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Equilibrium and Thermodynamics on Arsenic(III) Sorption Reaction in the Presence of Background Ions Occurring in Groundwater with Nanoparticle Agglomerates of Hydrous Iron(III) + Chromium(III) Mixed Oxide[†]

Tina Basu, Kaushik Gupta, and Uday Chand Ghosh*

Department of Chemistry, Presidency College, 86/1 College Street, Kolkata 700 073, India

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Agglomerated nanoparticles [(40 to 50) nm] of synthetic iron(III) + chromium(III) mixed oxide (NHICO) were investigated for the equilibrium and thermodynamics of arsenic(III) removal, respectively, at pH 7.0 (± 0.2) and temperature ($T \pm 1.6$) = (288 and 303) K from solutions with background ions that coexist in groundwater. Langmuir and Redlich−Peterson isotherm models described the equilibrium data better than Freundlich model. The Langmuir capacity ($\theta_0 \cdot 10^2$, $\text{mmol} \cdot \text{kg}^{-1}$) values estimated, 10.404 and 10.686 in the absence of ions at studied temperatures, were higher than that in the presence of ions (except for HCO_3^-) at background. The enthalpy (ΔH^0) and entropy (ΔS^0) changes were positive, indicating endothermic reactions driven by entropy increase at the solid−liquid interface. Negative values of free energy change (ΔG^0) indicated that the reactions were spontaneous, which increased with increasing temperature on reactions. The treatment of groundwater (arsenic concentration: 1.347 $\mu\text{mol} \cdot \text{dm}^{-3}$) by the NHICO packed fixed-bed column (height: 6.0 cm, i.d.: 1.0 cm, bed volume: 4.71 cm^3) yielded 4.7 dm^3 (~1000 BV) of water with an arsenic concentration of ≤ 0.133 $\mu\text{mol} \cdot \text{dm}^{-3}$. The used bed was regenerated up to a level 90 (± 1.5) % of its initial capacity with 0.350 dm^3 of optimized 0.25 M NaOH solution.

Introduction

Arsenic exists in the natural environment in four different oxidation states: As(V), As(III), As(0), and As(−III). The mobility and toxicity of arsenic are determined by its oxidation states;[1] thus, the behavior of arsenic species will change depending on biotic and abiotic conditions in water. The occurrence of arsenic in groundwater much exceeding the tolerance limit (10 $\mu\text{g} \cdot \text{dm}^{-3}$/0.133 $\mu\text{mol} \cdot \text{dm}^{-3}$) is a global problem[2] and poses 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. An accumulation of excess arsenic in groundwater in this delta region is presumably due to the microbial reduction of geogenic arsenopyrites and iron oxyhydroxide with adsorbed arsenic in an anoxic environment.[3,4] The aquifers thus become rich in this reduced As(III) along with Fe(II). The ratios of As(III)/$\text{As}_{(\text{Total})}$ at a depth of (30 to 40) m reported in these aquifers are in the range of 0.6 to 0.9,[4] which is a matter of great concern since the toxicity and mobility of arsenic(III) are greater than those of arsenic(V). The high toxicity of arsenic(III) is due to the high combining affinity with the thiol (−SH) part of the protein due to a soft−soft acid−base reaction.

Remembering the adverse health impact of arsenic toxicity for long-term drinking of groundwater contaminated with high arsenic, the researchers had paid attention for last two decades in developing methods for reducing arsenic level below or equal to the permissible value (10 $\mu\text{g} \cdot \text{dm}^{-3}$/0.133 $\mu\text{mol} \cdot \text{dm}^{-3}$). Consequently, several methods such as oxidation−precipitation, coagulation/electrocoagulation/precipitation, membrane filtration, surface sorption, and ion exchange, and so forth, were reported.[2,5,6] However, the surface sorption has been found to be an alternative option for the treatment of arsenic-rich groundwater and has been well-accepted by the rural people of under-developed countries like India and Bangladesh for its simplicity of operation, requirement of less space, and low recurring cost. Numerous sorbent materials,[5,6] namely, activated carbon, agricultural products and byproduct, biomasses and metal oxides, or metal ion loaded biomaterials were tested for the treatment of arsenic-rich (> 0.133 $\mu\text{mol} \cdot \text{dm}^{-3}$) ground/wastewater and industrial effluents. It has been found that different mineralogical forms of iron(III)/aluminum(III) oxide and hydroxide[7−22] in the bulk phase were used for arsenic sorption from aqueous solutions. Arsenic sorption or removal using some synthetic polyvalent metal oxides had also been investigated[22−27] in our laboratory. Zhang[28] demonstrated an overview on the use of nanoscale iron particles for environmental remediation for large surface areas and in situ reactivity. Consequently, the sorption behavior of arsenic from aqueous solutions had been reported using nanoscale zerovalent iron[29,30] and nanocrystalline titanium oxide.[31,32] On the basis of these studies, some filters for the treatment of arsenic-rich groundwater are developed and marketed by different companies. It had been reported[33] that the assessment performances of the filters at the field were not up to the level of specification given by the manufacturers. It is presumably due to the adverse influence of dissolved ions like sulfate, phosphate, chloride, calcium, magnesium, and so forth that those co-occur with arsenic in groundwater. Therefore, we have aimed for the sorption of arsenic by iron(III)-based sorbent materials to be investigated for removal from water in the presence of some background ions, which occur with arsenic in groundwater.

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* Corresponding author: Tel./Fax: +91-33-2241-3893. E-mail: ucghosh@yahoo.co.in.

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Thus, this manuscript reports herein the results of equilibrium and thermodynamics studies for the sorption reaction of arsenic(III) with nanoparticle [(40 to 50) nm] agglomerates of synthetic hydrous iron(III) + chromium(III) mixed oxide (NHICO) in the presence of some background ions occurring in groundwater with the column treatment of high arsenic groundwater by a NHICO packed fixed bed.

Materials and Methods

Chemicals. All chemicals used were of guaranteed reagent (G.R.) grade (E. Merck, India) except for arsenic(III) oxide (As_2O_3; 99.99 %, Analar Reagent, BDH, England), iron(III) chloride ($FeCl_3$; 98 %, laboratory reagent, E. Merck, India), sodium hydroxide (NaOH; 97 %, laboratory reagent, SD Fine Chemicals, India), and chromium(III) chloride ($CrCl_3$; 93 %, laboratory reagent, Loba Chemie, India).

Arsenic(III) Solution. A standard stock arsenic(III) solution (13.33 $mmol \cdot dm^{-3}$) was prepared by dissolving 1.76 mmol of arsenic(III) oxide in 0.1 dm^3 of arsenic-free 0.04 mass fraction sodium hydroxide solution, which was diluted with double-distilled water to 1.0 dm^3 into a volumetric flask. A measured volume of this stock solution was diluted with 0.002 volume fraction of HCl in water for a desired level of arsenic(III) concentration in solution prior to use in experiments. The stock was prepared fresh after every 15 days and frozen to prevent oxidation.

Arsenic Analysis. Concentrations of arsenic in sample solutions were analyzed using a UV–vis spectrophotometer (Hitachi, model U-3210) and atomic absorption spectrophotometer (Perkin-Elmer, model Analyst 200) by the methods described in the *Standard Methods for the Examination of Water and Wastewater*.[34]

Synthesis of NHICO. NHICO was synthesized by the method of chemical precipitation. Here, $FeCl_3$ (0.1 M in 0.1 M HCl) and $CrCl_3$ (0.1 M in 0.1 M HCl) were mixed together in 1:1 volume ratios and warmed at 353 (± 8) K. To the hot, well-stirred (speed: ~ 300 rpm) mixed solution, aqueous NH_4OH (1:1, volume fraction) was added carefully until the pH reached between 5.5 and 6.7. The brown jell-like precipitates that appeared were aged with liquid for 4 days, filtered, and washed three times with distilled water. It was dried inside an air oven at (333 to 343) K. The dried hot mass when treated with cold water was broken to the fine agglomerates. The grain size of agglomerates ranging from (140 to 290) μm were sieved out and characterized for the nanostructure. These grains were heat-treated at (323, 373, 473, 523, 573, 623, 673, 723, and 773) K for an hour in a muffle furnace and desiccated at room temperature (303 ± 1.6 K), which was used for the experiments.

Batch Experiments. To evaluate optimum temperature for the heat treatment on NHICO, 0.05 g of solid heat-treated at different temperatures was added with 0.05 dm^3 of arsenic(III) solution [concentration, $C_I = (0.10 \text{ and } 0.13)\ mmol \cdot dm^{-3}$ and $pH = 6.4 \pm 0.2$] into the polyethylene tetraphthalate (PET) bottles (capacity: 0.25 dm^3). Reaction mixtures in PET bottles were agitated (speed: 350 ± 5 rpm) using a thermostat shaker at temperature $(T) = 303 \pm 1.6$ K for 2.0 h and filtered. Arsenic concentration (C_e, $mmol \cdot dm^{-3}$) was analyzed in each filtered solution.

For the effect of initial solution pH (pH_i) on the removal of arsenic(III) from aqueous solutions, 0.05 g of NHICO (heat-treated at 623 K) was mixed with 0.05 dm^3 of arsenic(III) solutions of $C_I = (0.10 \text{ and } 0.13)\ mmol \cdot dm^{-3}$ adjusted separately at pH_i = 2.0, 3.0. 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 into the PET bottles (capacity: 0.25 dm^3) and agitated (speed: 350 ± 5 rpm) for a duration of 2.0 h at $T = 303 \pm 1.6$ K. The equilibrium solution pH (pH_f) value of each mixture was recorded immediately after 2 h of agitation by immersing the pH-meter electrode (model LI-127, ELICO India) and filtered to separate the solution from the solid particles. Each filtrate was analyzed for the arsenic concentration (C_e, $mmol \cdot dm^{-3}$) remaining at equilibrium.

Batch procedure, which was adopted for the determination of the equilibrium time of arsenic(III) removal reaction with NHICO (heat-treated at 623 K) from the solution of $C_I = (0.067 \text{ and } 0.172)\ mmol \cdot dm^{-3}$ including the background ion [SO_4^{2-} (2.08), Cl^- (11.27), PO_4^{3-} (0.53), HCO_3^- (4.92), Mg^{2+} (4.10), Ca^{2+} (2.5), SiO_3^{2-} (0.64)] at pH_i = 7.0 (± 0.2) and T = 303 (± 1.6) K was described in the Supporting Information (SI).

For equilibrium isotherm, experiments were set as described in the first paragraph in this subsection. Here, the arsenic(III) solution of C_I ranging from (0.13 to 3.33) $mmol \cdot dm^{-3}$ including a background ion [SO_4^{2-} (2.08), Cl^- (11.27), PO_4^{3-} (0.53), HCO_3^- (4.92), Mg^{2+} (4.10), Ca^{2+} (2.5), SiO_3^{2-} (0.64)] at pH_i 7.0 (± 0.2) was mixed separately with NHICO (heat-treated at 623 K). Values noted in parentheses against each background ion were the C_I ($mmol \cdot dm^{-3}$) of that ion added with arsenic(III) solution. A major change of pH during agitation, if any, in each set was checked at $t \approx$ (45 and 90) min from the time of start ($t = 0$) and adjusted (if required) by 0.1 M HCl or 0.1 M NaOH. Reaction mixtures were filtered immediately after 2.0 h of agitation, and the filtrates were analyzed for arsenic concentration (C_e, $mmol \cdot dm^{-3}$) remaining at equilibrium.

Calculation of Sorption Capacity. Arsenic(III) sorption capacity (q_e, $mmol \cdot kg^{-1}$) at the equilibrium of NHICO was calculated from the following mass balance relation (eq 1):

$$q_e = [C_I - C_e] \cdot (V/W) \cdot 10^3 \tag{1}$$

where C_I and C_e are the concentrations ($mmol \cdot dm^{-3}$) of arsenic in solution at $t = 0$ and equilibrium, respectively; V and W are the volume (dm^3) of solution and mass (g) of sorbent taken for the experiments. The multiplication factor 10^3 converted the q_e values in terms of $mmol \cdot kg^{-1}$.

Fixed-Bed Column Experiment for Arsenic Removal from Groundwater. A fixed-bed column was made by uniform packing of NHICO into a glass tube (i.d. 1.0 cm) up to a height of 6.0 cm (bed volume, BV: 4.71 cm^3). Groundwater sample that was collected from a tube well [depth: (40 to 45) m] from Kalinarayan pore at the Nadia district in West Bengal (India) was analyzed for arsenic (0.101 $mg \cdot dm^{-3}$/1.347 $\mu mol \cdot dm^{-3}$). Some analyzed parameters for water quality ($mmol \cdot dm^{-3}$, except pH) were pH (7.5), Fe^{2+} ($2.686 \cdot 10^{-3}$), F^- (0.034), and HCO_3^- (11.061), and hardness (2.92 as $CaCO_3$), Mg^{2+} (0.547) and Ca^{2+} (2.38). This water sample was passed through the NHICO packed bed for filtration (flow rate: 0.06 $dm^3 \cdot h^{-1}$). The filtered water collected by 0.1 dm^3 fractions was analyzed for arsenic concentration.

The arsenic-loaded NHICO bed in the column was regenerated by passing 0.25 M NaOH solution with an effluent rate of 0.06 $dm^3 \cdot h^{-1}$. Effluents were collected by a fraction of 0.05 dm^3 and analyzed for the arsenic released.

Results and Discussion

Physicochemical Characterization of NHICO. An analysis of the X-ray diffraction (XRD) pattern (figure omitted) of NHICO suggested that the material was amorphous. Absorbance bands (spectra a to d in Figure S1 of SI) at wavenumbers (ν, cm^{-1}) ranging from 3650 to 3120 and 1630 to 1400 were the stretching and bending modes of O–H bonds of lattice water and the hydroxyl groups, respectively. An absorption band appearing at $\nu \sim 521\ \text{cm}^{-1}$ in the spectrum of NHICO (marked as a) was absent in the spectra of the solid−solid mixture of iron(III) and chromium(III) oxides (marked as b), iron(III) oxide (marked as c), and chromum(III) oxide (marked as d). This indicated that the oxo/hydroxo bridge bond developed between iron(III) and chromium(III) in NHICO. Thus, it was found that the synthetic material was a hydrated mixed oxide. The thermogravimetric (TG) spectrum (Figure S2 of SI) showed a total weight loss by 24.75 % at temperatures between (80 and 800) °C which confirmed the hydrous nature of NHICO. Transmission electron microscopic (TEM) images (Figure S3 of SI) of NHICO confirmed the existence of nanoparticles [dimensions: (40 to 50) nm] in the agglomerates. Scanning electron microscopic (SEM) images (Figure S4 of SI) showed that the surface morphology of that material was irregular. The specific surface area, pH_{zpc}, and bulk density of NHICO, respectively, were estimated to be 601.6 (± 5.0) $\text{m}^2\cdot\text{g}^{-1}$ and [6.4 (± 0.2) and 2.20 (± 0.02)] $\text{g}\cdot\text{cm}^{-3}$ (SI). Taking the weight loss data from TG analysis at > 80 °C and chemical analyses by the wet method of dissolved NHICO in HCl for iron and chromium suggested that the percentage composition of NHICO was Fe_2O_3 (36.54 ± 0.45), Cr_2O_3 (35.84 ± 0.60), and H_2O (24.75 ± 0.35).

Effect of Heat Treatment Temperature. Arsenic(III) sorption capacity (q_e, $\text{mmol}\cdot\text{kg}^{-1}$) of heat-treated NHICO from aqueous solutions [C_I of arsenic(III) = (0.101 and 0.13) $\text{mmol}\cdot\text{dm}^{-3}$] at pH 6.4 (± 0.2) versus heat treatment temperature (Figure S5), described in the SI, showed that the value of q_e increased with increasing heat treatment temperature on NHICO from (323 to 623) K and decreased with that from (623 to 773) K. Thus, heat-treated NHICO at 623 K had the highest arsenic(III) removal capacity from the aqueous solutions, and that NHICO was used for the remaining experiments.

Effect of pH. The effect of initial solution pH (pH_i) on arsenic(III) removal capacity from aqueous solutions (Figure S6 of the SI) is discussed in detail in the SI. It was found that the NHICO (heat-treated at 623 K) had the highest arsenic(III) removal capacity from the aqueous solutions at $\text{pH}_i = 7.0$ (± 0.2) and $T = 303$ (± 1.6 K).

Equilibrium Modeling. Figures 1 and 2 demonstrate the values (as points) of sorption capacity at equilibrium (q_e, $\text{mmol}\cdot\text{kg}^{-1}$) against concentration at equilibrium (C_e, $\text{mmol}\cdot\text{dm}^{-3}$) of arsenic(III) for the sorption reaction with NHICO at T = [288 (± 1.6) and 303 (± 1.6)] K, respectively. To understand the sorption mechanism, equilibrium data shown as points were analyzed by the isotherm model equations,[35] namely, the Langmuir (eq 2), Freundlich (eq 3), and Redlich−Peterson (RP) (eq 4) with nonlinear regression fit method on origin spread sheet.

$$\text{Langmuir equation: } q_e = (\theta_0 K_a C_e)/(1 + K_a C_e) \qquad (2)$$

$$\text{Freundlich equation: } q_e = K_F C_e^{1/n} \qquad (3)$$

$$\text{RP equation: } q_e = (A C_e)/(1 + B C_e^{\,g}) \qquad (4)$$

where θ_0 and K_a are the Langmuir monolayer adsorption capacity ($\text{mmol}\cdot\text{kg}^{-1}$) and equilibrium constant ($\text{dm}^3\cdot\text{g}^{-1}$) and K_F and n are the Freundlich constants related to the adsorption capacity ($\text{mmol}^{1-1/n}\cdot\text{kg}^{-1}\cdot\text{dm}^{-3/n}$) and intensity (dimensionless), respectively. Significances of q_e and C_e are given above. The value of n is related to the affinity or binding strength of the solute with the solid surface. A ($\text{dm}^3\cdot\text{kg}^{-1}$) and B ($\text{dm}^3\cdot\text{mmol}^{-1}$) are the RP constants related to the adsorption equilibrium constant. The value of g, a dimensionless RP constant, should vary from 0 to 1.0. When $g = 0$, the RP eq 4 converts to Henry law, and when $g = 1$, that equation converts to Langmuir eq 2.

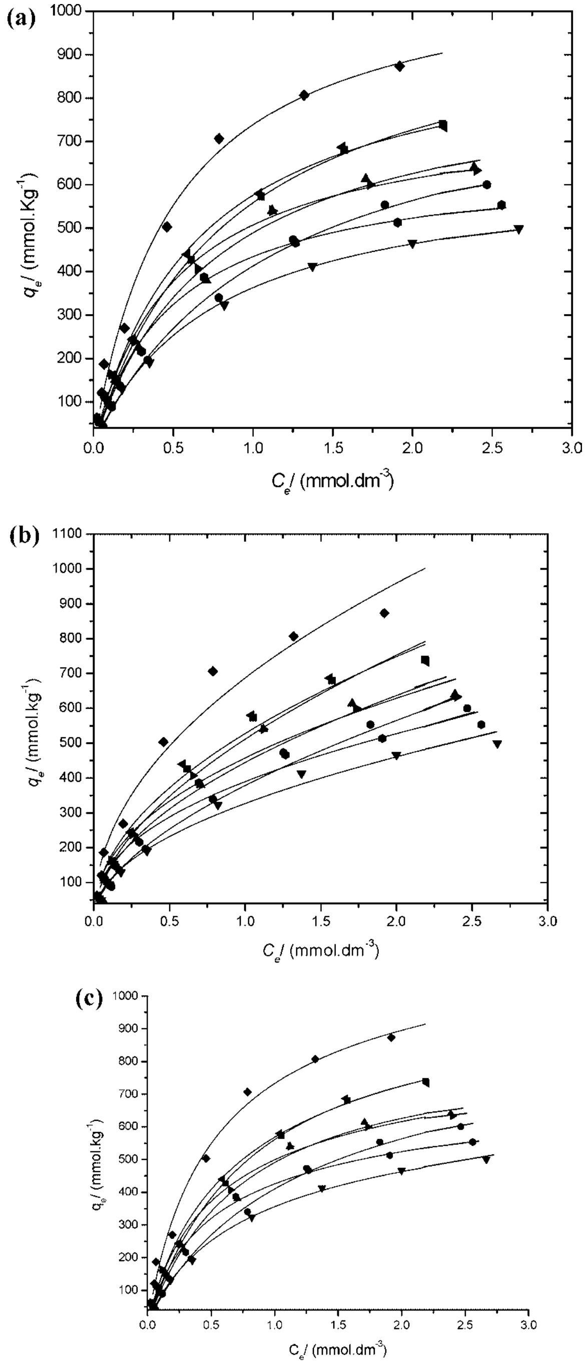

Figure 1. Plots of equilibrium sorption capacity (q_e) versus equilibrium concentration (C_e) of the arsenic(III) sorption reaction with NHICO at T = 288 (± 1.6) K and $\text{pH}_i = 7.0$ (± 0.2) in the presence of some background ions and nonlinear fits of the data with (a) Langmuir, (b) Freundlich, and (c) RP isotherm equations. ■, no ion; ●, SO_4^{2-}; ▲, Cl^-; ▼, PO_4^{3-}; ◆, HCO_3^-; left-pointing triangle, Mg^{2+}; right-pointing triangle, Ca^{2+}; and ⬢, SiO_3^{2-}.

Figures 1a−c and 2a−c show the nonlinear fits of the equilibrium data with the Langmuir (eq 2), Freundlich (eq 3), and RP (eq 4) equations. The estimated isotherm parameters for eqs 2 to 4 are shown in Tables 1 and 2 with the regression coefficient (R^2) and statistical error χ^2 values. On the basis of the values of χ^2 and R^2 (Tables 1 and 2), it was found that the present data described the Langmuir (eq 2) and the RP (eq 4) model isotherms very well ($R^2 \geq 0.99$). The goodness-of-fit of

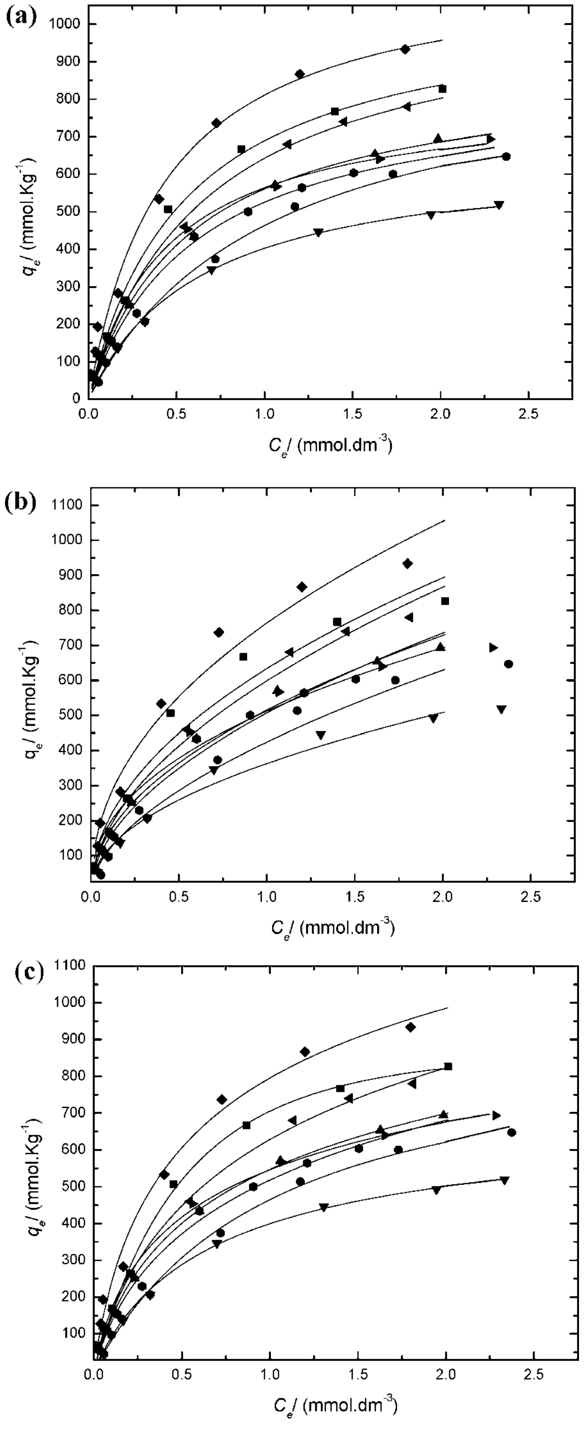

Figure 2. Plots of equilibrium sorption capacity (q_e) versus equilibrium concentration (C_e) of the arsenic(III) sorption reaction with NHICO at $T = 303$ (± 1.6) K and $pH_i = 7.0$ (± 0.2) in the presence of some background ions and nonlinear fits of the data with (a) Langmuir, (b) Freundlich, and (c) RP isotherm equations. ■, no ion; ●, SO_4^{2-}; ▲, Cl^-; ▼, PO_4^{3-}; ◆, HCO_3^-; left-pointing triangle, Mg^{2+}; right-pointing triangle, Ca^{2+}; and ⬢, SiO_3^{2-}.

the data with either the Langmuir (eq 2) or the RP (eq 4) model was comparatively better than that with the Freundlich model (eq 3; $R^2 = 0.97$ to 0.99). Assumptions based on which the Langmuir model (eq 2) is developed are (i) the monolayer adsorption of adsorbate on the adsorbent surface and (ii) the homogeneous energetic distribution of the active binding sites that are equally accessible to the solute. Good fits of the equilibrium data with the Langmuir model (eq 2) indicated that the adsorption sites of the NHICO surface were homogeneous and accessed equally by the arsenic species. Values of the dimensionless Freundlich constant (n) laid between 1.73 and 2.29, indicating a high affinity of arsenic(III) for the solid surface. Moreover, the values of g of the RP model were close to 1.0 ($0.78 < g < 1.20$), which helped us to understand that the Langmuir (eq 2) model is a better fit of the present equilibrium data. This confirmed that the active sites available on the NHICO surface are equally accessible to the solute particles. In contrast to the isotherm modeling of equilibrium data by Kuriakose et al.[19] and Zhang and Itoh,[36] the modeling of present data was found to be almost similar with the others.[8,9,12,18] Values for θ_0 ($\cdot 10^2$) obtained were (10.4 and 10.7) mmol$\cdot$kg^{-1} (Tables 1 and 2) for the arsenic(III) sorption reaction with NHICO in the absence of background ions, respectively, at T (± 1.6) = (288 and 303) K, which were higher than those obtained for the reaction in the presence of background ions (except for HCO_3^-). Thus, the background ions (except for HCO_3^-) had an adverse effect on the removal of arsenic(III) by NHICO. The obtained values of θ_0 ($\cdot 10^2$), (11.1 and 11.7) mmol$\cdot$kg^{-1}, respectively, at T (± 1.6) = (288 and 303) K (Tables 1 and 2) in the presence of HCO_3^- in the background on the arsenic(III) sorption reaction with NHICO, were higher than those obtained in the absence of background ions. It indicated that the HCO_3^- had a positive effect on the equilibrium of the arsenic(III) removal reaction. This is probably for the faster sorption of bicarbonate by NHICO ($\log K = 22.33 \pm 0.01$ for bicarbonate sorption on goethite)[37] than $As(OH)_3$ ($\log K = 4.91$, $\log K = 7.26$ for $As(OH)_3$ sorption on goethite),[38] which converted the negative solid surface and $As(OH)_3$ sorbed strongly thereon via an intermolecular type of hydrogen bond formation.

The separation factor,[39] R_L (a dimensionless parameter), which could predict the reaction feasibility had been expressed as,

$$R_L = (1 + K_a C_I)^{-1} \tag{5}$$

The significance of K_a and C_I has been given elsewhere in this manuscript. When the value of R_L is equal to (i) 0.0 to 1.0, the reaction is favorable, (ii) 0.0, the reaction is irreversible, and (iii) > 1.0, the reaction is unfavorable. Inserting the values of K_a (Tables 1 and 2) and C_I of arsenic(III) [= (0.13 to 3.33) mmol$\cdot$dm^{-3}] into the depicted relation (eq 5), the R_L values obtained were in the range of 0.0 to 1.0. This suggested that the arsenic(III) sorption reaction with NHICO, even in presence of background ions, was a favorable process at the conditions used for the experiments.

Mean Sorption Energy. Mean sorption energy (E_a, kJ$\cdot$mol^{-1}), which helps to predict the nature of a reaction, is defined as the free energy of transfer of one mole of solute from infinity (in solution) to the surface of the sorbent. The value of E_a is related with the Dubinin−Radushkevich[40] (DR) constant, B_D (mol$^2\cdot$kJ^{-2}) as $E_a = (2B_D)^{-0.5}$, which could be computed from the analysis of equilibrium data of a sorption reaction with the DR isotherm equation,[40]

$$\ln q_e = \ln q_m - B_D \varepsilon^2 \tag{6}$$

where q_m is the saturation sorption capacity (mmol$\cdot$kg^{-1}). The Polanyi potential (ε) expressed as $\varepsilon = RT \ln\{1 + (C_e)^{-1}\}$, where R is the molar gas constant and T, the absolute temperature.

The value of B_D was calculated from the slope of each linear plot of $\ln q_e$ against ε^2 (Figure S7 of SI) and evaluated the value for E_a. The values obtained are shown in Table 4. Values of E_a for the reaction of arsenic(III) sorption with NHICO in the

Table 1. Isotherm Parameters Estimated by the Nonlinear Method of Analysis of Equilibrium Arsenic(III) Sorption Data on NHICO at pH = 7.0 (± 0.2) and T = 288 (± 1.6) K

	Langmuir isotherm parameters				Freundlich isotherm parameters				RP isotherm parameters				
			θ_0 ($\cdot 10^2$)	K_a			K_F ($\cdot 10^2$)						
As(III) + ion added	R^2	χ^2 ($\cdot 10^2$)	$\mathrm{mmol \cdot kg^{-1}}$	$\mathrm{dm^3 \cdot mmol^{-1}}$	R^2	χ^2 ($\cdot 10^2$)	$(\mathrm{mmol \cdot kg^{1-}}) \cdot (\mathrm{dm^3 \cdot mg^{-1}})^{1/n}$	n	R^2	χ^2 ($\cdot 10^2$)	A ($\cdot 10^2$)	B	g
PO_4^{3-}	0.998	0.936	6.427	1.299	0.983	6.109	3.269	2.018	0.998	0.751	9.821	1.758	0.883
SiO_3^{2-}	0.992	3.685	6.58	1.944	0.975	11.423	3.899	2.291	0.993	3.968	15.191	2.569	0.901
Ca^{2+}	0.995	3.282	7.766	1.886	0.975	15.772	4.579	2.183	0.995	3.432	16.826	2.37	0.912
Cl^-	0.993	4.94	8.697	1.286	0.971	19.028	4.447	1.928	0.993	5.905	10.884	1.217	1.026
SO_4^{2-}	0.996	2.107	8.883	0.869	0.984	8.871	3.784	1.727	0.996	2.45	8.21	1.002	0.933
Mg^{2+}	0.997	2.715	9.614	1.495	0.983	14.303	5.276	1.982	0.997	2.798	16.318	1.872	0.904
no ion	0.998	1.419	10.404	1.159	0.979	18.566	5.115	1.793	0.998	1.65	11.679	1.082	1.037
HCO_3^-	0.99	11.775	11.128	1.973	0.972	34.479	6.87	2.075	0.991	13.868	24.021	2.279	0.938

Table 2. Isotherm Parameters Estimated by the Nonlinear Method of Analysis of Equilibrium Arsenic(III) Sorption Data on NHICO at pH = 7.0 (± 0.2) and T = 303 (± 1.6) K

	Langmuir isotherm parameters				Freundlich isotherm parameters				RP isotherm parameters				
			θ_0 ($\cdot 10^2$)	K_a			K_F ($\cdot 10^2$)						
As(III) + ion added	R^2	χ^2 ($\cdot 10^2$)	$\mathrm{mmol \cdot kg^{1-}}$	$\mathrm{dm^3 \cdot mmol^{-1}}$	R^2	χ^2 ($\cdot 10^2$)	$(\mathrm{mmol \cdot kg^{1-}}) \cdot (\mathrm{dm^3 \cdot mg^{-1}})^{1/n}$	n	R^2	χ^2	A	B	g
PO_4^{3-}	0.998	0.784	6.608	6.608	0.980	8.191	3.631	2.061	0.998	0.893	10.850	1.716	0.958
Ca^{2+}	0.991	6.699	8.166	2.231	0.979	15.054	5.122	2.289	0.993	5.907	25.625	3.693	0.835
SiO_3^{2-}	0.990	5.287	8.456	1.639	0.987	7.398	5.072	1.865	0.992	5.624	18.847	2.639	0.783
Cl^-	0.998	1.760	8.835	1.738	0.988	9.236	5.154	2.003	0.999	0.572	19.749	2.611	0.833
SO_4^{2-}	0.997	2.041	9.434	0.965	0.981	12.602	4.242	1.759	0.997	2.428	8.849	0.904	1.033
Mg^{2+}	0.996	3.951	10.676	1.510	0.991	8.930	5.985	1.873	0.997	3.463	20.711	2.298	0.812
no ion	0.996	4.959	10.686	1.815	0.962	42.036	6.335	2.018	0.997	3.963	16.742	1.375	1.162
HCO_3^-	0.989	15.223	11.669	2.276	0.977	31.651	7.637	2.150	0.991	15.984	36.047	3.533	0.839

presence of background ions were laid between (8.0 and 10.1) $\mathrm{kJ \cdot mol^{-1}}$ (Table S1 of SI), which indicated that the arsenic(III) sorption by NHICO took place with the ion-exchange/chemisorption[41] phenomenon.

Thermodynamic Parameters. Thermodynamic parameters for the arsenic(III) removal reaction with NHICO were estimated by using standard equations[42] on the basis of the assumption that the activity coefficient of solutes added for working in solution was unity.

The thermodynamic constant (K_c) was evaluated by using eq 7, taking the experimental data of equilibrium q_e and C_e determined at T (± 1.6) = (283, 293, 303, 313, and 323) K.

$$K_c = q_e/C_e \tag{7}$$

where q_e/C_e is called the sorption affinity ($\mathrm{dm^3 \cdot g^{-1}}$). The q_e and C_e have their usual significance and are given elsewhere. The values of the changes of entropy and enthalpy at standard conditions (ΔS^o and ΔH^o) were calculated from the slope and intercept of the plot of $\log(q_e/C_e)$ versus ($1/T$) (Figure 3) of the linear relation shown (eq 8).

$$log_{10}(q_e/C_e) = \Delta S^0/2.303R - (\Delta H^0/2.303R)1/T \tag{8}$$

Taking the values of ΔS^o and ΔH^o, the values of ΔG^o were calculated. The values of ΔG^o estimated for the thermodynamic parameters are shown in Table 3. It was found that the reactions in the presence and absence of ions at the background were endothermic (ΔH^o = positive), which took place with increasing entropy (ΔS^o = positive) at the solid−liquid interface, and spontaneous (ΔG^o = negative). The increase of entropy was due to the increase of randomness at the solid−liquid interface due to the release of aqua molecules when aquatic arsenic(III) species was distributed on the solid surface. The values of ΔG^o were found to be increasingly negative with increasing temperature on the reactions in the absence and presence of background ions, indicating the increase in spontaneity of the reactions.

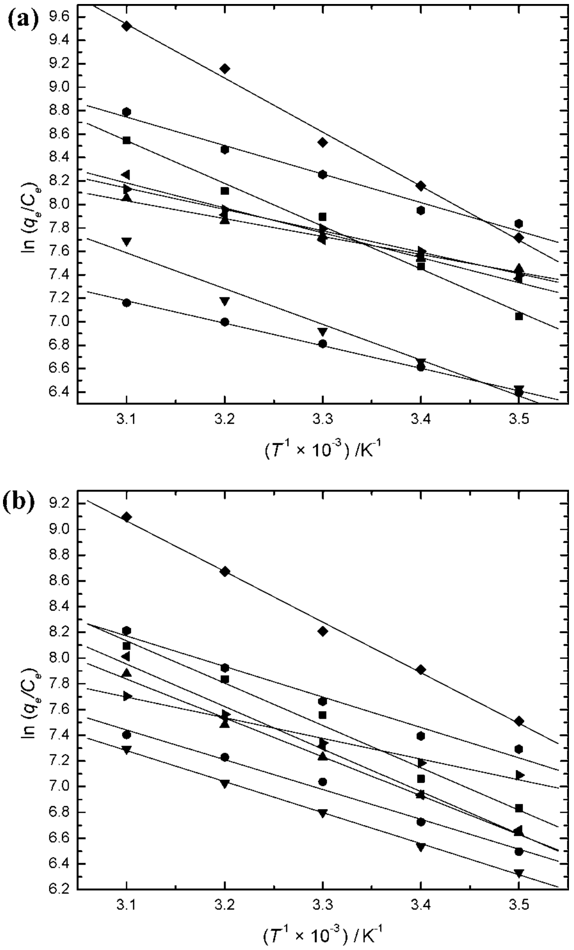

Figure 3. Plots of $\ln(q_e/C_e)$ versus $(T^{-1} \cdot 10^{-3})/K^{-1}$ for the sorption reaction of arsenic(III) with NHICO from arsenic(III) solutions at C_I ($\mathrm{mmol \cdot dm^{-3}}$) = (a) 0.067 and (b) 0.133 in the presence of some background ions. ■, no ion; ●, SO_4^{2-}; ▲, Cl^-; ▼, PO_4^{3-}; ◆, HCO_3^-; left-pointing triangle, Mg^{2+}; right-pointing triangle, Ca^{2+}; and ⬢, SiO_3^{2-}.

Table 3. Thermodynamic Parameters Estimated for Arsenic(III) Sorption on NHICO at Different Reaction Temperatures (K) and at pH_i 7.0 (± 0.2)

As(III) + ion added	C_I mmol·dm^{-3}	$\Delta H°$ kJ·mol^{-1}	$\Delta S°$ kJ·mol^{-1} K^{-1}	$-\Delta G°$/(kJ·mol^{-1}) 283 K	293 K	303 K	313 K	323 K
no ion	0.067	30.314	0.165	16.381	18.031	19.681	21.331	22.981
	0.134	27.353	0.152	15.776	17.300	18.824	20.348	21.872
SO_4^{2-}	0.067	15.952	0.109	14.923	16.014	17.105	18.742	19.287
	0.134	19.264	0.122	15.148	16.364	17.580	18.796	20.012
Cl^-	0.067	12.679	0.106	17.347	18.408	19.469	20.530	21.591
	0.134	25.117	0.143	15.352	16.782	18.212	19.642	21.072
PO_4^{3-}	0.067	24.775	0.140	14.788	16.885	17.584	18.982	20.380
	0.134	20.058	0.123	14.666	15.893	17.120	18.347	19.574
HCO_3^-	0.067	38.271	0.198	17.735	19.714	21.693	23.672	25.651
	0.134	32.721	0.177	17.31	19.081	20.849	22.617	24.385
Mg^{2+}	0.067	17.647	0.123	17.078	18.305	19.532	20.759	21.986
	0.134	27.461	0.151	15.357	16.870	18.383	19.896	21.409
Ca^{2+}	0.067	15.191	0.115	17.297	18.445	19.593	20.741	21.889
	0.134	13.354	0.105	16.474	17.528	18.582	19.636	20.690
SiO_3^{2-}	0.067	20.169	0.135	18.093	19.445	20.797	22.149	23.501
	0.1340	19.688	0.129	16.819	18.109	19.399	20.689	21.979

Mass Transfer Kinetics. The transfer of mass from the liquid to the solid phase carries out the uptake of a solute in the liquid phase by the surface of the sorbent, which may take place in a number of steps. McKay and Ho[43] developed a model based on the assumptions of the (i) mass transfers from the aqueous phase onto the solid surface, (ii) adsorption of solute onto the surface sites, and (iii) internal diffusion of the solute via either a pore diffusion model or homogeneous solid-phase diffusion model.

Taking into account these probable steps, the modified McKay and Ho[43] model eq 9 was used for the present investigation.

$$\ln[C_t/C_I - 1/(1 + mK_1)] = \ln[mK_1/(1 + mK_1)] - (1 + mK_1)\beta_1 S_S t \qquad (9)$$

where C_I and C_t are concentrations (mmol·dm^{-3}) of arsenic at time $t = 0$ and $t =$ equilibrium, respectively; m is the mass (g) of the adsorbent per unit volume, K_1 is a constant which is the product of the Langmuir monolayer capacity (θ_0) and Langmuir equilibrium constant (K_a). β_1 is the mass transfer coefficient (m·s^{-1}), and S_S is the outer specific surface (m^{-1}) of the adsorbate per unit volume. Taking the time-dependent residual arsenic(III) concentration (C_t, mmol·dm^{-3}) obtained from the sorption kinetics experiment (Figure S8a,b of SI), the values of $\ln[C_t/C_I - 1/(1 + mK_1)]$ were calculated and plotted against time, t (min). Figure 4a,b shows the linear plots with slopes $[\{(1 + mK_1)/mK_1\}\beta_1 S_S]$. The values of the correlation coefficient (R^2) ranged in 0.95 to 0.99 indicated good linearity of the plots. The values of mass transfer coefficients (β_1) calculated from the slopes are given in Table S2 of SI. It was found that the values of β_1 were in general of the order 10^{-13}. Only the prefix coefficients differed, indicating a slight effect on the mass transportation process. The values of β_1 (Table S2 of SI) for the case of C_I = 0.067 mmol·dm^{-3} were found to be higher in the presence of Mg^{2+}, Cl^-, SiO_3^{2-}, and HCO_3^- than in the presence of no or other background ions, while that was not clearly found when the C_I of arsenic(III) was 0.172 mmol·dm^{-3}; that is, the mass transportation of arsenic(III) from solution onto the solid surface was higher in the presence of Mg^{2+}, Cl^-, SiO_3^{2-}, and HCO_3^-, especially when C_I was less. Again, the value of β_1 was higher at C_I = 0.067 mmol·dm^{-3} than C_I = 0.172 mmol·dm^{-3} of arsenic(III) solution when no background ion was added, indicating higher mass transportation from the aqueous solution on the solid surface at low concentrations. This is presumably due to the increased coulombic inhibition between the solute species in solution and on solid surface being developed by rapid uptake at initial stages from the solution of high C_I value.

Filtration of High Arsenic Groundwater Using a Fixed-Bed NHICO Column. Figure 5 demonstrates the result that is obtained by filtering the collected groundwater contami-

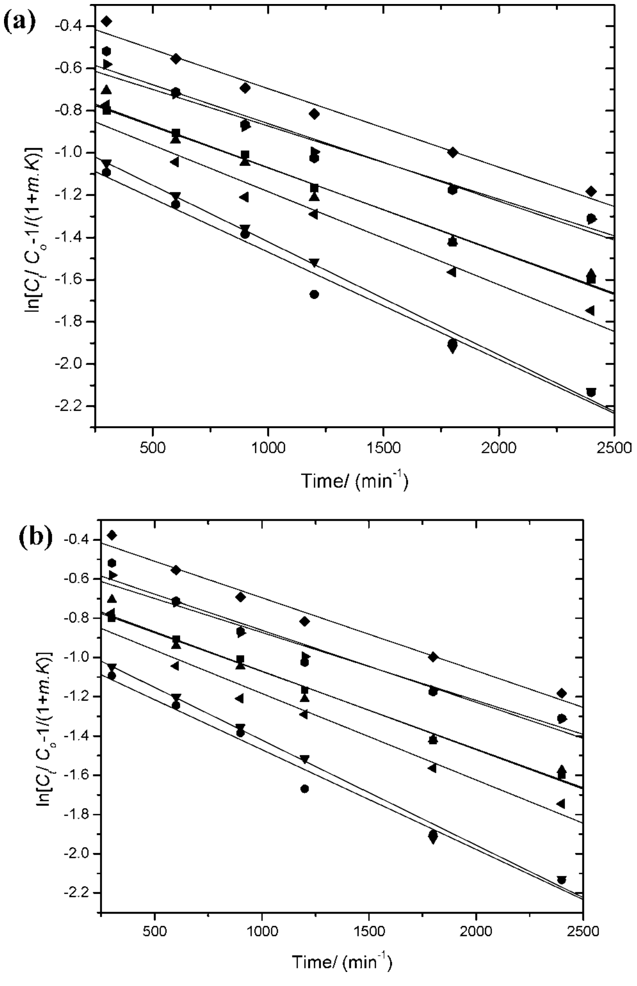

Figure 4. Mass transfer kinetic plots of arsenic(III) sorption on NHICO from the solutions of C_I (mmol·dm^{-3}) = (a) 0.067 and (b) 0.172 at T = 303 (± 1.6) K and pH_i = 7.0 (± 0.2) in the presence of some background ions. ■, no ion; ●, SO_4^{2-}; ▲, Cl^-; ▼, PO_4^{3-}; ◆, HCO_3^-; left-pointing triangle, Mg^{2+}; right-pointing triangle, Ca^{2+}; and ⬢, SiO_3^{2-}.

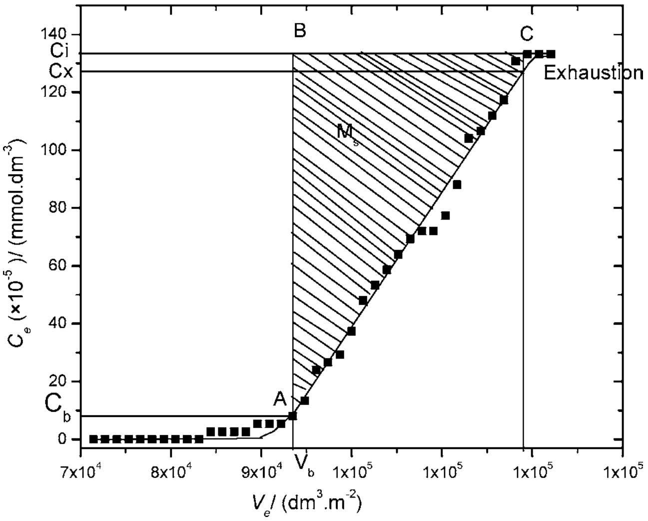

Figure 5. Breakthrough curve for the filtration of a groundwater sample by a NHICO packed fixed-bed column.

nated with high arsenic (1.347 μmol·dm^{-3}). To estimate the rate of attainment of equilibrium of arsenic concentration between mobile and stationary phases, the breakthrough curve (Figure 5) that is obtained by the treatment of field sample was analyzed.[44] The curve was idealized by the assumption that the removal of the solute is complete over the initial stages of operation. The break point was chosen at a point of arsenic concentration (C_b) crossed over 0.01 mg·dm^{-3} (0.133 μmol·dm^{-3}) in the effluent. At an arbitrarily selected effluent concentration, C_x, closely approaching C_I, the sorbent was considered to be essentially exhausted.

The primary adsorption zone (PAZ) in the fixed-bed adsorber represented by the breakthrough curve in Figure 5 is defined as that part of the bed over which there is a concentration reduction from C_x to C_b. It is assumed that this zone is of constant length or depth, δ. The total time, t_x, involved for the primary zone to establish itself and move down the length of the adsorber and out of the bed may be calculated by eq 10.

$$t_x = V_x/F_m \tag{10}$$

F_m is the mass rate of flow to the adsorber, expressed as mass per unit time per unit cross-sectional area of the bed. The time, t_δ, required for movement of the zone down its own length in the column after it has been established is simply (eq 11)

$$t_\delta = (V_x - V_b)/F_m \tag{11}$$

Thus, for a depth D of the adsorber, one may equate the depth and time ratios (eq 12):

$$\delta/D = t_\delta/(t_x - t_f) \tag{12}$$

where t_f is the time required for initial formation of the primary adsorption zone.

The portion marked by ABC in Figure 5 represents the amount of solute or impurity adsorbed by NHICO in the PAZ from the break point to exhaustion. This quantity, M_S, may be calculated by integrating the quantity ($C_i - C$) over V_e between the limits of V_X and V_b. This does not represent the total capacity of NHICO within the PAZ at the break point. However, the total capacity would be given by the product, $(V_X - V_b)\cdot C_i$. Thus, one can define a fractional capacity, f, of the adsorber in the adsorption zone at break point to continue to remove solute from solution by eq 13.

$$f = M_S/(V_X - V_b)\cdot C_i = \int (C_i - C)\cdot dV_e/(V_X - V_b)\cdot C_i \tag{13}$$

where C_i and C are input and effluent concentrations of solute in terms of the mass passing a unit cross-sectional area of the adsorber. The fractional capacity, f, approaches zero as the time required for initial PAZ formation, t_f, approaches the time, t_δ, required for the zone to move a distance in the bed equal to its own depth, δ. For systems in which the formation time, t_f, is very small (approaching zero), the value of f approaches unity.

$$f = 1 - t_f/t_\delta \tag{14}$$

Thus, by combining eqs 13 and 14, the following eq 15 results,

$$\delta/D = t_\delta/[t_x + t_\delta(f - 1)] \tag{15}$$

The percent saturation at this point is given by the eq 16

$$\%\ \text{saturation} = [D - \delta(f)]/D\cdot 100 \tag{16}$$

The experimental and calculated parameters for the fixed-bed sorption of arsenic by the NHICO bed were summarized respectively in Table 4a,b. It was found that the fixed-bed column of NHICO filtered 4.7 dm^3 (997.9 BV) of water with arsenic concentration below 0.01 mg·dm^{-3} (0.133 μmol·dm^{-3}). The column saturation at exhaustion point is estimated to be 81.5 %.

The used bed was regenerated up to level of 90 (± 1.5) % of its initial activity with 0.350 dm^3 of optimized 0.25 M NaOH solution.

Conclusion

Synthetic hydrous iron(III) + chromium(III) mixed oxide (NHICO), agglomerated nanoparticles (40 to 50 nm), heat-treated at 623 K showed the highest sorption affinity for arsenic(III) from aqueous solutions at pH = 7.0 (± 0.2) and T = 303 (± 1.6) K. Use of this material for estimating

Table 4

a. Observed Parameters for the Fixed-Ced Arsenic(III) Removal by NHICO Column

flow rate (·10^{-2})	C_o (·10^{-5})	C_x (·10^{-5})	C_b (·10^{-5})	V_x (·10^4)	V_b (·10^4)	($V_x - V_b$) (·10^4)	F_m (·10^3)	D (·10^{-2})
dm^3·h^{-1}	mmol·dm^{-3}	mmol·dm^{-3}	mmol·dm^{-3}	kg·m^{-2}	kg·m^{-2}	kg·m^{-2}	kg·h^{-1}·m^{-2}	m
6.0	134.667	127.701	8.108	11.904	9.350	2.553	1.558	6.0

b. Calculated Parameters for the Fixed-Bed Arsenic(III) Removal by NHICO Column

flow rate (·10^{-2})	t_x	t_δ		t_f	δ (·10^{-2})	
dm^3·h^{-1}	h	h	f	h	m	% saturation
6.0	76.381	16.383	0.831	2.768	1.335	81.5

equilibrium and thermodynamics arsenic(III) sorption from aqueous solutions in the presence of different background ions that occur in groundwater showed that the reactions took place obeying Langmuir and RP isotherm models. The estimated Langmuir monolayer capacity (θ_0; $10.636 \cdot 10^2$ $\text{mmol} \cdot \text{kg}^{1-}$) was higher than that obtained in the presence of investigated background ions except for HCO_3^-, which showed notable positive effects on the equilibrium. Whatever the background ion is, the changes of enthalpy (ΔH^0) and entropy (ΔS^0) were positive, indicating an endothermic arsenic(III) sorption reaction driven by entropy increase at the solid−liquid interface. The negative free energy (ΔG^0) changes indicated that the reactions were spontaneous and increased with increasing temperature on the reaction. The NHICO packed column (height: 6.0 cm, internal diameter: 1.0 cm, BV: 4.71 cm^3), when used for filtration of high arsenic groundwater (As concentration: 1.347 $\mu\text{mol} \cdot \text{dm}^{-3}$), yielded 4.7 dm^3 (∼ 1000 BV) of water with arsenic concentration of ≤ 0.133 $\mu\text{mol} \cdot \text{dm}^{-3}$. The bed after use was regenerated up to a level of 90 (± 1.5) % with 0.350 dm^3 of optimized 0.25 M NaOH solution.

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Supporting Information Available:

Some details of the characterization of NHICO, heat treatment, and pH effects with some figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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