

Adsorption of arsenic from aqueous solution on synthetic hydrous stannic oxide

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Abstract

The hydrated stannic oxide (HSO) was synthesized and arsenic adsorption behaviour is reported. HSO is found to be amorphous, and stable thermally up to 700 °C. The adsorption of As(III) is much higher than As(V) in the drinking water pH (6.5–8.5) range. The time required for reaching equilibrium is 4.0 and 3.0 h, respectively for As(III) and As(V). The adsorption kinetic data obtained at pH 7.0 (± 0.1) and temperature 27(± 1) °C follow the pseudo-second-order kinetic model best ($R^2 > 0.98$). The analyzes of isotherm adsorption data by two parameter isotherm model equations show the order to obey: Langmuir > Freundlich > Temkin for As(III), and Langmuir > Temkin > Freundlich for As(V). The monolayer adsorption capacities (mg/g) obtained for As(III) and As(V) are 15.85 and 4.30, respectively. Excepting phosphate, other anions studied show no adverse effect on adsorption of As(III) onto HSO. A fixed bed HSO packed column (internal diameter 0.70 cm, bed height 3.7 cm and particle size 0.14–0.29 mm) generates 2400 and 450 BV of potable water ($As < 0.01$ mg/L), respectively, for As(III) and As(V) from arsenic spiked (1.0 mg/L) water samples at pH 7.0 (± 0.1), which indicated that HSO can be used as an efficient scavenger for As(III) from the contaminated water.

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1. Introduction

Occurrence of arsenic in ground water much exceeding the tolerance limit (10 $\mu\text{g/L}$) is a global problem [1], and posed an ever increasing degree of health hazard. The Bengal delta basin [West Bengal in India and Bangladesh] has become infested with this menace, and in some pockets of this region it has assumed a life-threatening proportion causing deaths of a good number of inhabitants. The arsenic content in ground waters as reported [1] is wide in range (West Bengal in India: <10–3200 $\mu\text{g/L}$, and Bangladesh: <0.5–2500 $\mu\text{g/L}$). The cause of accumulation of arsenic in ground water in this delta region is an anoxic environment around its alluvial deposits of geogenic arsenic pyrites and iron oxyhydroxide with adsorbed arsenic undergoing microbial reduction [2–5]. The aquifers thus become rich in this reduced As(III) along with Fe(II). The reported ratios of As(III)/As_(Total) at a depth of 30–40 m in these aquifers [5] are in the range of

0.6–0.9. This high ratio is a matter of great concern since As(III) has much greater combining affinity with the thiol (–SH) group of proteins.

Treatment of arsenic-contaminated ground water by surface adsorption method has been found to be simple and cost effective suitable for catering to the needs of this people of rural areas of third world countries like India and Bangladesh. The adsorbents studied so far are many and include amorphous iron hydroxide [6], hydrous ferric oxide [7], granular ferric hydroxide [8], ferrihydrite [9], red mud [10], activated alumina [11–13], iron oxide coated polymeric materials [14], iron oxide coated sand [15], Fe(III)–Si binary oxide [16], iron oxide impregnated activated alumina [17], blast furnace slug [18], iron–cerium bimetal oxide [19], iron-coated sponge [20], nano-scale zerovalent iron [21–23], sulfate modified iron oxide-coated sand [24] and hydrous ferric oxide incorporated into naturally occurring porous diatomite [25]. In our laboratory, we have used crystalline hydrous ferric oxide [26], crystalline hydrous titanium oxide [27], granular hydrous zirconium oxide [28] and iron(III)–tin(IV) binary mixed oxide [29] for arsenic removal. A pilot-scale run

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Nomenclature

a_1, a_2, b_1, b_2	constants of power function and simple Elovich equation
A, B	Temkin constants
b	Langmuir constant
BV	bed volume
C_0	initial adsorbate concentration (mg/L)
C_e	equilibrium adsorbate concentration (mg/L)
C_t	the concentration (mg/L) of adsorbate at any time, t
K_0	constant
K_2	pseudo-second-order rate constant
K_{ad}	pseudo-first-order rate constant
K_f	Freundlich constant
M	mass of HSO added (g/L)
n	Freundlich constant
pH_{ZPC}	zero point surface charge pH
pK_a	negative logarithm of dissociation constant
q_e	uptake capacity at equilibrium (mg/g HSO)
q_t	uptake capacity at time t (mg/g HSO)
R_L	separation factor
R^2	correlation coefficient
V	volume of solution (mL)
<i>Greek symbols</i>	
α	constant
θ_0	Langmuir constant (mg/g)

for removal of excess iron and arsenic from contaminated water using manganese dioxide and crystalline hydrous ferric oxide packed columns has also been reported [30] from our laboratory.

Literature survey revealed that there are some adsorbents which have greater affinity for As(V) than for As(III) both in the acid and drinking water pH range; but hydrous oxides of tetravalent metals clearly showed the opposite property as reported from our laboratory [28]. Since the underground aquifers at the depth of 30–40 m in the Bengal delta basin region are reported [5] to contain arsenic mainly as As(III), the objective of the present work is to develop adsorbents for preferential removal of As(III) from water, and offers still a frontier area of research work. As(III) exists as $As(OH)_3$ [$pK_{a1} = 9.2$] in the pH range of potable water and is a softer Lewis base than the anionic As(V). Sn(IV) [$4s^2 4p^6 4d^{10}$] is a softer Lewis acid than either Fe(III) or Ti(IV). So hydrated stannic oxide (HSO) is expected to have greater affinity for As(III) than for As(V).

With this view, the present paper reports the synthesis, characterization and systematic arsenic adsorption behaviour of hydrous stannic oxide (HSO). Finally, a fixed bed column adsorption test on arsenic removal from water on a lab-bench scale has also been reported.

2. Materials and methods

2.1. Preparation of adsorbent

Hydrous stannic oxide (HSO) was prepared by neutralizing 0.1 M sodium stannate with drop-wise addition of 0.1 M ammonium chloride solution. The white gel-like precipitate of stannic hydroxide formed was aged for ten days with mother liquor. Decanting the mother liquor, thereafter, the precipitate was washed with de-ionized water till alkali free. The filtered white mass was dried in an air oven at 50–60 °C. The dried mass when treated with cold water was broken into fine particles, and sieved to collect the particles ranged between 0.14 and 0.29 mm.

2.2. Arsenic solutions

A standard stock As(III) solution (1000 mg/L) was prepared by dissolving 0.1320 g of As_2O_3 (99.9% Aldrich, USA) in 10 mL 4% (w/v) NaOH, acidified with 2.0 mL concentrated HCl and then diluted to 100 mL with arsenic free de-ionized water. The working solutions of As(III) of desired concentrations were made by diluting the stock with 0.2% (v/v) HCl. The stock solution was prepared freshly after every three days and frozen to prevent oxidation. The standard stock As(V) solution (1000 mg/L) was also prepared by dissolving 4.1601 g of sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$, E. Mark, Germany) with arsenic free de-ionized water in to a 1000 mL volumetric flask. The working solutions of As(V) of a required concentration were made by diluting the stock with de-ionized arsenic free water and frozen.

2.3. Analytical methods

Total arsenic as well as As(III) species was analyzed by hydride generation atomic absorption spectrophotometer (Perkin-Elmer-3100) and UV-vis spectrophotometer (HITACHI model-3210). Total dissolved inorganic arsenic in water sample was determined by adding HCl (32%, v/v) and KI (10%, w/v) where As(V) was reduced to trivalent state, which was converted to arsine with 3% (w/v) $NaBH_4$. The arsine gas was carried over to the flame of atomic absorption spectrophotometer, and absorbance value was noted at 193.7 nm against blank, and compared with standard for arsenic concentration. As(III) in water sample was determined by selective reduction with 3% $NaBH_4$ to volatile arsine at pH 4.8 in acetate buffer. This method allows rapid determination of arsenic species down to 1 $\mu\text{g/L}$ with $\pm 4\%$ accuracy [31]. In spectrophotometric method, the generated arsine gas was adsorbed in silver diethyl dithiocarbamate (SDDC) (G.R., E. Marck) solution in chloroform solvent, and absorbance was measured at 535 nm against blank and compared with the standard curve [31]. Some common ions, viz., phosphate, sulfate, nitrate, chloride, fluoride and bicarbonate in water sample were estimated by ion-chromatography (IC) using standard method [31]. Stannic ion in solution was determined colorimetrically. Here, a definite volume (40.0 mL) sample solution was concentrated to 10.0 mL, and used for developing color in dithiol method [32].

X-ray diffraction (XRD) analysis of the synthetic oxide was conducted by the powder method with Philips PW 1830 generator. Thermo gravimetric (TG) and differential thermal (DT) analyzes of the adsorbent were recorded using a seterm analyzer in argon atmosphere at a heating rate of 20 °C/min over a temperature range of 30–1000 °C. Point of zero charge (pH_{zpc}) was determined from electrophoretic mobility (EM) of the oxide using a Zeta-Meter. The electrophoretic mobility of solid sorbent suspensions containing 0.02% solid in 0.01 (M) NaCl was determined at various pH. Surface area of the sorbent particles was measured by Brunauer–Emmett–Teller (BET) method by adsorption of N_2 gas at liquid N_2 temperatures using Micromeritics high-speed surface analyzer.

2.4. Batch experiments

2.4.1. pH effect

The effect of pH in a range from 2 to 10 on arsenic adsorption was conducted by mechanical agitation (250–260 rpm) at room temperature, 27 (± 1) °C. Here, 0.1 g HSO (particle size: 0.14–0.29 mm) was added with 50.0 mL aliquots of As(III) and As(V) solutions (5.0 and 10.0 mg As/L) taking separately in well capped 100 mL polythene bottles. The required initial pH (pH_i) of test solutions were adjusted using 0.1 (M) HCl and/or 0.1 (M) NaOH. Agitating the reaction mixtures for 5.0 h for both As(III) and As(V), the solutions were filtered using 0.45 μm membrane filter; and analyzed for residual arsenic and equilibrium solution pH (pH_f).

2.4.2. Adsorption kinetic studies

Adsorption kinetic experiments were performed by batch method at pH_i 7.0 (± 0.1) and room temperature, 27 (± 1) °C. Here, 50.0 mL solution of arsenic [concentrations (mg/L): 5.0 and 10.0] was taken in to 100 mL polythene bottles with 0.1 g HSO, and agitated (250–260 rpm) using a shaker. A pH electrode was inserted into the solutions 10 min before withdrawing of samples for pH measurement, and 0.1 (M) NaOH or 0.1 (M) HCl was added, if required, for pH adjustment (~ 7.0) during experimental run. The reaction mixtures including bottle were withdrawn at a time interval of 15 min from starting till the equilibrium reached. The filtered sample solutions were analyzed for arsenic.

2.4.3. Adsorption isotherm

Adsorption isotherm experiments were conducted at room temperature, 27 (± 1) °C and at pH 7.0 (± 0.1) by batch adsorption procedure as described above. Here, six different concentrations ranging from 1.0 to 10.0 mg/L were used separately each for As(III) and As(V). The agitation time and speed used were 5.0 h and 250–260 rpm, respectively, for equilibrium. The solution pH was adjusted twice in the middle (after 1.0 and 4.0 h of agitation) using 0.1 M HCl and/or 0.1 M NaOH solution. Similar intermediate pH adjustment was made by Jang et al. [25] for arsenic adsorption isotherm experiment using 250 rpm shaking speed. Residual arsenic was determined in the filtered sample.

2.4.4. Column test

The glass columns (internal diameter: 0.70 cm) were packed with HSO (particle size: 0.14–0.29 mm, $\text{pH} \sim 7.0$) up to a height of 3.7 cm. The laboratory tap water of Presidency College (PC) was spiked with As(III) and As(V) separately up to a level of 1.0 mg/L. The tap water used for sample preparation was the ground water of PC. The tap water composition [27] was found to be almost the representative of the field samples of arsenic-contaminated belt of West Bengal in India. The arsenic spiked PC tap water samples were passed with a down flow (flow rate: ~ 100 mL/h; contact time: ~ 35 s) direction to evaluate column efficiency for As(III) and As(V) removal.

3. Results and discussions

3.1. Physico-chemical characteristics of HSO

The X-ray diffraction analysis showed that the synthesized hydrous stannic oxide (HSO) was of amorphous variety. The thermal stability of the hydrous oxide is shown in Fig. 1. Thermo gravimetric (TG) analysis recorded 8.26% and 6.81% weight loss in drying temperature range below 190 and 190–700 °C, respectively. The weight loss below and above 190 °C corresponds to dehydration and phase transition of the oxide. The calculated weight loss of 4.22% on drying up to 110 °C was attributed to the irreversible loss of physically adsorbed water molecules, and that would be the moisture content of the hydrous oxide. This is confirmed from a broad endoergic DTA peak (Fig. 1) at 110 °C. The differential thermal analysis (DTA) showed no exoergic peak (Fig. 1), so the chemical reactions, viz., polymerizations or crystallizations did not take place on drying up to 700 °C. Electrophoretic mobility studies of the oxide suspensions at various pH values showed that pH_{zpc} of the synthetic oxide was 4.6 to 6.4. The wide range of pH_{zpc} value of HSO is presumably owing to the lower basicity of tin(IV). Thus, HSO could be a surface-active oxide. The anion and cation exchange properties of HSO were also reported [33] at pH below 4.6 and above 6.4, respectively.

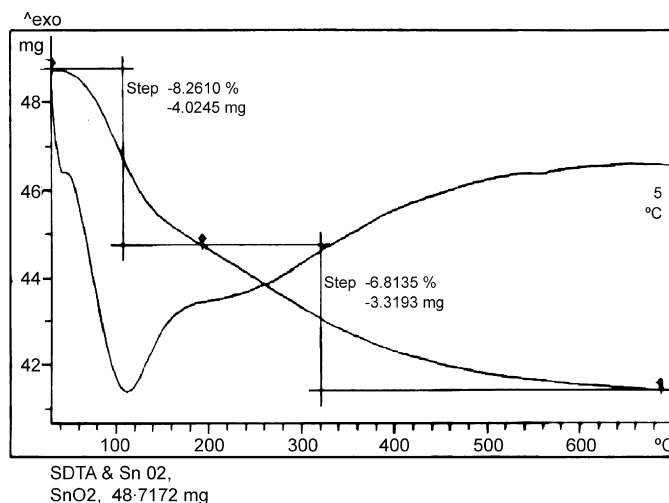


Fig. 1. Thermo gravimetric and differential thermal analysis of HSO.

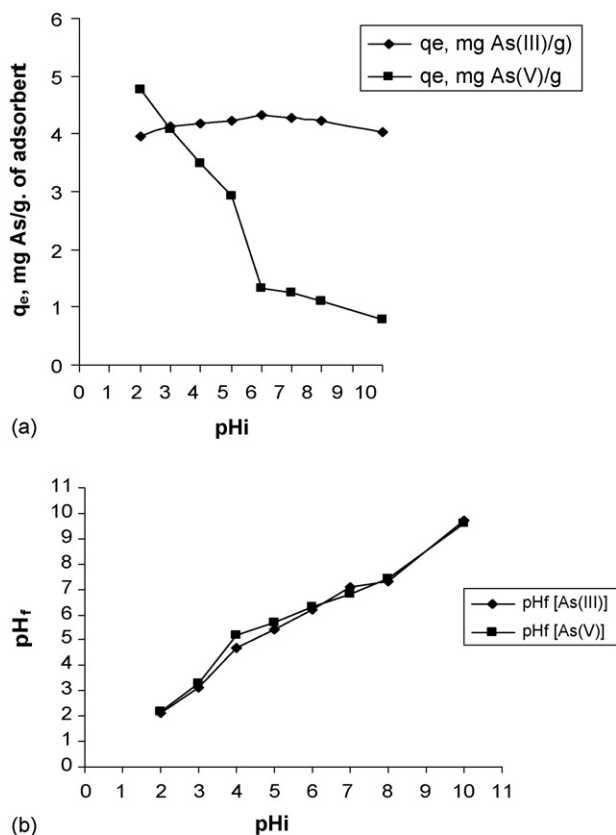


Fig. 2. (a) Effect of initial pH on arsenic adsorption by HSO at $27 (\pm 1) ^\circ\text{C}$ and (b) the plot of equilibrium pH (pH_f) vs. initial pH (pH_i).

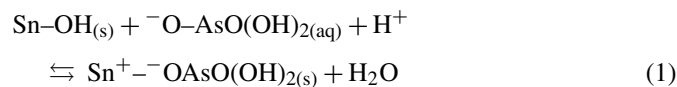
Some determined physico-chemical characteristics of HSO are: nature: amorphous; metal content: 61.60%; moisture content: 4.22%; bulk density: 1.38 g/cm^3 ; particle size: 0.14 to 0.29 mm; surface area: $140.8 \text{ m}^2/\text{g}$; pH_{zpc} : 4.6–6.4; solubility ($pH \text{ 6.5–8.0}$) = 0.02 mg/L .

3.2. Effect of pH

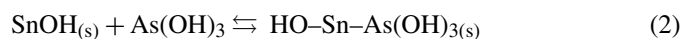
The effect of initial pH (pH_i) on adsorption of arsenic was determined by loading 5.0 mg As/g of adsorbent in the pH_i range of 2.0–10.0 and at temperature $27 (\pm 1) ^\circ\text{C}$. Fig. 2a demonstrates the efficiency of arsenic removal, and shows the increase in adsorption capacity (q_e , mg/g) for As(III) with increasing pH_i from 2.0 to 6.0, that remained almost same in the pH_i range 6.0 to 8.0 while that for As(V) decreased with increasing pH_i from 2.0 to 10.0. In general, the adsorption of As (III) is less pH dependent, while that of As(V) is highly pH dependent. The determined q_e -value for As(V) was significantly greater than As(III) at $pH_i = 2.0$, while that for As(III) was clearly greater than As(V) at $pH_i > 3.0$. Results (Fig. 2a) show that the percentage of As(V) adsorption was found to be about 12.0 to 13.0% of As(III) at $pH_i = 10.0$. Additionally, the equilibrium solution pH (pH_f) was found to increase (Fig. 2b) somewhat more for As(V) adsorption onto the HSO than the increase found for As(III) in the pH_i -range of 2.0–8.0.

The lower adsorption capacity for As(III) than As(V) of HSO at $pH_i = 2.0$ is due to the electrostatic hindrance between positive surface sites of the adsorbent [$pH_{zpc} = 4.6$ to 6.4] and $H^{\delta+}$ center of OH groups in $\text{As}(\text{OH})_3$ [$pK_{a1} = 9.2$]. For As(V), the positive surface sites of the adsorbent attracts the anionic adsorbate species [$pK_{a1} = 2.6$ and $pK_{a2} = 6.4$ of H_3AsO_4], and the adsorption capacity is high. With increasing pH_i , the positive charge density of adsorbent surface decreases and, therefore, the adsorption of non-ionic As(III) increases due to decrease in electrostatic hindrance while that of As(V) decreases due to decreasing electrostatic attraction. At $pH_i \sim 6.0$, HSO surfaces are to be negative and the As(V) anion being repelled due to like nature of charge, and the adsorption capacity for As(V) is about 50% less than that obtained at $pH_i = 5.0$. In contrast, that decrease for As(III) adsorption was not found, because the earlier noted adsorptive force persists up to $pH_i = 8.0$. At $pH_i > 8.0$, the less adsorption capacity of adsorbate ions are obviously due to (i) increase in electrostatic hindrance between like charges on adsorbent and adsorbate, and (ii) increase in competing OH^- concentration for sorption sites. Thus, the adsorption of As(III) and As(V) onto HSO takes place with different mechanisms.

The high value of As(III) adsorption data in the pH_i range of 4.0–8.0 resembled closely to our earlier studies [26,28]. The present observation on As(III) adsorption is similar to the literature available reports made by other workers using different adsorbents [6,14,16]. However, the pH_i value for maximum As(V) adsorption differ from the reports made by others [11,16,26]. The lower pH_i value for high arsenic adsorption compared to other literature available data may be due to the presence of $4d^{10}$ configuration in valence shell of the metal ion in HSO. The mechanisms for As(III) and As(V) adsorption are similar to that reported by others. In addition, As(V) adsorption at $pH_i \leq 6.0$ can be attributed by ligand (or anion) exchange [33] phenomenon. This supports the increase in pH of equilibrium solution.



The adsorption capacity for As(V) was very high at $pH_i = 2.0$ despite some solubilization loss of the HSO (0.03 mg/L) at that pH_i , because the anion-exchange property increases with decreasing pH. The high adsorption capacity of HSO for As(III) may be due to soft Lewis acid–base type interaction, where $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ (Sn^{4+} , a $4d^{10}$ species) functions as soft Lewis acid and $\text{As}(\text{OH})_3$ a soft Lewis base, giving a surface complex. Other workers, however, have earlier reported the probability of surface complex formation without specifying the stabilizing interaction.



where $\text{SnOH}_{(s)}$ stands for solid HSO in noted two adsorption reactions (Eqs. (1) and (2)) for mechanisms.

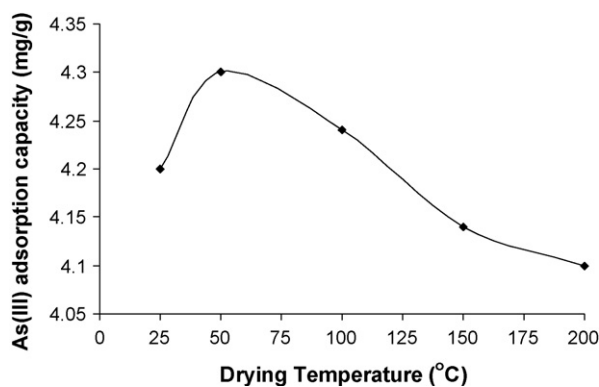


Fig. 3. Effect of drying temperature of adsorbent on As(III) adsorption at pH 7.0 (± 0.1).

3.3. Effect of drying temperature

The synthetic HSO was dried for an hour at the temperatures 25, 50, 100, 150 and 200 °C separately, and used for As(III) adsorption. Results (Fig. 3) show a small increase in adsorption capacity of As(III) when the drying temperature was increased from 25 to 50 °C, and that, thereafter, decreased slowly with increasing drying temperature of adsorbent. This indicates the increase of surface active sites for As(III) adsorption with increasing drying temperature from 25 to 50 °C which is due to the loss of physically attached (H-bonded) water molecules from the surface and, increases availability of surface active OH groups for arsenic adsorption. The decrease in adsorption capacity with increasing temperature for drying above 50 °C is due to the loss of surface active OH sites as water which agrees well with the loss of weight in thermal analysis (Fig. 1). Similar results were reported for As(III) adsorption using crystalline hydrous titanium oxide [27]. In contrast, crystalline hydrous ferric oxide showed an increase in arsenic adsorption capacity with increasing temperature for drying up to 300 °C [26]. Thus, it can be suggested that HSO, dried at 50 °C, could be used for As (III) removal.

3.4. Kinetic modeling

Fig. 4a and b show the time dependent arsenic adsorption data at pH 7.0 (± 0.1) and temperature 27 (± 1) °C. For the initial arsenic loads 2.5 and 5.0 mg per g adsorbent, the adsorption capacities (mg/g) nearly obtained were 1.80 and 3.33, 2.30 and 3.96, and 2.49 and 4.26 for As(III); and those were 0.47 and 0.74, 0.56 and 1.00, and 0.68 and 1.09 for As(V), respectively, at 1, 2 and 4 h of contact. The results show that the initial rate of adsorption was fairly rapid for both As(III) and As(V). ~70% of the adsorbed amount took place in an hour of agitation and, the remaining ~30% adsorption took place taking additional 3.0 and 2.0 h. That is, the time required for reaching adsorption equilibrium was 4 h for As(III), while that was 3 h for As(V). Results show (Fig. 4a and b) that the adsorption of As(V) onto HSO is faster than As(III) which is similar to the observation reported by Raven et al.[9]. However, the equilibrium time obtained in

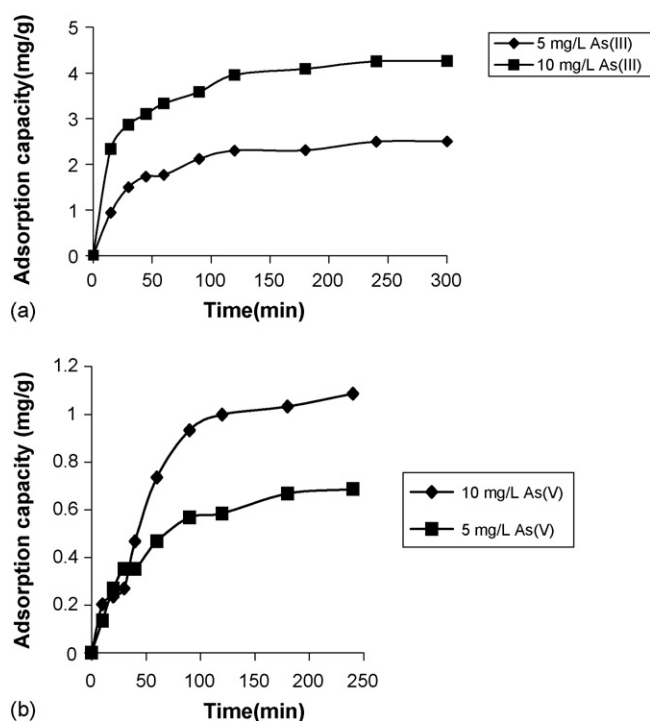


Fig. 4. Adsorption kinetic data for: (a) As(III) at pH 7.0 (± 0.1) and at 27 (± 1) °C and (b) As(V) at pH 7.0 (± 0.1) and at 27 (± 1) °C.

the present case is found to be less compared to the studies made using some other oxides [26,27].

The data shown in Fig. 4a and b are used for analysis taking the linear form of the following kinetic model equations:

The pseudo-first-order equation [34]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_{ad}}{2.303} \right) t \quad (3)$$

where q_e and q_t are the adsorption capacity (mg/g) at equilibrium and at time, t , respectively; and K_{ad} the pseudo-first-order rate constant (time^{-1}).

The pseudo-second-order equation [35]:

$$\left(\frac{t}{q_t} \right) = \left(\frac{1}{K_2 q_e^2} \right) + \left(\frac{1}{q_e} \right) t \quad (4)$$

where both q_e and q_t have the same meaning as above. K_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{time}^{-1}$).

The Bhattacharya–Venkobachar equation [36]:

$$\ln(1 - U(t)) = K_B t \quad (5)$$

where $U(t) = C_0 - C_t/C_0 - C_e$, where C_0 , C_t and C_e are the concentrations (mg/L) at $t=0$, t and equilibrium, respectively.

The power function equation [37]:

$$\log q_t = \log a_1 + b_1 \log t \quad (6)$$

where a_1 and b_1 are some constants, q_t the adsorption capacity (mg/g) at time, t .

The Elovich equation [38]:

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t = a_2 + b_2 \ln t \quad (7)$$

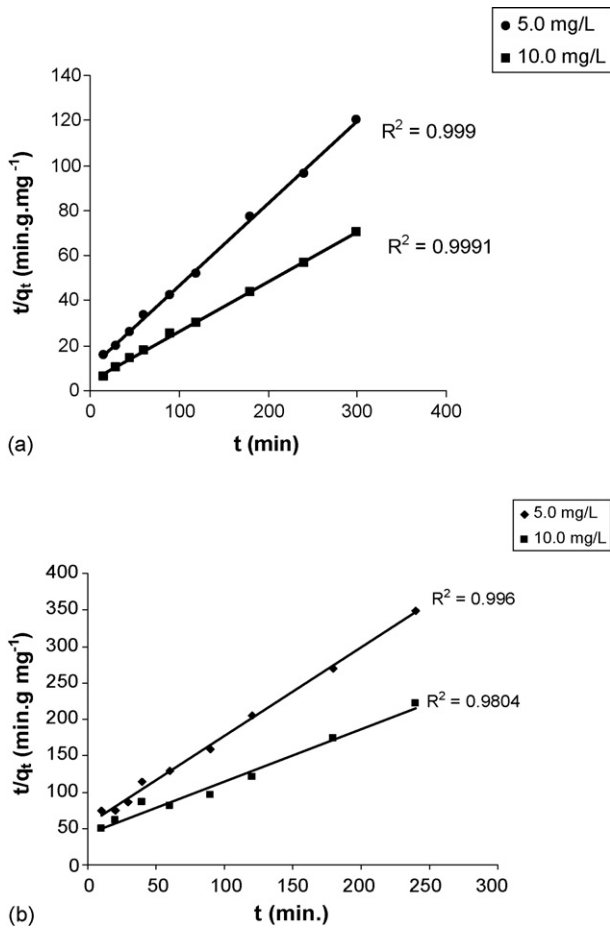


Fig. 5. Pseudo-second-order plot of: (a) As(III) adsorption at pH 7.0 (± 0.1) and at 27 (± 1) °C and (b) As(V) adsorption on HSO at pH 7.0 (± 0.1) and at 27 (± 1) °C.

where α and β have usual signification of the model equation, and $a_2 = \beta \ln(\alpha\beta)$ and $b_2 = \beta$.

The estimated kinetic models and related parameters with linear regression coefficient (R^2) are shown in Table 1. The present kinetic adsorption data for both As(III) and As(V) on HSO describe the pseudo-second-order model (Fig. 5a and b)

best ($0.98 < R^2 < 1.0$) while, those also describe the pseudo-first-order model well ($0.97 < R^2 < 0.98$). Other models tested describe the present kinetic data, in general, poorly. The simple Elovich equation explained the kinetic data fairly well. The regression coefficient (R^2) values obtained for As(III) are 0.9582 and 0.9919, and those for As(V) are 0.9932 and 0.9210, respectively for the studied initial arsenic loads 2.5 and 5.0 mg/g. The Bhattacharya–Venkobachar [36] kinetic model equation describes the kinetic data well ($R^2 = \sim 0.98$) obtained for 2.5 mg/g of As(III) while the power function kinetic model equation describes the kinetic data well ($R^2 = \sim 0.98$) obtained 5.0 mg/g of As(III). However, no systematic order is found for fitting the kinetic data with analyzed model equations. As the present kinetic data describe the pseudo-second-order model best, thus the arsenic adsorption onto HSO obeyed the pseudo-second kinetics.

3.5. Intra-particle (pore) diffusion

The adsorption process onto an adsorbent follows three steps, viz., film diffusion, macro and micro-pore diffusions phenomena. The slowest of the three-step controls the overall rate process. Generally, intra-particle (pore) diffusion is the rate-limiting step in batch process, while for a continuous flow system film diffusion is more likely to be the rate-limiting step. The intra-particle (pore) diffusion rate constant (k_i) can be defined as the gradient of the plot of sorption density versus square root of time [39,40]. The plot of q_t versus $t^{1/2}$ was found to be linear for a wide range of contact time for arsenic sorption indicating the presence of external mass transfer (Fig. 6). It shows three separate regions: initial part of the curve is attributed to mass transfer [41] (slope k_1) taking place with boundary layer (film) diffusion, while the final linear portion(s) of the curve indicate intra-particle diffusion (slope k_2 and k_3). The values of k_2 and k_3 indicate that the pores are micropore and intra-particle diffusional resistance is due the micro pores only which is more pronounced for large As(V) compared to small As(III) species. This is evident from smaller values of k_2 and k_3 for As(V). Moreover, pore sorption of As(III) and As(V) are concentration dependent and

Table 1
Adsorption kinetic model equations with different parameters evaluated on adsorption of arsenic by HSO at pH 7.0 (± 0.1) and at 27 (± 1) °C

Adsorption kinetic model equations	Parameters	Initial As(III) loads (mg/g of adsorbent)		Initial As(V) loads (mg/g of adsorbent)	
		2.5	5.0	2.5	5.0
Pseudo-first order: $\log(q_e - q_t) = \log q_e - K_{ad}/2.303t$	$K_{ad} \times 10^2$ (min^{-1}) R^2	1.36 0.9782	1.49 0.9822	1.75 0.9719	3.09 0.9723
Pseudo-second-order: $t/q_t = 1/K_2q_e^2 + t/q_e$	$K_2 \times 10^2$ ($\text{g}/(\text{mg min})^{-1}$) R^2	1.35 0.9990	1.16 0.9991	2.63 0.9960	1.20 0.9804
Bhattacharya–Venkobachar: $\ln(1 - U(t)) = K_B t; U(t) = C_0 - C_t/C_0 - C_e$	K_B (min^{-1}) $\times 10^2$ R^2	1.50 0.9811	1.36 0.8798	0.20 0.8522	1.88 0.9559
Power function: $\log q_t = \log a_1 + b_1 \log t$	a_1 b_1 R^2	0.4533 0.3284 0.9065	1.3478 0.2116 0.9811	0.0599 0.4776 0.9157	0.0432 0.6286 0.9098
Simple Elovich: $q_t = a_2 + b_2 \ln t$	a_2 b_2 R^2	-0.4181 0.5467 0.9582	0.4402 0.7067 0.9919	-0.2635 0.1780 0.9932	-0.7072 0.3383 0.9210

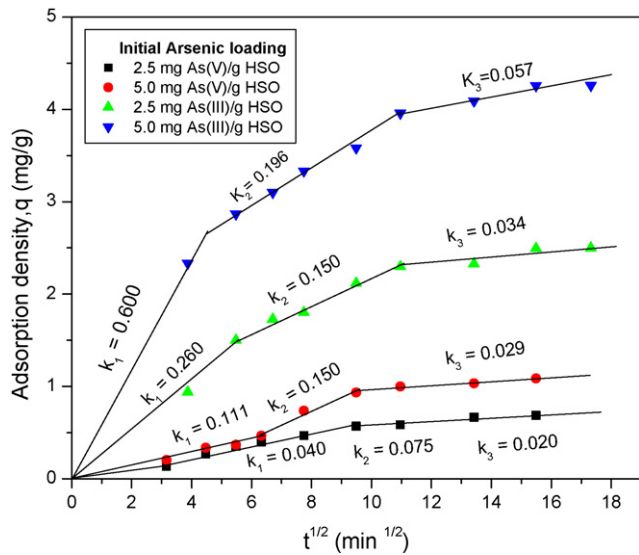


Fig. 6. Intra-particle diffusion rate constants (k_i , $\text{mg g}^{-1} \text{min}^{-1/2}$) of arsenic adsorption at pH 7.0 (± 0.1) and at 27 (± 1) °C.

the rate of pore diffusion increases with increasing concentration.

The Bangham's equation, furthermore, as suggested by Aharoni and Ungarish [42] (Eq. (8)) has been applied for verifying the pore-controlled adsorption phenomena,

$$\log \left(\frac{\log C_0}{C_0 - q_t m} \right) = \log \left(\frac{K_0 m}{2.303 V} \right) + \alpha \log t \quad (8)$$

where C_0 is the initial As(III) concentration (mg/L), V the volume of solution (mL), m the mass of adsorbent (g/L), q_t the amount of adsorbate retained in solid at time t , α and K_0 are constant. The plots of $\log(\log C_0)/(C_0 - q_t m)$ versus $\log t$ (Fig. 7a and b) obtained for As(III) and As(V) adsorption data show better correlation coefficient values for As(III) ($R^2 = 0.97-0.99$) than for As(V) ($R^2 = 0.73-0.75$). This supports the previous conclusion that the adsorption kinetics for the As(III) is more pore-diffusion controlled than As(V). This is presumably due to larger size of As(V) than As(III) in aqueous solution that hindered to enter into the pore.

3.6. Isotherm envelope

Fig. 8a and b show the equilibrium isotherm data for arsenic at pH 7.0 (± 0.1) and temperature 27 (± 1) °C. The following linear isotherm model equations are used for analyzing the equilibrium adsorption data of As(III) onto HSO:

Freundlich equation [43]: $q_e = k_f C_e^{1/n}$. The linear form of the equation is:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (9)$$

Langmuir equation [44]: $q_e = (\theta_0 b C_e)/(1 + b C_e)$. The linear form of the equation applied for isotherm data analysis is:

$$\frac{1}{q_e} = \frac{1}{\theta_0 b C_e} + \frac{1}{\theta_0} \quad (10)$$

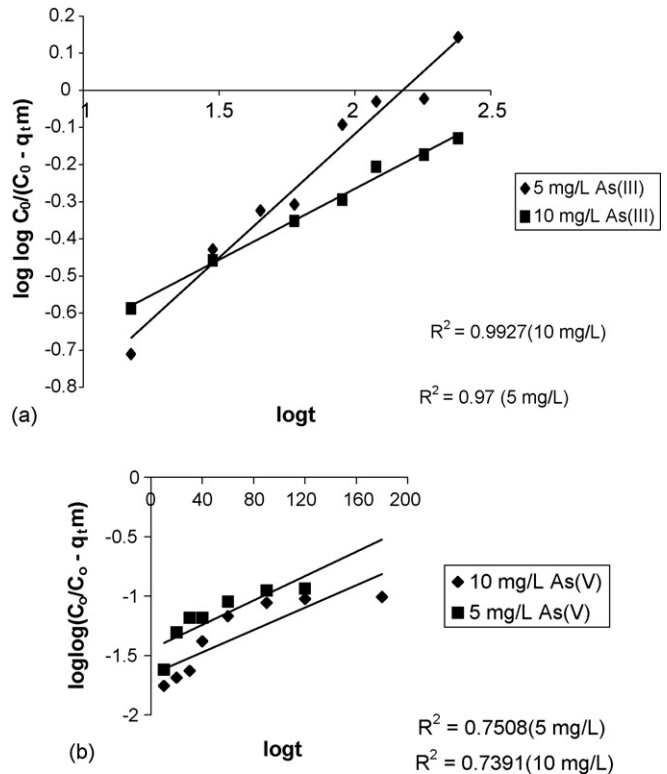


Fig. 7. Pore diffusion controlled adsorption kinetics of: (a) As(III) at pH 7.0 (± 0.1) and at 27 (± 1) °C and (b) As(V) at pH 7.0 (± 0.1) and at 27 (± 1) °C.

The Temkin isotherm equation applied for isotherm analysis in the following form [45]:

$$q_e = A + B \log C_e \quad (11)$$

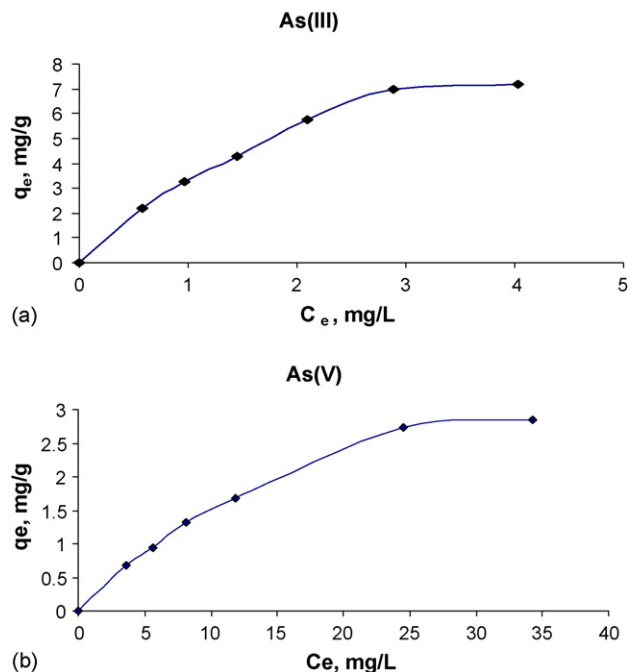


Fig. 8. Equilibrium isotherm data for: (a) As(III) adsorption at pH 7.0 (± 0.1) and 27 (± 1) °C and (b) As(V) adsorption at pH 7.0 (± 0.1) and 27 (± 1) °C.

Table 2
Estimated isotherm parameters for As(III)-sorption onto HSO at pH 7.0 (± 0.1) and at 27 (± 1) °C

	Estimated isotherm parameters	
	As(III)	As(V)
Langmuir		
R^2	0.9850	0.9707
θ_0 (mg/g)	15.850	4.303
b (L/mg)	0.2727	0.0488
Freundlich		
R^2	0.9720	0.8935
K_f	3.548	0.1521
n	1.569	1.0739
Temkin		
R^2	0.8069	0.9553
A	4.2472	-0.928
B	4.9862	2.4739

where q_e is the amount adsorbed at equilibrium (mg/g) and C_e the equilibrium concentration of adsorbate in solution (mg/L), K_f and n are the Freundlich constants corresponding to adsorption capacity and adsorption intensity, respectively; θ_0 and b are Langmuir constants related to maximum monolayer capacity and energy of adsorption, respectively; A and B are Temkin constants.

The isotherm parameters and linear regression coefficient (R^2) values obtained from the linear plots are shown in Table 2. The best-fit plots are shown in Fig. 8a and b. The results (Table 2) obtained from the isotherm analysis indicated that the Langmuir model describes the As(III) and As(V) adsorption isotherm data onto HSO best. The R^2 values were of 0.9850 and 0.9707 for As(III) and As(V), respectively. The order of fitting of the present data with the two parameter isotherm models is: Langmuir > Freundlich > Temkin for As(III), and Langmuir > Temkin > Freundlich for As(V). The Langmuir isotherm model describes the adsorption data for As(III) better than for As(V). Similar order on the fitting of the As(III) adsorption data was reported by Zeng [16] and Raven et al. [9] at pH 6.5 and 9.2, respectively. The better fit of As(III) adsorption data with the Langmuir isotherm was reported earlier [27,28]. The different trend found in describing the adsorption data with two-parameter isotherm models suggests different adsorption mechanisms for As(III) and As(V) adsorption onto HSO (Fig. 9).

The evaluated values for mono-layer adsorption capacity (θ_0) and adsorption energy (b) from the Langmuir isotherm plots show (Table 2) that the values for As(III) are much higher than for As(V). The higher values of the Freundlich and Temkin constants for As(III) compared to As(V) also support the fact that HSO has much greater affinity for the lower valent species at pH 7.0 (± 0.1). This agreed well to the results (Fig. 2a) obtained in the studies of pH effect.

Despite well-fit of adsorption data with used three different isotherm models, yet it can not high light the mechanistic implications. However, the dimensionless parameter, R_L [$=1/(1 + C_0b)$] [46], where b is the Langmuir constant and C_0 is the initial adsorbate concentration, can predict whether the

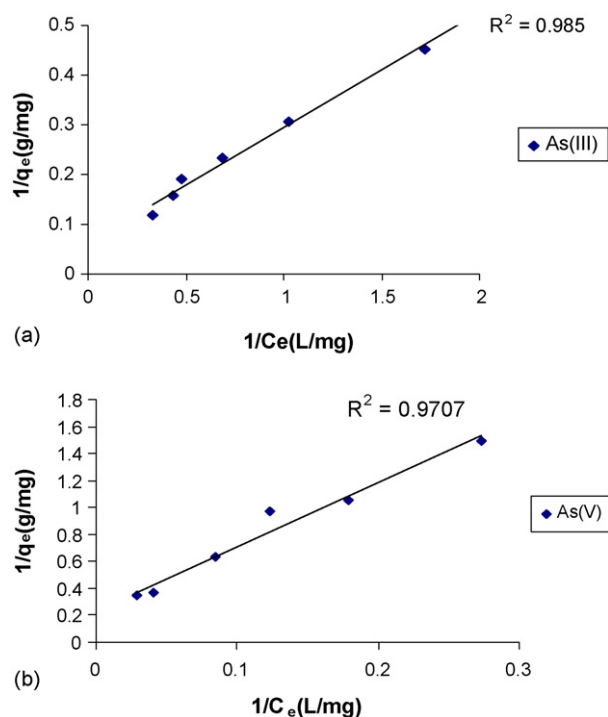


Fig. 9. Langmuir isotherm plot of: (a) As(III) at pH 7.0 (± 0.1) and at 27 (± 1) °C and (b) As(V) at pH 7.0 (± 0.1) and at 27 (± 1) °C.

adsorption is favorable or unfavorable. The calculated R_L -values for a range of initial concentrations (1.0–20.0 mg/L) of adsorbates are found to lie between 0 and 1.0, and indicate the favorable adsorption of both arsenic species onto HSO at pH 7.0 (± 0.1). The R_L -values for As(III) are found always lower than those for As(V) suggested the more adsorption favorability of the reduced arsenic compared to that of the oxidized species.

3.7. Adverse effect of some anions

The adverse effect of some anions (commonly found in groundwater) on As(III) adsorption onto the adsorbent were studied in the pH range 5.0–8.0. The studied sulfate, nitrate, chloride and fluoride ions show no significant interference while phosphate ion shows (Fig. 10) notable effect on As(III)-adsorption, particularly at higher phosphate concentrations. The arsenic(III) removal was found to decrease from 87.86 to 79.30%

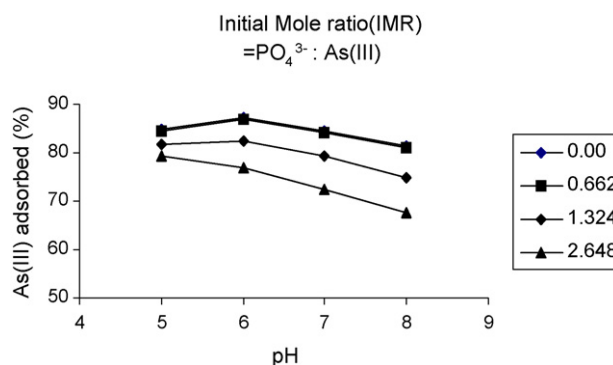


Fig. 10. Effect of phosphate on As(III) adsorption by HSO.

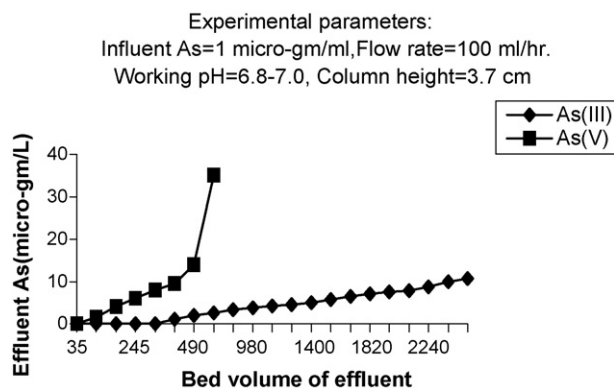


Fig. 11. As(III) and As(V) in effluent of HSO column.

at pH 5.0, and 84.52 to 67.50% at pH 8.0, when the mole ratio of PO_4^{3-} :As(III) was increased from 0.662 to 2.648. The phosphate mass balance for these experiments confirmed that the PO_4^{3-} ions adsorbed but barely on HSO probably through the formation of surface complexes with surface hydroxyl groups [47,48] reported similar significant adverse effect of phosphate on As(III) adsorption onto ferrihydrite. This indicates that the adsorbent, HSO can be used efficiently for As(III) removal from contaminated groundwater when phosphate concentration in that water is low.

3.8. Column study

The results (Fig. 11) obtained on the arsenic removal using fixed bed adsorbent columns show that the break-through and exhaustion point ($10 \mu\text{g/L}$ As in effluent) for As(V) were 120 and 450 bed volumes (BV), while those for As(III) were 400 and 2400 BV, respectively. The early attainment of break-through as well as exhaustion point clearly supported the obtained results that HSO has strong affinity for As(III) compared to that of As(V) in the drinking water pH range, and HSO can be used effectively in removing predominated As(III) species of the contaminated ground water of Bengal delta basin. In contrast, Joshi and Chaudhuri [49] reported that iron oxide coated sand removes both As(III) and As(V) with almost equal efficiency; and a simple fixed bed unit was treated about 160–190 BV of water containing $1000 \mu\text{g/L}$ arsenite and 150–165 BV of water with $1000 \mu\text{g/L}$ arsenate. Clifford [50] obtained 300 and 2300 BV of treated waters up to the As(III) and As(V) level of $<10 \mu\text{g/L}$ from the influent (As(III) and As(V) concentration: $100 \mu\text{g/L}$) water separately using activated alumina column at pH 6.0. Comparing the present results with the results reported by Joshi and Chaudhuri [49] and also by Clifford [50] have revealed that HSO is a better adsorbent for scavenging As(III) for the contaminated ground water treatment of Bengal delta basin of the river 'Ganga'.

3.9. Cost estimation of HSO

The cost (per kg) of raw materials used was $\sim\$6.0$ (for ordinary sodium stannate) and $\sim\$2.5$ (for ordinary ammonium chloride). Adding 10% additional with the above cost, the cost

for the preparation of HSO is $\sim\$9.35$. This cost could be reduced up to 50% if sodium stannate be prepared from waste metallic tin materials.

4. Conclusion

Hydrous stannic oxide (HSO), an amorphous variety, showed greater adsorption affinity for the As(III) than for As(V). The adsorption of As(III) was found almost pH insensitive, and maximum adsorption took place in the pH range of 3.0–8.0, whereas that of As(V) was highly pH sensitive and maximum adsorption took place at pH <3.0. There is a small change of As(III)-adsorption when HSO used was pre-dried up to the temperature of 200°C . The adsorption kinetic data for As(III) and As(V) at pH 7.0 (± 0.1) and at temperature $27 (\pm 1)^\circ\text{C}$ described the pseudo-second-order kinetic equation best. The As(III) and As(V)-adsorption equilibrium reached in 4.0 and 3.0 h, respectively, and adsorption isotherm data described the Langmuir isotherm model best. The competing ions, viz., sulfate, nitrate, chloride and fluoride showed no adverse effect on As(III)-adsorption up to their permissible concentration levels in groundwater whereas the phosphate ion showed a significant interference on As(III)-adsorption in the drinking water pH range. A fixed bed HSO column was produced 2400 and 450 BV of potable water (As content $<0.01 \text{ mg/L}$) for As(III) and As(V), respectively from the contaminated water (1.0 mg As/L). Thus, HSO can be used as an efficient adsorbent for more toxic and prevalent As(III) species from groundwater.

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