Simple and Efficient Synthesis of Iron Oxide-Coated Silica Gel Adsorbents for Arsenic Removal: Adsorption Isotherms and Kinetic Study

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Iron oxide (ferrihydrite, hematite, and magnetite) coated silica gels were prepared using a low-cost, easilyscalable and straightforward method as the adsorbent material for arsenic removal application. Adsorption of the anionic form of arsenic oxyacids, arsenite (AsO^{2-}) and arsenate (AsO_4^{3-}), onto hematite coated silica gel was fitted against non-linear 3-parameter-model Sips isotherm and 2-parameter-model Langmuir and Freundlich isotherm. Adsorption kinetics of arsenic could be well described by pseudo-second-order kinetic model and value of adsorption energy derived from non-linear Dubinin-Radushkevich isotherm suggests chemical adsorption. Although arsenic adsorption process was not affected by the presence of sulfate, chloride, and nitrate anions, as expected, bicarbonate and silicate gave moderate negative effects while the presence of phosphate anions significantly inhibited adsorption process of both arsenite and arsenate. When the actual efficiency to remove arsenic was tested against 1 L of artificial arsenic-contaminated groundwater (0.6 mg/L) in the presence competing anions, the reasonable amount (20 g) of hematite coated silica gel could reduce arsenic concentration to below the WHO permissible safety limit of drinking water of 10 µg/L without adjusting pH and temperature, which would be highly advantageous for practical field application.

Key Words : Arsenic, Iron oxide coated silica gel, Adsorption, Kinetic, Isotherm

Introduction

Arsenic is of serious concern due to its toxicity even at very low concentration. Clean water as one of the most fundamental elements for human survival is decreasing as global population already surpassed six billions people. The demand of clean water cannot be fulfilled by currently available surface water leading to increased dependence of groundwater usage. Arsenic contamination of surface and subsurface water has been reported in many parts of the world and has become global environmental issue as millions of people which have been exposed to contaminated drinking water develop several health problems such as skin, kidney, lung, liver cancer and neurological damage. The presence of arsenic, even at high concentration, is not accompanied by any change in taste, odor and visible appearance which makes it difficult to detect in drinking water. Arsenic can occur both organically and inorganically in the environment where organic arsenic species are considered to be very much less harmful to health compared to inorganic counterparts. The inorganic hydrolyzed form of arsenic include H3As3O3, H2AsO3⁻, HAsO3²⁻, AsO3³⁻, H3As3O4, H2AsO4⁻, HAsO4²⁻ and AsO4^{3-.1-4} Due to its toxicity and carcinogenic effect on human health, World Health Organization has revised the permissible safety limit of arsenic in drinking water from 50 µg/L to 10 µg/L in 1993. According to new directive, all drinking water supply system in European Union would had complied with this new limit while United States Environmental Protection Agency (USEPA) has also adopted the maximum arsenic contaminated level of 10 µg/

L which has been enforced since 2006.^{5,6}

There is an urgent need to improve current water treatment technology since both dissolved arsenite and arsenate ion are simultaneously present in the contaminated groundwater, Adsorption has become as an attractive and promising technology for arsenic removal due to its simplicity and safety, ease of operation, maintenance and handling, sludge-free operation, potential for regeneration and possibility of the use of low-cost adsorbent. It has been considered as the most effective treatment process for the removal of arsenic from aqueous environment at a lower cost applicable to individual sites serving households or small communities.^{4,7}

Due to its great affinity towards arsenic, various kinds of iron-based adsorbents have been developed for arsenic removal such as MnFe₂O₄ and CoFe₂O₄ magnetic ferrite nanoparticles,8 Fe-Mn binary oxide nanoparticles,9 mixed magnetite-maghemite nanoparticles,¹⁰ magnetite nano-particles,¹¹ akaganeite nanocrystals,12 hydrous ferric oxide,13 iron powder,^{14,15} hematite and goethite,¹⁶ etc. Extended x-ray absorption fine structure spectroscopy has provided evidence that arsenic can form inner sphere monodentate or bidendate-binuclear complexes with iron oxides during adsorption process.^{11,17} Despite its effectiveness in removing arsenic due to its larger surface area and high reactivity, their occurrence in fine or nanosized powder form causes difficulties when it comes to their separation in arsenic-contaminated water treatment process. This problem might be partly solved when using magnetic nanoparticles by installing magnetic separator at the expense of increasing the system cost.

Their use in fixed-bed column operation may also be limited due to low hydraulic conductivity. Direct application of adsorbents in fine powdery form may cause fast loss of adsorbent and iron pollution in drinking water (leaching) due to its tiny particle size. Therefore, it is necessary to load the adsorbent material on an inorganic or organic supporting material for the treatment of arsenic contaminated drinking water.¹⁸⁻²⁰

Various organic or inorganic supporters have been applied to improve arsenic adsorption capacity and to solve the aforementioned limitation such as cement,²¹ sand,²² slag,²³ resin,²⁴ cellulose bead,²⁵ alumina,²⁶ carbon²⁷ and chitosan.^{28,29} However some system suffered from multiple preparation steps, time-consuming process or requirement of reactor system to prepare the supporting matrices or matrix-supported adsorbant. For example, cement matrix³⁰ was prepared by mixing commercially available white cement with CaCl₂·2H₂O to accelerate hydration of silicate. For drying and setting, the slurry was then kept in ambient temperature for 48 h followed by curing (hardening) process for 7 days. The mixture of cement and ferric nitrate solution was kept in the oven at 100 °C for 16 h to obtain iron oxide coated cement. Iron oxide coated sand,²² available from nitrate removal system by zero-valent iron was generated from fluidized and air-aerated bed reactor. Iron oxide coated sand pellets were formed, discharged from the fluidized bed reactor, reclaimed and used for arsenic removal application. Amorphous FeOOH was loaded onto solid waste melted slag²³ via chemical processes and high temperature coating technique. The slag was generated from a municipal solid waste incinerator at a melting temperature of 1400-1600 °C. After aging the mixture of slag and NaOH for 48 h at 80 °C, FeCl₃ solution was added and aging process was extended for another 12 h at 25 °C to obtain neutral adsorbent. The slurry was filtrated and heated at 105 °C for 2 h and then 550 °C for 1 h. Upon cooling, the composite was broken to separate the grains and sieved, vacuum-dried at 105 °C for 24 h and stored in a capped bottle for use. Bead cellulose loaded iron oxyhydroxide²⁵ was prepared by dropwise addition of NaOH into mixture of FeCl3 solution and wet bead cellulose. Fe was continuously loaded into the cellulose bead in the form of akaganéite and the Fe content could be increased by repeating the loading process. The bead cellulose was prepared via several steps (2-3 days), i.e. preparation of alkalized cotton, cellulose esterification, and purification of esterified cellulose through heating and filtering to obtain white-colored cellulose bead. Iron oxide modified activated carbon²⁷ was prepared by precipitation of FeCl₃ solution with NaOH followed by heating the mixture at 105 °C overnight. The activated carbon was previously oxidized by strong acid solution at room temperature. Zero valent iron modified carbon was prepared by reduction of Fe²⁺ by NaBH₄ on coal-derived activated carbon previously pretreated in nitric acid for 24 h.

Silica-containing iron oxide adsorbent for arsenic removal application³¹ had been prepared based on simultaneous *insitu* generation of hydrous ferric oxide (FeOOH) sol and

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Si(OH)₄ sol (via reaction of sodium silicate and hydrochloric acid) in one reactor in one reactor in which detailed study on adsorption behavior was not discussed. Goethite coated silica³² had been prepared by adsorption and precipitation method for nickel ion removal application, in which the preparation time varied from one to several days depending on experimental parameters. In this study, a simple, quick and reproducible method to prepare iron oxide coated silica gel is reported. Micron-size silica gel, commonly used in the purification and separation of organic mixtures in chromatography, was chosen due to its good adsorption capability, high surface area and porosity. Silica may act as a binding agent through Fe-Si complexes which would enhance physical and binding strength of the adsorbent produced. The adsorption isotherm, adsorption kinetics, its effectiveness as well as applicability to remove arsenic from real life ground water were also discussed.

Experimental

Preparation of the Ferrihydrite Coated Silica Gel (SiO₂-Fh). Ferrihydrite was prepared based on the method commonly employed in our laboratory. Briefly, 20 g of silica gel and 2.8 g of Fe(NO₃)₃·9H₂O and 50 mL de-ionized water were loaded into 250 mL flask. The pH of the mixture was increased to neutral pH (7) by adding NH₄OH solution. The mixture was stirred for 2 h at room temperature. The solid was then washed and purified with de-ionized water using low speed centrifugation to remove free ferrihydrite from the mixture. The dried ferrihydrite coated silica gel was obtained by vacuum drying at 60 °C for 2 h and the solid were stored in a glass vial for further use.

Preparation of the Hematite Coated Silica Gel (SiO₂-Hm). The hematite coated silica powder was prepared *via* annealing of purified ferrihydrite coated silica gel in ambient atmosphere at 600 °C for 4 h. After cooling down to room temperature, the hematite coated silica gel was then stored in a glass vial for further use.

Preparation of the Magnetite Coated Silica Gel (SiO₂-Mt). Magnetite was prepared according to commonly employed method in our laboratory. Briefly, 20 g of silica powder, 2.7 g of FeCl₃·6H₂O, 1 g of FeCl₂·4H₂O, 4.34 g of CH₃COONa and 100 mL ethylene glycol were loaded into 250 mL flask. Reflux was performed in N₂-protected atmosphere overnight. The solid was then washed with de-ionized water and purified by low speed centrifugation to remove



Figure 1. Physical appearance of silica gels coated with (a) ferrihydrite, (b) hematite, and (c) magnetite.

free magnetite from the mixture. The dried magnetite coated silica gel was obtained by vacuum drying at 60 $^{\circ}$ C for 2 h and the solid was stored in a glass vial for further use.

Batch Adsorption Isotherm and Adsorption Kinetic Experiment. Adsorption isotherm and kinetic studies of arsenic on iron oxide coated silica gel were performed in plastic tube containing 1.5 g of oxide coated silica gel and 30 mL arsenic solution. The mixture was then shaken at 250 rpm with at room temperature. No pH adjustment was made for all batch adsorption experiments. Adsorption isotherm studies were conducted by varying initial arsenic concentration from 1-80 mg/L for As(III) and 5-120 mg/L for As(V). Reaction was allowed to proceed for 3 h at room temperature. The 3 h reaction time was found to be adequate for equilibrium to be attained. Time-dependant As(III) and As(V) adsorption kinetics were investigated by varying contact time from 5, 15, 25, 45, 60, 120 and 180 min. using initial arsenic concentration of 10 mg/L at room temperature. Effect of co-existing anions such as SO₄²⁻, HCO₃⁻, PO₄³⁻, SiO_3^{2-} , Cl⁻ and NO₃⁻ was analyzed with initial arsenic concentration of 3 mg/L. This arsenic concentration was higher than those commonly found real natural groundwater so that complete removal of arsenic could be avoided and the effect of competing anions could be observed. The molar concentration of competing anion was prepared 25 and 250 times higher than that of arsenic. The experimental procedure was similar to those of batch isotherm experiment with addition of competing anion.

Characterization. All experiments were triplicately performed and similar results were obtained within 5% difference range. All batch samples from adsorption isotherm and kinetic experiment were collected by centrifugation and the supernatant was filtered through nylon cellulose filter. The remaining arsenic concentration was then analyzed by Inductive Couple Plasma-Atomic Emission Spectrometer (Shimadzu ICPS-7510) with arsenic detection limit of 10 µg/L. Morphology of uncoated silica gel and iron oxide coated silica gel were characterized by Scanning Electron Microscope (Hitachi S-4300). Crystal structure of iron oxide phase present on the surface of silica gel was analyzed using powder X-Ray Diffractometer (M18XHF-SRA). Nitrogen adsorption-desorption isotherm and pore size distribution measurement were measured by Micromeritics ASAP 2020. All adsorption data were analyzed using Microsoft Excel 2007 and Origin Pro 8.0 Software.



Figure 2. SEM images showing the surface morphologies of silica gels: (a and e) untreated, (b and f) ferrihydrite-coated, (c and g) hematite-coated, and (d and h) magnetite-coated samples.

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Results and Discussion

Characterization of Iron Oxide Coated Silica Gel Adsorbent. The physical appearance of the iron oxide coated silica gel is shown in the Figure 1. The original white color of silica gel turned vellow-brown, dark red-brown, and black after being coated with ferrihydrite, hematite, and magnetite, respectively, confirming the coated iron oxide phases by their characteristic colors.³³ The morphology of the adsorbents was characterized using scanning electron microscope (SEM) and was found to have irregular granular shape as shown in Figure 2. The iron oxide coated silica gel (b-d) had rougher surface and was covered by nanometer sized aggregate structure (f-h) compared to the uncoated silica gel with smooth surface in the absence of any noticeable nanometersized features, implying the successful coating of silica gel with various iron oxide phases. The iron content on the surface of silica gel was determined by acid treatment of the iron oxide coated silica gel followed by quantitative analysis of iron by ICP-AES. The phase of iron oxides coated on the surface of silica gel was analyzed using powder X-Ray



Figure 3. (a) Comparison of equilibrium adsorption capacities achieved by ferrihydrite-, hematite-, and magnetite-coated silica gels (treated volume: 50 mL, arsenic concentration: 1 mg·L⁻¹, total mass of iron oxide-coated silica gel: 5 g, and treatment time: 2 h); (b) Effect of pH on arsenic adsorption for hematite-coated silica gel (treatment volume: 30 mL, initial arsenic concentration: 5 mg·L⁻¹, and treatment time: 2 h).

diffraction. However, only broad peak of silica gel between 20 of 20-30° was observed since the actual amount of iron oxides was very small compared with the silica. Pure iron oxide phases were then prepared using the same method previously described in the absence of the silica gel. These iron oxide phases were analyzed using powder X-Ray diffraction and were confirmed as ferrihydrite, hematite, and magnetite phases based on the JCPDS card reference of number 00-029-0712, 04-003-2900 and 01-076-0957, respectively (supporting information Figs. S1-S3).

Effect of Iron Oxide Phase on Arsenic Removal. Preliminary experiment was carried out in order to determine which iron oxide phase had the largest arsenic adsorption capability at equilibrium condition. It can be seen from Figure 3(a) that the hematite coated silica gel has the largest equilibrium adsorption capacity and could effectively remove both arsenite and arsenate compared to those of ferrihyditre or magnetite coated silica gel. Magnetite coated silica gel has the smallest arsenic equilibrium adsorption capacity despite its highest iron content (Table 1). It is interesting to observe that the magnetite coated silica gel could be employed to remove arsenite while arsenate ions could not be adsorbed effectively. These results might be related with the crystallinity and porosity of magnetite structure prepared at different conditions. Uncoated silica gel was also tested as a reference and it was found that more than 99% of arsenic ion still remained in the solution (supporting information Table S1). Uncoated silica gel did not possess the ability to remove or adsorb the anionic form of arsenic oxyacids which further emphasized its role as a supporter in the system. Hematite coated silica gel was chosen for further adsorption kinetics and adsorption isotherm batch-mode experiments since it has the largest arsenic adsorption capacity over ferryhydrite or magnetite coated silica gels.

Effect of pH. It is evident from Figure 3(b) that both arsenite and arsenate adsorption onto hematite coated silica gel was independent over a wide range of pH from 3 to 8 which is beneficial for practical real field application. Speciation of both arsenite and arsenate in aqueous solution is known to be a function of pH. Arsenate exists as H_3AsO_4 at pH lower than 2, $H_2AsO_4^-$ (at 2 < pH < 7), $HAsO_4^{2-}$ (at 7 < pH < 11) and As_3O_4 pH higher than 11 while arsenite is stable as neutral species H_3AsO_3 at pH lower than 9 and $H_2AsO_3^-$ at pH between 9 and 12.³ It has also been previously reported that point of zero charge (P_{zc}) of hematite falls between pH from 8.8 to 9.5 below which the adsorbent

Table 1. Measured amount of iron or iron oxide within coating materials on silica gel by ICP-AES (Fh = ferrihydrite (Fe₃HO₈· 4H₂O), Hm = hematite (Fe₂O₃), Mt = magnetite (Fe₃O₄)

Material	Fe coating	Fe-oxide coating		
Wateriai	(mg/g of SiO ₂)	(mg/g of SiO ₂)		
SiO ₂ -Fh	21	37		
SiO ₂ -Hm	21	31		
SiO ₂ -Mt	34	47		



Figure 4. (a) Time dependent arsenic adsorption on hematitecoated silica gel. (b) Pseudo first-order, and (c) pseudo secondorder models for adsorption kinetics of arsenic on hematite-coated silica gel.

has net surface positive charge and net surface negative charge above the P_{zc} .³⁴ Arsenate anion was readily adsorbed to adsorbent surface through boundary of solid/liquid interface *via* electrostatic interaction at pH range from 3 to 8 while arsenite adsorption occurred through Lewis acid-base reaction onto non-ionized surface functional group. Arsenite adsorption is governed by deprotonation of H_3AsO_3 below P_{zc} ,²⁰ where electrostatic attraction did not play important role since arsenite dominantly occurs as neutral species at pH range from 3 to 8. Both arsenite and arsenate adsorption significantly decreased at pH between 10 to 11 due to electrostatic repulsion between arsenic anions and net negatively-charged adsorbent surface in the presence of hydroxyl group.

Adsorption Kinetics. Time-dependence equilibrium adsorption capacity of the hematite coated silica gel for both arsenite (up) and arsenate (down) adsorption at room temperature and neutral pH condition is shown in Figure 4(a). Both arsenite and arsenate adsorption kinetics profiles can be divided into 2 stages; the first stage where rapid adsorption occured with increasing contact time up to 45 min and 25 min for arsenite and arsenate, respectively, and the second stage at which adsorption process reached plateau condition and no significant increase in equilibrium adsorption capacity was observed even though the contact time was further extended to 3 h. Silica gel (for column chromatography), used in this study, possesses both high porosity (pore size of 60 angstrom) and high surface area (approximately 500 m²/g) (supporting information Figs. S4 and S5), therefore it is highly probable that the iron oxide (hematite phase) was present in both the exterior and interior pores of the silica gel. After most of active adsorption sites on the outer part had been occupied during the initial adsorption stage, diffusion barrier was created when arsenic anions started to diffuse through the pore of silica gel. This process further decreased overall diffusion rate with the increase of contact time under the studied initial arsenic concentration and eventually arsenic anions got adsorbed by hematite phase present in inner part of the silica gel. The decrease of diffusion rate was more pronounced as the arsenic concentration in the solution decreased. Diffusion process eventually stopped and adsorption process reached equilibrium condition as gradient concentration of arsenic became significantly lower. The much slower adsorption process may also have been attributed to coulombic repulsion between initially adsorbed arsenic species on the adsorbent surface and the remaining arsenic in the solution.^{25,29}

Various kinetics models was employed to describe the nature of arsenic adsorption onto hematite coated silica gel. Pseudo-first-order and pseudo-second-order kinetic models are the most widely used and both had been successfully applied to describe adsorption of various metal ions, dyes and organic substance from aqueous solution. Recent mechanism study of arsenic adsorption using ATR-FTIR³⁴ had indicated that protonated and deprotonated bidendate bridging inner-sphere complexes dominate the arsenate surface speciation with small additional fraction of outer-sphere H₂AsO₄⁻ while arsenite predominantly adsorbs as bidendate inner-surface complexes on the hematite surface. The kinetic of arsenic adsorption onto hematite coated silica gel can be simply written in general form as

$$Fe-OH(s) + As(aq) \rightarrow Fe-As(s)$$
(1)

And the overall rate law of adsorption kinetics can be

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 Table 2. Estimated value of several kinetic model parameters for arsenic adsorption on hematite-coated silica gel

Kinetic	Daramatara	Arsenic species		
model	Farameters -	As ³⁺	As ⁵⁺	
Pseudo	K_{1-ads} (min ⁻¹)	0.074	0.043	
first-order	$q_e \operatorname{calc}(mg \cdot g^{-1})$	1.821	0.241	
	$q_e \exp(mg \cdot g^{-1})$	4.434	6.624	
	\mathbb{R}^2	0.898	0.898	
	standard error of estimate (SE)	0.678	0.392	
Pseudo	K_{2-ads} (g·mg ⁻¹ ·min ⁻¹)	0.188	0.621	
second-order	h (mg·g ⁻¹ ·min ⁻¹)	3.765	27.32	
	$q_e \operatorname{calc}(mg \cdot g^{-1})$	4.467	6.632	
	$q_e \exp(mg \cdot g^{-1})$	4.434	6.624	
	\mathbb{R}^2	0.999	0.999	
	standard error of estimate (SE)	0.053	0.0067	

described as

$$r = d[As(aq)]/dt = -K_{ads}$$
. [Fe-As (s)]^a. [As (aq)]^b (2)

where [] is the molar concentration of arsenic in aqueous solution, a and b are constant representing the order of reaction and K_{ads} is adsorption kinetic rate constant. The adsorption kinetics can be viewed as a^{th} order with respect to Fe-As(s) and b^{th} order with respect to As(aq). The sum of power of concentration terms involved in the rate law expression is defined as the total rate $[(a+b)^{th}]$ of reaction.

Assuming that the adsorption sites is present in the large excess compared to the concentration of arsenic in the solution, the availability of surface adsorption sites is virtually unchanged during the adsorption process, therefore, the rate law can be treated as pseudo-order reaction.³⁵ The change of available surface adsorption site can be ignored throughout the reaction such as $[Fe-As(s)] \approx [Fe-As(s)]_{initial}$ and the rate equation simplifies to

$$\mathbf{r} = -\mathbf{K'}_{ads} \cdot [\mathbf{As}(aq)]^b \tag{3}$$

where $K'_{ads} = K_{ads} \cdot [Fe-As(s)]^a$

It has also been reported that adsorption followed by formation of inner-sphere complex are not much influenced by ionic strength and pH (shown in Fig. 3(b)). In order to analyze arsenic adsorption onto hematite coated silica gel, the adsorption kinetic data was fitted against the linearized form of pseudo-first-order kinetic model (Lagergren equation) and pseudo-second-order kinetic model according to Eqs. (4)-(5), respectively.³⁶

$$\log (q_e - q_t) = \log q_e - (K_{1-ads}/2.303)$$
(4)

$$t/q_t = [1/(K_{2-ads} \cdot q_e^2)] + t/q_e$$
 (5)

The value of equilibrium adsorption capacity, initial sorption rate and adsorption kinetic reaction rate constant can be experimentally determined from the slope and intercept of adsorption kinetic plot shown in Figure 4(b) and 4(c) and the result was summarized in Table 2. Both pseudo kinetic



Figure 5. Isotherm plots for arsenic adsorption on hematite-coated silica gel based on (a) Langmuir, (b) Freundlich, (c) Sips, and (d) Dubinin-Raduskevich models.

models was tested against least-square regression analysis to determine which model better describe the adsorption behavior and standard error of estimation was calculated for each model to provide a degree of agreement between calculated and experimentally obtained values.

The correlation coefficient of the pseudo-second-order kinetic model for both arsenite and arsenate adsorption were above 0.999 and the calculated values of equilibrium adsorption capacity (4.434 mg/g and 6.624 mg/g) agreed well with the experimental values (4.458 mg/g and 6.631 mg/g) for arsenic and arsenate, respectively, compared to those obtained from the pseudo-first-order kinetic model. The higher value of initial sorption rate (h) and pseudo-second-order constant (K2-ads) of arsenate adsorption indicates that it required shorter time for arsenate adsorption to attain equilibrium condition than arsenite adsorption. The higher correlation coefficient values and lower value of standard error of estimate for both arsenic adsorption and agreement between experimental and calculated values of equilibrium adsorption capacity provided evidence that the adsorption process could be well described by the pseudo-second-order kinetic model. This model assumes that adsorption occurs on localized sites with no interaction between arsenic anions, maximum adsorption represents saturated monolayer adsorption and negligible rate of desorption compared to adsorption rate leading to the chemisorptions through sharing or exchange of valence electrons between hematite coated silica gel and arsenic anions *via* covalent bond formation.³⁷ The amount of removed arsenate anion was higher than that of arsenite which was also supported by the data from adsorption isotherm.

Adsorption Isotherm. Equilibrium arsenic adsorption data onto hematite coated silica gel was fitted against threeparameter Sips isotherm model and two-parameter Langmuir and Freunlich isotherm models²¹ as shown in Figures 5(a)-

Table 3. Estimated value of several isotherm parameters for arsenic adsorption on hematite-coated silica gel

Isotherm	Daramatara	Arsenic species		
model	Farameters	As ³⁺	As ⁵⁺	
Langmuir	$Q_o (mg \cdot g^{-1})$	27.82	45.75	
	$b (L \cdot mg^{-1})$	0.077	1.2	
	\mathbb{R}^2	0.993	0.987	
	χ^2	0.513	7.521	
Freundlich	$K_F [(mg \cdot g^{-1})(L \cdot mg^{-1})^{1/n}]$	3.49	19.86	
	n	2.03	3.94	
	\mathbb{R}^2	0.991	0.9	
	χ^2	0.585	34.575	
Sips	$Q_s (mg \cdot g^{-1})$	33.09	50.95	
	As	0.024	0.792	
	N_s	0.7	0.7	
	\mathbb{R}^2	0.999	0.992	
	χ^2	0.04681	2.767	
Dubinin	K_{D-R} (mol ² ·kJ ⁻²)	0.0045	0.0021	
-Raduskevich	E_{D-R} (kJ·mol ⁻¹)	10.55	15.43	
	Q_d (mol·kg ⁻¹)	1.363	1.375	
	R^2	0.998	0.946	
	χ^2	1.89×10^{-4}	0.0033	

5(c). Langmuir isotherm model assumes that monolayer adsorption process takes place at specific homogenous sites of equal energy on which there is no interaction between adsorbed species. Adsorption forces is similar to that of chemical interaction and once sorption sites was occupied by adsorbate species, no further adsorption can take place at that same site. The Freundlich isotherm model is the oldest known empirical model describing the adsorption process. It assumes that multilayer adsorption process occurs on the heterogeneous surface with exponential distribution of adsorption active sites and non-uniform heat of adsorption over the adsorbent surface. Three-parameter Sips isotherm model,¹⁹ a combination of both Langmuir and Freundlich model having features of both, was developed to improve the performance of both Langmuir and Freundlich models over a wide range of arsenic concentration. The mathematical representation of these isotherm models are given in Eqs. (6)-(8):

$$q_e = (b \cdot Q_o \cdot C_e) / (1 + b \cdot C_e)$$
(6)

$$q_e = K_F \cdot C_e^{1/n} \tag{7}$$

$$q_{e} = [Q_{s} \cdot (a_{s} \cdot C_{e})^{s}] / [1 + (a_{s} \cdot C_{e})^{s}]$$
(8)

The estimated parameters from each isotherm model are summarized in Table 3. The determination of optimal parameters from each isotherm model was performed using a non-linear optimization approach. This is particularly important for Langmuir isotherm model in which the term $1/C_e$ in the linearized-form underweights data from high initial

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A dearbart motoriale	Adsorption ca	pacity (mg·g ⁻¹)	IIa	Daf	
Adsorbent materials	As ³⁺ As ⁵⁺		рп	Kel	
Fe supported on carbon	18.19	12.02	7	20	
Iron oxide-loaded slag	2.9-30	18.8-78.5	$10(As^{3+}), 2.5(As^{5+})$	23	
Fe(III)-loaded resin	62.93	55.44	9(As ³⁺), 3.5(As ⁵⁺)	24	
Bead cellulose-loaded iron-oxy-OH	99.6	33.2	7	25	
Iron hydroxide-coated alumina	7.64	36.64	6.6-7.2	26	
Iron-modified activated carbon	39.2	51.3	8 (As ³⁺), 6 (As ⁵⁺)	27	
Iron oxide-doped chitosan composite	22.47	16.1	7	38	
Iron oxide-doped chitosan spacer granules	22.57	25.84	7	39	
Natural goethite	10.1	12.1	7.5	40	
Natural hematite	10	31.3	7.3	40	
Activated alumina	3.5	15.9	7(As ³⁺), 5.2(As ⁵⁺)	41	
Alumina-coated chitosan	56.5	96.46	4	42	
Iron oxide-coated sponge	3.85	4.5	6.5-7.3	43	
Iron oxide-impregnated activated carbon	4.67	4.5	7	44	
This work	27.82	45.75	7		

Table 4. Comparison of Langmuir adsorption capacities of different adsorbent materials

arsenic concentration in the overall optimization. The threeparameter Sips model provides better fit to experimental data compared to two-parameter isotherm model indicated by higher value of correlation coefficient (\mathbb{R}^2) and lower statistical error (χ^2).

The performance of the hematite coated silica gel in removing both arsenite and arsenate was compared with other adsorbents from other literature works and the result was summarized in Table 4. Some adsorbents should be applied at certain pH range (acid or base) to attain maximum adsorption capacity. Our adsorbent offers several advantages such as: (i) quick, simple and straight-forward preparation which can be easily scale-up for mass production, (ii) neither pH nor temperature adjustment is needed during the adsorption process yet it still maintains high adsorption capacity which is advantageous for practical field applications.

While both Langmuir and Freundlich adsorption models predicted favorability of the arsenic adsorption onto the hematite coated silica gel, the adsorption energy (E) calculated from Dubinin-Radushkevich (D-R) isotherm could provide important information regarding the physical or chemical nature of adsorption process (Fig. 5(d) and Table 3). The mathematical representation of D-R isotherm and the calculation of adsorption energy (E_{D-R}) is given by Eqs. (9)-(11):

$$q_e = Q_d. \exp\left(-K_{D-R} \cdot e^2\right) \tag{9}$$

$$e = R. T. \ln[1 + (1/C_e)]$$
 (10)

$$E_{D-R} = (2K_{D-R})^{-0.5}$$
(11)

It has been reported that the adsorption process should be of chemisorption if adsorption energy has value between 8.0 and 16.0 kJ/mol or physisorption if the value is below 8.0 kJ/ mol.⁴⁵ The adsorption process of arsenic onto hematite coated silica gel implies chemisorption nature with estimated value of adsorption energy (E_{D-R}) of 10.55 and 15.43 kJ/mol



Figure 6. Interference effect of coexisting anions on adsorption process of (a) arsenite and (b) arsenate on hematite-coated silica gel.

for arsenite and arsenate, respectively, which implies the formation of a monolayer of adsorbate on the surface through residual valence forces of surface molecules.

Effect of Competing Anions. The effect of co-existing anions on arsenic adsorption onto the hematite coated silica gel was investigated. Since both arsenite and arsenate dissociate and occur in anionic form in aqueous solution, the adsorption competition onto active sites on the surface of adsorbent materials should mainly arise from anions especially the oxyanions while the effect of cations can be neglected. The effect of competing anions on arsenic adsorption process was summarized in the Figure 6. Sulfate, chloride and nitrate did not inhibit both arsenite and arsenate adsorption process even though they coexisted at very high concentration suggesting that they had low affinity toward the adsorbent. Phosphate anions exerted the highest negative effect while bicarbonate and silicate anions gave moderate negative effects in adsorption process during which the amount of both adsorbed arsenite and arsenate were greatly reduced when they were present at very high concentration. Phosphate and arsenic ion always compete with each other in aqueous system (in this case for sorption sites on the hematite adsorbent surface) since they belong to the same group in the periodic table therefore having similar chemical properties and atomic structure resemblance. In addition, arsenate, phosphate and silicate are all tetrahedral anions which compete with each other for active adsorption sites on the adsorbent surface resulting in a decreased of equilibrium adsorption capacity.^{25,46} Incomplete arsenic removal is more pronounced in case of arsenate than arsenite when phosphate anions are present at very high concentration. Excess iron oxide should be used to ensure complete removal of arsenic in the presence of strongly competing anions.

Arsenic Removal from Artificial Arsenic-Contaminated Groundwater. The applicability of our adsorbent to remove both arsenite and arsenate from natural system was tested using artificial arsenic-contaminated groundwater prepared from distilled water spiked with arsenic and other commonly found cations and anions as shown in Table 5.47 Triplicate experiment of one liter of artificial arsenic-contaminated groundwater spiked with either arsenite or arsenate (0.6 mg/ L) along with various cations and anions was treated with 20 g of hematite coated silica gel adsorbent for 2 h of equilibration time in batch-mode experiment. The treated water was then separated from adsorbent material by filtration through nylon cellulose membrane and the remaining arsenic concentration was determined from ICP-AES. The result of remaining arsenic concentration for both arsenite and arsenate was "ND" (not detectable) implying that our adsorbent was successfully applied to effectively remove both arsenite and arsenate from artificial groundwater to WHO drinking water permissibility safety limit of arsenic concentration of below 10 µg/L. (The ICP-AES has detection limit of arsenic of 10 µg/L). Excess adsorbent was needed to ensure complete removal of arsenic as the concentration of remaining arsenic became smaller in the presence of competing anions in solution which has also been

 Table 5. Composition of artificial arsenic-contaminated ground-water

ion	Na ⁺	Mg^{2+}	Ca^{2+}	HCO_{3}^{-}	SiO ₃ ²⁻	PO4 ³⁻	$\mathrm{SO_4}^{2-}$	Cl-
mg/L	144.44	8	51	362.95	12.46	1.82	32	89.55

observed when NHITO was employed as adsorbent to remove arsenic from aqueous solution. 28

Conclusion

A study on the removal of arsenic from aqueous solution using iron oxide coated silica gel, in particular hematite coated silica gel, was presented. Arsenic removal was investigated through adsorption at neutral pH condition at room temperature in equilibrium-batch mode system. Equilibrium data were fitted against Langmuir, Freundlich and Sips isotherm and various model parameters were evaluated. Adsorption energy calculation from Dubinin-Radushkevich isotherm indicated chemisorptions and arsenic adsorption kinetics could be well described by the pseudo-second order kinetic model. The presence of competing anions such Cl-, NO₃⁻, SO₄²⁻ and CO₃²⁻ did not greatly interfere on arsenic adsorption while the presence of PO43- and SiO32- significantly decreased the arsenic adsorption. One liter of artificial arsenic-contaminated artificial groundwater was successfully treated with 20 g the hematite coated silica gel yielding groundwater which complied with WHO drinking water arsenic permissible limit of 10 µg/L. It is expected that this adsorbent material can be applied for removing arsenic compound from aqueous environment at a lower cost applicable to individual sites in rural communities or small-scale water treatment system.

Supporting Information. Nomenclature used in the main text. XRD pattern of iron oxide phase on silica gel, arsenic removal by bare silica gel, Brunauer-Emmett-Teller (BET) and pore size measurements of bare silica gel, determination of rate-limiting step during arsenic adsorption on hematite-coated silica gel, affinity of arsenic towards hematite-coated silica gel

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