Adsorption of As(V) and As(III) from aqueous solution by lepidocrocite (γ-FeOOH) nanoparticle

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ABSTRACT

γ-FeOOH nanorods an adsorbent for As(V) and As(III) removal was prepared by a chemical co-precipitation method. The maximum adsorption capacities at pH6 for As(V) and As(III) were 63.75 and 88.99 mg/g, respectively, higher than those of Fe_2O_3, Fe_3O_4... The adsorption data accorded with Freundlich isotherms. At the study pH, for arsen, the adsorption equilibrium was gained after 90 min. Kinetic data fitted well to the pseudo-second-order reaction model. The adsorption of γ-FeOOH for As (V) and As(III) could be competed by some other ion such as sulfate, ammonium and chloride. The high adsorption capability and good performance on other aspects make the γ-FeOOH nanorod a promissing adsorbent for the removal of As (V) and As(III) from the groundwater.

Keywords: *As (V), As(III), sorption, kinetic, γ-FeOOH nano*

INTRODUCTION

Geogenic arsen (As) contamination in the groundwater is a major health problem that has been recognized in several regions of the world, especially in Bangladesh, West Bengal [1, 2], Vietnam [3-5], Cambodia [6, 7], Myanmar [8], and Mexico, where a large proportion of groundwater is contaminated with arsen at levels from 100 to 2000 µg L^{-1} [9].

In natural water, arsen is primarily present in inorganic forms and exists in two predominant species, arsenate As(V) (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$) and arsenic As(III) (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$) [10, 11]. As(III) is much more toxic and mobile than As(V). However, in the groundwater in nature, after exposure to air, the majority As(III) was transferred to As(V) [12].

Iron oxides indeed have been used for arsen removal [13-17] as well as, alumina [15], zeolite, titanium dioxide [18], and akaganeite [19]. In most cases, these low cost materials were used as filters [10, 20]; while their modelling was attempted by the mechanism of surface complexation [21].

Among the possible treatment processes, the adsorption is considered to be less expensive than the membrane filtration, easier and safer to handle as compared to the contaminated sludge produced by precipitation, and more versatile than the ion exchange [22]. Adsorption process is considered to be one of the most promising technologies because the system can be simple to operate and low cost [23].

Among a variety of adsorbents for arsen removal, iron (hydro)oxides including amorphous hydrous ferric oxide, poorly crystalline hydrous ferric oxide (ferrihydrite) [24], goethite [25] and akaganeite [19] are well-known for their ability to removal inorganic arsen from aqueous system with low cost. Among these adsorbents the As(III) adsorption is normally less effective than the As(V) adsorption [15, 17, 18]. FeOOH has high adsorption capacity on arsenic [26], but it could not effectively remove both As(V) and As(III) simultaneously.

In the present study, a γ-FeOOH nanoparticle adsorbent was prepared by a chemical co-precipitation method, which was easy to operate and economic. The adsorbent was characterized and evaluated for its adsorption behavior of arsen. It exhibited high adsorption capacity for both As(V) and As(III).

MATERIALS AND METHODS

Materials

Stock solutions of As(V) and As(III) 1000 mg/L (Merk). The working solutions were freshly prepared by diluting $Na_2HAsO_4·7H2O$ and As_2O_3 with bidistilled water.

HNO_3 (0.1–0.5 N) and NaOH (0.1–0.5 N) were used for adjusting the pH of the arsenic solution as necessary.

The ammonium (NH+) stock solution (500 mg $NH4^+$/L), the chloride (Cl^-) stock solution (500 mg Cl^-/L) and the sulfate (SO_4^{2-}) stock solution (500 mg SO_4^{2-}/L) were prepared separately from ammonium chloride (NH_4Cl) (Fisher, certified A.C.S.) and sodium sulfate (Na_2SO_4) (Fisher, certified A.C.S.). Both solutions were used as the competing ions in some arsenic adsorption experiments.

Arsen in solutions was measured with Atomic Absorption Spectrometer (AA 7000 – HVG1 Shimadzu).

All adsorption data were analysed by the Originlab 8.5.1 software.

Methods

Preparation of γ-FeOOH

The γ-FeOOH adsorbent was prepared according to the following procedure [33]:

Dissolve 12 g $FeCl_2$ $4H_2O$ in 300 mL distilled water with vigorous stirring. The beaker should be equipped with a glass electrode connected to a pH meter, a gas inlet connecting an air or oxygen cylinder and a dropping funnel containing 125 mL 1M NaOH. Adjust the pH of the system to 6.5- 6.8 by adding NaOH dropwise, then open the gas cylinder and aerate the air blowing rate 2 L/min. The initial greenish black precipitate becomes orange after 20 min. Throughout the reaction, the pH of the suspension must be maintained at 6.5-6.8, by adding NaOH from the dropping funnel as needed, centrifuge, wash and dry. The dried material was stored in a desiccator for use.

γ-FeOOH nanoparticle

Powder X-ray diffraction (XRD) was recorded on a Scintag-XDS-2000 diffractometer with Cu Kα radiation (λ=1.54059), scan rate at 2θ of 44.9°. Sample morphology was detected by scanning electron microscopy (SEM) on Hitachi H-7500.

Batch sorption tests

To determine the amount of adsorbed arsen (As(V) or As(III)) under the given conditions, approximately 0.1 g of adsorbent was weighed and placed in a 250-mL Erlenmeyer flask. One hundred millilitres of As(V) or As(III) solution was added into the flask. The concentration of the As(V) or As(III) solution ranged from 40 to 1000 mg/L depending on the type of experiment. Ionic strength was not adjusted during the absorption. The flask was capped and shaken at 180 rpm on an orbital shaker for 24 h to ensure the approximate equilibrium. All batch experiments were conducted at room temperature (20 °C) unless stated otherwise. The pH was manually maintained at a designated value pH= 6.0 in such a way: pH was initially adjusted to a defined value with 0.01 N HNO_3 and NaOH and then measured and adjusted at an interval of 2 h. After 24 h of the period reaction, all samples were centrifuged at 10.000 rpm for 5 minutes and filtered through a 0.45-µm membrane filter and the filtrate was analyzed for arsen. This procedure was used in all adsorption experiments for evaluating isotherms and interferences of competing ions, except for kinetic experiments. The quantity of adsorbed arsen was calculated by the difference of the initial and residual amounts of arsen in the solution divided by the weight of the adsorbent.

The amount of adsorbed metal was calculated from the following expression:

$$q = V\,(C_i - C_e)/B$$

Where q is the metal uptake or sorption capacity of adsorbent (in mg/g of adsorbent); C_i and C_e are the metal concentrations before and after adsorption, respectively, B is the mass of adsorbent used and V the solution volume used.

The pseudo-first-order adsorption and pseudo-second-order adsorption were used to test the adsorption kinetics data. The pseudo-first-order rate expression of Lagergern is given as [27].

$$\log\,(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (1)$$

or

$$\boxed{\ln(q_e - q_t) = \ln q_e - k_1 t}$$

Where q_e and q_t are the amount of arsenic adsorbed on adsorbent (mg/g) at equilibrium and time, and k_1 is the rate constant of pseudo-first-order adsorption. The pseudo-second-order rate model is expressed as [28]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (2)$$

Where k_2 is the constant of pseudo-second-order rate (g/mg·min). The experimental data of q_e, q_t and k_2 can be determined from the slope and the intercept of the plot of t/q_t against t.

Studies of adsorption isotherm effect

Experiments for studying the arsenic adsorption isotherm were conducted at 20 °C and pH= 6.0 by following the batch adsorption procedure. A series of different initial concentrations of As(V) or As(III) solutions (40–1000 mg/L) at pH= 6.0 were used. For estimating the thermodynamic parameters of arsenic adsorption, the isotherm experiments were also conducted at 20 °C.

Studies of adsorption time effect

The effects of time on arsenic adsorption were examined in a series of batch sorption experiments that used the same initial As(V) or As(III) concentration (100 mg/L) while maintaining the time at different values from 0 to 180 minutes.

Adsorption kinetics studies

Arsenic adsorption kinetics was evaluated at 20 °C and pH= 6.0. The initial As(V) or As(III) solution concentrations were 100 mg As/L. The kinetic experiments were conducted in a 250-mL flask. The flask was shaken at 180 rpm. With this experimental setup the temperature of the solution inside the flask was well maintained at 20 °C, pH was maintained at around pH= 6.0.

Arsenic adsorption with competing other ions

The interference of ammonium (NH_4^+), chloride (Cl^-) and sulfate (SO_4^{2-}) on As(V) or As(III) adsorption was evaluated in batch experiments, respectively. The experimental method was similar to the batch adsorption method described previously. The difference was that the arsenic working solutions for these competing adsorption experiments were prepared with the separate addition of ammonium, chloride and sulfate solutions into the arsen solution. The initial addition of arsen was 100 mg/g adsorbent using an arsenic solution in 100 mg As/L and the pH was maintained at approximately pH= 6.0. The concentrations of the competing anions used in the experiments were from 1 to 120 mg/L for ammonium, chloride and sulfate.

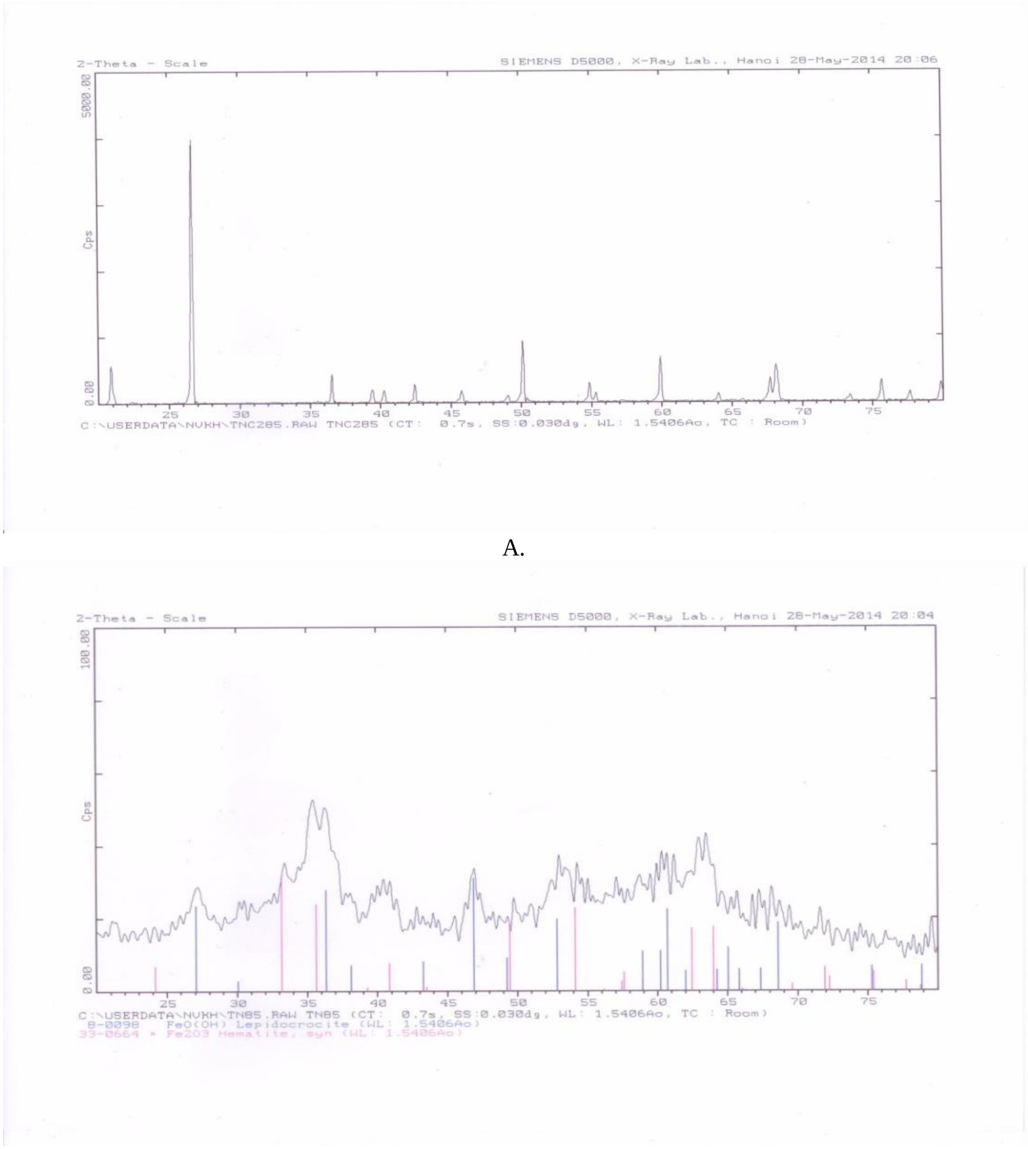
RESULTS AND DISCUSSION

Characterization of γ-FeOOH adsorbent

Lepidocrocite nanoparticles applied in this work consisted mainly of γ-FeOOH, characterized by the basic reflection appearing at 2θ of 44.9◦, as shown in the XRD diagram in (Fig. 1A) and (Fig. 1B)

This is evident from the XRD diagram in Fig. 1B, where the oxide appears in the form of lepidocrocite (γ -FeOOH) and hematite (α-Fe_2O_3) (Fig. 1B). The α-Fe_2O_3 percentage is very low. It is a by product of the synthesis process, and thus the corresponding peaks might be of γ -FeOOH (Fig. 1A).

A typical SEM image of the prepared sample was shown in Fig. 2, which reveals that the Lepidocrocite was a nanorod with the diameter of 20 nm and the length of 100 nm.



A.

B.

Figure 1. A) XRD patterns of γ-FeOOH synthesized samples; B) XRD patterns of synthesized samples

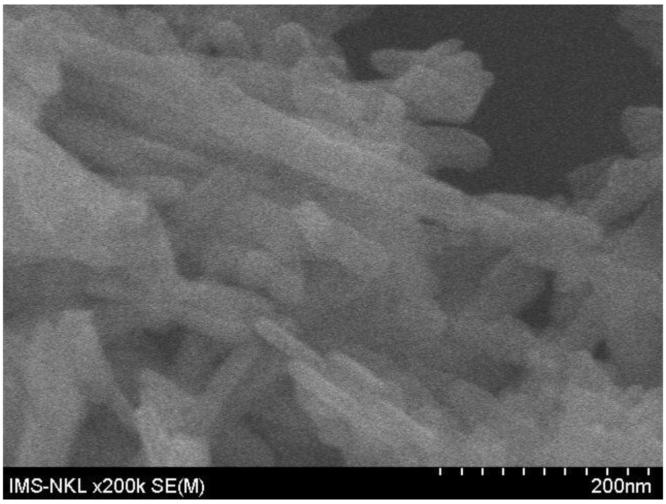


Figure 2. The SEM of γ-FeOOH samples

Batch sorption tests

Adsorption isotherm of γ-FeOOH adsorbent

The adsorbents were tested for adsorption of As(V) and As(III), as shown in Fig. 3A and Fig. 3B. The sorption capacity of As(III) by γ-FeOOH was higher than As(V) and the sorption capacity of γ-FeOOH was high compared to goethite (72.4 mg/g) [29].

The Langmuir expression was:

$$q = \frac{q_m b C_e}{1 + bC_e}$$

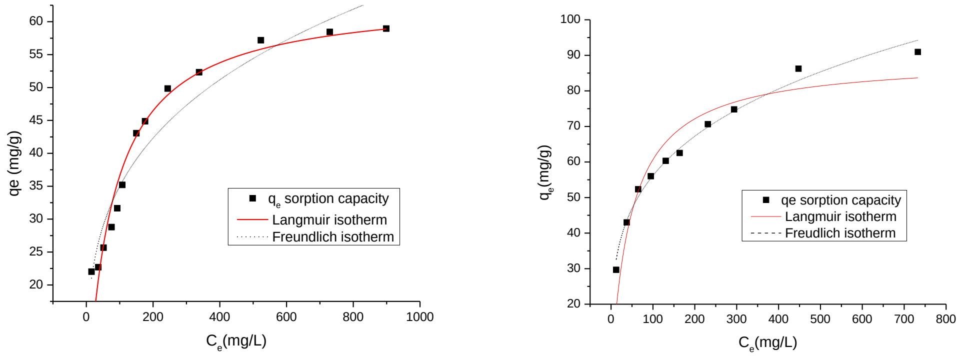
Where q is the amount of As(V) adsorbed, mg/g; q_m the maximum As(V) and As(III) uptake value corresponding to sites saturation, mg/g; Ce the equilibrium As(V) and As(III) concentration in solution, mg/L; and b is the ratio of adsorption/desorption rate. The result sorption of As(V) and As(III) by γ-FeOOH was shown in the Table 1.

The Freundlich expression was:

$$q_e = KC_e^{1/n}$$

K = equilibrium constant indicative of adsorption capacity

n = adsorption equilibrium constant



A.

B.

Figure 3. A) Langmuir and Freundlich sorption isotherm of As(V) on γ-FeOOH; B) Langmuir and Freundlich sorption isotherm of As(III) on γ-FeOOH

The adsorption isotherm of γ-FeOOH for As(V) and As(III) were presented in Fig. 3A and Fig. 3B. In this study, both Langmuir and Freundlich isotherms were used to describe the adsorption isotherms. The adsorption constants obtained from the isotherms are listed in Table 1. The correlation coefficient (R^2) values of the Langmuir isotherms for As(V) was 0.92 and for As(III) was 0.89, while that of the Freundlich isotherms for As(V) was 0.93 and for As(III) was 0.98. High regression coefficients suggested that the Freundlich model was suitable for describing the adsorption behavior of As(V) and As(III) by γ-FeOOH.

The coefficient value (R^2) of the Freundlich isotherms for As(III) was higher than (R^2) value of Langmuir isotherms, in the sorption system due to a part of As(III) was transferred to As(V) [12].

Table 1. Langmuir and Freundlich isotherm parameters for As(V) and As(III) adsorption on γ-FeOOH adsorbent at pH= 6.0

Langmuir model			
As species	q_m (mg/g)	b (L/mg)	R^2
As(V)	63.75	0.90	0.92
As(III)	88.99	1.01	0.89
Freundlich model			
As species	K_F (L/mg)	n	R^2
As(V)	9.88	3.64	0.93
As(III)	16.95	3.84	0.98

Adsorption kinetics of As(V) by γ-FeOOH adsorbent

The kinetics of adsorption is one of the important characteristics that define the adsorption efficiency. Hence, in the present study, the kinetics of arsenic adsorption was analyzed to understand the adsorption behavior of γ-FeOOH. Fig. 4 shows the adsorption data of As(V) and As(III) by γ-FeOOH at different time intervals. The adsorptions of both As(V) and As(III) by γ-FeOOH were found to be time dependent. The adsorption of As(V) and As(III) was rapid for the first 45 min, when the removal rate reached 87 % for As(V), and 76 % for As(III), the removal reach was 97 %, after 90 min and the adsorption equilibrium was approached for both of As(V) and As(III).

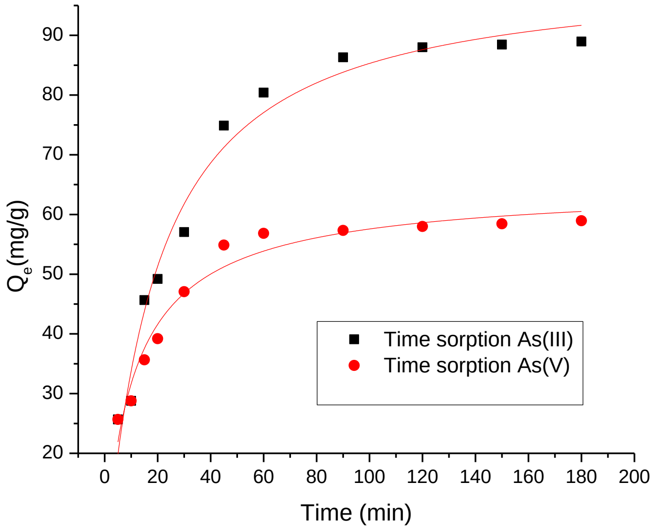


Figure 4. Time effect sorption of As (V) and As(III) by γ-FeOOH

Table 2, lists of the results of rate constant studies for As(V) and As(III) by pseudo-first-order and pseudo-second-order. The values of correlation coefficient R^2 for the pseudo-first-order adsorption model are 0.97 for As(V) and 0.96 for As(III), (Fig. 5) and the adsorption capacities calculated by the model are different to those determined by experiments. The values of R^2 for the pseudo-second-order are extremely high (>0.99) (Fig. 6), for both As(V) and As(III), the experimental data fitted the pseudo-second-order model better than the pseudo-first-order model. Therefore, it can be concluded that the pseudo-second-order model is more suitable to describe the adsorption kinetics of arsenic on γ-FeOOH. The rate of adsorption depends on the driving force and concentration gradient. In case of pseudo-first-order the rate is proportional to the concentration (ΔC) and in pseudo-second-order, it is proportional to the square of concentration gradient (ΔC^2) which refers to both external as well as internal mass transfer [30]. This evidence shows that both the external and internal mass transfer is taken place. The As(V) ions existe as negative ions [31] in the experimental conditions. Therefore, As(V) ions may be easy to diffuse into the external and internal adsorption sites of adsorbent. So there was fast removal rate percentage of As(V) before 45 min. This was not contradictory with the adsorption isotherms.

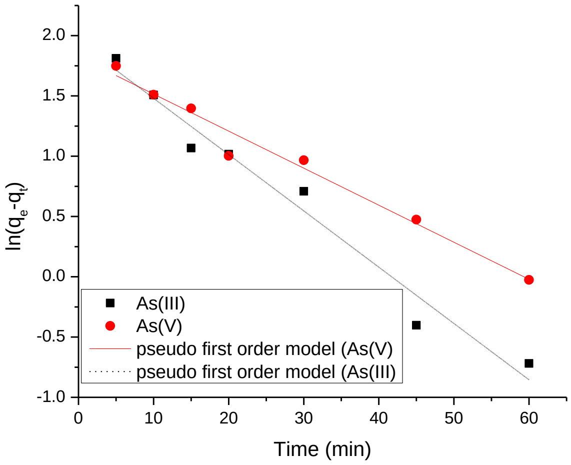


Figure 5. Pseudo-first-order model adsorption of As(V) and As(III) by γ-FeOOH

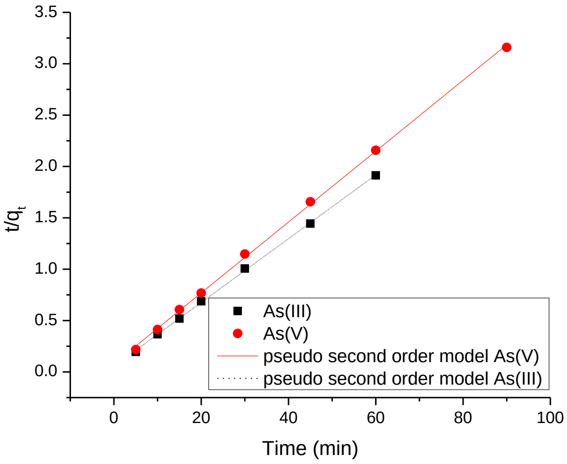


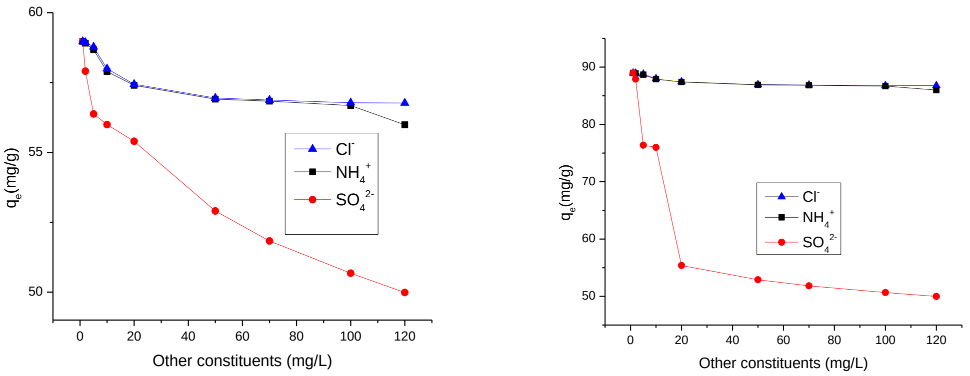
Figure 6. Pseudo-second-order model adsorption of As(V) and As(III) by γ-FeOOH

Table 2. Composition of pseudo-first and pseudo-second-order adsorption rate constants

	Pseudo-first-order model			
As species	$q_{e.\ exp}$ (mg/g)	k_1 (min^{-1})	$q_{e.\ cal}$ (mg/g)	R^2
As(V)	61.79	0.03	58.17	0.97
As(III)	88.68	0.04	91.33	0.96
	Pseudo-second-order model			
As species	$q_{e.\ exp}$ (mg/g)	k_2 (g/mg·min)	qe.cal (mg/g)	R^2
As(V)	61.79	0.02	63.75	0.99
As(III)	88.68	0.02	88.93	0.99

Effect of other constituents on arsenic removal

In natural groundwater or waste water several component might exist, which could compete with arsen for the available adsorption sites or interact with arsenic itself. In this study we select some ions (Cl^-, SO_4^{2-}, and NH_4^+) to test the effect of co-existing constituents. Fig. 7A and Fig. 7B show the results of the effect of co-existing ions. Cl^- had little or no effect on the arsen removal performance of the adsorbent. This is probably that the ions do not compete with the arsen ions. The oxyanions SO_4^{2-} were selected to assess the effects of co-existing anions on As(V) and As(III) removal. At pH 6, the effects of those oxyanions increased the concentration level were illustrated in(Fig. 7A and 7B). The NH_4^+ also had little effect on the arsenate removal performance of the adsorbent. This result is in agreement with previous studies [32].



A. B.

Figure 7. A) Other constituents effect sorption of As(V) by γ-FeOOH; B) Other constituents effect sorption of As(III) by γ-FeOOH

CONCLUSION

A novel γ-FeOOH nanorod an effective adsorbent for As(V) and As(III) removal, has been prepared by a chemical co-precipitation method. At pH 6 the maximum adsorption capacities for As(V) and As(III) were 63.75 and 88.99 mg/g respectively. At this pH, for arsen, the removal rate reached 95 % after 90 min. In order to reveal useful informations for the sorption mechanism, typical adsorption isotherms (Langmuir and Freundlich) were determined and X-ray photoelectron spectroscopy analysis was used. The mechanism of the removal seemed rather to be a chemisorption, based on the kinetics sorption.

The sulfate was a competitor with arsenic for adsorptive sites on the adsorbent. These results indicated that the γ-FeOOH nanorod was an attractive adsorbent for the removal of arsenic from aqueous solutions.

Hấp thu As(V) và As(III) từ dung dịch nước bởi lepidocrocite (γ-FeOOH) dạng nano

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TÓM TẮT

γ-FeOOH dạng nano dùng làm vật liệu hấp phụ As(V) và As(III) được điều chế bằng phương pháp đồng kết tủa. Tại pH = 6,0, dung lượng hấp phụ cực đại của vật liệu đối với As(V) và As(III) lần lượt là 63,75 và 88,99 mg/g, cao hơn so với một số vật liệu làm chất hấp phụ arsen như Fe_2O_3, Fe_3O_4. *Mô hình hấp phụ đẳng nhiệt Freundlich mô tả quá trình hấp phụ As(v) và As(III) bởi γ-FeOOH, thời gian đạt cân bằng hấp phụ là 90 phút. Động học hấp phụ tuân theo phương trình động học hấp phụ bậc 2. Quá trình hấp phụ của γ-FeOOH đối với As(V) và As(III) có thể bị cạnh tranh bởi các ion khác như sulfate, ammonium và chloride (theo thứ tự giảm dần). Vật liệu γ-FeOOH dạng nano, với dung lượng hấp phụ As(V) và As(III) cực đại, việc điều chế dễ dàng với giá thành thấp, là chất hấp phụ đầy tiềm năng trong việc xử lý arsen trong nước ngầm.*

Từ khóa: *As(V); As(III), hấp phụ, động học hấp phụ, γ-FeOOH nano*

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