Arsenic removal from groundwater by Anjili tree sawdust impregnated with ferric hydroxide and activated alumina

P. Dhanasekaran, P. M. Satya Sai, C. Anand Babu, R. Krishna Prabhu and K. K. Rajan

ABSTRACT

Arsenic is a toxic element found naturally in groundwater. Due to its carcinogenicity, risk for heart diseases and diabetes, arsenic needs to be removed from groundwater for potable application. ‘Anjili’ tree sawdust was chemically modified with ferric hydroxide and activated alumina (SFAA) and used as an adsorbent for the removal of arsenic from groundwater. The adsorbent was characterized using scanning electron microscopy (SEM), Fourier transform infrared (FTIR) to study the pore structure and surface functional groups. Effect of contact time, initial concentration, pH, particle size and temperature was studied. Arsenic adsorbed by SFAA followed Freundlich adsorption isotherm. Maximum sorption of arsenic by SFAA adsorbent occurred at pH 6.5. Arsenic sorption kinetics followed a pseudo-second-order model. The maximum sorption capacity at 303 K was found to be 54.32 mg/g for As(III) and 77.60 mg/g for As(V). Interference of other ions on the adsorption was in the order of PO_4^{3-} > SO_4^{2-} > HCO_3^- > NO_3^-.

Key words | adsorption, arsenate, arsenic, arsenite, sawdust

INTRODUCTION

Groundwater contamination with arsenic is a globally acknowledged environmental hazard with an adverse impact on human health. Erosion of arsenic containing rocks, industrial and mine discharges are the sources of groundwater contamination with arsenic (Jameel et al. 2009). Arsenic exists in different forms viz., arsenate (As(V)), arsenite (As(III)), dimethylarsinic acid (DMA), and monomethylarsonic acid (MMA). Inorganic forms of arsenic viz., As(V) and As(III), are more toxic than organic forms (DMA and MMA) (Smedley 2006). In aqueous systems, arsenic is normally in the highest oxidation state, therefore the focus is on As(V) removal. Continuous exposure to arsenic results in increased blood levels of asymmetric dimethylarginine (ADMA) amino acid, which is associated with cardiovascular risk (Del Razo et al. 2011). Those who consume arsenic-contaminated water for a long time since childhood, have a greater chance of developing diabetes and cardiovascular problems at a young age (Desarrollo 2014). Lifetime exposure to low-level (15–20 μg/L) inorganic arsenic in drinking water has also been associated with increased risk for coronary heart and cardiovascular diseases (James et al. 2014).

These health effects have prompted the World Health Organization to reduce the limit of arsenic in drinking water from 50 to 10 μg/L (Saqib et al. 2015). Highly efficient technologies capable of selectively removing arsenic have to be developed for meeting this stringent requirement.

Conventional technologies used for metal ion removal from aqueous solution, such as precipitation, ion exchange, adsorption on activated alumina, co-precipitation with iron or alum, reverse osmosis, membrane filtration, modified coagulation/filtration, and enhanced lime softening have been used for arsenic removal in drinking water (Malik et al. 2009; Ali Khan et al. 2011; Mudhoo et al. 2011; Jiang
et al. 2013). Among these, adsorption is preferred for As(V) removal, due to its low cost, good performance and the relatively low secondary waste generation (Jun et al. 2014). Biological materials, mineral oxides, activated carbons and polymer resins have been extensively investigated as adsorbents for arsenic removal (Mohan & Charles 2007).

Iron oxides, oxyhydroxides and hydroxides, including amorphous hydrous ferric oxide (FeO–OH), goethite (FeO–OH) and haematite (Fe₂O₃), are known for their ability to remove both As(V) and As(III) from aqueous solutions (Ying et al. 2009; Litter et al. 2010). Several iron-based materials such as Fe-treated activated carbon, Fe-treated gel beads (FeGB) and iron oxide-coated sand have been reported for arsenic removal from drinking water (Zeng 2004; Kumar et al. 2008; Yao et al. 2014). Other materials such as red mud, calcined bauxite and activated alumina have also been effectively used for arsenic removal from drinking water (Altundogan et al. 2002; Ayoob et al. 2007; Darban et al. 2013).

Iron and aluminium oxides based sorbents, salts and impregnated adsorbents were found effective in removing arsenic from aqueous environment (Jeong et al. 2007; Arias et al. 2008; Simsek et al. 2013). Impregnating activated alumina with iron oxide significantly enhanced the effectiveness of adsorbing both As(V) and As(III) (Singh & Pant 2006). Further, several iron(III)oxides, such as amorphous hydrous ferric oxide, poorly crystalline hydrous ferric oxide (ferrihydrite) and goethite have been reported for removing both As(V) and As(III) from aqueous solutions (Pierce & Moore 1982; Raven et al. 1998; Sun & Doner 1998). However, most of these oxides are available as fine powders or are generated in situ as gels or suspensions in aqueous solutions. To improve the column properties of these oxides, silica sol has been reported as a binding material (Zeng 2003).

In view of the growing demand for drinking water, application of naturally available resources for water purification is warranted for cost effective process development. Although activated carbon has been used extensively for arsenic removal, the process is not economic. Chemically treated natural adsorbents have been reported for arsenic removal from drinking water as an alternative to activated carbon (Pokhrel & Viraraghavan 2006; Pandey et al. 2009; Urik et al. 2009).

The aim of the present work was to develop a cost-effective adsorbent based on iron and alumina with a biosorbent as a binding material for adsorption of arsenic from aqueous solutions. As biosorbents contribute additional hydroxyl groups for arsenic trapping, they improve the arsenic adsorption capacity, when used as binding materials. This study investigates the effectiveness of locally available ‘Anjili’ tree sawdust chemically modified with ferric hydroxide and activated alumina (SFAA) as an adsorbent for the removal of arsenic from groundwater.

MATERIALS AND METHODS

Chemicals

Chemicals used in this study were of analytical grade. Arsenic stock solution of 1,000 mg/L was prepared from sodium arsenite (NaAsO₂) and sodium arsenate (Na₂HAsO₄·7H₂O) using demineralized (DM) water. This stock solution was diluted with DM water to prepare arsenic solutions of desired concentration.

Sawdust

Sawdusts of different trees were collected for assessing their suitability as a base material for the adsorbent. The sawdust sample was washed with DM water and then soaked in 0.1 N NaOH for 24 h to remove lignin based colour material. Subsequently, it was filtered and excess NaOH was neutralized by washing with 0.1 N H₂SO₄, followed by DM water. The sawdust was dried to constant weight in an air oven at 80 ± 5 °C for 12 h and cooled to room temperature. These sawdust samples were tested for their capacity for adsorption of arsenic from a solution of 1 mg/L As(V) and the results are presented in Table 1.

Based on these adsorption capacities, Artocarpus hirsutus, called ‘Anjili’ locally, was selected for preparation of the adsorbent. Artocarpus hirsutus had the highest adsorption capacity of the sawdust for As(V) of 38.0% and was thus selected as the adsorbent in further experiments. The Brunauer–Emmett–Teller (BET) surface area of the Anjili sawdust was determined using Sorptomatic 1990 of Thermo Electron (USA), and was found to be 22.5 m²/g.
Synthesis of adsorbent

For optimization of the composition of the adsorbent, mass ratio of the constituents was varied and arsenic adsorption capacities were determined. Mass ratios studied were 2:1:1, 1.5:1:1 and 1:1:1 of sawdust: ferric hydroxide: activated alumina. Based on these studies, chemically treated sawdust (*Artocarpus hirsutus*), ferric hydroxide and activated alumina were mixed in 1.5:1:1 mass ratio and made into a paste with sufficient quantity of water (1.2 L water for 1 kg solids). The paste was dried in an oven to constant weight and the dried mass was sieved to obtain different particle sizes. Adequate quantity of the adsorbent was prepared and samples from the same lot were used for all the experiments, thus avoiding uncertainties in the results due to variation in the method of preparation of adsorbent.

Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) were used to study the interaction between arsenic and the adsorbent.

**Batch sorption experiments**

Sorption experiments were performed by adding dry sorbent of 0.1 g to 10 mL of solution containing As(III) and As(V). The pH of the synthetic arsenic solution was maintained at 6.5. The sample vials were agitated at 40 rpm in a thermostatically controlled orbital shaker (Remi, India). The temperature was maintained at 303 K. Samples were removed at predetermined time intervals, centrifuged, filtered using 90 mm Whatman filter paper and analyzed for residual arsenic concentration by inductively coupled plasma mass spectrometry (ICP-MS) (Model-ELAN 250). Some of the experiments were repeated to check the reproducibility, which was found to be within ±2%.

The amount of arsenic adsorbed at equilibrium, $q_e$ (mg/g), was computed by

$$q_e = \frac{(C_i - C_e)V}{m}$$

where $C_i$ is the initial concentration (mg/L), $C_e$ is the equilibrium concentration (mg/L), $V$ is the volume of solution (L) and $m$ is the mass of adsorbent (g).

**Determination of point of zero charge**

The point of zero charge of adsorbent was found by mass titration method developed by Noh and Schwarz (*Noh & Schwarz 1989*). Different masses of SFAA from 0.1 to 2.0 g and 10 mL of 0.1 N sodium chloride solution were added to different vials of 50 mL and stirred continuously for 24 h in a thermostatic shaker. The final pH was plotted against the mass of the adsorbent and the final pH approached an asymptotic value with increase in the mass of adsorbent. This asymptotic value is taken as the point of zero charge (PZC).

**RESULTS AND DISCUSSION**

**Characterization of adsorbent**

The surface morphology before and after arsenic adsorption was characterized using Philips XL-30 scanning electron microscope at 15 kV. The SEM image shown in Figure 1 indicates that in SFAA the pores are in the range of 0.1 to 2 μm in diameter (macroporous). The SEM images of the SFAA adsorbent after adsorption of As(V) and As(III) are shown in Figures 2 and 3, respectively. From these SEM images, it can be seen that the granules remained intact after grafting, except for the appearance of some pores on the surface of SFAA.

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**Table 1** As(V) adsorption by different tree sawdusts

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of the tree</th>
<th>Binomial name</th>
<th>As(V) adsorbed (mg/g)</th>
<th>As(V) adsorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Coconut</td>
<td><em>Cocos nucifera</em></td>
<td>0.003</td>
<td>6.0</td>
</tr>
<tr>
<td>2</td>
<td>Teak</td>
<td><em>Tectona grandis</em></td>
<td>0.004</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>Karuvelam</td>
<td><em>Acacia arabica</em></td>
<td>0.006</td>
<td>12.0</td>
</tr>
<tr>
<td>4</td>
<td>Eucalyptus</td>
<td><em>Eucalyptus obliqua</em></td>
<td>0.007</td>
<td>14.0</td>
</tr>
<tr>
<td>5</td>
<td>Patauk</td>
<td><em>Pterocarpus</em></td>
<td>0.007</td>
<td>14.0</td>
</tr>
<tr>
<td>6</td>
<td>Poovarasam</td>
<td><em>Thespesia populnea</em></td>
<td>0.013</td>
<td>26.0</td>
</tr>
<tr>
<td>7</td>
<td>Aanjili</td>
<td><em>Artocarpus hirsutus</em></td>
<td>0.019</td>
<td>38.0</td>
</tr>
</tbody>
</table>
To study the surface of SFAA, FTIR spectra were recorded in a range between 500 and 4,000 cm\(^{-1}\) with 16 cm\(^{-1}\) resolution using ABB-MB3000 FTIR instrument. Figure 4 shows the FTIR spectra of SFAA before and after arsenic adsorption. The broad and intense peak at 3,060–3,600 cm\(^{-1}\) was assigned to hydroxyl stretching vibration of water and that at 1,640 cm\(^{-1}\) represents HOH bending vibration of water. The FTIR spectrum shows the prominence of the peaks in the adsorbent and decrease in the peak height after arsenic adsorption. The small peaks at 1,504 and 1,427 cm\(^{-1}\) were assigned to C\(=\)C aromatic stretching. FTIR results also indicated that mainly hydroxide in the carboxylic groups were involved in arsenic sorption.

Surface characterization of biosorbents was studied by various researchers and the results of FTIR studies on SFAA showed similar trends, as sawdust is its major component. Biomass-based sorbents contain a high amount of polysaccharides and some of them are associated with proteins and other components (Ilahi et al. 2005). These bio-macromolecules on the sorbent surfaces have several functional groups such as amino, carboxyl, thiol, sulphydryl, alcohol, phenol and phosphate groups (Kumar & Gaur 2011).

Optimization of sawdust, ferric hydroxide and activated alumina ratio

Adsorption capacities for various combinations of sawdust, ferric hydroxide and activated alumina are presented in Figure 5 along with adsorption capacities of only activated
alumina. Also, sawdust and activated alumina could not be mixed into a solid without addition of ferric hydroxide. From the results, it can be seen that adsorbent of 1.5:1:1 ratio of sawdust, ferric hydroxide, activated alumina results in an effective removal of arsenic, the uptake of arsenic being higher than that of only activated alumina. However, as activated alumina is less than 30% of this adsorbent, the present adsorbent is economical compared to activated alumina. It may be noted that about 45% by weight, of the adsorbent is Anjili tree sawdust. Maximum uptake of arsenic by the adsorbent is estimated by using 3,000 mg/L arsenic solution and 0.1 g of adsorbent and equilibrating for 4 hours. The maximum uptake is found to be 77.60 mg/g in case of SFAA and 59.06 mg/g in case of activated alumina for As(V) removal. Thus, SFAA proves to be cost effective in comparison to activated alumina. Water treated by SFAA was analysed for Fe and Al and was found to contain less than 0.1 mg/L, which is within the permissible limit for drinking water.

All the remaining experiments were conducted to study the effect of operating parameters, with SFAA of 1.5:1:1 composition.

**pH study**

The effect of pH on arsenic removal by SFAA was studied using 0.10 g of adsorbent in 10 of 25 mg/L arsenate and arsenite solutions. The pH of the solution was adjusted by adding dilute NaOH or HNO₃ dropwise to obtain pH of 2.0 through 10.0. The percentage removal of arsenic from solutions of different pH is shown in Figure 6(a).

Uptake of As(V) was almost constant in the pH range of 2 to 6, whereas for As(III) the uptake increased in the range of 2 to 7. Maximum uptake was observed in pH range of 6.5–7 for both As(V) and As(III). Maximum As(V) removal was found to be more than 95%, whereas for As(III), it was only 45%. The results can be explained using arsenic chemical forms in different pH ranges. In the pH range of 3–8.5 arsenate (As(V)) exists mostly in its anionic form (H₂AsO₄⁻, HAsO₄²⁻). The PZC of the adsorbent is determined to be 5.85, as shown in Figure 6(b). The adsorbent has positive charge on the surface up to the point of zero charge which attracts negatively charged H₂AsO₄⁻, HAsO₄²⁻ (electrostatic attraction) thereby favouring adsorption. In the As(V) adsorption as pH increases amount of negative arsenic species increases, while the number of positively charged adsorbent surface sites decreases (up to pH₁₇₃) (Yu et al. 2013). At neutral pH, both H₂AsO₄⁻, HAsO₄²⁻ are present equally hence the adsorption is maximum at this pH. Up to pH ≤ 9, arsenite (As(III)) exists as stable and neutral H₃AsO₃, and therefore no electrostatic interaction between As(III) and adsorbent surface up to pH₂₃₀ (Anirudhan & Senan 2011). In case of As(V) adsorption, both electrostatic attraction and chemical bonding take place. But in case of
As(III), only chemisorption takes place, and hence the As(III) adsorption is less compared to As(V).

It is interesting to note that arsenic adsorption is maximum in the pH range of 6.5 to 7, which is greater than pH_{PZC}. At this pH, the surface of the adsorbent is negatively charged and hence the adsorption is not due to electrostatic interaction. This indicates that the adsorption in this range may be due to chemisorption. This indication is supported by the thermodynamic study presented subsequently in section 3.7. Similar observation of maximum uptake of arsenic at a pH greater than pH_{PZC} was reported by Zheng et al. (2012) in their studies on zirconia nanoparticles.

**Effect of adsorbent dose**

The effect of adsorbent dose on arsenic removal was studied for an initial arsenic concentration of 2 mg/L for a contact time of 4 h. The results obtained are shown in Figure 7 as percentage removal for adsorbent dose ranging from 1 to 30 g/L. The removal of As(V) increased from 27.33 to 98.64 percent with increase in the adsorbent dose from 1 to 10 g/L and with further increase in dose, % removal remained constant. A greater dosage of sorbent implies a greater amount of available binding sites, which result in increased sorption. The optimum adsorbent dose was taken as 10 g/L for complete removal of As(V) from an initial solution concentration of 2 g/L.

The distribution coefficient ($K_{DC}$) for As(V) on adsorbent was calculated by

$$K_{DC} = \frac{q_e}{C_e}$$

(2)

where $q_e$ is mass of As(V) adsorbed per unit mass of adsorbent and $C_e$ is the concentration of As(V) in the solution at equilibrium.

The distribution coefficient reflects the binding ability of the surface for an element and is dependent on pH and type of surface (Alagumuthu & Rajan 2010; Yu et al. 2013). The $K_{DC}$ values for As(V) on SFAA at initial pH of 6.5 were calculated and presented in Figure 8. It can be seen that $K_{DC}$ values increased with an increase in adsorbent dose, indicating that the adsorbent has a heterogeneous surface (Allison & Allison 2005). $K_{DC}$ value is 7271.43 L/kg at the dose rate of 10 g/L which increased to 9263.96 L/kg at the dose rate of 30 g/L.

**Equilibrium isotherms**

Equilibrium isotherms for As(V) and As(III) adsorption on SFAA are shown in Figure 9. The initial concentration of the solutions was varied from 0 to 870 mg/L at an initial pH of 6.5. The temperature for the equilibrium was maintained at 303 K. The maximum equilibrium uptake...
capacities were found to be 77.60 mg/g and 54.32 mg/g for As(V) and As(III), respectively for an initial concentration of 3,000 mg/L. These capacities are better than most adsorbents reported in the literature, as can be seen from Table 2.

Langmuir and Freundlich isotherms were used to model the adsorption in order to have an insight of adsorption mechanism. The Langmuir isotherm, which is valid for a monolayer sorption on to a surface, is given below:

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

where \( q_e \) is the equilibrium uptake of arsenic per unit mass adsorbent (mg/g), \( q_m \) is the maximum value of \( q \), \( K_L \) is the Langmuir constant (L/mg) and \( C_e \) is the equilibrium concentration (mg/L).

Freundlich isotherm is an empirical equation based on sorption on a heterogeneous surface and is expressed as

\[
q_e = K_F C_e^{1/n}
\]

where \( q_e \) is the equilibrium uptake of arsenic per unit mass of adsorbent (mg/g), \( K_F \) is the Freundlich constant ((mg/g)

### Table 2 | Arsenic adsorption capacity comparison

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>As(III) (mg/g)</th>
<th>As(V) (mg/g)</th>
<th>Temp (°C)</th>
<th>pH</th>
<th>Conc. (mg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFAA</td>
<td>54.32</td>
<td>77.60</td>
<td>30</td>
<td>6.5</td>
<td>20–3000</td>
<td>Current study</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>44.77</td>
<td>59.06</td>
<td>30</td>
<td>6.5</td>
<td>20–3000</td>
<td>Current study</td>
</tr>
<tr>
<td>Activated alumina (grains)</td>
<td>3.48</td>
<td>15.9</td>
<td>25</td>
<td>7, 5.2</td>
<td>4.9, 11.5</td>
<td>Lin &amp; Wu (2001)</td>
</tr>
<tr>
<td>Alumina Al_{10} SBA15</td>
<td>–</td>
<td>20.98</td>
<td>25</td>
<td>6.5</td>
<td>10–100</td>
<td>Jang et al. (2003)</td>
</tr>
<tr>
<td>Alumina Fe_{10} SBA15</td>
<td>–</td>
<td>12.74</td>
<td>25</td>
<td>6.5</td>
<td>10–100</td>
<td>Jang et al. (2003)</td>
</tr>
<tr>
<td>Meso porous alumina</td>
<td>47.20</td>
<td>121.37</td>
<td>30</td>
<td>3–7</td>
<td></td>
<td>Kim et al. (2004)</td>
</tr>
<tr>
<td>Nano Alumina</td>
<td>40.00</td>
<td>–</td>
<td>25</td>
<td>7.5</td>
<td>10</td>
<td>Darban et al. (2013)</td>
</tr>
<tr>
<td>La(III), Y(III) impregnated alumina</td>
<td>–</td>
<td>25.00</td>
<td>–</td>
<td>6–8</td>
<td>140</td>
<td>Wasay et al. (1996a, b)</td>
</tr>
<tr>
<td>La(III) impregnated alumina</td>
<td>–</td>
<td>12.88</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Wasay et al. (1996a, b)</td>
</tr>
<tr>
<td>Shirasu zeolite</td>
<td>–</td>
<td>65.93</td>
<td>24</td>
<td>3–10</td>
<td>97.4</td>
<td>Wasay et al. (1996a, b)</td>
</tr>
<tr>
<td>Al-Loaded Shirasu zeolite</td>
<td>–</td>
<td>10.49</td>
<td>24</td>
<td>3–10</td>
<td>97.4</td>
<td>Xu et al. (2002)</td>
</tr>
<tr>
<td>Iron hydroxide coated alumina</td>
<td>7.64</td>
<td>36.64</td>
<td>25</td>
<td>6.6–6.8</td>
<td>7.5–135</td>
<td>Hlavay &amp; Polyak (2005)</td>
</tr>
<tr>
<td>Red mud</td>
<td>0.88</td>
<td>0.94</td>
<td>25</td>
<td>7.3,3.5</td>
<td>2.5–30</td>
<td>Altundogan et al. (2002)</td>
</tr>
<tr>
<td>TiO_2</td>
<td>32.40</td>
<td>41.00</td>
<td>25</td>
<td>7</td>
<td>0.4–80</td>
<td>Bang et al. (2005)</td>
</tr>
<tr>
<td>Granular ferric hydroxide</td>
<td>–</td>
<td>8.50</td>
<td>25</td>
<td>8–9</td>
<td>5–100</td>
<td>Driehaus et al. (1998)</td>
</tr>
<tr>
<td>Ferricydrite</td>
<td>–</td>
<td>68.75</td>
<td>–</td>
<td>7</td>
<td>0–150</td>
<td>Raven et al. (1998)</td>
</tr>
<tr>
<td>Bead cellulose loaded FeOOH</td>
<td>99.60</td>
<td>33.20</td>
<td>25</td>
<td>7</td>
<td>75–7500</td>
<td>Guo &amp; Chen (2005)</td>
</tr>
<tr>
<td>Zr-Loaded chelating resin</td>
<td>49.15</td>
<td>88.73</td>
<td>25</td>
<td>9.4</td>
<td>–</td>
<td>Balaji et al. (2005)</td>
</tr>
<tr>
<td>Rice husk</td>
<td>0.14</td>
<td>0.15</td>
<td>20</td>
<td>7</td>
<td>–</td>
<td>Ranjan et al. (2009)</td>
</tr>
<tr>
<td>Plants – <em>Calami rhizoma</em></td>
<td>–</td>
<td>22.04</td>
<td>–</td>
<td>8</td>
<td>1000</td>
<td>Chiban et al. (2012)</td>
</tr>
<tr>
<td>Plants – <em>Withania frutescens</em></td>
<td>–</td>
<td>16.88</td>
<td>–</td>
<td>8</td>
<td>1000</td>
<td>Chiban et al. (2012)</td>
</tr>
<tr>
<td>Iron impregnated Chitosan beads</td>
<td>6.48</td>
<td>22.60</td>
<td>8</td>
<td>1</td>
<td>1</td>
<td>Pontoni &amp; Fabbricino (2012)</td>
</tr>
<tr>
<td>Chitosan coated ceramic alumina</td>
<td>56.50</td>
<td>96.46</td>
<td>–</td>
<td>–</td>
<td></td>
<td>Ponnal &amp; Fabbricino (2012)</td>
</tr>
<tr>
<td>Char carbon</td>
<td>89.00</td>
<td>34.50</td>
<td>25</td>
<td>2–3</td>
<td>992,737</td>
<td>Pattanayak et al. (2000)</td>
</tr>
<tr>
<td>Granulated activated carbon</td>
<td>0.09</td>
<td>4.50</td>
<td>23</td>
<td>7</td>
<td>1</td>
<td>Reed et al. (2000)</td>
</tr>
<tr>
<td>Fresh biomass</td>
<td>128.1</td>
<td>–</td>
<td>30</td>
<td>6</td>
<td>50–2500</td>
<td>Kamala et al. (2005)</td>
</tr>
</tbody>
</table>
(L/mg)\(^{1/n}\), \(C_e\) is the equilibrium concentration (mg/L) and \(n\) is a constant.

The Langmuir and Freundlich models were applied to the experimental results and the model coefficients calculated are given in Table 3. The Langmuir constant \((K_L)\) and the Freundlich constant \((K_F)\) are indicators of sorption capacity. From the regression coefficient \((R^2)\), it was observed that Freundlich isotherm fits the adsorption data well, as shown in Figure 10.

**Adsorption kinetics**

The effect of contact time for As(V) adsorption on SFAA was studied with varying feed concentrations (0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 2.0 mg/L) for the adsorbent dose of 0.1 g/10 mL at pH of 6.5. The sorption capacity of the SFAA adsorbent with time is shown in Figure 11. As can be seen, the uptake was rapid in the first 10 min and was constant after 10 min. The adsorption capacity increased from 0.019 to 0.188 mg/g with increasing the initial As(V) concentration from 0.2 to 2 mg/L.

Different kinetic models like pseudo-first order, pseudo-second order and intra-particle diffusion adsorption kinetic models were tested by various researchers to find the mechanisms of the adsorption and rate controlling steps (Lagergren 1898; Ho & McKay 2000).

The pseudo-first-order and second-order equations are represented as

\[
\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}
\]

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]

where \(q_e, q_t\) are the adsorption capacity (mg/g) at equilibrium and at time \(t\) respectively. \(K_1\) (1/min) and \(K_2\) (g/mg.min) are the pseudo-first- and second-order rate constants for adsorption. The plot of \(\log(q_e - q_t)\) versus \(t\) gives a linear relationship from which \(K_1\) and \(q_e\) can be determined from the slope and intercept of the plot, respectively. From the plot of \(t/q_t\) versus \(t\), \(K_2\) and \(q_e\) of pseudo second order kinetic model are found. The model parameters are given in Table 4. It was observed that the adsorption of As(V) on SFAA adsorbent follows second order kinetics and hence it is inferred that the process is chemisorption.

The contribution of particle diffusion on As adsorption by SFAA was tested using the Weber–Morris model. The plot of \(q_t\) against \(t^{0.5}\) presents linear form of the model (Weber & Morris 1963).

\[
q_t = K_{id}t^{1/2} + C
\]

where \(q_t\) is adsorption capacity (mg/g) at time \(t\), \(K_{id}\) intra-particle (pore) diffusion rate constant (mg/g.min \(^{0.5}\)) and \(C\) is the intercept that gives an idea about the thickness of the boundary layer. A larger \(C\) value indicates greater boundary layer effect.

It was observed that the intra-particle diffusion model has a poor coefficient of correlation as shown in Table 4.

**Thermodynamic study**

To study the effect of temperature on the extent of As sorption on SFAA, temperature was varied from 303 to 318 K for 0.1 g of adsorbent (SFAA) in 10 mL of As(V) solution. When the temperature was increased from 303 K to 313 K, the adsorption was almost constant (Figure 12). However, when temperature was increased from 313 to 318 K, there was a slight decrease in the uptake of As(V). This may be due to a shift in the adsorption mechanism, in the temperature range of 313–318 K.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Langmuir and Freundlich isotherm model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir parameters</strong></td>
<td></td>
</tr>
<tr>
<td>(K_L) (L/mg)</td>
<td>(q_{max}) (mg/g)</td>
</tr>
<tr>
<td>As(V)</td>
<td>0.0013</td>
</tr>
<tr>
<td>As(III)</td>
<td>0.0011</td>
</tr>
<tr>
<td><strong>Freundlich parameters</strong></td>
<td></td>
</tr>
<tr>
<td>(K_F) ((mg/g)(L/mg)(^{1/n}))</td>
<td>(1/n)</td>
</tr>
<tr>
<td>As(V)</td>
<td>1.748</td>
</tr>
<tr>
<td>As(III)</td>
<td>1.033</td>
</tr>
</tbody>
</table>

\(q_{exp}\) – experimental equilibrium uptake.
To evaluate the thermodynamic feasibility and to confirm the nature of the adsorption process, three basic thermodynamic parameters, standard enthalpy ($\Delta H^\circ$), standard entropy ($\Delta S^\circ$), and standard free energy ($\Delta G^\circ$) were calculated.

Van’t Hoff plot of $\ln(K_d)$ against reciprocal of temperature ($1/T$) is shown in Figure 13. The thermodynamic equilibrium constant $K_d$ is dimensionless and is obtained by multiplying $K_D$ (in the units of L/g) with water density, 1,000 g/L (Slobodan 2007). The value of $\Delta H^\circ$, and $\Delta S^\circ$ were obtained from the slope and intercept of the plot. The thermodynamic parameters were determined using the following equations (Han et al. 2015) and given in Table 5.

$$\Delta G^\circ = -RT \ln K_d$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

where $\Delta G^\circ$ is the standard free energy, $R$ is universal gas constant (8.314 J/mol K) and $T$ is the absolute temperature in Kelvin (K).

From Figure 13, $\Delta H^\circ$ and $\Delta S^\circ$ were calculated to be 13.57 KJ/mol and 0.138 KJ/mol.K respectively. The endothermic nature of adsorption is indicated by an increase in $K_d$ with the temperature and the positive value of $\Delta H^\circ$. The value of $\Delta H^\circ$ indicates that the process is chemisorption. The negative value of $\Delta G^\circ$ confirms the feasibility of adsorption at all the temperatures and indicates that it is a spontaneous process. The value of $\Delta S^\circ$ being positive indicates that both enthalpy and entropy are responsible for making $\Delta G^\circ$ negative, which showed the increasing randomness at the solid–solution interface during adsorption. The adsorption mechanism of arsenic is mainly by $\text{H}_2\text{AsO}_3^-$ and $\text{OH}^-\text{exchange. Desorption of OH}^-\text{attached to active sites on the surface needs some activation energy to leave the surface, which might explain the endothermic nature of the adsorption process.}$

### Effect of particle size

The effect of particle size on As(V) adsorption on SFAA was studied with different particle sizes, viz., 89, 152, 210, 354

---

**Table 4** | Chemical reaction and diffusion based kinetic model parameters

<table>
<thead>
<tr>
<th>C (mg/L)</th>
<th>$K_1$ (1/min)</th>
<th>$q_e$ (mg/g)</th>
<th>$R^2$</th>
<th>$K_2$ (g/mg.min)</th>
<th>$q_e$ (mg/g)</th>
<th>$R^2$</th>
<th>$K_{id}$ (mg/g.min$^{0.5}$)</th>
<th>$R^2$</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.0689</td>
<td>0.041</td>
<td>0.99</td>
<td>413.933</td>
<td>0.0188</td>
<td>1</td>
<td>$8 \times 10^{-5}$</td>
<td>0.89</td>
<td>0.018</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0626</td>
<td>0.046</td>
<td>0.99</td>
<td>293.992</td>
<td>0.0398</td>
<td>1</td>
<td>$1 \times 10^{-4}$</td>
<td>0.88</td>
<td>0.039</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0557</td>
<td>0.071</td>
<td>0.96</td>
<td>97.124</td>
<td>0.0999</td>
<td>1</td>
<td>$3 \times 10^{-4}$</td>
<td>0.87</td>
<td>0.097</td>
</tr>
<tr>
<td>1.4</td>
<td>0.0537</td>
<td>0.091</td>
<td>0.99</td>
<td>54.401</td>
<td>0.1391</td>
<td>1</td>
<td>$5 \times 10^{-4}$</td>
<td>0.93</td>
<td>0.135</td>
</tr>
<tr>
<td>2.0</td>
<td>0.0435</td>
<td>0.113</td>
<td>0.98</td>
<td>30.841</td>
<td>0.1879</td>
<td>1</td>
<td>$1 \times 10^{-3}$</td>
<td>0.89</td>
<td>0.180</td>
</tr>
</tbody>
</table>
and 500 μm. The uptake capacities of the adsorbent and the percentage of As(V) removal for different particle sizes are shown in Figure 14. Both removal percentage and adsorption capacities of the adsorbent decreased with increase in the particle size of the adsorbent. Decrease in particle size increases the external surface area for adsorption and hence the uptake.

Interference of other ions

Interference of other ions on As adsorption by SFAA was studied for different anions (nitrate, sulphate, bicarbonate, carbonate, phosphate). The concentration of other ions was increased from 10 to 500 mg/L, while keeping the As(V) concentration at 2 mg/L. Figure 15 shows the percentage removal of As(V) in the presence of different anions.

It was seen that presence of nitrate did not effect As adsorption over a wide range of concentration. Bicarbonate and sulphate showed little effect on As adsorption at lower concentrations but with increase in their concentrations the removal of As(V) decreased. The effect of phosphate is the most significant, as can be seen from Figure 15. As(V) adsorption decreased from 99% to 58% with increase in phosphate concentration from 25 to 500 mg/L. The effect of other ions on As adsorption by SFAA adsorbent was observed to be in the order of $PO_4^{3-} > SO_4^{2-} > HCO_3^- > NO_3^-.$

CONCLUSIONS

Locally available sawdust impregnated with ferric hydroxide and activated alumina (SFAA) can be used very effectively for arsenic removal of groundwater to meet the drinking water standards laid down by WHO. Maximum removal of As(V) and As(III) was observed in the pH range of 6.5–7. Adsorption capacity of SFAA is 54.32 mg/g for As(III) and 77.60 mg/g for As(V) which is better than most adsorbents reported. An adsorbent dose of 10 g/L and contact time of 5 minutes are found to be the optimum for arsenic removal from water having arsenic concentration up to 2 mg/L. From the batch equilibrium and kinetic studies, it was observed that As(V) adsorption by SFAA follows Freundlich

<p>| Table 5 | Van’t Hoff plot parameters |</p>
<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>1/T (1/K)</th>
<th>$C_e$ (mg/L)</th>
<th>$q_e$ (mg/g)</th>
<th>$K_d$</th>
<th>$\ln K_d$</th>
<th>$\Delta G$ (KJ/mol.K)</th>
<th>$\Delta H$ (KJ/mol)</th>
<th>$\Delta S$ (KJ/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>0.00330</td>
<td>0.027</td>
<td>1.975</td>
<td>73074</td>
<td>11.20</td>
<td>-28.21</td>
<td>13.57</td>
<td>0.138</td>
</tr>
<tr>
<td>308</td>
<td>0.00325</td>
<td>0.025</td>
<td>1.975</td>
<td>79000</td>
<td>11.28</td>
<td>-28.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.00319</td>
<td>0.023</td>
<td>1.977</td>
<td>85956</td>
<td>11.36</td>
<td>-29.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>0.00314</td>
<td>0.021</td>
<td>1.979</td>
<td>94238</td>
<td>11.45</td>
<td>-30.28</td>
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<td></td>
</tr>
</tbody>
</table>
isotherm and pseudo-second-order kinetics. Presence of phosphate and sulphate decreases the adsorption of As(V) by SFAA.

REFERENCES


Balaji, T., Yokoyama, T. & Matsunaga, H. 2005 Adsorption and removal of As(V) and As(III) using Zr-loaded lysine diacetic acid chelating resin. Chemosphere 59 (8), 1169–1174.


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