Removal of Arsenic from Aqueous Phase by Nanoparticle Agglomerates of Hydrous Iron(III)-Chromium(III) Bimetal Mixed Oxide: Effects of Background Ions on the As(V) Sorption Kinetics and Equilibrium

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The influence of some groundwater occurring ions was investigated on As(V)-sorption by agglomerated nanoparticles (40-50 nm) of synthetic hydrous iron(III)-chromium(III) mixed oxide (NHICO). Solubility tests of NHICO suggested that it could be used safely for As(V) removal at pH = 6.4 ± 0.1 by agitation (speed: 350 ± 5 rpm) for an hour. Kinetic data obtained in the presence of applied ions for this reaction were well described by the pseudo-second order equation (0.98 < r² <1.00, 0.04 < χ² < 0.18). Good agreement of the equilibrium data with the Freundlich isotherm (0.96 < r² <1.00, 0.41 < χ² < 6.30) suggested that the NHICO surface was heterogeneous. Adequate fitting of the data with the Redlich-Petterson (0.96 < r² <1.00, 0.65 < χ² < 7.83) isotherm with g < 1.0 confirmed the conclusion drawn. The positive enthalpy (ΔH°) and entropy (ΔS°) changes indicated that the endothermic As(V)-sorption reaction in the absence/presence of ions was driven by an entropy increase at the solid-liquid interface. Negative values of free energy change (ΔG°) indicated that the reaction spontaneity increased with increasing temperature. The sorption of As(V) by NHICO occurred via an ion-exchange mechanism (mean sorption energy, E_sor = 8.98 to 11.47 kJ. mol⁻¹) involving surface M—OH groups.

Key words: arsenic(V), groundwater ions, influence, iron(III)-chromium(III) bimetal oxide, sorption behaviour

Introduction

The occurrence of arsenic in spring and ground waters far exceeding the tolerance level of 10 μg.L⁻¹ is a global problem (Smedley and Kinniburgh 2002). This has affected a large area of the Bengal Delta Basin (West Bengal in India and Bangladesh), where arsenic content in the ground water varies widely (West Bengal in India is less than 10-3,200 μg.L⁻¹ and Bangladesh is less than 0.5-2,500 μg.L⁻¹) (Smedley and Kinniburgh 2002). Arsenic exists mainly in the +3 and +5 valence states depending upon the Eₚₑ–pH conditions of the ground water (Mohan and Pittman Jr. 2007). Long-term ingestion of these groundwaters can be fatal to the people of underdeveloped countries like India. This demands cost-effective and environmentally safe technology for the treatment of ground waters with high arsenic concentrations (greater than 10 μg As.L⁻¹).

Consequently, various treatment technologies such as coagulation and filtration, reverse osmosis, electrodialysis, ion-exchange, and surface sorption have been reported (Smedley and Kinniburgh 2002; Mohan and Pittman Jr. 2007). Among them, surface sorption technology has been found to be an attractive option for the treatment of arsenic-rich groundwater. It has also been accepted by rural people of third-world countries like India and Bangladesh because of low recurring cost, easy operation, lesser space requirements, and no need for trained personnel. Sorbent materials such as activated carbon, agricultural products and by-products, biomasses, and metal oxides or metal ion loaded biomaterials have been developed (Mondal et al. 2006; Mohan and Pittman Jr. 2007). Materials used in bulk phases for arsenic removal from aqueous solutions are mainly iron (III)/aluminium(III) oxides and hydroxides (Willkie and Hering 1996; Driehaus et al. 1998; Raven et al. 1998; Lin and Wu 2001; Lenoble et al. 2002; Manna et al. 2003; Sing and Pant 2004; Kuriakose et al. 2004; Manna and Ghosh 2005; Lashmipathiraj et al. 2006), mixed rare earth oxides (Raichur and Penvekar 2002), iron oxide coated materials (Katsoyiannis and Zouboulis 2002), nanostructured akaganeite (Deliyanni et al. 2003) for the arsenic sorption. This has encouraged us in the synthesis of nanostructured mixed metal oxides for the application in water purification. Hence, the synthetic oxides of nanostructured iron(III)-zirconium(IV) (Gupta et al. 2008) and iron(III)-titanium(IV) (Gupta and Ghosh, 2009) have been investigated for the arsenic removal/sorption from the contaminated water.
Based on the lab-bench data, some filters for the pilot-scale treatment of high arsenic groundwater are designed and marketed in different trade names by various companies. Field assessment performances of the filters reported (Hossain et al. 2005) showed that the filters are not working up to the specification level of the manufacturers. It is presumably due to the adverse influence of dissolved solutes co-existing with arsenic in groundwater. Therefore, we have aimed to investigate the sorption/removal of arsenic in the presence of ions occurring in groundwater.

This manuscript reports the results of kinetics and equilibrium studies for the As(V) sorption reaction with agglomerated nanoparticles (40-50 nm) of synthetic hydrous iron(III)-chromium(III) bimetal oxide (NHICO) in the presence of major ions that occur in groundwater with arsenic.

Materials and Methods

Preparation of NHICO

NHICO was prepared by chemical precipitation method. Here, the solutions of 0.1 M FeCl₃ (in 0.1 M HCl) and 0.1 M CrCl₃ (in 0.1M HCl) were mixed together by a volume ratio of 1:1. To the hot (80±5° C) and well-stirred (speed: ~300 rpm) mixture, aqueous ammonia (1:1) was added slowly until the pH of solution including precipitate reached 5.5-6.7. The precipitate was aged with mother liquid for four days, filtered, washed three times with distilled water, and dried inside an air-oven at 60-70°C. The cold water treatment of dried hot mass converted to the fine agglomerated particles. The agglomerates of grain size ranging between 140-290 μm were collected by sieving, and then used for the sorption experiments.

As(V) Stock Solution

The standard As(V) solution (1,000 mg.L⁻¹) was prepared as stock by dissolving 4.1601 g of disodium hydrogen arsenate (Na₂HAsO₄.7H₂O; E. Merck, Germany) in arsenic-free distilled water into a 1,000 mL volumetric flask and frozen. A measured volume of this stock solution was diluted with arsenic-free distilled water for a desired level of As(V) concentration prior using for the experiments.

Arsenic Analysis

The total arsenic concentrations in solutions were analyzed by the methods as described in ‘Standard Methods for the Examination of Water and Wastewater’ (APHA et al. 1998).

Analytical Instruments

An x-ray powder diffractometer (Philips Analytical PW-1710, Alemelo, Netherlands) was equipped with copper Kα radiation at a scanning speed 2°/minute between 20 values 10° and 90°, and operated at voltage 40 kv. Applied potential current 30mA was used for the crystal phase analysis of NHICO. Thermogravimetric (TG) and differential thermal (DT) spectra of NHICO were recorded using a Setaram analyzer in argon atmosphere at a heating rate of 20°C min⁻¹ over a temperature range 50-800°C. Föurier transform infra red (FT-IR) spectrophotometer (Jasco 680 plus, Albany, Oreg., USA) with a resolution of 2 cm⁻¹ was used for the identifications of functional groups of NHICO and As(V)—NHICO with KBr pellet method. Scanning electron micrograph (SEM) (Tescan Vega, UK) was used for recording the surface morphology of the material. A FEI high-resolution electron microscope (Tecnai STWIN, Hillsboro, Oreg., USA) was used for the transmission electron micrograph image for the particle size of NHICO. A UV-Vis spectrophotometer (Hitachi, model-3210U, Hitachi, Japan) and an atomic absorption spectrophotometer (Perkin-Elmer, AAnalyst-200, Waltham, Mass., USA) were used for analysis of total arsenic concentration in samples.

Zero-Point Surface Charge pH (pH_{zpc})

The pH drift method (Babic et al. 1999) was used for the analysis of zero-point surface charge pH (pH_{zpc}) of NHICO.

Specific Surface Area

The method described by Sears Jr. (1956) was used for the specific surface area of NHICO.

Experimental procedures

Experiments for the As(V)-sorption by NHICO were carried out inside the well capped PET bottles (capacity: 250 mL) with agitation speed (Sₚ) 350 ± 10 rpm. 0.1g of NHICO was placed with 50 mL As(V) solution of a desired level of initial concentration (Cₒ)/load at pHᵢ = 6.4 (± 0.1) (excepting the pH effect experiment) and temperature (T) = 303 (± 1.6) K, and then agitated by placing it inside a thermostatic orbital shaker for 2.0 hours (excepting the kinetics experiment). Once the agitation period was over, NHICO particles were separated using a 0.45-mu membrane filter. The total arsenic concentration remained in the filtrates was analyzed by the standard methods (APHA et al. 1998).

The sorption amount of arsenic (qₜ, mg.g⁻¹) at any time (t) was calculated by:

\[ qₜ = (wₒ - wₜ) / m' \]  

where wₒ and wₜ are the amount (in mg) of arsenic present in solution at t = 0 hours and t = 2.0 hours, respectively, and m' is the mass (g) of NHICO added.
Experiments for the effect of agitation speed (S<sub>j</sub>) were conducted by varying S<sub>j</sub> from 100-400 rpm with As(V) load 7.5 mg/g NHICO in the reaction mixtures at a fixed pH and T.

Experiments for the pH effect of As(V) removal by NHICO were carried out by varying pH<sub>i</sub> from 2.0-10.0 with As(V) loads 3.75 and 7.5 mg/g of sorbent. Other conditions were remained same as specified above. Equilibrium pH (pH<sub>f</sub>) and the remaining arsenic concentrations were analyzed in the filtered sample solutions. The amount of arsenic removed was calculated using equation 1.

For the effect of incinerating temperature on NHICO for As(V) sorption, 0.5 g fractions of the solid were heat-treated separately at T (± 3.2) = 373, 423, 473, 523, 573, 623, 673, 723, and 773 K for an hour inside a muffle furnace, and cooled to room temperature inside the desiccators. Each incinerated NHICO was used to carry out the sorption experiments at pH<sub>i</sub> = 6.4 ± 0.1 taking As(V) load 3.75 or 7.50 mg/g of sorbent. Other conditions for the experiments were same (as described in the first paragraph of Experimental Procedures).

Kinetic experiments for the As(V) sorption (load: 13.20 mg per g sorbent) by NHICO incinerated at 623 K were conducted in the presence of groundwater occurring ions. Ions including concentration (mg.L<sup>-1</sup>) in parenthesis added with As(V) at background were chloride (400), sulphate (200), phosphate (10.0), iron(III) (3.0), magnesium (100), calcium (200), manganese (3.0). The set up of experiments with other conditions has been described earlier. The pH change, if any, was monitored by inserting a pH meter electrode, and adjusted using 0.1 N NaOH and/or HCl 15 minutes before withdrawing the sample. Reaction mixtures including the bottles were taken out at pre-fixed time intervals from the start and filtered immediately. The filtrates obtained were analyzed for the residual arsenic, and calculated the q<sub>e</sub> values using equation 1.

Isotherm experiments for the As(V) sorption by NHICO in presence of the ions (specified above) at background were conducted at T = 298 (±1.6) K and pH<sub>i</sub> = 6.4 (± 0.1) by batch method. Initial concentrations (C<sub>i</sub>) of the As(V) solutions varied from 5.0-250.0 mg.L<sup>-1</sup>. Experimental set up and other conditions were the same as specified in the first paragraph of Experimental Procedures earlier. The pH change of each reaction mixture was checked at ~45 and ~90 minutes from the start of agitation (t = 0), and if required, adjusted to 6.4 (± 0.1) using 0.1 N HCl and/or 0.1N NaOH. The reaction mixtures including the container were taken out from the agitator immediately after 2.0 hours and filtered. The filtrates were analyzed for the residual arsenic concentrations.

The sorption amount at equilibrium (q<sub>e</sub>, mg g<sup>-1</sup>) was calculated by:

\[ q_e = (C_i - C_e) \left( \frac{V}{m'} \right) \]  

where C<sub>i</sub> and C<sub>e</sub> are the initial and the equilibrium concentrations (mg L<sup>-1</sup>) of As(V) in solution, respectively. V, the volume (L) of solution and m' is the mass (g) of NHICO.

**Results and Discussion**

**Characterization of NHICO**

X-ray diffraction patterns (figure omitted) of NHICO showed that the synthetic material was microcrystalline. It was found that the crystallites size increased with increasing incineration temperature in that material. Figure 1 demonstrates the TG and DT spectra of NHICO. It was seen that the weight loss percentages were 13.67, 21.55, and 1.24 at temperatures ranged in 30-100°C, >100-270°C, and > 400-430°C, respectively. The weight loss at first-step was due to the irreversible elimination of physically attached water molecules, which is the moisture content in NHICO. The weight loss at second-step was presumed due to the elimination of chemically bound water with dehydroxylation of metal hydroxide. The endothermic and sharp DT peak had supported the major weight loss at the second-step. Low percentage of weight loss recorded at temperatures greater than 400°C were presumed for the elimination of water from bridged hydroxo groups with phase transformation. The total weight loss calculated was found to be 36.46%. An exothermic DT peak observed at 450-550°C was presumed due to the chemical reaction such as polymerization or crystallization. This indicated that NHICO was stable up to the temperature 450°C. Analysis of the FTIR spectrum (figure omitted) suggested that the broad absorption band at wave numbers ranged between 3,000-3,700 cm<sup>-1</sup> was due to the stretching mode of O–H bond indicating hydrous nature of NHICO. Variations of pH<sub>f</sub> against pH<sub>i</sub> (plot omitted) showed that the pH<sub>zpc</sub> value of NHICO appeared to be 6.4 ± 0.1. Thus, the NHICO surface should be positive at pH < 6.4 ± 0.1, negative at pH > 6.4 ± 0.1 and neutral at pH = 6.4 ± 0.1. Comparison of the FTIR spectrum (plot omitted) of NHICO with that of pure chromium(III) and iron(III) oxides showed that NHICO was hydrous mixed oxide, because the bands in spectrum of the bimetal oxide showed some differences from either of the pure oxides at wave number values ranged between 400-1,000 cm<sup>-1</sup>. This indicated that some chemical interactions took place between hetero metal centers via oxo/hydroxo bridge in synthetic bimetal oxide. Figure 2 (a and b) demonstrates the transmission electron micrograph and the SEM (c) pictures of NHICO. It appeared from these images that the spherical nanoparticles of size between 40-50 nm were agglomerated together appearing with irregular surface morphology. The specific surface area estimated for NHICO was high (608.6 m<sup>2</sup>.g<sup>-1</sup>) and agreed well with the presence of nano size particles.
Fig. 1. TG and DT spectra of NHICO.

Fig. 2. Transmission electron microscopic images (A) 50 nm scale and (B) 20 nm scale; and (C) SEM image of NHICO.
Effect of Agitation Speed

Increase of agitation speed ($S_T$) increases the frequency of interaction between sorbate and sorbent, indicating the increase of solute distribution from solution on the surface. Thus, there shall be an optimum $S_T$ value for every heterogeneous system. It was found that the $q_e$ values increased from 6.65-7.43 mg As(V) per g of NHICO with increasing $S_T$ from 100-400 rpm. Highest $q_e$ value was found at $S_T \geq 350$ rpm. Therefore, the experiments remaining are conducted using $S_T = 350 \pm 5$ rpm.

Effect of pH

Variations of pHf versus pHi, and $q_e$ (mg. g$^{-1}$) versus pHi are demonstrated in Fig. 3 (a and b, respectively). It was found that the pHf values were greater than the pHi between 2.0-5.0, and lesser than the pHi between 7.0-10.0 (Fig. 3a). There is a small difference between the values at pH 5.0 and 7.0.

The plots shown in Fig. 3b indicate that the $q_e$ (mg. g$^{-1}$) values decreased with increasing pHi, which had been found to be similar with the observations that found for the As(V) sorption by hydrous stannic oxide (Manna and Ghosh 2007). The decrease of $q_e$ with increasing pHi was due to the lowering of positive charge density on NHICO surface, which reduced the columbic attraction between the surface charge of solid and the anionic As(V) species in solution. Highest $q_e$ value noted at pHi 2.0 was due to the strong columbic attraction between the positive charge on the solid surface (pH ZPC = 6.4 ± 0.1) and ($\text{HO}_2$)$\text{AsO}_2^-\text{ species}$ (pK$_1$ of OAs(OH)$_3$ = 2.1). At pH$_{ZPC}$, the As(V) sorption by NHICO was presumed to take place by the intermolecular hydrogen bonding with outer sphere surface complex formation. A sharp reduction of $q_e$ at pHi > pH$_{ZPC}$ was found, which was due to the columbic repulsion of anionic As(V) species by the negative charge on solid surfaces.

Solubility of NHICO

The solubility test of NHICO was conducted by estimation of total iron and chromium concentrations from solutions that obtained by filtration in the pH effect experiments. It was found that the concentrations (mg.L$^{-1}$) analyzed for Fe$_{\text{total}}$ were 0.12, 0.89, 0.03, 0.01, and < 0.01, for Cr$_{\text{total}}$ they were 0.15, 0.10, 0.04, 0.01 and <0.01 at pH$_i$ 2.0, 3.0, 4.0, 5.0, and 6.0–10.0, respectively. The concentrations of the metal ions analysed was found to be significantly lower than their maximum permissible values at pH$_i$ ranged between 4.0-10.0. Thus, the NHICO bed could be used safely for the filtration of arsenic-rich groundwater.

Effect of Heat Treatment on NHICO

Figure 4 demonstrates the variation of $q_e$ (mg. g$^{-1}$) against the temperature of incineration on NHICO. It was found that the $q_e$-values increased with increasing temperature of incineration on NHICO from 373-623 K (100-350º C), and decreased steadily with increasing that from 623-773 K (350-500º C). This indicated that the available active sites per g solid for sorption enhanced with increasing temperature of incineration from 373-623 K (100-350º C), which reduced with increasing that from 623-773 K (350-500º C). This is presumably due to: (i) removal of physically attached (H-bonded) and coordinated water molecules from the solid up to 623 K (350ºC), and (ii) elimination of water from the surface M–OH bonds above 623 K (350ºC). The weight loss at first and second stages in TG analysis agreed well with the broad exothermic DT peak at incinerating temperature between 323-573 K (50-300ºC) (Fig. 1). The phase change of the material indicated at ~500º C (773 K) was confirmed by the exothermic DT band (Fig. 1). The results were found similar with that of crystalline hydrous ferric oxide (Manna et al. 2003), but somewhat
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different from that of hydrous stannic oxide (Manna and Ghosh 2007) and crystalline hydrous titanium oxide (Manna et al. 2004).

**Sorption Kinetics**

Figure 5 demonstrates the variation of $q_t$ (mg. g$^{-1}$) values with increasing contact time ($t$, min) of As(V) sorption reaction with NHICO at $T = 303$ (± 1.6) K and pH$\text{I} = 6.4$ (± 0.1) in the presence of ions (at background) specified previously. It was found that ~90% of the equilibrium sorption amount ($q_e$, mg.g$^{-1}$) took place in 20 min, and the remaining ~10% took place in next 20 minute. Thus, the time required in reaching dynamic equilibrium ($t_e$) was 40 minutes. The $t_e$ (minute) obtained was found to be much lower than the results that had been reported by other workers (Raven et al. 1998; Raichur and Penvekar 2002; Zhang et al. 2003; Zeng 2004; Kundu and Gupta 2006).

In order to understand the reaction quantitatively, the kinetic data shown as points in Fig. 5 were analyzed using non-linear forms of the following kinetic equations (Lakshmipathraj et al. 2006; Pokhrel and Viraraghavan 2008):

Lagerrgen pseudo-first order: $q_t = q_e(1-e^{-k_1t})$  \( (3) \)

Pseudo-second order: $q_t = \frac{t_k_2q_e^2}{(1 + t.k_2.q_e)}$  \( (4) \)

where $q_t$ and $q_e$ have their usual significance noted earlier; $k_1$ (min$^{-1}$) and $k_2$ (g.mg$^{-1}$.min$^{-1}$) are respectively, the pseudo-first and the pseudo-second order rate constants.

Nonlinear fits of kinetic data with the pseudo-first order (equation 3) and the pseudo-second order (equation 4) equations are shown, respectively in Fig. 5a and b. The kinetic parameters estimated are presented in Table 1. It was found that the regression coefficient ($r^2$) and the chi-square ($\chi^2$) error values, respectively, ranged from 0.94-0.98 and 0.24-0.63 for the pseudo-first order equation 3, and 0.98-1.00 and 0.04-0.18 for the pseudo-second order equation 4. Thus, better fits of kinetic data were found with the pseudo-second order equation 4 than with the pseudo-first order equation 3. Therefore, the reaction for As(V) sorption with NHICO in the absence/presence of ions at background took place obeying the pseudo-second order kinetic model. Values of the $q_e$ (mg. g$^{-1}$) were always found to be higher in the absence of ions than in the presence of ions at background (Table 1). Thus, the As(V) removal efficiency of NHICO declined in presence of the background ions. Values of the $q_e$ (obtained according to the pseudo-second order kinetic
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...model) were close with that of the \( q_e \) (experimental), indicating fits of kinetic data with the pseudo-second order equation 4. It was revealed from the modeled \( q_e \)-values (obtained from the pseudo-second order equation 4 [Table 1]) that the ions added at the background had adverse influence in removing As(V) by NHICO. Among them, the sulfate ion showed the strongest adverse effect relative to any other ions tested.

Diffusion kinetics

The functional relationship (Weber and Morris 1963) applied to predict the rate-controlling step (RCS) of the reaction is:

\[
q_t = k_{id} \cdot t^{0.5} \tag{5}
\]

where \( k_{id} \) is the intra-particle diffusion rate constant \( \text{(mg.g}^{-1}. \text{time}^{-0.5}) \). If the RCS is intra-particle diffusion, the plot of \( q_t \) against \( t^{0.5} \) should be a straight line with intercept value zero. Deviation of plot from the linearity will indicate that the RCS should not be intra-particle diffusion.

Figure 6 demonstrates the plots of \( q_t \) versus \( t^{0.5} \) (Weber and Morris plot) for this sorption reaction. The points could be described by joining with two straight lines, indicating two stages of sorption phenomena. The joining of points for any specific case (as shown in Fig. 6) with a single line gave a poor straight line over the range of contact time, which did not pass through the origin. Thus, RCS was not the intra particle (pore) diffusion; instead it might be considered as the boundary layer (film) diffusion or multistage process. To confirm RCS, the coefficients of intra-particle (pore) diffusion (\( D_p \), \( \text{cm}^2.\text{s}^{-1} \)) and film diffusion (\( D_f \), \( \text{cm}^2.\text{s}^{-1} \)) were calculated using the following relationships (Helffrich 1962; Crank 1979):

\[
D_p = \frac{(0.03r_e^2)}{t_{0.5}} \tag{6}
\]

\[
D_f = \frac{(0.23r_e^2, \delta, C_s)}{(C_L, t_{0.5})} \tag{7}
\]

where \( r_e (1.08 \times 10^{-2} \text{ cm}) \) is the mean radius of nanoparticle agglomerates (assumed spherical), \( \delta (=10^{-3} \text{ cm}) \) (Helffrich 1962) is the film thickness, and \( C_s \) and \( C_L \) are the solid and liquid phase solute concentrations at \( t=t_e \) and \( t=0 \), respectively. Here, \( t_{0.5} \) corresponds to the time of 50% of solute sorption by the sorbent. If the calculated value of \( D_p \) is ranged in \( 10^{-11} \) to \( 10^{-13} \text{ cm}^2.\text{s}^{-1} \), RCS should be intra-particle (pore) diffusion and if that of \( D_f \) is ranged in \( 10^{-6}-10^{-8} \text{ cm}^2.\text{s}^{-1} \), then RCS should be the boundary layer (film) diffusion (Helffrich 1962; Crank 1979).

Taking the rate constant values that estimated for the pseudo-second order model (best fit) equation 4, the time for 50% sorption reaction (\( t_{50} \)) was calculated, and used to calculate the values of diffusion coefficients. The values (\( \text{cm}^2.\text{s}^{-1} \)) of \( D_p \) and \( D_f \) calculated were \((1.25-3.16) \times 10^{-8}\) and \((1.52-5.65) \times 10^{-9}\) in the presence of no or any ion at background, respectively. Whatever be the ions at background in the reaction of As(V) sorption with NHICO, the values of \( D_p \) were in the order of \( 10^{-8} \text{ cm}^2.\text{s}^{-1} \), and that were greater than the \( 10^{-11} \text{ cm}^2.\text{s}^{-1} \). Again, the values of \( D_f \) were in the order \( 10^{-9} \text{ cm}^2.\text{s}^{-1} \), which was outside the range of \( 10^{-6}-10^{-8} \text{ cm}^2.\text{s}^{-1} \). Thus, the RCS of As(V) sorption reactions with NHICO in the absence or presence of any ion at background were controlled neither by the intra-particle diffusion nor by the boundary-layer diffusion phenomenon. Instead, it should be multi-stage controlled phenomenon. The results obtained were
Basu et al. found to be similar with that reported earlier (Gupta et al. 2008; Gupta and Ghosh 2009).

**Sorption isotherm**

Figures 7 and 8 demonstrate the variation of equilibrium sorption capacity ($q_e$, mg/g) versus equilibrium concentration ($C_e$, mg/L) for As(V) sorption by NHICO in the presence/absence of ions added at background at pH$_i$ = 6.4 ($\pm$ 0.1) and T = 303 ($\pm$ 1.6) K. To understand the reactions mechanism, the equilibrium data were analyzed by the non-linear regression method of data fit using the following model equations (Ozacar et al. 2008; Vaghetto et al. 2009):

Freundlich equation: $q_e = K_F C_e^{1/n}$  
(8)

Langmuir equation: $q_e = (\theta_o K_a C_e)/(1 + K_a C_e)$  
(9)

Temkin equation: $q_e = (RT/b) \ln(A_T C_e)$  
(10)

Redlich-Peterson equation: $q_e = (A C_e)/(1 + B C_e^g)$  
(11)

where $K_F$ is the Freundlich constant (mg$^{1-1/n}$ .g$^{-1}$ .L$^{-3/n}$) related to the sorption capacity, and ‘n’ is the Freundlich sorption intensity related to the affinity or binding

**Fig. 7.** Equilibrium data of As(V)-sorption by NHICO at T = 303 ($\pm$ 1.6) K and pH$_i$ = 6.4 ($\pm$ 0.1) in the presence of some background ions with non-linear isotherm analyses of (a) Freundlich (b) Langmuir model equations. Without ion, $\bullet$ SO$_4^{2-}$, $\blacktriangledown$ Cl$^-$, $\blacktriangle$ PO$_4^{3-}$, $\blacklozenge$ Fe$^{3+}$, $\blacktriangleleft$ Mg$^{2+}$, $\star$ Ca$^{2+}$ and $\diamondsuit$ Mn$^{2+}$.

**Fig. 8.** Equilibrium data of As(V)-sorption by NHICO at T = 303 ($\pm$ 1.6) K and pH$_i$ = 6.4 ($\pm$ 0.1) in the presence of some background ions with non-linear isotherm analysis of (a) Temkin (b) Redlich-Peterson model equations. Without ion, $\bullet$ SO$_4^{2-}$, $\blacktriangledown$ Cl$^-$, $\blacktriangle$ PO$_4^{3-}$, $\blacklozenge$ Fe$^{3+}$, $\blacktriangleleft$ Mg$^{2+}$, $\star$ Ca$^{2+}$ and $\diamondsuit$ Mn$^{2+}$.
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θ₀ and K a are the Langmuir constants related to maximum monolayer sorption capacity (mg.g⁻¹) and the sorption equilibrium constant (L.g⁻¹). A₀ and 'b' are the Temkin constants related to sorption equilibrium constant (L.g⁻¹) and a dimensionless quantity. A (L.g⁻¹) and B (L.mg⁻¹) are the Redlich-Peterson constants, which are related to the sorption equilibrium constants, respectively. 'g' is the third dimensionless constant of Redlich-Peterson isotherm. The value of g should vary from 0-1.0. When g = 0, equation 11 converts to the Henry law, and when g = 1, equation 11 converts to the Langmuir form. The meanings of qe and C e are given earlier. Non-linear statistical fits of equilibrium data with the models such as Freundlich (equation 8), Langmuir (equation 9), Temkin (equation 10) and R-P (equation 11) are demonstrated in Figs. 7 and 8, respectively. The parameters related to the isotherm equations (8-11) including regression coefficient (r²) and statistical error chi-square (χ²) values estimated as shown in Table 2. Based on the values of r² and χ², it was found that the equilibrium data of As(V) sorption reactions with NHICO described the Freundlich (equation 8) and the R-P isotherm (equation 11) models well (0.96 < r² > 1.00, χ² = 0.41-7.83) (Table 2). The fits of equilibrium data were found to be better with the Freundlich and the R-P models than either the Langmuir or the Temkin models. Thus, the active sites available on the surface of NHICO for As(V) sorption were heterogeneous and not equally accessible to all species. Again, the values of g (= 0.52-0.71) estimated from the R-P equation were well below 1.0, which inclined to the better fit of equilibrium data with the Freundlich equation than to the Langmuir equation. The Freundlich isotherm equation that developed based on the consideration of chemisorption of solute onto the solid surface, described the equilibrium data poorly, and ruled out the chemisorption of As(V) by NHICO. The modeling of present equilibrium data was found to be similar with results that had been reported by Zhang et al. (2003). The value of K a obtained in the absence of ions was found greater than that obtained in the presence of any ion at the background (Table 2), indicating negative effect of the ions on the As(V) sorption by NHICO.

Energy of sorption

The equilibrium data shown as points (Figs. 7 and 8) were analyzed by the Dubinin-Radushkevich (D-R) isotherm equation 12 (shown below) (Singh and Pant 2004; Kundu and Gupta 2006) for estimating mean free energy of sorption (E des, kJ.mol⁻¹):

\[
\ln Q_e = \ln Q_m - K_{DR} \varepsilon^2
\]

where Q_m and K_{DR} are the sorption capacity (mol.kg⁻¹) and the D-R isotherm constant (mol².kJ⁻²), respectively. ε is the Polanyi potential and expressed according to equation 13:

\[
\varepsilon = RT \ln (1 + 1/C_e)
\]

where R is the molar gas constant (8.31 x 10⁻³ kJ. K⁻¹.mol⁻¹), T the absolute temperature (K) and, Q_e and C_e are the equilibrium capacity (mol.Kg⁻¹) and the equilibrium concentration (mol.L⁻¹), respectively.

Figure 9 shows the plots of ln q_e versus ε² which show good linearity (r² = 0.96 – 0.99) in presence of

<table>
<thead>
<tr>
<th>Background ion</th>
<th>Freundlich isotherm parameters.</th>
<th>Background ion</th>
<th>Langmuir isotherm parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ As(V)</td>
<td>r²</td>
<td>χ²</td>
<td>Kₑ ± SD (mg.g⁻¹)(dm³.mg⁻¹)²</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.98</td>
<td>3.43</td>
<td>28.3 ± 0.59</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1.00</td>
<td>0.90</td>
<td>3.39 ± 0.31</td>
</tr>
<tr>
<td>SiO₄³⁻</td>
<td>0.99</td>
<td>0.41</td>
<td>3.30 ± 0.31</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.98</td>
<td>0.52</td>
<td>3.71 ± 0.38</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.99</td>
<td>1.70</td>
<td>4.35 ± 0.55</td>
</tr>
<tr>
<td>Cr⁺⁺</td>
<td>0.97</td>
<td>5.20</td>
<td>5.07 ± 0.97</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.96</td>
<td>6.26</td>
<td>5.30 ± 1.15</td>
</tr>
<tr>
<td>No ion</td>
<td>0.99</td>
<td>2.05</td>
<td>5.83 ± 0.55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Background ion</th>
<th>Temkin isotherm parameters.</th>
<th>Background ion</th>
<th>Redlich-Peterson isotherm parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ As(V)</td>
<td>r²</td>
<td>χ²</td>
<td>A</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.88</td>
<td>23.58</td>
<td>0.54 ± 0.28</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.89</td>
<td>23.93</td>
<td>0.59 ± 0.30</td>
</tr>
<tr>
<td>SiO₄³⁻</td>
<td>0.94</td>
<td>17.85</td>
<td>0.85 ± 0.31</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.93</td>
<td>2.10</td>
<td>1.46 ± 0.68</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.84</td>
<td>23.13</td>
<td>2.02 ± 1.70</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.91</td>
<td>2.30</td>
<td>2.89 ± 1.88</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.74</td>
<td>50.38</td>
<td>7.44 ± 10.53</td>
</tr>
<tr>
<td>Mn³⁺</td>
<td>0.75</td>
<td>36.60</td>
<td>8.41 ± 12.21</td>
</tr>
</tbody>
</table>
no or any ion, excepting the case of \( \text{PO}_4^{3-} \) \((r^2 = 0.92)\). The values of \( Q_m \) (mol. kg\(^{-1}\)) and \( K_{\text{DR}} \) (mol\(^2\). kJ\(^{-2}\)) were calculated from the intercepts and slopes. It was found that the \( K_{\text{DR}} \) values were ranged in \((4.0 \text{ to } 6.0) \times 10^{-3} \) mol\(^2\).kJ\(^{-2}\) in the absence/presence of ions at background. Taking the \( K_{\text{DR}} \) values, the \( E_{\text{DR}} \) values calculated using equation 14 ranged between 8.98-11.47 kJ.mol\(^{-1}\).

\[
E_{\text{DR}} = 1 / (2 K_{\text{DR}})^{1/2}
\]

The magnitude of \( E_{\text{DR}} \) is useful for understanding the type of a sorption reaction. If the value of \( E_{\text{DR}} \) be: (i) between a range of 8.0-16.0 kJ.mol\(^{-1}\), then sorption should occur with ion/ligand exchange mechanism (Singh and Pant 2004; Kundu and Gupta 2006), (ii) less than 8.0 kJ. mol\(^{-1}\), sorption should occur with hydrogen bonding or van der Waal type of physical interaction, and (iii) greater than 16 kJ.mol\(^{-1}\), then the reaction should be chemisorption type. The \( E_{\text{DR}} \) values calculated in the absence/presence of any ion at background ranged from 8.0-16.0 kJ.mol\(^{-1}\), suggesting anion/ligand exchange mechanism of As(V) sorption by NHICO.

**Thermodynamic parameters**

Thermodynamic parameters such as \( \Delta G^0 \), \( \Delta H^0 \) and \( \Delta S^0 \) for the present heterogeneous reaction were evaluated by the literature available standard equations 15 and 16 below (Atkins and de Paula 2006) based on assumptions that the activity coefficient of the working solutes in the solution was in unity.

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0
\]

\[
\Delta G^0 = - 2.303RT \log K_c
\]

The combination of equation 15 and 16 gives equation 17 as shown below:

\[
\log K_c = \Delta S^0/ 2.303R - (\Delta H^0/2.303R) 1/T
\]

The changes of standard enthalpy (\( \Delta H^0 \)) and standard entropy (\( \Delta S^0 \)) are assumed to be constant within the temperature range where the reaction was studied.

The thermodynamic equilibrium constant (\( K_c \)) was calculated using equation 18:

\[
K_c = q_e / C_e
\]

where \( q_e/C_e \) is called the sorption affinity (L.g\(^{-1}\)). \( q_e \) and \( C_e \) have the same significance given previously. So, the relation (equation 18) above can be written as equation 19:

\[
\log( q_e/C_e) = \Delta S^0/2.303R - (\Delta H^0/2.303R) 1/T
\]

The values of \( \Delta S^0 \) and \( \Delta H^0 \) were calculated from the slope and intercept of the linear plots of \( \log (q_e/C_e) \) versus (1/T) (Fig. 10). The values of \( \Delta S^0 \), \( \Delta H^0 \) and \( \Delta G^0 \) estimated are shown in Table 3. It has been suggested from the estimated values of thermodynamic parameters that the As(V) sorption reaction by NHICO was endothermic (\( \Delta H^0 = \) positive), and spontaneous (\( \Delta G^0 = \) negative), which took place with increasing entropy at liquid-solid interface (\( \Delta S^0 = \) positive). The \( \Delta G^0 \) values were increasingly negative with temperature, which indicated the increase of reaction spontaneity. Again, the present reaction was increasingly endothermic but spontaneous at \( T = 303 (\pm 1.6) \) K with increasing solute load per g of NHICO. The increase of + \( \Delta S^0 \) value has indicated that the randomness at the solid-liquid interface increased with increasing solute load per g of NHICO, which might be due to the release of aqua molecules with hydroxyl ions when aquatic As(V) was sorbed by the solid.

**Sorption mechanism**

Figure 11 demonstrates the FTIR spectra of NHICO (Fig. 11a) and As(V)–NHICO (Fig. 11b). It was found that the stretching and the bending absorption bands for the O-H group at wave number 3,300–3,700 cm\(^{-1}\) and around 1,625 cm\(^{-1}\), respectively, of spectrum a (Fig.11a) were weak in spectrum b (Fig.11b). Additionally, the area occupied by the O-H stretching band reduced, indicating the disappearance of some O-H groups from the solid surface with As(V) sorption by NHICO. Also, the weakness of absorption band at a wave number 843 cm\(^{-1}\) in spectrum b (Fig. 11b) might be for the presence of As-O bond. Disappearance of the O-H groups from the NHICO surface with As(V) sorption supported the proposed anion/ligand exchange mechanism. The increase of pHf over the pHi (Fig. 3a) during As(V) sorption by NHICO at pHi = 6.4 (± 0.1) also supported that mechanism. Thus, the mechanism for the As(V) sorption by NHICO at working conditions can be presented as below.
Removal of Arsenic from Aqueous Phase by Nanoparticle Agglomerates

\[ \text{Fe(OH)}_3 + \text{HAsO}_4^{2-} \rightarrow \text{FeAsO}_4^{2-} + 2 \text{OH}^- \]

The inner sphere bidentate surface complex formation mechanism suggested for the As(V) sorption by NHICO had been found to be similar with that made by Pena et al. (2006).

**Conclusion**

Agglomerated nanoparticles (40-50 nm) of hydrous iron(III)-chromium(III) bimetal oxide (NHICO) was synthesized by the chemical precipitation method at low temperature, and used for the As(V) sorption at pH \( p_\text{H} = 6.4 \pm 0.1 \) and \( T = 298 \pm 1.6 \) K. High specific surface area (608.6 m\(^2\).g\(^{-1}\)) with irregular surface morphology indicated the presence of nanostructure in the material. The zero point surface charge \( p_\text{H} = 6.4 \pm 0.1 \) indicated good possibility of As(V) removal efficiency with increasing pH \( p_\text{H} \) of solution. The pseudo-second order equation described the kinetics of As(V) sorption reaction with NHICO in the absence/presence of background ions. Well fits of the equilibrium data (obtained in the presence/absence of ions at background) with the Freundlich and the Redlich-Peterson (\( g < 1.0 \)) models suggested surface heterogeneity of NHICO. Thermodynamic analyses of data showed that the As(V) sorption reaction with NHICO was endothermic and spontaneous, which took place with increasing entropy. The reaction of As(V)-sorption by NHICO had taken place with ion/ligand exchange mechanism.

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**References**


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