



Arsenic removal using hydrous nanostructure iron(III)–titanium(IV) binary mixed oxide from aqueous solution

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ABSTRACT

The synthetic bimetal iron(III)–titanium(IV) oxide (NHITO) used was characterized as hydrous and nanostructured mixed oxide, respectively, by the Fourier transform infra red (FTIR), X-ray diffraction (XRD) pattern and the transmission electron microscopic (TEM) image analyses. Removal of As(III) and As(V) using the NHITO was studied at pH 7.0 (± 0.1) with variation of contact time, solute concentration and temperature. The kinetic sorption data, in general, for As(III) described the pseudo-first order while that for As(V) described the pseudo-second order equation. The Langmuir isotherm described the equilibrium data (303 ± 1.6 K) of fit was well with the Langmuir model. The Langmuir capacity (q_m , mg g^{-1}) value of the material is $85.0 (\pm 4.0)$ and $14.0 (\pm 0.5)$, respectively, for the reduced and oxidized species. The sorption reactions on NHITO were found to be endothermic and spontaneous, and took place with increasing entropy. The energy (kJ mol^{-1}) of sorption for As(III) and As(V) estimated, respectively, is $9.09 (\pm 0.01)$ and $13.51 (\pm 0.04)$. The sorption percentage reduction of As(V) was significant while that of As(III) was insignificant in presence of phosphate and sulfate. The fixed bed NHITO column ($5.1 \text{ cm} \times 1.0 \text{ cm}$) sorption tests gave 3.0, 0.7 and 4.5 L treated water (As content $\leq 0.01 \text{ mg L}^{-1}$) from separate As(III) and As(V) spiked ($0.35 \pm 0.02 \text{ mg L}^{-1}$) natural water samples and from high arsenic ($0.11 \pm 0.01 \text{ mg L}^{-1}$) ground water, respectively when inflow rate was (0.06 L h^{-1}).

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1. Introduction

Occurrence of arsenic in ground water much exceeding the tolerance limit (0.01 mg L^{-1}) 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. Accumulation of excess arsenic in ground water in this delta region is presumably due to the reduction of geogenic arsenopyrites and iron oxyhydroxide with adsorbed arsenic in anoxic environment [2–4], and the aquifers thus become rich in this reduced As(III) with Fe(II). The ratios of As(III)/As_(Total) at a depth of 30–40 m reported in these aquifers are in the range of 0.6–0.9 [4], which is a matter of great concern since As(III), more toxic than As(V), has much greater combining affinity with the thiol (–SH) part of the protein due to soft–soft acid–base reaction.

Several methods namely coagulation–filtration, surface sorption, membrane filtration, ion exchange, etc. had been tested to

reduce arsenic level below the tolerance value; and the surface sorption has been found to be an alternative cost effective option for the third world countries like India and Bangladesh. The surface sorption property of many natural, synthetic and surface modified materials including biomasses had been used for arsenic removal studies [5–24] including the synthetic materials developed and used for arsenic removal from our laboratory [18–23].

Zhang [25] demonstrated an overview on the use of nano-size iron particle for environmental remediation. The recent increasing use of nanostructured materials for arsenic removal studies [26–30] has encouraged us for synthesizing nanostructured oxide materials for application in arsenic removal. Literature showed the maximum use of iron(III) oxide in this field. Thus, the incorporation of some other metal ions into the lattice structure of iron(III) oxide might be the good material for the sorption science. Therefore, the present work takes attempt to synthesis and use of nanostructured hydrous iron(III)–titanium(IV) bimetal mixed oxide agglomerates for the arsenic sorption studies, because titanium(IV) incorporated iron(III) oxide agglomerate might have enhanced material properties namely surface sorption, photo-induced catalysis, etc.

Thus, the communication herein reports (i) the synthesis with characterization of hydrous iron(III)–titanium(IV) bimetal mixed

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Nomenclature

C_0	initial sorbate concentration (mg L^{-1})
C_e	equilibrium sorbate concentration (mg L^{-1})
C_s	solid phase solute concentration (mg g^{-1})
C_L	liquid phase solute concentration (mg g^{-1})
D_F	film diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
D_P	pore diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
k_1	pseudo-first order rate constant (min^{-1})
k_2	pseudo-second order rate constant ($\text{mg g}^{-1} \text{min}^{-1}$)
k_{id}	intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$)
K_{DR}	Dubinin–Radushkevich constant ($\text{mol}^2 \text{KJ}^{-2}$)
K_f	Freundlich constant (mg g^{-1})
K_L	Langmuir constant related to sorption energy (L mg^{-1})
n	Freundlich constant
q_e	sorption capacity at equilibrium (mg g^{-1})
q_t	sorption capacity at time t (mg g^{-1})
Q_e	Dubinin–Radushkevich sorption capacity at equilibrium (mol kg^{-1})
Q_m	Dubinin–Radushkevich saturation capacity (mol kg^{-1})
r_0	the mean diameter solid particles
R_L	separation factor
R^2	correlation coefficient
t	time (min)
$t_{0.5}$	time for 50% completion of the reaction
T	temperature (K)
<i>Greek letters</i>	
δ	the film thickness (10^{-3} cm)
θ_0	Langmuir constant related to monolayer capacity (mg g^{-1})
χ^2	statistical error

oxide (NHITO) as nanocrystalline agglomerate, and (ii) the use of it for arsenic removal by sorption from the aqueous solution.

2. Materials and methods

2.1. Preparation of NHITO

The material was prepared by slow injection of 10 mL TiCl_4 (liquid) into a liter of hot ($\sim 60^\circ\text{C}$) 0.5 M FeCl_3 in 0.1 M HCl solution with constant mechanical mixing. When TiCl_4 addition was over, 1.0 M NaOH solution was added slowly into the hot mixture with mechanical stirring till the pH of the supernatant liquid was ranged in 5.0–6.0, and the stirring was continued more 0.5 h. The gel-like yellow-to-brown precipitate formed was aged for 6 days in mother liquor. The filtered precipitate was washed with deionized water till alkali free, and dried in an air oven at $60\text{--}70^\circ\text{C}$. The hot dried mass when treated with ice cold water was broken into fine agglomerated particles of size mostly ranged in $140\text{--}290 \mu\text{m}$, and sieved for use in the experiments. The method used for the synthesis of the present bimetal mixed oxide is a low temperature process and that is different from the methods reported [31,32].

2.2. Arsenic solutions

The standard stock As(III) and As(V) solutions (1000 mg/L) were separately made and preserved as described earlier [19,21]. The arsenic solutions of required concentrations for working were made

from the stocks by appropriate dilution with deionized arsenic free water.

2.3. Analytical methods

2.3.1. Arsenic analysis

Arsenic (total) as well as arsenic(III) in solution was analyzed by hydride generation atomic absorption spectrophotometer (PerkinElmer-3100) (detection limit: $1 \mu\text{g L}^{-1}$ with $\pm 4\%$ accuracy) and UV-vis spectrophotometer (Hitachi model-3210) (detection limit: $10 \mu\text{g L}^{-1}$ with accuracy $\pm 5\%$) using the methods described in “Standard Methods for the Examination of Water and Wastewater” [33]. Total dissolved arsenic in samples was analyzed by adding HCl (32%, v/v) and KI (10%, v/v) where As(V) was reduced to As(III), which was converted to arsine with NaBH_4 (3%, w/v). 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, that was compared with the standard curve made from the standard arsenic solution. The As(III) in samples was analyzed by the selective reduction to arsine with NaBH_4 (3%, w/v) solution at pH 4.8 in acetate buffer. In the spectrophotometric method, the arsine gas generated was absorbed in solution of silver diethyldithio carbamate (SDDC) (G. R., E. Merck, Germany) in chloroform solvent, and absorbance was measured at 525 nm against blank taking into 1 cm quartz glass cell. The absorbance value was compared with a standard calibration curve.

2.3.2. Adsorbent characterization

X-ray diffraction (XRD) analysis of NHITO was made using an X-ray powder diffractometer (Philips Analytical PW-1710) equipped with Cu $K\alpha$ radiation at a scanning speed of $2^\circ/\text{min}$ from 10° to 90° , operated at voltage 40 kV and applied potential current 30 mA. Thermo gravimetric (TG) and differential thermal (DT) analyses of the NHITO were recorded using a setaram analyzer in argon atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$ over a temperature range of $30\text{--}1000^\circ\text{C}$. The pH_{zpc} (pH for zero-surface charge) was determined according to procedure as described by Babic et al. [34]. The surface area of the NHITO particles was analyzed by Brunauer–Emmett–Teller (BET) method by N_2 gas adsorption at 77 K using high-speed surface analyzer (model: ASAP 2000, Norcross, USA). The Fourier transform infra red (FTIR) spectra of the mixed oxide and the associated pure oxides were recorded on a PerkinElmer (U.S.) system 2000 spectrophotometer with a resolution of 2 cm^{-1} . The transmission electron micrograph (TEM) image for the particle size was recorded on a H800 transmission electron micrograph (Hitachi, Japan) operating at 200 kV.

2.4. Batch experiments

2.4.1. Sorption kinetics

Batch method was used at pH 7.0 (± 0.1) for sorption kinetics reaction with NHITO separately at temperatures 288, 303 and 313 K with a maximum ($\pm 1.6 \text{ K}$) fluctuation. Here, 500.0 mL of arsenic solution [concentrations (mg L^{-1}): 5.0 or 10.0] was taken with 1.0 g NHITO (agglomerated particle: $140\text{--}290 \mu\text{m}$) in 1000 mL glass vessel, and placed inside a thermostat bath to attain the desired temperature. The reaction mixture was agitated ($300 \pm 5 \text{ rpm}$) using a speed adjustable agitator. A pH-meter (model LI-127, ELICO, India) electrode was inserted into the solutions 10 min before withdrawing of samples for pH check, and 0.1 (M) NaOH or 0.1 (M) HCl was added, if required, for pH adjustment (~ 7.0) during the run of the experiment. A measured volume of the reaction mixture, 2.0 mL at initial three stages and 5.0 mL in the later stages, was withdrawn at an interval of 0.25 h from the start till a plateau reached. The sample solutions were filtered using $0.45 \mu\text{m}$ -membrane filter and

the filtrates were analyzed for arsenic [33]. The adsorption capacity (q_t mg g⁻¹) at any time, t was calculated using the following equation,

$$q_t = (C_0 - C_t)(V/m) \quad (1)$$

where C_0 is the initial concentration (mg L⁻¹) of the solute in aqueous solution, C_t the solute concentration (mg L⁻¹) in aqueous phase at any time, t (min), V the solution volume (L) and m is the mass (g) of solid sorbent added.

The high arsenic concentration was used in this work as the review [1] showed in many natural water sources scattered throughout the world are associated with high arsenic concentration even higher than 10 mg L⁻¹ and, the review [24] showed many authors had used higher arsenic concentration in their work.

2.4.2. Sorption isotherm

The sorption isotherm experiments were conducted at a temperature of 303 (±1.6)K and at pH 7.0 (±0.1) by batch sorption procedure. Here, 50-mL of arsenic solution in concentration (mg L⁻¹) range 5.0–250.0 was used separately. The sorbent dose added was 2.0 g L⁻¹. The agitation (speed: 300 ± 5 rpm) time used for As(III) was 3.5 h and that for As(V) was 6.0 h for equilibrium. The solution pH was adjusted twice in the middle (at 1.0 and 3.0 h of agitation from zero time) using 0.1 M HCl and/or 0.1 M NaOH as required. Residual arsenic was determined in the filtered sample [33]. The equilibrium adsorption capacity (q_e , mg g⁻¹) was calculated using the following equation,

$$q_t = (C_0 - C_e)(V/m) \quad (2)$$

where C_e is the equilibrium concentration (mg L⁻¹) of solute in solution and the significance of other terms are as given above.

2.5. Quality assurance

All samples were analyzed in 2 days and analyzed in triplicate indicated a precision better than ±5%. The data analyzes were made with a computer for kinetics by excel soft ware work sheet and those for isotherm by origin soft ware work sheet. The linear regression coefficient values for analysis indicate the fitting of the experimental data to the theoretical. The closer the regression coefficient value to unity greater is the data fit with the model analyzed. The chi-square values were obtained from the nonlinear analysis of the data for a model in origin. The lower is the chi-square value for a set of data higher is the accuracy.

3. Results and discussions

3.1. Determined physicochemical parameters

The determined physicochemical parameters are shown in Table 1. The FTIR and thermal (TG and DT) analyzes (figures omitted) indicated the hydrous nature of synthetic NHITO. The total mass loss (23.77 ± 0.25%) found from the TG analysis of the material in the drying temperature range 30–1000 °C is the water loss and that was supported from the exothermic peak in DT spectrum. The chemical composition determination by classical analytical methods showed the studied material contained 59.85 (±0.91)% Fe₂O₃ and 14.68 (±0.76)% TiO₂. The XRD pattern (figure omitted) obtained for the synthetic oxide (NHITO) showed seven peaks at diffraction angle (2θ , °) values 27.13°, 35.76°, 39.79°, 46.95°, 56.54°, 61.99° and 64.95° with good relative intensity (%) of 77.3, 100.0, 50.0, 38.5, 52.4, 38.5 and 36.4, respectively. This suggested the synthetic material is crystalline. The peaks position obtained for the synthetic mixed oxide showed the presence of magnetite (Fe₃O₄),

Table 1

Some determined physicochemical parameters of nanostructure hydrous Fe(III)–Ti(IV) bimetal mixed oxide (NHITO)

^a Chemical composition (%)	Fe ₂ O ₃ : 59.85 (±0.105); TiO ₂ : 14.68 (±0.32); H ₂ O: 23.77 (±0.25)
Nature	Microcrystalline
Particle diameter (nm) calculated from X-ray diffraction pattern peaks data	~11.0 (±2.0)
Particle diameter (nm) obtained from the TEM image analysis	7.0 (±1.0)
BET surface area (m ² g ⁻¹)	77.8 (±0.2)
pH _{ZPC}	6.0 (±0.05)

^a (±S.D.) is the average of three analyzes.

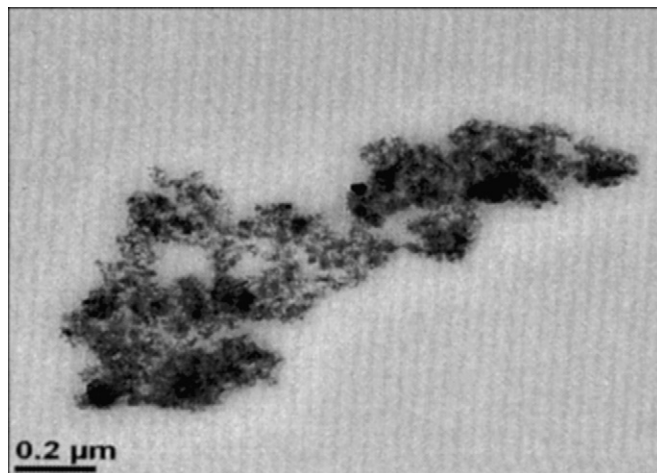


Fig. 1. High resolution electron transmission microscopic (TEM) image of NHITO.

γ -FeO(OH) and anatase (TiO₂) phases corresponding to the peaks at diffraction angle (2θ , °) values 35.76°, 56.54°, and 61.99°, and the peak positions agreed well with the Joint Committee on Powder Diffraction (JCPDS) file (no. 3-863 and 21-1272). The peaks position at some other diffraction angle (2θ , °) values were neither for the iron oxide nor for the titanium oxide, which indicated the presence of some new phases of iron(III)–titanium(IV) mixed oxide with the phases noted. The particles size calculated from the XRD peaks data were ~9–13 nm, and that obtained from the TEM image (Fig. 1) was ranged between 6 and 8 nm. The BET surface area determined was 77.8 m² g⁻¹. The pH_{ZPC} value estimated for the NHITO was 6.0 (±0.05) (Fig. 2), which is one unit less than the neutral pH. The pH_{ZPC} values suggest the surface of the mixed oxide material should

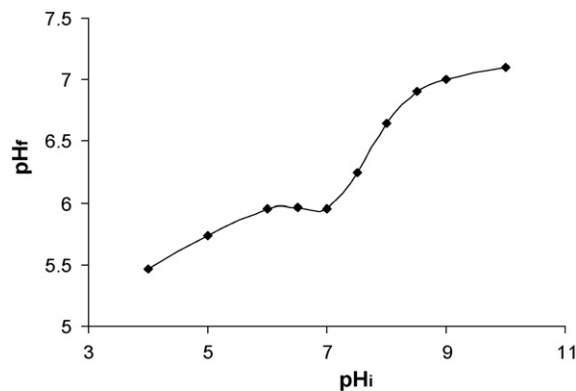


Fig. 2. The plot of final solution pH (pH_f) versus initial solution pH (pH_i) in presence of 0.1 M NaCl.

be predominantly positive and negative, respectively, at below and above the pH 6.0 (± 0.05). The surface charge density of the material should increase or decrease with decreasing or increasing pH from the pH_{ZPC} .

3.2. Kinetic analysis

The points shown in Fig. 3a and b demonstrate the arsenic sorption kinetic data on NHITO obtained at pH 7.0 (± 0.1) and at temperatures (± 1.6 K) 288, 303, and 318. It was found that the sorption capacity (q_t , $mg\ g^{-1}$) at any time (t) of As(III) was found to be greater than that of As(V). The time (h) required was 3.5 and 6.0, respectively, for reaching equilibrium for As(III) and As(V). The data (Fig. 3a and b) were analyzed by the non-linear method using the Microsoft origin spread sheet according to the Lagergren pseudo-first order and pseudo-second order equations [35]. The kinetic parameters obtained from the analysis are shown in Table 2. It is found that the kinetics of the sorption reactions with NHITO has been taken place, in general, by obeying (i) the pseudo-first order reaction for the As(III) and (ii) the pseudo-second order reaction for the As(V).

The pseudo-first order rate constant (k_1 , min^{-1}) and the equilibrium sorption capacity (q_e , $mg\ g^{-1}$) estimated for the As(III) from the kinetic analysis of pseudo-first order equation are found to increase (Table 2) with increasing temperature on the reactions.

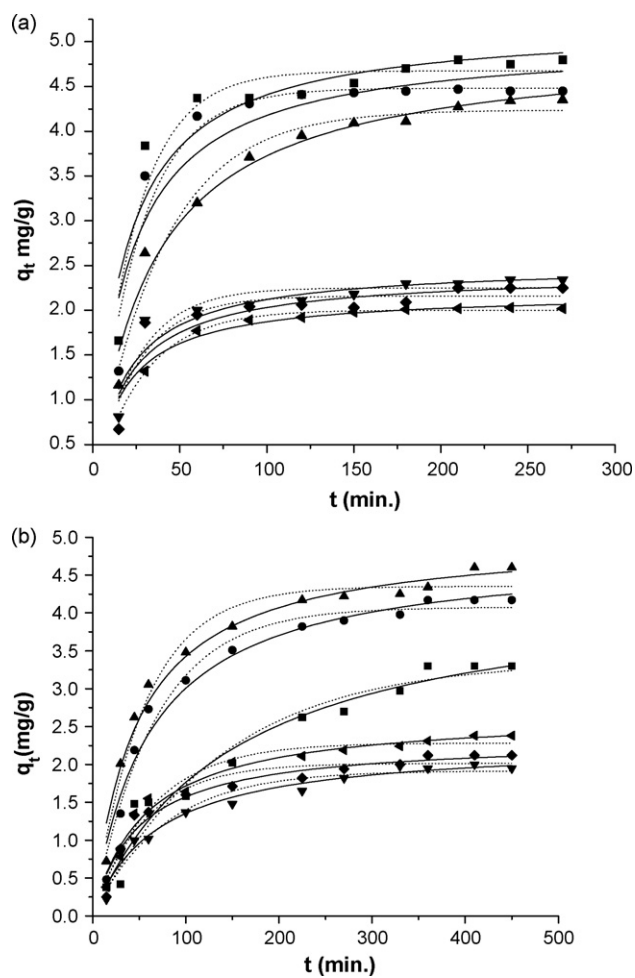


Fig. 3. The arsenic sorption capacity of NHITO with the change of contact time at pH 7.0 (± 0.1) for (a) As(III) and (b) As(V) at different temperatures and concentrations ($mg\ L^{-1}$). Non-linear kinetic plots: (—) pseudo-second order, (---) pseudo-first order. For $10.0\ mg\ L^{-1}$: (\blacklozenge) 318 K, (\blacksquare) 303 K, (\blacktriangle) 288 K; and for $5.0\ mg\ L^{-1}$: (\times) 318 K, (\times) 303 K, (\bullet) 288 K.

Table 2
The kinetic model parameters (significance of each terms given in nomenclature) for the sorption of As(III) and As(V) on NHITO at pH 7.0 \pm 0.1

Kinetic model equations	Kinetic parameters	Arsenic concentration ($mg\ L^{-1}$) studied												
		As(III)						As(V)						
		5.0	10.0	288 K	318 K	303 K	318 K	288 K	303 K	318 K	288 K	303 K	318 K	
Pseudo-first order $q_t = q_e(1 - e^{-k_1 t})$	$k_1 \times 10^{-2} (min^{-1})$	3.53 \pm 0.00	4.07 \pm 0.01	4.11 \pm 0.01	4.16 \pm 0.01	3.78 \pm 0.01	4.16 \pm 0.01	1.31 \pm 0.06	1.79 \pm 0.00	1.58 \pm 0.00	1.58 \pm 0.00	0.73 \pm 0.00	1.51 \pm 0.00	1.83 \pm 0.00
	$q_e (mg\ g^{-1})$	2.00 \pm 0.01	2.16 \pm 0.07	2.29 \pm 0.06	4.68 \pm 0.11	4.48 \pm 0.11	4.68 \pm 0.11	1.92 \pm 0.06	2.01 \pm 0.06	2.27 \pm 0.05	2.27 \pm 0.05	3.37 \pm 0.20	4.08 \pm 0.08	4.35 \pm 0.09
	R^2	0.99	0.87	0.89	0.92	0.94	0.92	0.95	0.94	0.97	0.97	0.95	0.97	0.97
	$\chi^2 (\times 10^{-2})$	0.1	3.4	2.5	8.4	7.8	8.4	1.6	2.0	1.4	1.4	6.2	4.5	4.4
Pseudo-second order $q_t = tq_e q_e^2 / (1 + tk_2 q_t)$	$k_2 \times 10^{-2} (g\ mg^{-1}\ min^{-1})$	2.60 \pm 0.00	2.17 \pm 0.01	2.14 \pm 0.01	1.07 \pm 0.00	1.00 \pm 0.00	1.07 \pm 0.00	0.63 \pm 0.00	0.88 \pm 0.00	0.67 \pm 0.00	0.67 \pm 0.00	0.15 \pm 0.00	0.34 \pm 0.00	0.43 \pm 0.00
	$q_e (mg\ g^{-1})$	2.20 \pm 0.03	2.42 \pm 0.13	2.52 \pm 0.11	5.20 \pm 0.23	5.02 \pm 0.26	5.20 \pm 0.23	2.29 \pm 0.08	2.33 \pm 0.09	2.68 \pm 0.09	2.68 \pm 0.09	4.41 \pm 0.35	4.82 \pm 0.17	5.01 \pm 0.13
	R^2	0.97	0.83	0.86	0.87	0.86	0.87	0.97	0.96	0.97	0.97	0.96	0.97	0.98
	$\chi^2 (\times 10^{-2})$	0.2	4.3	2.8	12.7	15.6	12.7	1.0	1.6	1.2	1.2	5.0	4.5	3.8

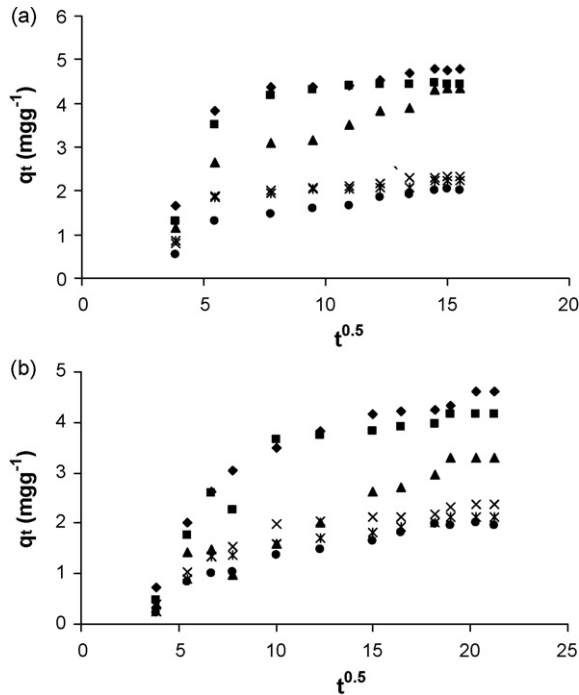


Fig. 4. The Weber–Morris plots for intra-particle diffusion of the arsenic sorption kinetic data on NHITO for the (a) As(III) and (b) As(V) at studied two different concentrations [5 mg L⁻¹: (×) 318 K, (X) 303 K, (●) 288 K and 10 mg L⁻¹: (◆) 318 K, (■) 303 K, (▲) 288 K] and at three different temperatures.

The values are again found greater than those obtained for the case of the As(V). Apart from that, the values of the pseudo-second order rate constant (k_2 , g mg⁻¹ min⁻¹) (Table 2) for As(V) is found to decrease with increasing temperature on the sorption reaction. The comparison of rate constant values estimated from either of the kinetic equation analysis suggests that the rate of As(III) sorption by NHITO is faster than As(V) at any of the studied temperature. Thus, it has been concluded that the sorption of reduced arsenic by NHITO is kinetically more favorable than the oxidized species from the aqueous solution.

3.3. Intra-particle (pore) diffusion

The over all reaction kinetics for the sorption by NHITO of As(III) is a pseudo-first order process while that of As(V) is a pseudo-second order process. However, those could not highlight on the rate-limiting step. The rate-limiting step (slowest step of the reactions) may be either the boundary layer (film) or the intra-particle (pore) diffusion of solute on the solid surface from bulk of the solution in a batch process. The theoretical treatments of intra-particle diffusion yield rather complex mathematical relationships, which differ in form as functions of the geometry of the sorbent particle [36]. The functional relation (Eq. (3)) which had been used by many workers [5,6,11,36,37] to predict the rate-controlling step of the reactions is,

$$q_t = k_{id} t^{0.5} \quad (3)$$

where k_{id} is the intra-particle diffusion rate constant (mg g⁻¹ time^{-0.5}). If the rate-limiting step be the intra-particle diffusion, the plot of q_t against square root of time should be straight line and pass through the origin. The deviation of the plot from the linearity indicates the rate-limiting step should be boundary layer (film) diffusion controlled.

Fig. 4a and b shows the plots of q_t versus $t^{0.5}$ for the As(III) and As(V), respectively. It was found that the plots are non-linear and do not pass through the origin, which suggest the present sorption reactions rates are not controlled by the pore diffusion instead it is controlled by the boundary layer (film) diffusion [38] at the all working temperatures.

3.4. Pore and film diffusion coefficients

In order to confirm the evaluated rate controlling step above, the pore diffusion coefficient (D_p , cm² s⁻¹) and the film diffusion coefficient (D_f , cm² s⁻¹) have been calculated, respectively, for the sorption of As(III) and As(V) by NHITO using following relations (Eqs. (4) and (5)) [39,40]:

$$D_p = \frac{(0.03r_0^2)}{t^{0.5}} \quad (4)$$

$$D_f = \frac{(0.23r_0 \times \delta \times C_s)}{(C_L \times t_{0.5})} \quad (5)$$

where r_0 ($=1.075 \times 10^{-2}$ cm) is the mean radius of agglomerated nanostructure particles (assumed spherical), δ ($=10^{-3}$ cm) [39,40] is the film thickness and C_s and C_L are the solid and liquid phase solute concentrations at $t = t$ and $t = 0$, respectively. Here, $t_{0.5}$ corresponds to the time of 50% of solute sorption on the sorbent. If the D_p -value be ranged in 10^{-11} to 10^{-13} cm² s⁻¹, the sorption process should be controlled by the pore-diffusion; and if the D_f -value be ranged in 10^{-6} to 10^{-8} cm² s⁻¹, the sorption process should be controlled by the boundary-layer (film) diffusion [40,41].

The values for the D_p and D_f have been calculated using the relations (Eqs. (4) and (5)) above and shown in Table 3. It has been found that the D_p and D_f values (cm² s⁻¹) are ranged in 10^{-9} to 10^{-10} and 10^{-6} to 10^{-7} , respectively. Thus, the results (Table 3), in general, has suggested that the sorption reactions of either the As(III) or the As(V) with NHITO at the studied reaction conditions are taken place with the boundary-layer (film) diffusion. The results reported herein is similar to the results that published by Lgwe and Abia [42] on the sorption of As(III) by the modified and unmodified coconut fiber.

3.5. Isotherm analysis

Fig. 5 shows the equilibrium isotherm data as points for the sorption of As(III) and As(V) by NHITO at pH 7.0 (± 0.1) and at a

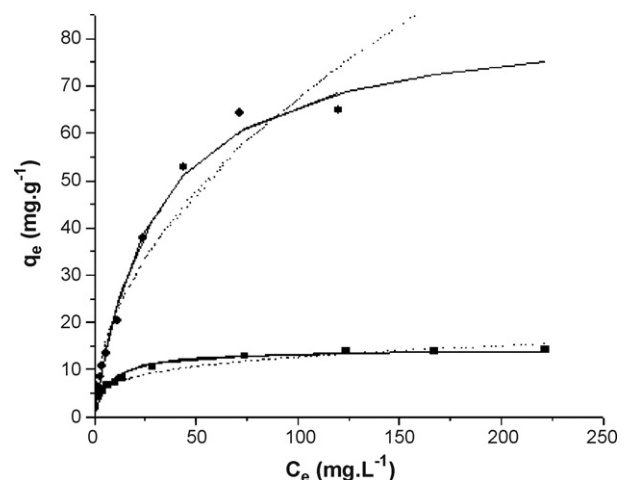


Fig. 5. The equilibrium isotherm data shown as points of arsenic sorption by NHITO at pH 7.0 (± 0.1) and temperature 303 K, and the non-linear isotherm analysis of the data for the (●) As(III) and (■) As(V). Plots: (—) Langmuir (---) Freundlich.

Table 3
Pore and film diffusion coefficients calculated for the arsenic sorption on NHITO at pH 7.0 (± 0.1)

Species	Concentration (mg L^{-1})	D_p ($\text{cm}^2 \text{s}^{-1}$)			D_f ($\text{cm}^2 \text{s}^{-1}$)		
		288 K	303 K	318 K	288 K	303 K	318 K
As(V)	5.0	8.4×10^{-10}	1.2×10^{-9}	1.1×10^{-9}	2.7×10^{-7}	3.9×10^{-7}	4.0×10^{-7}
	10.0	3.9×10^{-10}	7.2×10^{-10}	1.3×10^{-9}	1.2×10^{-7}	2.4×10^{-7}	4.5×10^{-7}
As(III)	5.0	4.1×10^{-9}	45.1×10^{-9}	25.4×10^{-9}	1.2×10^{-6}	1.6×10^{-6}	8.6×10^{-6}
	10.0	6.3×10^{-9}	9.9×10^{-9}	1.1×10^{-8}	1.9×10^{-7}	3.1×10^{-7}	3.7×10^{-6}

temperature 303 (± 1.6) K, respectively. These isotherm data (Fig. 5) have been analyzed for the Freundlich and the Langmuir isotherms [43] by the non-linear method of analysis using the Microsoft origin spread sheet.

The non-linear fits of the equilibrium data are also shown in Fig. 5. The estimated isotherm parameters related to the model equations are shown in Table 4 with regression coefficient (R^2), and the statistical error chi-square (χ^2) values. In general, the results (Table 4) based on either χ^2 or R^2 values have indicated that the sorption data for either of the arsenic species has described the Langmuir model well. The Langmuir monolayer sorption capacity (θ_0 , mg g^{-1}) and sorption energy (K_L , L mg^{-1}) values evaluated from the Langmuir isotherm plots showed (Table 4) that the Langmuir capacity of As(III) is ~ 6 (six) times greater than As(V) and the sorption energy of As(III) is ~ 0.25 times of As(V).

Despite the well fit of the sorption data with the used two-parameter isotherm a model, the mechanistic implication has not been highlighted. However, the dimensionless parameter, R_L [$=1/(1 + C_0 K_L)$] [44], where K_L = the Langmuir constant (L mg^{-1}) and C_0 = initial arsenic concentration (mg L^{-1}), can predict whether the sorption is favorable or unfavorable. The R_L -values for the range of arsenic concentration (mg L^{-1}) 0.05–1.0 or at any higher concentration, if calculated, shall be found to lie between 0 and 1.0, which indicated the sorption of As(III) and As(V) by NHITO is favorable at pH 7.0 (± 0.1) and temperature 303 (± 1.6) K. The arsenic-sorption performance of NHITO has also been compared on the basis of the Langmuir monolayer sorption capacity (θ_0 , mg g^{-1}) with some reported data (Table 5) and, that revealed the present material has higher affinity for the As(III), which is a major concern of ground-water contaminant in Bengal delta [4] basin.

3.6. Thermodynamic parameters

The thermodynamic parameters for the present sorption reactions had been evaluated by using the literature available standard relations [43] based on the assumptions that (i) the activity coefficient of the working solutes in solution is unity and (ii) the ΔS° and ΔH° are to be constant within the range of temperature studied. The calculated values of ΔS° and ΔH° from the slope and intercept of

Table 4
The isotherm parameters estimated by the non-linear method of analysis of equilibrium arsenic sorption on NHITO at pH 7.0 ± 0.1 and at 303 K (significance and unit of each term is given in nomenclature)

Isotherm equation	Different parameters	Estimated parameters	
		As(V)	As(III)
Langmuir model $q_e = (\theta_0 K_L C_e)/(1 + K_L C_e)$	R^2	0.97	0.99
	χ^2	0.71	5.26
	θ_0	14.3 (± 0.5)	85.0 (± 4.0)
	K_L	0.13 (± 0.02)	0.03 (± 0.00)
Freundlich model $q_e = K_f C_e^{1/n}$	R^2	0.95	0.95
	χ^2	1.00	31.25
	K_f	4.17 (± 0.40)	6.75 (± 1.46)
	n	4.12 (± 0.37)	2.00 (± 0.21)

Table 5
Comparison of Langmuir monolayer sorption capacity for arsenic of NHITO with some reported data

Sorbent material	pH	Langmuir capacity (mg/g)		Reference
		As(III)	As(V)	
NHITO	7.0	85.0	14.3	Present work
Crystalline hydrous ferric oxide	7.0	33.3	25.0	18
Crystalline hydrous titanium oxide	7.0	31.7	–	19
Nanoscale zero valent iron	7.0	2.47	–	26, 27
Nano-TiO ₂	7.0	59.9	37.5	28, 29
Hydrous stannic oxide	7.0	15.9	4.3	21
Akaganeite nanocrystal	7.5	–	134.1	30

the straight line plot of $\log_{10}(q_e/C_e)$ versus $(1/T)$ (plots omitted) and the values for ΔG° obtained there from are shown in Table 6. Results (Table 6) showed the increase in magnitude of $-\Delta G^\circ$ with rising temperature on the sorption reactions, which indicate the increase in spontaneity of the sorption reactions with increasing temperature. Based on the ΔH° , it can be concluded that the sorption reaction of either As(III) or As(V) with NHITO is endothermic (ΔH° positive), and takes place with increasing entropy (ΔS° positive). This suggests the increase in number of species during sorption process at the solid–liquid interface, which is presumably due to the release of water molecules at solid–liquid interface when hydrated solutes being sorbed by the solid phase.

3.7. Energy of sorption

In order to evaluate the sorption energy and to understand the sorption mechanism of arsenic on NHITO, the equilibrium data shown in Fig. 5 have been analyzed by Dubinin–Radushkevich (D–R) equation (Eq. (6)) below [45]:

$$\ln Q_e = \ln Q_m - K_{DR} \varepsilon^2 \quad (6)$$

where Q_e and Q_m are the equilibrium and saturated sorption capacities in (mol kg^{-1}), respectively, and K_{DR} is the free energy of

Table 6
Thermodynamic parameters evaluated for arsenic sorption on NHITO at pH 7.0 ± 0.1 and at 303 K (significance and unit of each thermodynamic parameter is given in nomenclature)

Arsenic species	Concentration (mg L^{-1})	ΔH°	ΔS°	ΔG°		
				288 K	303 K	318 K
As(V)	5.0	+35.81	+0.13	–1.34	–3.28	–5.21
	10.0	+36.48	+0.13	–0.39	–2.31	–4.23
As(III)	5.0	+25.90	+0.10	–2.04	–3.49	–4.95
	10.0	+26.57	+0.10	2.75	–4.28	–5.80

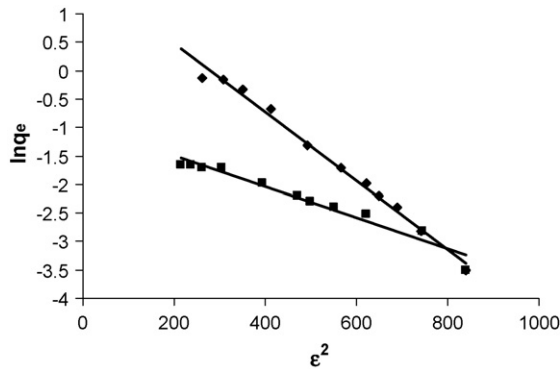


Fig. 6. The Dubinin–Radushkevich (D–R) plot of arsenic sorption by NHITO at pH 7.0 (± 0.1) and at temperature 303 K: (\blacklozenge) As(III), (\blacksquare) As(V).

sorption. The ε is expressed by the equation (Eq. (7)) below:

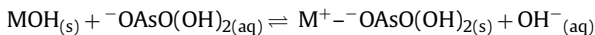
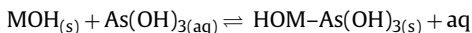
$$\varepsilon = RT \ln \left\{ 1 + \left(\frac{1}{C_e} \right) \right\} \quad (7)$$

where R is the gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and T the temperature (K).

A plot of $\ln Q_e$ against ε^2 will be a straight line that was used to confirm the model. The intercept and slope of the plot give the value for Q_m and K_{DR} , respectively. The plots of the present data showed straight lines (Fig. 6) with good linear regression coefficient values (Table 7). If the mean free energy (E , kJ mol^{-1}) of the sorption reactions, which can be calculated by computation of K_{DR} in the following relation (Eq. (8)), be ranged in 8.0–16.0, the sorption reactions should be chemisorptions [5,11,45]:

$$E_{DR} = (-2K_{DR})^{-0.5} \quad (8)$$

The values of mean free energy of sorption (E_{DR}) calculated for the present cases are shown in Table 7 with other evaluated parameters. It has been found that the E_{DR} value (kJ mol^{-1}) for As(III) is $9.09 (\pm 0.1)$ and for As(V) is $13.51 (\pm 0.04)$. These E_{DR} values are indicated that the arsenic sorption by NHITO is the chemical sorption [11,46]. The mean free energy of sorption found for the As(III) and the As(V) is higher than that reported by the other workers [5,11]. Thus, the plausible mechanism of arsenic sorption could be suggested as below:



(s) stands for the solid phase. The suggested mechanism agreed well with the significant increase of equilibrium solution pH for As(V) sorption. The higher energy of sorption of As(V) than As(III) is presumably due to the chemisorptions with ion-exchange.

3.8. Effect of NHITO dose

The efficiency of NHITO how far it is capable to reduce arsenic concentration from a solution of $50.04 (\pm 0.10) \text{ mg As(III) L}^{-1}$ to

Table 7
The Dubinin–Radushkevich (D–R) isotherm parameters evaluated for arsenic sorption on NHITO at pH 7.0 ± 0.1 and at 303 K (unit each term is given in nomenclature)

Parameters	As (III)	As (V)
R^2	0.99	0.96
E_{DR}	$9.09 (\pm 0.01)$	$13.51 (\pm 0.04)$
$K_{DR} (\times 10^{-3})$	6.0	3.0
Q_m	$5.31 (\pm 0.02)$	$2.63 (\pm 0.03)$

Table 8

Effect of NHITO dose on arsenic removal from an arsenic solution of concentration = $50.04 (\pm 0.10) \text{ mg L}^{-1}$ [volume of solution = 50.0 mL, pH $7.0 (\pm 0.1)$, agitation speed = $300 (\pm 5) \text{ rpm}$, agitation time = 4 h]

Dose (g L^{-1})	As _(Total) concentration (mg L^{-1})	Dose (g L^{-1})	As _(Total) concentration (mg L^{-1})
2.0	$6.30 (\pm 0.10)$	18.0	$0.20 (\pm 0.04)$
4.0	$2.80 (\pm 0.10)$	20.0	$0.16 (\pm 0.02)$
6.0	$1.90 (\pm 0.12)$	24.0	$0.13 (\pm 0.01)$
8.0	$0.65 (\pm 0.05)$	28.0	$0.08 (\pm 0.02)$
10.0	$0.45 (\pm 0.04)$	32.0	$0.04 (\pm 0.01)$
12.0	$0.32 (\pm 0.05)$	36.0	$0.02 (\pm 0.01)$
14.0	$0.30 (\pm 0.02)$	38.0	$0.01 (\pm 0.01)$
16.0	$0.29 (\pm 0.03)$	40.0	$0.00 (\pm 0.01)$

the permissible value (0.01 mg L^{-1}) has been investigated with varying the dose of solid with maintaining the other parameters unchanged by the batch procedure. The results obtained are shown in Table 8. It is found that the concentration (mg L^{-1}) of the solute has decreased to $6.30 (\pm 0.20)$ from $50.04 (\pm 0.10)$ when the dose of the sorbent used is 2.0 g L^{-1} . But, the decrease in arsenic concentration in the later stages is found less and that becomes $0.01 (\pm 0.01) \text{ mg L}^{-1}$ when the dose of NHITO used is 38 g L^{-1} . The decrease of arsenic concentration has been found very high ($\sim 87.5\%$) at the first stage, and that is low at the later stages.

3.9. Effect of some other ions

The effect of phosphate and sulfate ions on arsenic sorption (amount loaded = 5.0 mg g^{-1} sorbent) at pH $7.0 (\pm 0.1)$ has showed no significant effect on As(III) removal while those ions have reduced the As(V) removal percentage from $83.0 (\pm 1.5)$ to $23.4 (\pm 1.1)$ and $35.0 (\pm 1.0)$ with increasing mole ratio of (i) $\text{PO}_4^{3-}:\text{As}$ from 0 to 1.6 and (ii) $\text{SO}_4^{2-}:\text{As}$ from 0 to 27.3, respectively. The significant interference on As(V) sorption by phosphate and sulfate is due to the similar chemistry of As(V) with phosphate and sulfate in aqueous solution at pH $7.0 (\pm 0.1)$.

3.10. Case study

3.10.1. Arsenic removal from the spiked sample

Natural water sample has been collected from a hand pump attached well from the College Square area of Kolkata (India) and analyzed for some water quality parameters. The analyzed data (mg L^{-1} except pH) are pH (7.6 ± 0.1), suspended solids (6.4 ± 0.1), total dissolved solids (1200 ± 50), total hardness (704 ± 10), calcium (221.2 ± 5.1), magnesium (37.5 ± 1.5), chloride (357.5 ± 7.4), fluoride (0.35 ± 0.01), arsenic(III) (0.023 ± 0.004), arsenic(V) (0.008 ± 0.005), iron (0.06 ± 0.01), alkalinity (total) (722.0 ± 12.5), phosphate (0.05 ± 0.01) and sulfate (25.5 ± 0.1). The As(III) and As(V) have been spiked (mg L^{-1}) separately into that water sample up to a level of $0.35 (\pm 0.02)$. The spiked water samples are passed through the separate columns packed (height: 5.1 cm, internal diameter: 1.0 cm) with NHITO for evaluating arsenic removal efficiency with a down flow rate 0.06 L h^{-1} and analyzed for arsenic. The results obtained (Fig. 7) show the columns specified give the treated water volume (L) 3.0 and 0.7 with arsenic level up to 0.01 mg L^{-1} , respectively, from the As(III) and As(V) spiked samples. This reveals the NHITO material is more than four times efficient in removing the reduced arsenic than the oxidized form from the natural water.

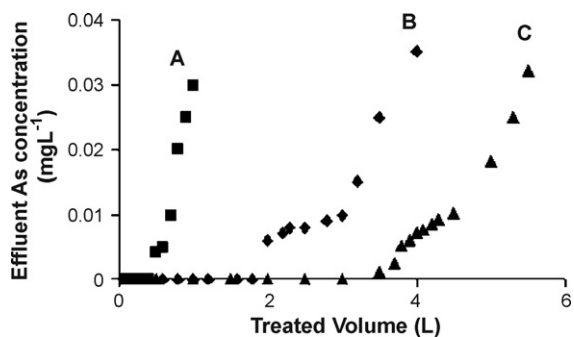


Fig. 7. Column tests on arsenic removal from the (A) As(V) (■) and (B) As(III) (◆) spiked ($0.35 \pm 0.02 \text{ mg L}^{-1}$) natural water samples, and (C) arsenic contaminated ($0.11 \pm 0.01 \text{ mg L}^{-1}$) ground water (▲) sample. Column specification (cm): height 5.1, internal diameter 1.0. Flow rate (L h^{-1}): 0.06.

3.10.2. Arsenic removal from the contaminated ground water sample

The ground water sample for the test has been collected from a tube well (depth: $\sim 30 \text{ m}$) of Chakkda area of district Nadia (West Bengal, India). The water quality parameters estimated (mg L^{-1} except pH) are pH (7.5 ± 0.1), suspended solids (7.1 ± 0.1), total dissolved solids (400 ± 5), total hardness (360 ± 10), calcium (56.5 ± 2.3), magnesium (18.7 ± 1.0), chloride (60.5 ± 1.5), fluoride (0.65 ± 0.03), arsenic_{total} (0.11 ± 0.01), iron (0.45 ± 0.02), alkalinity (total) (185.6 ± 7.5), phosphate (0.15 ± 0.01) and sulfate (31.5 ± 0.1). This sample water has been passed through the NHITO packed column (specification given above) with a down flow rate noted earlier. The effluents collected in 0.5 L fractions are analyzed for the total arsenic. The results obtained have also been shown in Fig. 7. It has been found that the column of NHITO specified produces filtered water volume 4.5 L with arsenic below the permissible value (0.01 mg L^{-1}).

4. Conclusions

The synthetic bimetal Fe(III)–Ti(IV) oxide (NHITO) is hydrated and nanostructured material. The pseudo-first order and pseudo-second order kinetic equations describe well, respectively, the As(III) and As(V) sorption kinetic data on NHITO. The boundary-layer (film) diffusion is the rate-determining step. The Langmuir isotherm model fit of equilibrium data is well. The Langmuir sorption capacity of As(III) is nearly six times greater than the As(V). The reactions are endothermic and of spontaneous nature. The nature of the sorption reactions is chemisorptions. The phosphate and sulfate show the significant interference in removing As(V) from the aqueous solution. A fixed bed NHITO packed column gives the greater volume of treated water (arsenic: 0.01 mg L^{-1}) for the case of As(III) than the As(V) spiked natural water sample. The same column treats 4.5 L of a groundwater sample (As concentration = $0.11 \pm 0.01 \text{ mg L}^{-1}$).

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