Adsorption of arsenic from aqueous solution on naturally available red soil

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Abstract: In the present study arsenate and arsenite removal from naturally available red soil in and around Western Ghats of Maharashtra near Mumbai has been investigated. The parameters like adsorbent dose, operating pH, contact time, initial arsenite concentration, adsorbent particle size, etc. on the removal of arsenite and arsenate are examined. Kinetic study in centrifuge vessel reveals that uptake of As (III) ions is rapid in the first two hours and slows down thereafter. Maximum removal efficiency of As (III) achieved is 98% at an adsorbent dose of 45 g l\(^{-1}\) with initial As (III) concentration of 1000 µg l\(^{-1}\) in batch studies and 95% at 25 g l\(^{-1}\) adsorbent dose under the same conditions. Equilibrium time is almost independent of initial arsenite concentration. Equilibrium studies show that As (III) ions have high affinity towards red soil even at very low concentration of arsenite. In speciation study, about 25% conversion to As (V) from As (III) is observed, with initial As (III) concentration of 1000 µg l\(^{-1}\) and at 25 g l\(^{-1}\) adsorbent dose. The results suggest that red soil could be used as effective filter medium for removal of arsenic from water.

Key words: Arsenite removal, Red soil, Kinetic study, Adsorption, Arsenic speciation

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Introduction

A hazardous arsenic concentration in natural waters is now a worldwide crisis and often referred to as a 20\(^{th}\)--21\(^{st}\) century catastrophe. There have been widespread reports of arsenic poisoning in Bangladesh (Nickson et al., 1998), West Bengal (Chatterjee et al., 1995), China (Guo et al., 2003), Mexico (Del Razo et al., 1990), the upper midwest and the western United States (Welch et al., 1988), Argentina, Chile, Taiwan and Japan. The chronic health effects commonly include skin diseases i.e. pigmentation, dermal hyperkeratosis, and skin cancer (Singh et al., 2007; Flora et al., 2007), and other cardiovascular, neurological, hematological, renal and respiratory diseases, (Tseng, 2007), as well as lung, bladder, liver, kidney, prostate cancers. The World Health Organization set a provisional guideline limit of 10 µg l\(^{-1}\) for As in drinking water (WHO, 1993; Smedley and Kinniburgh, 2002). In India, a maximum arsenic level of 50 µg l\(^{-1}\) is permitted in ground water supplies for drinking purpose as per Bureau of Indian Standards (IS:10500:91) (Jiang et al., 2001; Nordstrom, 2002).

In natural water, usually inorganic arsenic in the form of As (III) and/or As (V) is found to be prevalent. Arsenite As (III) is much more toxic (Ferguson and Gavis, 1972) and more soluble and mobile than arsenate As (V). In the pH range of most natural waters (6.5-7.5), As (III) predominantly exists as an uncharged (H\(_2\)AsO\(_3\)) specie due to which this form of arsenic is very difficult to be removed by the conventionally applied physicochemical treatment methods than As (V).

The major current methods include coagulation, precipitation, ion exchange, and adsorption using a variety of Fe-containing solids as adsorbents. These adsorbents include hydrous iron oxide (Wilkie and Hering, 1996; Nemade et al., 2007), femihydrate (Jessen et al., 2005), zero valent iron (Nikolaidis et al., 2003), Fe oxide (Zang et al., 2003). New methods like construction soil filter (CSF) (Nemade et al., 2008) for As removal. Also low cost adsorbents like agricultural byproducts, clay minerals (Mohan and Pittman, 2007) coconut husk carbon (Manju et al., 1998), orange juice residue (Ghimire et al., 2002) are used for arsenic removal from water. Each technology has its own merits and demerits. Therefore, addition of an oxidizing agent is required to oxidize As (III) to As (V) to achieve higher arsenic removal. Due to their low hydraulic permeability iron oxides are unsuitable as filter medium. So it is crucial to discover a low alternative to knock out arsenic from water.

Natural red soil comes from disintegration of laterite rock which is a heterogeneous, anisotropic rock consisting of hard ferruginous skeletal framework impregnated with soft clayey material. Typical properties of laterite are shown in Table 1. Red soil is naturally available in Western Ghats of Maharashtra (India) which was used as the adsorbent for As (III) and As (V) removal. Red soil (Laterites) are product of intense sub aerial weathering whose iron and/or aluminium content is higher and silicon content are lower than in merely kaolized parent rocks. Red soil consists of mineral assemblages of iron oxides, aluminium hydroxide, kaolinite mineral and quartz and is abundantly available in the Konkan (Western Ghats) of Maharashtra (India).

In the present study, suitability of naturally occurring, low cost natural red soil is explored as potential arsenic adsorbent. Compared to iron oxide, it is harder (due to presence of silica) and can be separated from aqueous medium easily. This natural medium may be highly suitable for column adsorption for both ground and wastewater. Both equilibrium and kinetic study over a wide range of
operating conditions are undertaken to evaluate the effectiveness of red soil to remove As (III) from water. Speciation study of arsenic is also carried out to quantify the conversion from As (III) to As (V) state during a kinetic study. Various isotherms are studied to have more insight into the process.

**Materials and Methods**

**Reagent preparation:** Stock solutions of arsenite (1000 mg l−1) were prepared by dissolving appropriate quantity of arsenic trioxide, As₂O₃, (S.D. Fine Chem Ltd., India) in distilled water containing 1% (w/w) NaOH and the solution was then diluted up to 1 liter with tap water before use. The arsenate stock solution (1000 mg l−1) was prepared from the sodium arsenate, Na₃H₂AsO₆·7H₂O (Loba Chemie, India). The working solutions containing arsenic were prepared by dissolving appropriate amount of arsenic from stock solutions in tap water. Tap water analysis showed that pH varied from 7.1 to 7.6, bicarbonate alkalinity was approximately 40-50 mg l⁻¹ as CaCO₃, dissolved iron, phosphate and arsenic were not detected. Experiments were performed at ambient temperatures ranging from 29-30°C.

**Preparation of adsorbent:** Red soil was collected from Tambati village district Alibag 100 km away from Mumbai, Red soil crushed, washed several times by tap water until loosely bound particles were removed dried in hot-air oven at 100°C for overnight. Screened material was stored in capped bottle.

**Procedure:** For equilibrium studies, 100 ml solution of As(III) of known concentration (0.25-4.0 mg l⁻¹) was used as in natural water arsenic found in the wide range of 0.2 to 3.2 mg l⁻¹ in West Bengal, India. The dose is first optimized from experiment carried with varying dose concentration. It is found that the 25 g l⁻¹ gives maximum arsenic removal; and used same concentration for further studies. In a series of 250 ml Erlenmeyer flasks kept at constant temperatures of 290 K (17°C), 305 K (33°C), and 314 K (41°C). The solution was agitated at 130 rpm by orbital shaker with temperature controller for a predetermined equilibrium time of 24 hr. As (III) adsorption on red soil surface was functions of pH, adsorbent dosage and operating temperature. Effect of pH on adsorption of arsenite was studied and the pH of the As (III) solution was maintained at 7.1±0.05 for subsequent equilibrium studies. Samples were withdrawn after 24 hr and filtered though 0.45 μm membrane filters.

The filtrates were analyzed by rapid colorimetric method Dhar et al. (2004) for residual total arsenic concentration and As (V) (with detection limit 2 μg l⁻¹). Kinetic study was carried out in 1.5 l beaker which was kept at a constant temperature using magnetic stirrer. The effects of various process parameters on the rate of adsorption of the As (III) ions were observed by stirrer speed 80-130 rpm, initial absorbate concentration (1 mg l⁻¹), at ambient temperature (31°C) and adsorbent dose (5-45 g l⁻¹). For each experiment, 1000 ml As (III) solution of required concentration at fixed pH of 7.2±0.05 was used. Each experiment was repeated twice and the average of two values was used.

**Results and Discussion**

**Adsorbent characterization:** The various other properties of red soil are also presented in Table 1. Mineral constitution of the red soil was investigated by powder X-ray diffraction (XRD) using X’Pert Pro XRD system diffractometer with a curved position-sensitive detector config. d in vertical geometry with a 2θ detection range of 3-6°. Tube operating conditions were 40 kV and 30 mA. Measurements were made in reflection geometry with the sample surge at an angle of 1° to the incident beam as shown in Fig. 1. XRF results shows that the major constituents of red soil are quartz, magnetite, hematite, iron oxide / h ydroxide, goethite, iron silicon and aluminium oxide etc.

**Adsorbent dose:** The criteria for selection of suitable adsorbent include: the cost of the medium, the ease of operation or handling, the cost of operation, the useful service life per cycle / the adsorption capacity of the adsorbent, the potential of reuse and the possibilities of regeneration of adsorbent. Based on this naturally available red

### Table 1: Various properties of laterite rock/soil

<table>
<thead>
<tr>
<th>Properties</th>
<th>Colour</th>
<th>Structure</th>
<th>Rebound number</th>
<th>Compressive strength (MPa)</th>
<th>Specific gravity</th>
<th>Water absorption (%)</th>
<th>Hardness (Moh scale)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values</td>
<td>Reddish brown</td>
<td>Vermicular</td>
<td>40 - 6 2</td>
<td>1.13-2.42</td>
<td>1.85 - 2.60</td>
<td>9.74 - 13.92</td>
<td>2 - 4</td>
</tr>
</tbody>
</table>

### Table 2: Characterization of red soil as adsorbent

<table>
<thead>
<tr>
<th>Property</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface area (m²/g)</td>
<td>16.05</td>
</tr>
<tr>
<td>Point of zero charge (pHpzc)</td>
<td>7.41</td>
</tr>
<tr>
<td>Particle size (spherical), mm</td>
<td>0.5 - 0.32</td>
</tr>
<tr>
<td>Bulk density (g ml⁻¹)</td>
<td>1.30</td>
</tr>
<tr>
<td>True density (g ml⁻¹)</td>
<td>2.40</td>
</tr>
<tr>
<td>Conductivity (1:5, laterite: water mixture), μS cm⁻¹</td>
<td>12.0</td>
</tr>
<tr>
<td>pH (1:5, laterite: water mixture)</td>
<td>6.58</td>
</tr>
</tbody>
</table>

### Table 3: Characterization of red soil as adsorbent

<table>
<thead>
<tr>
<th>Inorganic composition (only metals)</th>
<th>Values (%, w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>42.74</td>
</tr>
<tr>
<td>Si</td>
<td>31.25</td>
</tr>
<tr>
<td>Al</td>
<td>10.08</td>
</tr>
<tr>
<td>Mn</td>
<td>1.32</td>
</tr>
<tr>
<td>K</td>
<td>1.01</td>
</tr>
<tr>
<td>Ti</td>
<td>2.25</td>
</tr>
</tbody>
</table>
soil was used in this study as a low cost adsorbent and it is available locally in West Bengal, India.

Figure 2 shows the effect of adsorbent dose on percentage removal of As (III). The figure reveals that uptake of As (III) increases rapidly from 5 to 25 g l⁻¹, and marginally thereafter due to more surface area with increase in adsorbent dose (Gupta et al., 2005). Further increment of adsorbent does not affect much due to non-availability of adsorbate. In the subsequent studies, the adsorbent dose selected was 25 g l⁻¹. This will help to carry out pilot studies in the field for arsenic removal from ground water. Effect of particle size on adsorption of As (III) having concentration of 1.0 mg l⁻¹ is very small.

**Effect of pH of the solution:** Fig. 3 shows the effect of pH on adsorption of As (III) and percentage removal of As (III). From the figure, it is evident that about 92% of As (III) was adsorbed on the red soil surface in a pH range of 4.0-10 at an initial As (III) concentration of 1.0 mg l⁻¹. The percentage removal decreases rapidly with further increase in pH. As (III) adsorption on red soil surface was almost pH independent in the range of 4-10, with slight higher adsorption in the acidic pH range. At higher pH (>9.8), laterite surface is negatively charged and arsenite adsorption becomes less due to repulsion of similar charge, as arsenite exists as anion in that pH range. Similarly maximum adsorption was observed for As (III) adsorption in the pH range 7-7.6 on activated alumina (Singh and Pant, 2004) and iron-oxide coated sand (Gupta et al., 2005) as both iron and aluminium oxide present in the red soil are primarily responsible for arsenite adsorption.

The detailed nature of chemisorption, either by ligand or ion exchange is studied next. For this purpose, the speciation study
of arsenic is carried out. The results are presented in Fig. 4. It is found from this figure that maximum about 21% of the initial arsenic (III) is converted to (V) state due to the presence of manganese oxide in laterite similar results obtained elsewhere (Maji et al., 2008). At the studied pH (about 7.0), As (III) is found primarily as H₃AsO₃ (pKₐ 1 = 9.2). 22% of this arsenic is converted to As (V) state which is anionic at pH about 7.0. Therefore, adsorption at this pH is a combination of ligand exchange of As (III) and ion exchange of As (V). This nature of adsorption of a neutral and/or charged species on natural hydrous metal oxide is well described in literature (Stumm and Morgan, 1981).

**Adsorption isotherms:** From equilibrium studies the isotherm data were obtained using As(III) concentration in the range of 0.25-4.0 mg l⁻¹ with fixed adsorbent dose 25 g l⁻¹ at three different temperatures, 290 K, 305 K and 314 K, similar studies conducted earlier (Singh and Pant, 2004). The results are presented in Fig. 5. These data can be fitted to Freundlich and Langmuir isotherm models shown by equation 1 and 2. The equation of Freundlich isotherm is given as follows:

\[
q_e = k q_o^{1/n}
\]  

(1)

Where, \(k\) and \(n\) are Freundlich isotherm constants representing the adsorption capacity and intensity of the adsorbent, respectively. Langmuir isotherm equation is given as,

\[
q_e = \frac{Q_0 c_e}{1 + b c_e}
\]  

(2)

Where, \(Q_0\) and \(b\) are the Langmuir constants representing the adsorption capacity and energy of adsorption. The values of \(k\), \(n\) and \(Q_0\) and \(b\) obtained by non-linear regression and are presented in Table 4 showing Freundlich constant \(k\) increases with temperature. The other constant \(n\) remains almost constant (about 1) in the temperature range studied here. This indicates that the adsorption capacity increases with temperature.

**Effect of adsorbent dose in the kinetic study:** The effect of adsorbent dose in the feed on the removal of arsenic is presented in Fig. 6. The removal is more for higher adsorbent dose due to availability of more adsorption sites (Singh and Pant, 2004). Arsenic removal is about 90% for red soil concentration of 25 g l⁻¹ and it increases up to 98% for adsorbent dose of 45 g l⁻¹ at 1 mg l⁻¹ arsenic, reduce to a level of 20 µg l⁻¹, which is very near to maximum permissible limit (10 µg l⁻¹) recommended by WHO and well below the recommended value in India (50 µg l⁻¹) according to IS 10500:91.

**Thermodynamic parameters:** From the experiments, at different temperatures thermodynamic parameters, were calculated like standard Gibb’s free energy (\(ΔG^o\)), change in enthalpy (\(ΔH^o\)) and entropy change (\(ΔS^o\)) are estimated (Singh and Pant, 2004) by the following equation:

\[
ΔG^o = ΔRT \ln K_o
\]  

(3)

Where, \(K_o = \frac{C_{ad}/C_e}{K_o}\) is the equilibrium constant; \(C_{ad}\), is the reduction of adsorbate concentration (mg l⁻¹) of the solution at
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Fig. 4: Speciation study of As (III) on red soil, initial As (III) = 1.0 mg l⁻¹, pH 7.2, adsorbent dose = 25 g l⁻¹, shaker speed, 130 rpm

Fig. 5: Langmuir isotherm plots for adsorption of As (III) on red soil, C₀, 0.25-4.0 mg l⁻¹, pH 7.2, adsorbent dose 25 g l⁻¹, shaker speed 130 rpm

Fig. 6: Estimation of thermodynamic parameters from a graph of ln Kᵢ vs. (1/T)

Fig. 7: Effect of adsorbent dose on As (III) adsorption [temperature, 290 K, C₀, 1.0 mg l⁻¹, pH 7.2, stirrer speed, 130 rpm coated cement (IOC) media. Also statistical variation shown in Table 6 and 7.

It may also be noted that the free energy values obtained for the system decreases with increasing temperature which shows that the reaction is easier at higher temperatures. The positive values of enthalpy change (ΔH°) for the processes further confirm the endothermic nature of the process, while positive values of entropy change (ΔS°) suggest the increase in randomness at the solid-solution interface during the adsorption of As (V) on red soil. The negative (ΔG°) values confirm feasibility of the arsenite adsorption on the red soil surface.

\[ \ln Kᵢ = \Delta S° R / Δ H° R T \] (4)

The values of entropy change (ΔS°) and enthalpy change (ΔH°) were obtained from intercept and slope of the plot of ln Kᵢ versus (1/T) (Fig. 7). The estimated values of the thermodynamic parameters for the three operating temperatures are presented in Table 5, similar study have been carried out by Kundu and Gupta (2006) indicating that the adsorption process is spontaneous for As (V) with high affinity for iron oxide.
Arsenic adsorption using naturally occurring red soil is given in this work. Equilibrium studies reveal that the operating pH should be around 7.1. Both Langmuir and Freundlich isotherms fit the adsorption data adequately. From the kinetic study it is observed that the maximum adsorption occurs within two hours of the operation. About 98% arsenic can be removed using an adsorbent dose of 45 g l⁻¹, for an initial arsenite concentration of 1.0 mg l⁻¹. It is established that both ligand and ion exchange may be the mechanism of the adsorption. The controlling step of arsenic adsorption is by both external film diffusion and intraparticle pore diffusion (Maji et al., 2008). It has been observed that from speciation study near about 21% of As (III) is converted to As (V). Consequently, red soil plays a role of natural oxidant for arsenite and additional step of pre-oxidation of As (III) is not required.

In the present study the adsorbent selected was a naturally occurring material. Thus, the cost of procuring the commercial material was minimized. Laterite soil is abundantly found in different parts of West Bengal (Maji et al., 2008).

The results obtained in this study will be useful for its further extension to field scale column study or for designing pilot plant as future studies. It is worth mentioning here that the laterite soil does not cause any increase in pH, or any increase in Fe (III)/Al (III) concentration (due to leaching) in the effluent water. In addition, on column adsorption the effluent water quality is much improved.

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References


