

## 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<sup>-1</sup> 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<sup>-1</sup>. 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<sub>3</sub><sup>-</sup>. 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<sup>-1</sup>) natural water are reported systematically. Lab-bench mini-pilot scale application of a fixed-bed (bed volume=30.0 cm<sup>3</sup>) CHTO column is reported at a down flow-rate of 33 to 34 B.V. (bed volume) h<sup>-1</sup> using an As(III) spiked (320 µg l<sup>-1</sup>) 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

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### 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<sub>2</sub>), realger (As<sub>4</sub>S<sub>4</sub>) 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<sub>2</sub>O<sub>3</sub> 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<sub>4</sub> 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 at 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:  $72.94 \text{ mg g}^{-1}$ ) 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,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{HPO}_4$  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  $\text{TiO}_2$ . The peak intensity of 80% at  $2\theta$  value of  $26^\circ$  indicates the crystalline nature of the oxide.

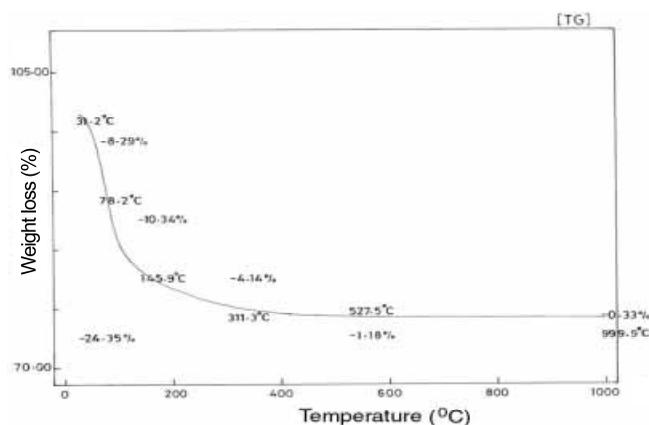


Figure 1 | Thermal gravimetric analysis of CHTO.

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  $\mu\text{m}$ . 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  $68.3^\circ\text{C}$ , which corresponds to the loss of physically adsorbed water, confirming the hydrous nature of the synthesized product. The sharp endoergic (downward) DTA peak at  $68.4^\circ\text{C}$  further supports this. A broad exoergic DTA peak (Figure 2) between  $68.4$  and  $200^\circ\text{C}$  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  $200^\circ\text{C}$  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:  $1.21 \text{ g cm}^{-3}$ ,



**Table 1** | Effect of pH on adsorption of As(III) at 30±2°C

As(III) loaded (mg)*	Initial pH	Final pH	Adsorption density of As(III) (mg g <sup>-1</sup> )
1.25	2	2.12–2.15	10.70–10.76
	3	3.24–3.27	10.85–10.90
	4	4.40–4.44	11.05–11.15
	5	5.65–5.72	11.20–11.24
	6	6.58–6.62	11.36–11.40
	7	6.85–6.89	11.40–11.42
	8	7.52–7.59	11.26–11.32
	9	8.50–8.57	11.14–11.20
	10	8.80–8.89	10.90–10.93
	12	10.85–10.92	8.40–8.44
2.50	2	2.21–2.23	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	6.80–6.83	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.

11.20±0.18 mg g<sup>-1</sup>) 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<sup>-1</sup>) 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 2** | Pre-drying of CHTO and effect on As(III) sorption at pH 7.0

Drying temperature (°C)	25	50	100	150	200	250	300	350	400	500
Adsorption density (mg g <sup>-1</sup> )	11.50±0.10	11.45±0.12	11.35±0.05	11.20±0.18	10.78±0.15	10.55±0.11	10.23±0.07	8.98±0.05	8.90±0.10	8.15±0.17

Drying time=1 h; CHTO dose used=0.1 g; agitation speed=160 rpm.  
 sorbate loaded=1.25 mg in 50 ml solution; agitation time=6 h.  
 Results replicate of three experiments. Adsorption density (mg g<sup>-1</sup>)=value±SD.

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<sup>-1</sup> (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 Ca<sup>2+</sup> (or Mg<sup>2+</sup>) 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<sup>-1</sup>) 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 Mn<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> and Pb<sup>2+</sup> 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<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> on sorption of the sorbate showed that F<sup>-</sup> did not interfere while the other anions had little effect. Adsorption density (mg g<sup>-1</sup>) 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<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> for As(III) sorption sites on CHTO is somewhat greater than that for either PO<sub>4</sub><sup>3-</sup> or SO<sub>4</sub><sup>2-</sup>, which is probably due to the presence of high levels of

**Table 3** | Time of equilibration and effect on As(III) sorption by CHTO at pH 7.0 and temperature of 30±2°C

Agitation time (h)	0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0	6.0
Adsorption density (mg g <sup>-1</sup> )	8.50±0.20	9.62±0.15	9.95±0.12	10.25±0.25	10.92±0.08	11.21±0.10	11.60±0.15	11.65±0.12	11.62±0.12

Sorbent dose=0.1 g; sorbate load=1.25 mg in 50 ml solution.  
 Agitation speed=160 rpm. Results replicate of three experiments.  
 Adsorption density (mg g<sup>-1</sup>)=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<sub>3</sub><sup>-</sup> 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<sub>ad</sub>) 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<sup>-1</sup>) 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<sub>ad</sub> for the

adsorbent are given in Table 5 compared with some of our earlier works (Manna *et al.* 1999, 2003). The comparative K<sub>ad</sub> 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  $\sqrt{t}$  (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.

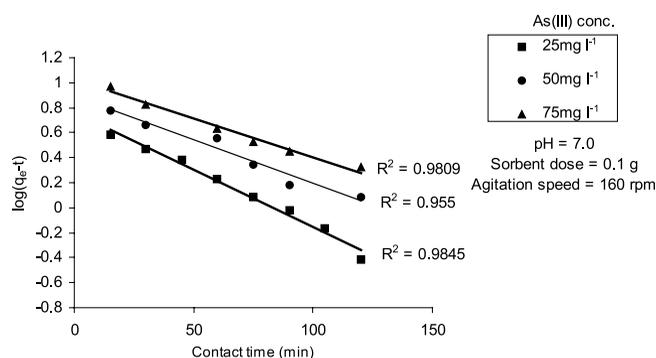
### Pore diffusion coefficient

The pore diffusion coefficient ( $D$ ) for intraparticle transport of As(III) sorption onto CHTO has been calculated

**Table 4** | Effect of some interfering ions on adsorption of As(III) by CHTO at pH 7.0

Interfering ion (I.I)	Mole ratio (I.I):As(III)	Adsorption density (mg g <sup>-1</sup> )
Mn <sup>2+</sup>	0.0273	10.67±0.02
	0.0546	9.81±0.10
	0.1365	9.62±0.05
	0.2732	9.25±0.10
Fe <sup>3+</sup>	0.0268	10.25±0.16
	0.0536	9.97±0.08
	0.1340	9.69±0.03
	0.2681	9.65±0.34
Cr <sup>3+</sup>	0.0288	11.02±0.01
	0.0578	10.84±0.03
	0.1452	10.87±0.06
	0.2883	10.40±0.10
Pb <sup>2+</sup>	0.0073	10.91±0.04
	0.0145	10.59±0.02
	0.0363	10.39±0.10
	0.0736	10.19±0.07
PO <sub>4</sub> <sup>3-</sup>	0.75	11.25±0.05
	1.50	10.90±0.07
	3.00	10.88±0.03
	4.50	10.50±0.15
SO <sub>4</sub> <sup>2-</sup>	4.67	10.62±0.03
	9.42	10.47±0.01
	14.23	10.37±0.05
	18.81	10.40±0.10
HCO <sub>3</sub> <sup>-</sup>	4.92	10.10±0.02
	9.84	9.56±0.08
	14.76	9.56±0.12
	19.68	9.50±0.10

Calcium, magnesium and fluoride showed no effect and are not given in the table. As(III) sorption density in the absence of any interfering ion=11.35±0.35. Initial As(III) load=1.25 mg in 50 ml solution; CHTO dose=0.1 g; experimental temperature=30±2°C.

**Figure 3** | Kinetic study of As(III) sorption by CHTO at 30±2°C.

using the following equation assuming spherical geometry for the adsorbent particles (Healfferich 1963; Bhattacharya and Venkobacher 1984)

$$t_{1/2} = 0.03r_0^2/D$$

where  $t_{1/2}$ =time of half sorption,  $r_0$ =mean radius of sorbent particles and  $D$ =pore diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>). Table 5 shows the calculated values for  $D$ , found to be in the range of 10<sup>-9</sup> to 10<sup>-12</sup> cm<sup>2</sup> s<sup>-1</sup> 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.

$$q_e = a_f c_e^{1/n} \quad (I)$$

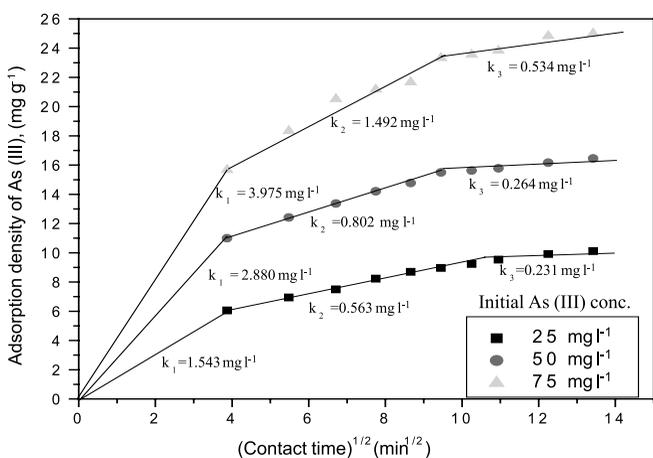
$$c_e/q_e = c_e/Q_0 + 1/(Q_0b) \quad (II)$$

where  $c_e$  (mg l<sup>-1</sup>) and  $q_e$  (mg g<sup>-1</sup>) are the concentration and adsorption density for As(III) at equilibrium, respectively.  $a_f$  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

**Table 5** | Adsorption rate constant ( $K_{ad}$ ) compared with some reported data, intraparticle diffusion rate constant ( $k_i$ ) and pore diffusion constant ( $D$ ) for As(III) sorption onto CHTO at  $30\pm 2^\circ\text{C}$ 

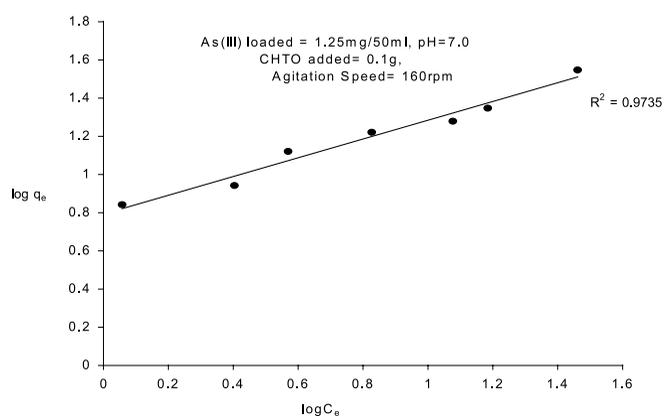
Initial As(III) conc. ( $\text{mg l}^{-1}$ )	Adsorption rate constant ( $K_{ad}$ ), $\text{min}^{-1}\times 10^{-2}$			Pore diffusion constant ( $D$ ) $\times 10^{-10}$ $\text{cm}^2 \text{s}^{-1}$ (for CHTO)	Intraparticle diffusion rate constant ( $k_i$ ), $\text{mg g}^{-1}, \text{min}^{-1/2}$ for CHTO		
	CHTO	CHFO	GHZO		$K_1$	$K_2$	$K_3$
25	1.842	—	—	33.991	1.543	0.563	0.231
50	1.833	1.163	1.512	38.524	2.880	0.802	0.264
75	1.811	1.154	1.483	44.452	3.976	1.492	0.534

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  $30\pm 2^\circ\text{C}$ .

high values of correlation coefficients ( $R^2$ ) indicating linear relationships, which confirm the applicability of both the adsorption isotherms. The  $R^2$  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).

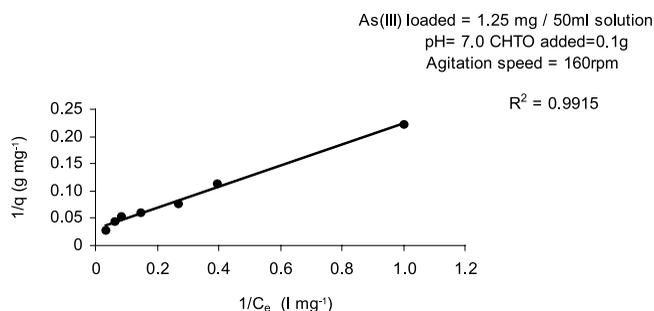
The values for the Freundlich and Langmuir constants for As(III) sorption at pH 7.0 clearly indicate that CHTO like other hydrous oxides should be a good adsorbing medium for As(III).  $1/n < 1$  supports the high As(III) sorption capacity and the value of  $b$  also indicates favourable As(III) sorption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

**Figure 5** | Freundlich adsorption isotherm of As(III) on CHTO at  $30\pm 2^\circ\text{C}$ .

The essential characteristics of the Langmuir isotherm may be expressed in terms of the dimensionless equilibrium parameter,  $R_L = 1/(1+bC_0)$  where  $C_0$ =initial adsorbate concentration ( $\text{mg l}^{-1}$ ). 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  $82.00\pm 1.00$  and  $77.50\pm 1.30\%$ , 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  $90.00\pm 0.80\%$  and  $82.50\pm 0.80\%$ , respectively. An increase



**Figure 6** | Langmuir 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  $\text{Na}^+$  than bigger  $\text{K}^+$ . The results of column regeneration by recycling 33.33 BV of 1.0(M) NaOH thrice (down flow-rate 3.3–3.4  $\text{BV h}^{-1}$ ) 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

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

pH	$7.40 \pm 0.25$
Hardness (as $\text{CaCO}_3$ )	$254 \pm 3.0$
Turbidity (NTU)	$5.10 \pm 0.50$
Dissolved oxygen	$6.65 \pm 0.35$
Biological oxygen demand (25°C)	$2.56 \pm 0.25$
Total dissolved solids	$810 \pm 3.8$
Total suspended solids	$4.12 \pm 0.3$
Iron	$0.25 \pm 0.05$
Manganese	$0.03 \pm 0.01$
Chloride	$210 \pm 7.0$
Sulphate	$84 \pm 3.0$
Nitrate	$10.2 \pm 1.0$
Phosphate	$0.07 \pm 0.01$
Bicarbonate	$117.0 \pm 3.0$
Fluoride	$0.38 \pm 0.04$

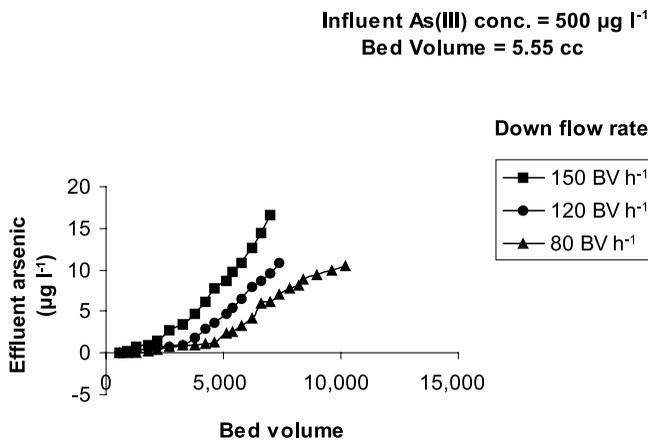
All values are in  $\text{mg l}^{-1}$ , except pH and turbidity.

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 6** | Adsorption constants and Langmuir parameter ( $R_L$ ) values at pH 7.0 and temperature 30±2°C

Adsorbent	Freundlich constants		Langmuir constants		Initial As(III) conc. ( $\text{mg l}^{-1}$ )	$R_L$ value (CHTO)
	$a_f$	1/n	$Q_0$ ( $\text{mg g}^{-1}$ )	b (l/mg)		
CHTO	2.187	0.538	31.74	0.645	25	0.0584
GHZO	1.819	0.666	29.41	0.202	50	0.0301
CHFO	2.754	0.514	33.33	0.396	75	0.0135

Sorbent dose=0.1 g; agitation speed=160 rpm; agitation time=4 h.



**Figure 7** | Flow rate variation on As(III) sorption by CHTO.

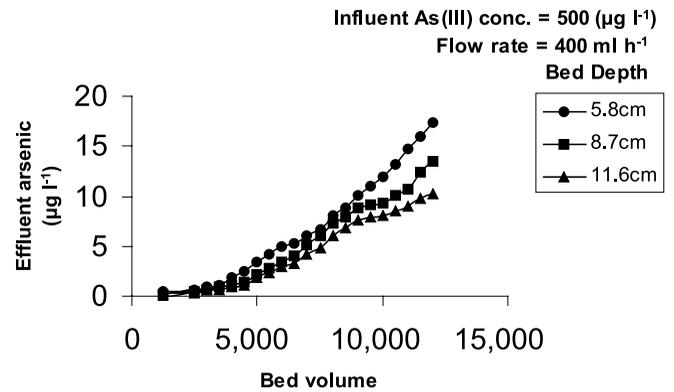
the experiments. Here the parameters studied were: flow-rate, bed depth and lab-bench mini-pilot scale As(III) removal.

### Flow-rate variation

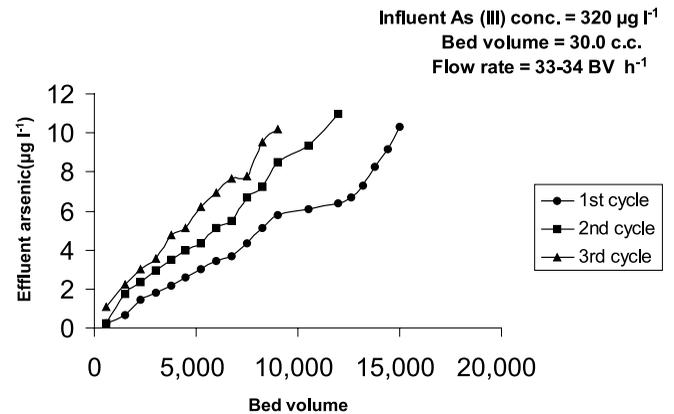
Three fixed adsorbent beds (particle size: 0.14 to 0.29 mm) each of volume 5.55 cm<sup>3</sup> and a tap water sample spiked with As(III) (influent As(III) concentration=500  $\mu\text{g l}^{-1}$ ) were used. Down flow-rates were 80, 120 and 150 BV h<sup>-1</sup>, respectively. The results (Figure 7) showed that ~10,000, 7,000 and 5,500 BV of water with arsenic  $\leq 10$  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  $\mu\text{g l}^{-1}$ ) tap water described above were used for the study. Here, the flow-rate of influent water



**Figure 8** | Sorption of As(III) by CHTO at different bed depth.



**Figure 9** | Lab bench scale removal of arsenic by fixed bed CHTO.

was arbitrarily fixed at 400 ml h<sup>-1</sup>. The results (Figure 8) showed that 9,000, 10,500 and 12,000 BV of water with arsenic  $\leq 10$  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 cm<sup>3</sup> and an As(III) spiked PCC tap water sample (As(III) content: 320  $\mu\text{g l}^{-1}$  and pH=7.5) were used for conducting these experiments. Down flow-rate of influent water was maintained at 33 to 34 BV h<sup>-1</sup>. 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<sup>-1</sup>. 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 As<sub>2</sub>S<sub>3</sub> by the method described in our earlier work (Manna *et al.* 2003).

## CONCLUSIONS

The findings of the laboratory bench scale tests have demonstrated the following:

1. Synthesized titanium (IV) oxide is purely crystalline and hydrated in nature.
2. Absolute As(III) sorption capacity of CHTO at pH 7.0 is very high (72–75 g kg<sup>-1</sup>), determined from 1,000 mg l<sup>-1</sup> of As(III) solution.
3. As(III) sorption decreases by a substantial amount when pre-dried CHTO at above 200°C is used.
4. Initial As(III) sorption onto CHTO is rapid. More than 70% of As(III) sorbed at half an hour although equilibrium time for maximum sorption is found to be 4.0 hours.
5. Some anions and cations, those commonly available in groundwater, decrease As(III) sorption to some extent at their possible high level of contamination.
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.

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