Crystalline hydrous titanium (IV) oxide (CHTO): An arsenic (III) scavenger from natural water

Biswaranjan Manna, Monotosh Dasgupta and Uday Chand Ghosh

ABSTRACT

Arsenic contamination (>10 ppb) in groundwater poses a risk to public health globally. The problem is apparently the greatest in the Bengal basin of the Ganga River. As(III) is a major contaminant in anoxic groundwater. Here, a systematic report on As(III) removal using synthetic crystalline hydrous titanium(IV) oxide (CHTO) is made. Absolute As(III) sorption capacity is 72 to 75 g kg\(^{-1}\) at a pH of 7.0. CHTO has nearly the same sorption density in the pH range of 6.0 to 9.0. Use of pre-dried CHTO above 350°C shows a decrease in sorption density from 11.50 (±0.10) to <9.0 mg g\(^{-1}\). Approximately 70% of As(III) sorption takes place within 0.5 hour. Interfering effect studies of some ions show a poor effect on the sorption process except for HCO\(^{-}\). As(III) sorption follows the Lagergren first-order kinetic model and the sorption data fit the Freundlich and Langmuir isotherms well. Batch and column methods for regeneration of arsenic rich CHTO with 1.0 M NaOH solution show ~90% and 75 to 80% regain of its initial efficiency, respectively. Flow-rate and bed depth variation effects on As(III) removal from a spiked (500 µg l\(^{-1}\)) natural water are reported systematically. Lab-bench mini-pilot scale application of a fixed-bed (bed volume=30.0 cm\(^3\)) CHTO column is reported at a down flow-rate of 33 to 34 B.V. (bed volume) h\(^{-1}\) using an As(III) spiked (320 µg l\(^{-1}\)) natural tap water sample from Presidency College, Kolkata. Reuse of the bed after regeneration shows a decrease in As(III) removal efficiency to the extent of 20–25% of that of a fresh column. Arsenic recovery (~99.25%) from the regenerate is also reported.

Key words | arsenic(III), crystalline titanium(IV) oxide, natural water, recovery, removal, sorption

INTRODUCTION

Contamination by arsenic in groundwater above toxic levels (10 ppb) in six districts of West Bengal (India) and also in major parts of Bangladesh pose a threat to public health. Chatterjee et al. (1995) reported that at least 800,000 people are at a high risk of arsenical skin diseases due to drinking highly arsenic-contaminated groundwater and among them 175,000 people are suffering from arsenical skin diseases that are the last stages of manifestation of arsenic toxicity. Besides West Bengal (India) and Bangladesh, arsenic contamination in groundwater above 10 ppb has been reported (Smedley & Kinniburgh 2002) in many other countries scattered throughout the globe.

The source of arsenic in groundwater is thought to be geochemical. The Earth’s crust contains arsenic in sulfide bearing ores and minerals (Ferguson & Davis 1972; Smedley & Kinniburgh 2002) such as arsenopyrites (FeAsS\(_2\)), realger (As\(_4\)S\(_8\)) and orpiment. Arsenic comes out from these minerals into groundwater mainly due to pyrite oxidation by air or water rich in dissolved oxygen and by oxyhydroxides reduction where arsenic is bound to ferric oxyhydrates in subsoil in a manner similar to that of phosphate.

Numerous methods reported so far for reducing arsenic content below the allowed level are of the coagulation–filtration type using alum and ferric salt (Harper & Kingham 1992; Rajakovic et al. 1993), lime softening (Dutta & Chaudhuri 1991) and surface adsorption using activated alumina (Rosenblum & Clifford 1984),...
activated carbon (Huang & Fu 1984), amorphous and granular ferric hydroxide (Wilkie & Hering 1976; Pierce & Moore 1982; Driehaus et al. 1998), crystalline hydrous ferric oxide (Manna et al. 2003), goethite (Matis et al. 1997), manganese oxides (Driehaus et al. 1995), geological materials (Xu et al. 1988; Bowell 1994), silica gel impregnated with ferric hydroxide (Joshida et al. 1976), basic yttrium carbonate (Wasay et al. 1996), lanthanum compounds (Tokunaga et al. 1997), hydrated zirconium oxide (Manna et al. 1999), hydrotalcite (Manju & Anirudhan 2000) and lanthanum impregnated sawdust carbon (Raji & Anirudhan 1999). In some cases arsenic removal from contaminated groundwater via oxidation of As(III) to As(V) has been reported. Since As(III) is the main contaminant (>90% As(III)) in anoxic groundwater in the Bengal basin (Harvey et al. 2002), direct removal from groundwater is important in the context of public health. Hydrous titanium(IV) oxide is a non-toxic compound and has been found to be selective for As(III) sorption.

Thus, in the present communication, synthesis of crystalline hydrous titanium (IV) oxide (CHTO), some of its physicochemical characterizations, systematic As(III) sorption behaviour, competing effect of some other ions, regeneration of the adsorbent and lab bench fixed bed As(III) removal from spiked tap water have been reported. Reuse of the regenerated fixed bed column has also been shown.

**METHODS**

**Preparation of standard As(III) solution**

Standard stock As(III) solution was prepared by dissolving 0.1320 g of As$_2$O$_3$ in 10 ml of 4% (w/v) NaOH, acidified with 2.0 ml of conc. HCl and then diluted to 100 ml with pure water. Working solution for As(III) of a desired concentration was made by diluting the stock with 0.2% (v/v) HCl. The stock solution was freshly prepared after every 3 days and frozen to prevent oxidation.

**Synthesis of sorbent**

Crystalline hydrous titanium(IV) oxide (CHTO) was prepared by slow addition of 25 ml of TiCl$_4$ per 2.0 l of water with constant mechanical stirring followed by dropwise addition of 0.1(M) aqueous ammonia until the pH of the supernatant liquid was 4.0 to 5.0. The white gelatinous precipitate was kept as such for 7 days with mother liquor for ageing. Decanting the supernatant liquid, the precipitate was washed with deionized water until free from acid. Filtering the precipitate, it was dried at 40°C in an air oven; the gelatinous cake shrinks on drying and cracks to give glassy and transparent granular products; on immersion in water the granules break down with the release of air bubbles entrapped to give granular materials. It was then ground to the particle size of 0.14 to 0.29 mm and used throughout the experiments.

**Arsenic estimation**

As(III) was estimated by standard methods using SDDC in chloroform and also by hydride generator atomic absorption spectrophotometer (Standard Methods 1998).

**Sorption study**

Sorption experiments were conducted at 30 ± 2°C by both batch and column methods. Here, initial pH of the test solutions as well as of the sorbent particles was adjusted near to the same value as per requirement in each test using dilute HCl and/or NaOH solution as necessary.

**Batch adsorber test**

Fifty-millilitre aliquots of solutions containing 1.25 mg As(III) were taken with 0.1 g of CHTO into 100-ml polythene containers and then agitated mechanically (agitation speed: 160 rpm) for equilibration. The experiment for pH effect was conducted using an initial As(III) load of 1.25 and 2.50 mg separately. The solution was filtered and the filtrate analysed for arsenic. All the batch experiments, except for pH influence, were conducted at an initial pH of 7.0.

**Column test**

Column sorption tests were conducted by packing glass columns, 1 cm internal diameter (i.d.), with CHTO up to a
desired bed depth and/or bed volume; then, As(III) spiked tap water from the Presidency College Campus (PCC) was passed through the adsorbent bed. Using the columns, down flow-rate and bed depth variation experiments were conducted. Lab-bench mini-pilot scale application was carried out using a column (2.0 cm i.d.) packed with CHTO up to a definite bed volume.

**Determination of absolute adsorption capacity**

Absolute As(III) sorption capacity of CHTO was determined by a number of batch experiments. Fifty millilitres of As(III) solution (total As(III) content: 50 mg) per 0.5 g of the sorbent at an initial working pH of 7.0 was agitated (agitation speed: 160 rpm) mechanically for 6 hours. The filtered solution was analysed for residual arsenic. Arsenic(III) sorption capacity was then calculated.

**Regeneration of used adsorbent**

Regeneration of As(III) saturated-CHTO (arsenic content: 72.94 mg g⁻¹) was performed first by batch test. Here, 0.1 g of As(III) saturated sorbent was equilibrated (agitation speed: 160 rpm) for an hour separately with a 50 ml aliquot of 0.5(M) different regenerating solutions. Regenerating agents used were: NaOH, KOH, Na₂CO₃, Na₂HPO₄ and NaCl solutions. The best results were obtained using NaOH and, hence, the concentration was varied thereafter for optimization of regeneration condition.

Column regeneration was conducted with 1.0(M) NaOH solution. Here, a definite volume of the regenerating solution was recycled thrice through the bed to give the best possible result.

**RESULTS AND DISCUSSION**

The XRD pattern of synthesized crystalline hydrous titanium oxide (CHTO) showed a close resemblance to the anatase form of TiO₂. The peak intensity of 80% at 20 value of 26° indicates the crystalline nature of the oxide. The extent of crystallization depends mainly on the mode of preparation, time and condition of ageing and drying temperature. With an increase in ageing time and temperature, hydrous oxide gradually transforms into the more ordered anatase form with correspondingly large crystal sizes and reduced surface area.

The scanning electron micrograph (SEM) revealed the surface morphology of the oxide particles. The average particle diameter is found to be 0.20–0.22 mm. The particles are of irregular shape with triangular, rectangular, square and pentagonal plane surfaces.

TG analysis (Figure 1) of the adsorbent showed a rapid first step weight loss of 8.29% at drying temperatures below 68.3°C, which corresponds to the loss of physically adsorbed water, confirming the hydrous nature of the synthesized product. The sharp endoergic (downward) DTA peak at 68.4°C further supports this. A broad exoergic DTA peak (Figure 2) between 68.4 and 200°C and a second step weight loss of 12.25% in TG analysis is attributed to a chemical change indicating polymerization. Another slow step weight loss of 3.89% at temperatures above 200°C is found which presumably occurs due to the condensation of layers through the release of exchangeable hydroxyl groups as water with a consequent decrease in sorption sites.

Some physicochemical characteristics of CHTO determined are as follows: titanium content: 53.39%, moisture content: 15.06%, bulk density: 1.21 g cm⁻³.
Effect of pH

The effect of pH on adsorption of As(III) by CHTO was studied in the pH range of 2.0 to 12.0 with initial loads of 1.25 and 2.5 mg arsenic. The results (Table 1) showed that the adsorption density increased somewhat with an increase in pH up to 6.0, remained nearly same up to pH 9.0, and thereafter decreased sharply in the highly alkaline pH range. As(III) in aqueous solution up to pH 9.0 exists mainly as non-ionic As(OH)₃ and then dissociates increasingly with increased pH forming the predominant species H₂AsO₃⁻ [pK₁ = 9.2]. Though the adsorbent possesses an anion-exchange property (Sasaki 1985) up to pH ≤ 6.0, the adsorption of As(III) cannot take place through the ion-exchange mechanism due to lack of anionic As(III) species. The adsorption presumably occurs up to that pH through the ion-dipole type of non-specific interactions (Equation 1). This is in conformity with the increase in the final pH of the solution (Table 1).

\[
\begin{align*}
\text{HO}^- \cdot \text{(TiO)}_n \cdot \text{OH}^- + \text{H}^+ + \text{As(OH)}_3^- & \rightleftharpoons \\
\text{HO}^- \cdot \text{(TiO)}_n \cdot \text{O}^\delta + \text{H}_2 \ldots \text{O}^\delta - \text{As(OH)}_2^- & \\
\delta^\uparrow & \text{H} \quad 2.0 < \text{pH} \leq 6.0 \quad (1)
\end{align*}
\]

An increase in pH leads to a slight increase in As(III) sorption density which is due to the decrease in surface positive charge on CHTO particles resulting in a decrease in electrostatic repulsion between sorbent and sorbate.

Sorption of As(III) in the range of pH 6.0 to 9.0 is thought to take place via Na⁺ (present in working solutions) sorption at cation-exchange sites of CHTO because the cation exchange property (Sasaki 1985) appears just above pH 6.0 and persists throughout the higher pH range and, thereon, As(OH)₃ binds electrostatically (Equation 2). This agreed well with the decrease in final pH of the solution.

\[
\begin{align*}
\text{OH}^- \cdot \text{(TiO)}_n \cdot \text{OH}^- + \text{Na}^+ + \text{As(OH)}_3^- & \rightleftharpoons \\
\text{OH}^- \cdot \text{(TiO)}_n \cdot \text{O}^\delta \ldots \text{O}^\delta - \text{As(OH)}_2^- & \\
\delta^\uparrow & \text{H} \quad 6.0 < \text{pH} \leq 9.0 \quad (2)
\end{align*}
\]

In the pH range of 9.0 to 12.0, As(III) exists predominantly as (HO)₂AsO⁻ which adsorbs onto CHTO presumably as given in Equation (3). CHTO adsorbs Na⁺ and thereon anionic As(III) species bind via ion-dipole interactions. The clear decrease in pH from the initial value supports the mechanism (Equation 3). A rapid decrease in As(III) sorption density with increasing experimental pH is due to the competing effect of OH⁻ with (HO)₂AsO⁻ for the sorption sites. The Fourier Transform Infrared Spectroscopic (FTIR) study for both CHTO and arsenic sorbed CHTO showed the change of the Ti-O and O-H absorption peak frequency value, which supports these mechanisms (Equations 1–3).

\[
\begin{align*}
\text{OH}^- \cdot \text{(TiO)}_n \cdot \text{OH}^- + \text{Na}^+ + \text{As(OH)}_3^- & \rightleftharpoons \\
\text{OH}^- \cdot \text{(TiO)}_n \cdot \text{O}^\delta \ldots \text{O}^\delta - \text{As(OH)}_2^- + \text{H}_2 \text{O} & \\
9.0 < \text{pH} \leq 12.0
\]
\]

Effect of drying temperature on adsorbent

Adsorbent was dried at a pre-fixed temperature for an hour and then used for As(III) sorption at an initial pH of 7.0. The results show (Table 2) that As(III) sorption density remained nearly the same (11.50±0.10 to
11.20±0.18 mg g⁻¹) in the drying temperature range of 25–150°C of the adsorbent, but decreased remarkably when the adsorbent used was dried at 200°C or above. This is attributed to the loss of adsorption sites (hydroxyl groups) due to polymerization with the increase in drying temperature. The sharp decrease in adsorption density (<9.0 mg g⁻¹) at a drying temperature of above 350°C is due to the phase transition. Thus, initially dried CHTO at a temperature between 50 and 150°C should be a good adsorbent for As(III) and it will decrease the chance of

<table>
<thead>
<tr>
<th>As(III) loaded (mg)*</th>
<th>Initial pH</th>
<th>Final pH</th>
<th>Adsorption density of As(III) (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>2</td>
<td>2.12–2.15</td>
<td>10.70–10.76</td>
</tr>
<tr>
<td>3</td>
<td>3.24–3.27</td>
<td>10.85–10.90</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4.40–4.44</td>
<td>11.05–11.15</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5.65–5.72</td>
<td>11.20–11.24</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.58–6.62</td>
<td>11.36–11.40</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>6.85–6.89</td>
<td>11.40–11.42</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>7.52–7.59</td>
<td>11.26–11.32</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>8.50–8.57</td>
<td>11.14–11.20</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>8.80–8.89</td>
<td>10.90–10.93</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>10.85–10.92</td>
<td>8.40–8.44</td>
<td></td>
</tr>
</tbody>
</table>

| 2.50                 | 2          | 2.21–2.25 | 10.90–10.95 |
| 3                    | 3.16–3.18  | 11.40–11.44 |
| 4                    | 4.51–4.55  | 11.48–11.52 |
| 5                    | 5.76–5.80  | 11.53–11.56 |
| 6                    | 6.77–6.80  | 11.60–11.66 |
| 7                    | 6.80–6.85  | 11.60–11.65 |
| 8                    | 7.50–7.54  | 11.50–11.58 |
| 9                    | 8.38–8.43  | 11.20–11.25 |
| 10                   | 8.75–8.80  | 10.95–10.98 |
| 12                   | 10.80–10.86| 8.50–8.52  |

*The As(III) loaded was in 50 ml volume of solution and CHTO added=0.1 g. Agitation time and speed were 6 h and 160 rpm, respectively.
dissolution of the adsorbent over a long contact time with water.

Effect of contact time

Contact time for As(III) sorption was conducted up to 6.0 hours in half hour increments. The results showed (Table 3) that the sorption density increased from 8.50±0.20 (at 0.5 hour) to 11.60±0.15 mg g⁻¹ (at 4.0 hours), and then remained nearly the same. Thus, CHTO needs a minimum of 4.0 hours of contact for maximum As(III) sorption from solution. Initial rapid As(III) sorption is due to the surface phenomenon and then becomes very slow probably due to pore diffusion controlled process.

Effect of interfering ions

The interfering effect of some ions (those commonly found in groundwater) on As(III) sorption onto CHTO was investigated separately by varying the initial molar ratio (IMR) of each interfering ion to As(III). The results (Table 4) show that Ca²⁺ (or Mg²⁺) showed no adverse effect on As(III) sorption when IMR was varied from 0 to 8 (or 12.66). As(III) sorption density (mg g⁻¹) decreased from 11.35±0.35 to, respectively, 9.25±0.10, 9.65±0.34, 10.40±0.10 and 10.19±0.07 when IMR for Mn²⁺, Fe³⁺, Cr³⁺ and Pb²⁺ was varied from 0 (no interfering ions) to 0.2732, 0.2681, 0.2883 and 0.0736, respectively. This decrease in sorption density with increase in IMR values is presumably due to the surface coverage of CHTO by the metal hydroxide precipitate or by cation adsorption at the working initial pH of 7.0.

Investigation of the interfering effect of $F^-$, $PO_{4}^{3-}$, $SO_4^{2-}$ and $HCO_3^-$ on sorption of the sorbate showed that $F^-$ did not interfere while the other anions had little effect. Adsorption density (mg g⁻¹) of As(III) was found to decrease from 11.35±0.35 to, respectively, 10.50±0.15, 10.40±0.10 and 9.50±0.10 when IMR for $PO_{4}^{3-}$, $SO_4^{2-}$ and $HCO_3^-$ was varied from 0 (no interfering ions) to 4.5, 18.8 and 19.68, respectively. Thus, it indicates that the competing effect of $HCO_3^-$ for As(III) sorption sites on CHTO is somewhat greater than that for either $PO_{4}^{3-}$ or $SO_4^{2-}$, which is probably due to the presence of high levels of

Table 2 | Pre-drying of CHTO and effect on As(III) sorption at pH 7.0

<table>
<thead>
<tr>
<th>Drying temperature (°C)</th>
<th>Adsorption density (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>11.50±0.10</td>
</tr>
<tr>
<td>50</td>
<td>11.45±0.12</td>
</tr>
<tr>
<td>100</td>
<td>11.20±0.18</td>
</tr>
<tr>
<td>150</td>
<td>10.78±0.15</td>
</tr>
<tr>
<td>200</td>
<td>10.23±0.07</td>
</tr>
<tr>
<td>250</td>
<td>10.55±0.11</td>
</tr>
<tr>
<td>300</td>
<td>8.90±0.10</td>
</tr>
<tr>
<td>350</td>
<td>8.15±0.17</td>
</tr>
<tr>
<td>400</td>
<td>8.15±0.17</td>
</tr>
<tr>
<td>500</td>
<td>8.15±0.17</td>
</tr>
</tbody>
</table>

Drying time=1 h; CHTO dose used=0.1 g; agitation speed=160 rpm. Results reported are of three experiments. Adsorption density (mg g⁻¹)=value±SD.
bicarbonate in the experimental solutions. Hence, As(III) removal efficiency of the adsorbent from the contaminated water will decrease to some greater extent with increasing HCO$_3^-$ concentration.

**Adsorption dynamics**

To rationalize the adsorption dynamics for the present investigation, the following approaches have been used: (a) kinetic modelling using Lagergren equation, (b) intraparticle diffusion rate constant, and (c) pore diffusion rate constant.

**Kinetic modelling**

The kinetic study for As(III) sorption onto CHTO was conducted by batch method at an initial pH of 7.0 by varying adsorbate concentration at 30(±2)°C. The adsorption rate constant ($K_{ad}$) was calculated using the model proposed by the Lagergren first order rate process:

$$\log_{10}(q_e - q) = \log_{10}q_e - (K_{ad}/2.303)t$$

where $q_e$ and $q$ (both in mg g$^{-1}$) are the sorption densities for the sorbate at equilibrium and at time $t$ (min), respectively. The straight line plots of $\log_{10}(q_e - q)$ versus time ($t$) at different initial As(III) concentrations have a high correlation coefficient, $R^2 > 0.95$ (Figure 3) showing the validity of the model and suggesting that As(III) sorption obeys first order kinetics. The rate constants, $K_{ad}$ for the adsorbent are given in Table 5 compared with some of our earlier works (Manna et al. 1999, 2003). The comparative $K_{ad}$ values on the sorption process indicate that CHTO is a good medium as an adsorbent for As(III).

**Intraparticle diffusion rate constant**

The intraparticle diffusion rate constant ($k_i$) can be defined as the gradient of the plot of the amount of the sorbate sorbed per unit weight of the adsorbent versus the square root of time (Weber and Morris 1963; Allen et al. 1989). The plot of $q$ versus $vt$ (Figure 4) is found to be linear for a wide range of contact times for As(III) sorption investigated indicating the presence of external mass transfer. Figure 4 shows three separate regions. The initial part of the curve is attributed to mass transfer effects (Crank 1983) (slope $k_1$) taking place with boundary layer diffusion, while the final linear portions of the curve indicate intraparticle diffusion (slope $k_2$ and $k_3$). Table 5 shows the diffusion rate parameters $k_1$, $k_2$ and $k_3$ obtained. The values for $k_2$ and $k_3$ indicate that the pores are micropore and the intraparticle diffusional resistance is due to micropores only. Moreover, pore sorption of As(III) onto CHTO is concentration dependent; with the increase in As(III) concentration, rate of pore diffusion increases.

**Pore diffusion coefficient**

The pore diffusion coefficient ($D$) for intraparticle transport of As(III) sorption onto CHTO has been calculated.
using the following equation assuming spherical geometry for the adsorbent particles (Healfferich 1963; Bhattacharya and Venkobacher 1984)

\[ t_{1/2} = 0.03 \frac{r_0^2}{D} \]

where \( t_{1/2} \) = time of half sorption, \( r_0 \) = mean radius of sorbent particles and \( D \) = pore diffusion coefficient (cm² s⁻¹).

Table 5 shows the calculated values for \( D \), found to be in the range of \( 10^{-9} \) to \( 10^{-12} \) cm² s⁻¹ for As(III) sorption onto CHTO, indicating that the adsorption phenomenon is controlled by pore diffusion (Poots et al. 1976).

### Adsorption isotherms

The equilibrium data in adsorbing As(III) onto CHTO were analysed by using Freundlich(I) and Langmuir(II) isotherms.

\[ q_e = a_t c_e^{1/n} \quad (I) \]

\[ q_e = \frac{c_e}{q_e} = \frac{Q_0}{b} + \frac{1}{Q_0 b} \quad (II) \]

where \( c_e \) (mg l⁻¹) and \( q_e \) (mg g⁻¹) are the concentration and adsorption density for As(III) at equilibrium, respectively. \( a_t \) and \( n \) are Freundlich constants which indicate adsorption capacity and intensity. \( Q_0 \) and \( b \) are Langmuir constants indicating adsorption capacity and equilibrium adsorption constant, respectively. The plots of log \( c_e \) versus log \( q_e \) (Figure 5) and \( 1/q_e \) versus \( 1/c_e \) (Figure 6) show
high values of correlation coefficients (R²) indicating linear relationships, which confirm the applicability of both the adsorption isotherms. The R² values for the Freundlich and Langmuir models were 0.9735 and 0.9915, respectively, indicating that the adsorption data fitted the Langmuir equation best. The evaluated values of the Freundlich and Langmuir constants are given in Table 6 compared with our reported data (Manna et al. 1999, 2003).

The values for the Freundlich and Langmuir constants for As(III) sorption at pH 7.0 clearly indicate that CHTO like other hydrous oxides should be a good adsorbing medium for As(III). 1/n < 1 supports the high As(III) sorption capacity and the value of b also indicates favourable As(III) sorption taking place through monolayer coverage onto the adsorbent surface.

The essential characteristics of the Langmuir isotherm may be expressed in terms of the dimensionless equilibrium parameter, \( R_L = \frac{1}{1 + bC_0} \) where \( C_0 \) is initial adsorbate concentration (mg l⁻¹). The \( R_L \) values (Table 6) lie between 0 and 1 at different initial As(III) concentrations indicating favourable sorption onto CHTO.

### Regeneration of As(III)-Rich Absorbent

Batch regeneration showed that a 0.5(M) solution of NaOH and KOH could regenerate to the extent of 82.00±1.00 and 77.50±1.30%, respectively, while other regenerating agents achieved less than 31.00%. The increase in concentration of NaOH and KOH solutions showed that 1.0(M) of each regenerant regenerated 90.00±0.80% and 82.50±0.80%, respectively. An increase

---

### Table 5

<table>
<thead>
<tr>
<th>Initial As(III) conc. (mg l⁻¹)</th>
<th>Adsorption rate constant (kad), min⁻¹×10⁻²</th>
<th>Pore diffusion constant (D)×10⁻¹⁰ cm² s⁻¹ (for CHTO)</th>
<th>Intraparticle diffusion rate constant (ki), mg g⁻¹, min⁻¹/² for CHTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHTO</td>
<td>CHFO</td>
<td>GHZO</td>
<td>K₁</td>
</tr>
<tr>
<td>25</td>
<td>1.842</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>50</td>
<td>1.833</td>
<td>1.163</td>
<td>1.512</td>
</tr>
<tr>
<td>75</td>
<td>1.811</td>
<td>1.154</td>
<td>1.483</td>
</tr>
</tbody>
</table>

Sorbent dose=0.1 g, working pH=7.0; agitation speed=160 rpm; agitation time=4 h.

---

### Figure 4

Intraparticle diffusion rate constants of As(III) sorption by CHTO at 30±2°C.

### Figure 5

Freundlich adsorption isotherm of As(III) on CHTO at 30±2°C.
in concentration of the alkali solutions used above 1.0(M) did not improve the extent of regeneration of the adsorbent. Thus, the results on regeneration of CHTO indicate that NaOH is a better regenerating agent than KOH. This is presumably due to the greater combining affinity of arsenite with smaller Na\(^+\) than bigger K\(^+\). The results of column regeneration by recycling 33.33 BV of 1.0(M) NaOH thrice (down flow-rate 3.3–3.4 BV h\(^{-1}\)) showed that the extent of regeneration was 75 to 80%. The 20 to 25% lower regeneration is possibly due to chemisorption. Higher regeneration of As-loaded CHTO in the batch method than in the column method is due to the intimate mixing of regenerant and adsorbent during agitation.

**Column study on As(III) removal**

A CHTO packed column was used for conducting the study on As(III) removal from the spiked tap water of PCC (Kolkata, India). Some analysed water quality parameters of used tap water are shown (Table 7). The pH of As(III) spiked tap water sample was 7.3 to 7.5 during

### Table 7 | Some parameters of Presidency College tap water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value ± Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.40 ± 0.25</td>
</tr>
<tr>
<td>Hardness (as CaCO(_3))</td>
<td>254 ± 3.0</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>5.10 ± 0.50</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>6.65 ± 0.35</td>
</tr>
<tr>
<td>Biological oxygen demand (25°C)</td>
<td>2.56 ± 0.25</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>810 ± 3.8</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>4.12 ± 0.3</td>
</tr>
<tr>
<td>Iron</td>
<td>0.25 ± 0.05</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>Chloride</td>
<td>210 ± 7.0</td>
</tr>
<tr>
<td>Sulphate</td>
<td>84 ± 3.0</td>
</tr>
<tr>
<td>Nitrate</td>
<td>10.2 ± 1.0</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>117.0 ± 3.0</td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.38 ± 0.04</td>
</tr>
</tbody>
</table>

All values are in mg l\(^{-1}\), except pH and turbidity.

### Table 6 | Adsorption constants and Langmuir parameter (R\(_L\)) values at pH 7.0 and temperature 30±2°C

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>(a_I)</th>
<th>1/n</th>
<th>(Q_m) (mg g(^{-1}))</th>
<th>b (l/mg)</th>
<th>Initial As(III) conc. (mg l(^{-1}))</th>
<th>(R_L) value (CHTO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHTO</td>
<td>2.187</td>
<td>0.538</td>
<td>31.74</td>
<td>0.645</td>
<td>25</td>
<td>0.0584</td>
</tr>
<tr>
<td>GHZO</td>
<td>1.819</td>
<td>0.666</td>
<td>29.41</td>
<td>0.202</td>
<td>50</td>
<td>0.0301</td>
</tr>
<tr>
<td>CHFO</td>
<td>2.754</td>
<td>0.514</td>
<td>33.33</td>
<td>0.396</td>
<td>75</td>
<td>0.0135</td>
</tr>
</tbody>
</table>

Sorbet dose=0.1 g; agitation speed=160 rpm; agitation time=4 h.
the experiments. Here the parameters studied were: flow-rate, bed depth and lab-bench mini-pilot scale As(III) removal.

**Flow-rate variation**

Three fixed adsorbent beds (particle size: 0.14 to 0.29 mm) each of volume 5.55 cm³ and a tap water sample spiked with As(III) (influent As(III) concentration=500 µg l⁻¹) were used. Down flow-rates were 80, 120 and 150 BV h⁻¹, respectively. The results (Figure 7) showed that ∼10,000, 7,000 and 5,500 BV of water with arsenic ≤10 ppb were obtained, respectively. Thus, it appears that the decrease in down-flow rate gives a greater volume of potable water with arsenic at a permissible level. This is due to the effect of an increase in contact time between sorbate and sorbent. The increase in contact time permits the sorbate to enter the bulk to a greater extent through pore diffusion. Though the flow rate was increased by 50 and 87.5% of the initial rate, respectively, the decrease in effluent BV of water was not found to be proportionately less. This agrees with the initial rapid uptake of As(III).

**Bed-depth variation**

Three adsorbent beds of depth 5.8, 8.7 and 11.6 cm and As(III) spiked (500 µg l⁻¹) tap water described above were used for the study. Here, the flow-rate of influent water was arbitrarily fixed at 400 ml h⁻¹. The results (Figure 8) showed that 9,000, 10,500 and 12,000 BV of water with arsenic ≤10 ppb were obtained. Thus, the results indicate that more water of a potable standard can be obtained with the increase in bed-depth if the flow-rate were kept constant. This is due to the increase in contact time between adsorbent and adsorbate.

**Lab bench mini-pilot scale study**

A fixed adsorbent bed of volume 30 cm³ and an As(III) spiked PCC tap water sample (As(III) content: 320 µg l⁻¹ and pH=7.5) were used for conducting these experiments. Down flow-rate of influent water was maintained at 33 to 34 BV h⁻¹. The results (Figure 9) showed that a fresh
CHTO column specified above gave water of ∼15,000 BV with arsenic < 10 ppb.

At this stage, the adsorbent bed was regenerated with 33.33 BV of 1.0(M) NaOH solution allowing a down-flow rate of 3.33 BV h⁻¹. The same solution was recycled thrice through the bed under identical conditions. Then the bed was made alkali free by washing with deionized water and used for the experiment again. Reuse of the regenerated bed in the column gave water of ∼11,500 BV with arsenic ≤ 10 ppb. Here, ∼20–25% less water of potable standard was obtained compared with that from a fresh bed in the column. This is agreed to the extent of regeneration reported elsewhere.

Regenerating the bed again as above, it was reused taking the water sample as specified above. Here, the regenerated bed in column gave potable water of 9,000 BV. Thus, using the same bed in column three times, a total of 35,500 BV of water were obtained. To avoid the disposal problem of arsenic-rich regenerates, arsenic was recovered (99.25%) as As₂S₃ by the method described in our earlier work (Manna et al. 2003).

6. The sorption phenomenon obeys the first-order Lagergren kinetic model and the data fit better with Langmuir than with the Freundlich isotherm.
7. Column regeneration up to ∼80% of arsenic(III) rich sorbent is possible by the cyclic use of 1.0(M) NaOH solution three times.
8. Reuse of a fixed-bed CHTO column after regeneration is found to decrease As(III) removal efficiency by 20–25% from a natural groundwater sample.

ACKNOWLEDGEMENTS

The authors are thankful to UGC (New Delhi) for financial support and also to the Head, Department of Chemistry, Presidency College, Kolkata for facilities. The authors wish to acknowledge Dr K. L. Ghatak for suggestions.

REFERENCES


First received 8 August 2003; accepted in revised form 23 July 2004