td>
</tr>
<tr>
<td>Ho’s pseudo-second order</td>
<td></td>
<td>0.9718</td>
<td>0.9807</td>
</tr>
<tr>
<td></td>
<td>k2 × 10^{-3}</td>
<td>7.34</td>
<td>20.95</td>
</tr>
<tr>
<td>Lagergren pseudo-first</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>order</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>log(qe-q)</td>
<td>0.9556</td>
<td>0.9170</td>
</tr>
<tr>
<td></td>
<td>k1 × 10^{-2}</td>
<td>3.270</td>
<td>1.934</td>
</tr>
</tbody>
</table>

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