Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20869

77 (2017) 342–348
May

Removal of aqueous arsenic using abundant boehmite coated zeolite

Acong Chen, Xin Xin, Jie Xu, Yu Bian, Aizhong Ding, Zhaoyong Bian*

College of Water Sciences, Beijing Normal University, Beijing 100875, China, Tel. +86 10 58802736; emails: bian@bnu.edu.cn (Z. Bian), 2446110448@qq.com (A. Chen), 894596244@qq.com (X. Xin), 1157030205@qq.com (J. Xu), 524701214@qq.com (Y. Bian), ading@bnu.edu.cn (A. Ding)

Received 1 December 2016; Accepted 28 April 2017

ABSTRACT

The potential use of synthetic boehmite coated zeolites for the removal of arsenic from water has been investigated. The boehmite coated zeolite was characterized by scanning electron microscopy and X-ray diffraction. The mechanism of aqueous arsenic adsorption was revealed. Additionally, experiments were conducted to examine the extent of arsenic removal as a function of pH, adsorbents dose, coexisting ions. The adsorption behavior followed the Langmuir isotherm model. The kinetic process of adsorption was well fitted with the Elovich equation. The boehmite coated zeolite showed great performance on the aqueous arsenic removal.

Keywords: Adsorption; Arsenic; Boehmite; Zeolite

1. Introduction

Arsenic is one of the contaminants found in the environment which is notoriously toxic to plants, animals, and human beings. Arsenic aqueous contamination is usually caused by mining activity, combustion of fossil fuels, and the use of arsenical pesticides and herbicides [1,2]. Generally, inorganic arsenic is mostly found in natural environment, especially inorganic arsenate and arsenite, referred to As(V) and As(III) which were most common in natural waters [3]. Although As(V) tends to be less toxic compared with As(III), As(V) ions were thermodynamically more stable under normal conditions and cause the major contamination in aqueous environment [4]. Hence, the As(V) removal from aqueous environment such as drinking water becomes urgent on behalf of human health [5].

Numerous treatment efforts have been made to treat the aqueous arsenic contamination such as redox processes [6,7], precipitation [8], adsorption [9], solvent extraction [10], ion exchange [11]. Among these methods, adsorption technique is generally considered as a promising method, because the adsorbent could be easily removed from aqueous media after treatment [12–14]. So far, various adsorbents for arsenic removal have been developed such as metal-loaded coral limestone [15], alginate beads [16], hematite and feldspar [17], sandy soils [18,19], coal fly ash [20], activated carbon [21,22], activated alumina [23], silica gel [24], etc. [25,26]. However, natural adsorbents were not quite efficient for arsenic removal and synthetic adsorbents usually need complex preparation procedures with quite high cost. Hence, developing adsorbents with easy making and high efficiency has attracted much attention to facilitate the arsenic removal using the adsorption process. Zeolite has the advantage of low cost, simple preparation, easy for surface modification, and no secondary pollution. Alswat et al. [27] found that zeolite modified with copper oxide and iron oxide has remarkable adsorption ability for arsenic and lead. Awuah et al. [28] reported a theoretical study in which arsenic immobilization is showed to depend on Si/Al ratio in the Al(III)-modified zeolite. As a non-traditional mineral resource, the research on zeolite has received wide attention. However, it is necessary to improve the adsorption capacity and stability of zeolite modified by a kind of low-cost method.

In the present study, a new adsorbent, boehmite coated zeolite, has been synthesized and investigated for the As(V) removal from aqueous solution. During the process of the immobilization of boehmite on zeolite surface, the aluminiferous compounds such as hydroxyl group (AlOOH) and alumina species (Al_2O_3) would be coated on the surface as the activated adsorption site for adsorption of arsenic. Pseudoboehmite is

---

* Corresponding author.

1944-3994/1944-3986 © 2017 Desalination Publications. All rights reserved.

a low-cost alumina precursor and a hydrated aluminum oxyhydroxide (AlOOH), which can be easily synthesized and dispersed on the surface of porous zeolite [29]. Based on these advantages, the boehmite coated zeolite was prepared by treating zeolite with pseudoboehmite suspension instead of boehmite for their similar chemical composition and characterized as an adsorbent. Batch experiments were performed to evaluate the arsenic removal property of the boehmite coated zeolite under different operational conditions. The adsorption isotherm models and kinetic processes were calculated and discussed to assess the present system.

2. Materials and methods

2.1. Materials

Natural zeolite (200 mesh) was used as received. Analytical reagent grade chemicals were used for the preparation of all solutions with deionized water. Stock solution of As(V) (500 mg/L) was prepared by dissolving disodium hydrogen arsenate in deionized water and further diluted to suitable concentration before use. Arsenic in solution was determined by an AFS-230E atomic fluorescence spectrometry. Calibration standards are prepared using standard solutions certified by the supplier.

2.2. Preparation of samples

Natural zeolite and water with proper mixture ratio were mixed together and grounded into fine powder with pore-forming agent (polyethylene particle, 2–3 mm) in a mortar. The well-mixed powder was calcined at 110°C for 2 h. The result solid was grounded into powder again and calcined at 1,150°C for 3 h to achieve the mesoporous zeolite. The zeolite was then ultrasonic treated to remove some present small species on the surface and in the cavity. The treated zeolite was mixed with pseudoboehmite suspension at 60°C for 30 min. Then the solid was centrifuged to remove excess pseudoboehmite on the surface and dried at 110°C for 2 h. Finally, the dried samples were calcined at proper temperature to give the boehmite coated zeolite.

2.3. Characteristics of samples

The surface of the prepared zeolite was characterized by a Hitachi S-4800 scanning electron microscopy (SEM). X-ray diffraction (XRD) pattern of the prepared zeolite particles was analyzed by a X'Pert PRP MPD multi-purpose X-ray diffractometer. The surface potential was estimated by using batch equilibrium techniques. 0.1 g of adsorbent was treated with 0.05 M $NaClO_3$ solution which was used as an inert electrolyte. The initial pH values are adjusted in the range of 4–9 by adding minimum amounts of 0.1 M NaOH or 0.1 M HCl solutions. The suspensions are allowed to equilibrate for 72 h in a rotary shaker at room temperature. After completion of equilibration time, the mixtures are filtered and potential of the filtrates is measured. The adsorption experiment was repeated for seven stock solutions with different initial pH levels varying from 4 to 9. After 3 h of adsorption, the removal efficiency of arsenic was calculated. The adsorption kinetic study was carried out at pH 4 and 9. The initial concentration of arsenic was 1 mg/L. To investigate the effect of coexisting anions, sodium chloride, sodium sulfate, and monopotassium phosphate were chosen and added to the arsenic solution. A mass of 2 g of boehmite coated zeolite was mixed with 100 mL of arsenic solution. The mixtures were shaken with an over-head shaker for 3 h and centrifuged. Then the arsenic concentration in supernatant was analyzed.

3. Results and discussions

3.1. Characterization of boehmite coated zeolite

The prepared zeolite was modified by loading with various amounts of pseudoboehmite via a wet-impregnation method. Fig. 1 shows the SEM micrographs of the raw zeolite (a), boehmite coated zeolite (b) and (c), and over-loaded sample (d), respectively. It was clearly shown that there were many microcavities in the sample (a) which contributed to high surface area, and some of them remained in the sample (b) after the boehmite was coated on the surface of zeolite. Sample (c) showed in detail highly boehmite coverage with many flaws on the surface which increases the effective surface area. However, too much boehmite loaded on the surface of sample (d) decreased the stability of coating which will leak boehmite species.

The structure and properties of the coated boehmite species play an important role in the adsorption properties of modified zeolite. XRD patterns of prepared boehmite coated zeolites were illustrated in Fig. 2. The structure of boehmite species changed with the calcination temperature on the preparation processes. The sample treated at 350°C showed major peaks at about 2θ = 14.5°, 28.2°, 38.4°, and 49.2° which attributed to the (020 reflection), (021), (130), and (150/002 doublet) crystal phase of boehmite, respectively [30]. In addition, the size of boehmite species could be calculated as 3.7 nm from XRD data. The samples treated at 450°C presented as activated alumina with two characterized XRD 2θ peaks at ca. 45° and 66°. Hence, high temperature resulted in the transformation of coated hydroxyl group (AlOOH) to alumina species (Al_2O_3) as shown in Eq. (1) [31]. During the coating process, AlOOH molecule combined with the oxygen-containing group on the surface of the zeolite by the hydroxyl group. The chemical bond would be reinforced and a stabilized boehmite coated zeolite would be obtained by calcining at a proper temperature. The content of hydroxyl group in boehmite is greater than alumina when the boehmite coated zeolite was calcined at 350°C.

$$\text{Pesuoboehmite} \xrightarrow{350°\text{C}} \text{AlOOH} \xrightarrow{450°\text{C}} \text{Al}_2\text{O}_3 \tag{1}$$

As(V) mainly exists in the form of H_3AsO_4 (pH < 2), $H_2AsO_4^-$ (2 < pH < 7), and $HAsO_4^{2-}$ (pH > 7). AsO_4^{3-} hardly ever exists even in the aqueous solution pH is closed to 14. Hydroxide anion could be replaced by the As(V) ion with different hydrochemical speciation in aqueous solution, which can be described as follows:

$$\text{Al(OH)}_2^+ + \text{H}_2\text{AsO}_4^- \rightarrow \text{AlO}_2\text{HAs(OH)}_2 \tag{2}$$

$$\text{Al(OH)}_4^- + \text{HAsO}_4^{2-} \rightarrow \text{AlO}_2\text{As(O)OH}^- \tag{3}$$

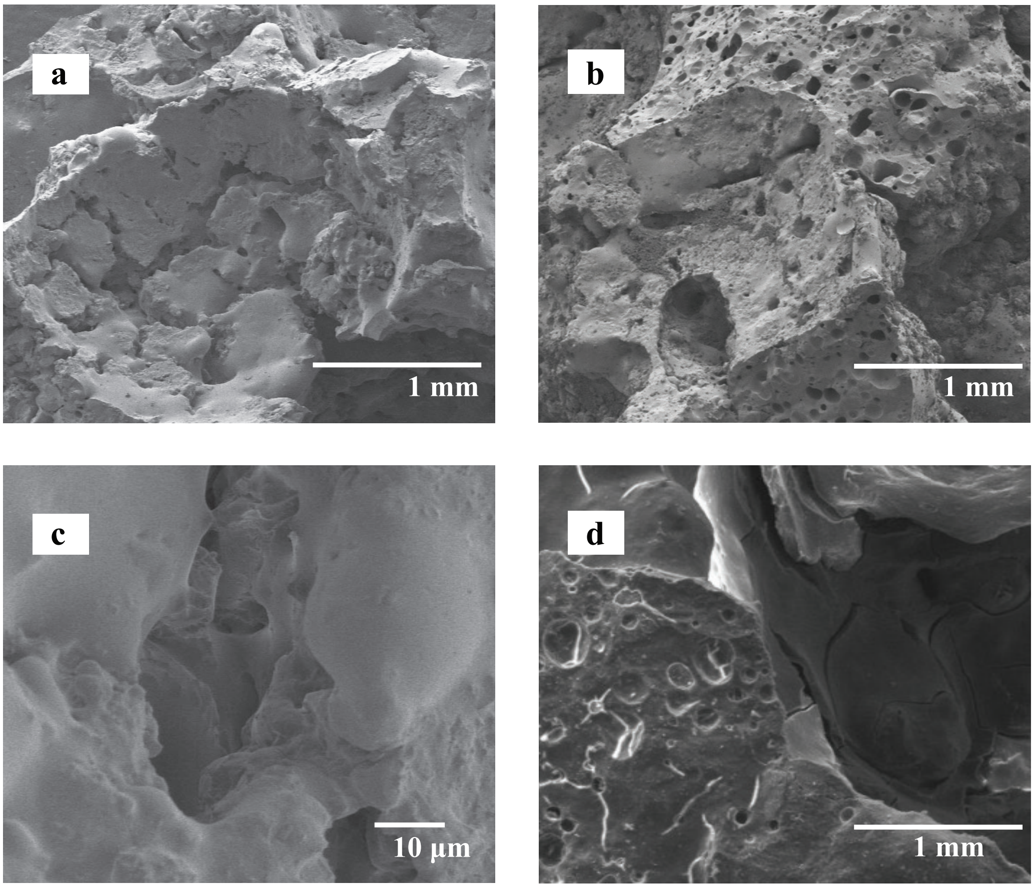

Fig. 1. SEM micrographs of raw zeolite and boehmite coated zeolites: (a) raw zeolite; (b) and (c) modified zeolite; (d) over-loaded zeolite.

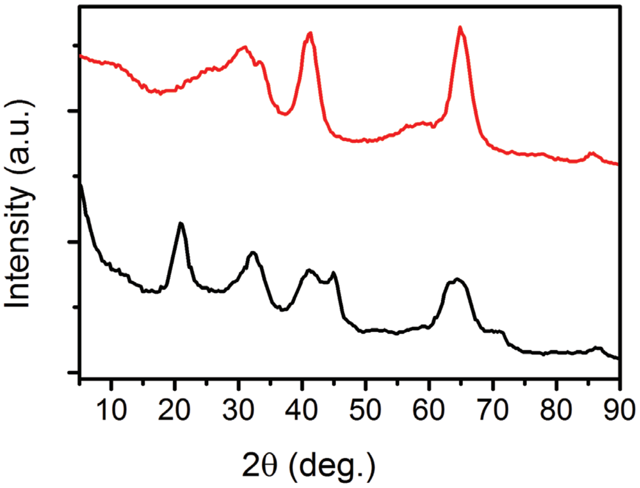

Fig. 2. XRD patterns of boehmite coated zeolite treated at different temperature: above red line 450°C; below black line 350°C.

As arsenic adsorption via anion exchange, the hydroxyl group in boehmite may play a crucial role in the removal of arsenic from aqueous environment. The adsorption of As(V) onto boehmite coated zeolite occurred by ligand exchange reactions, and most of the hydroxide groups were involved in ligand exchange reactions. Hydroxyl group coated zeolites showed better arsenic adsorption performance compared with alumina modified one.

3.2. Surface potential of boehmite coated zeolite

The acid–base properties of boehmite coated zeolites are important when they are used as adsorbents for arsenic removal. One parameter for characterization of adsorbents' acid–base properties is their surface potential. A plot of potential of filtered solution after equilibrium as a function of initial pH values provides surface potential of the adsorbents as shown in Fig. 3. The zero point surface potential values of the boehmite coated zeolite presented at pH 9. Due to arsenic species present as anion in solutions, pH below zero point surface potential favored the adsorption of arsenic anion on adsorbents. At pH 5.5, the surface potential was the most positive which indicated that boehmite coated zeolite had strong adsorption capacity for arsenic anion.

3.3. Effect of solution pH on arsenic adsorption

From the view of surface potential, when pH value was less than 9, the adsorption of arsenic was favorable. In this pH range, the dependence of removal percentage for As(V) upon pH of the aqueous solution was shown in Fig. 4. At pH of 5.5, the most efficient arsenic removal efficiency was achieved, due to the strongest acid of the surface of boehmite

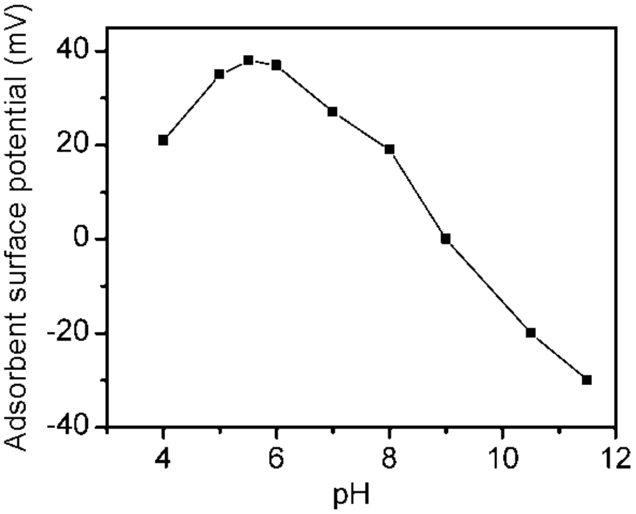

Fig. 3. Relationship of surface potential of adsorbent and solution pH values.

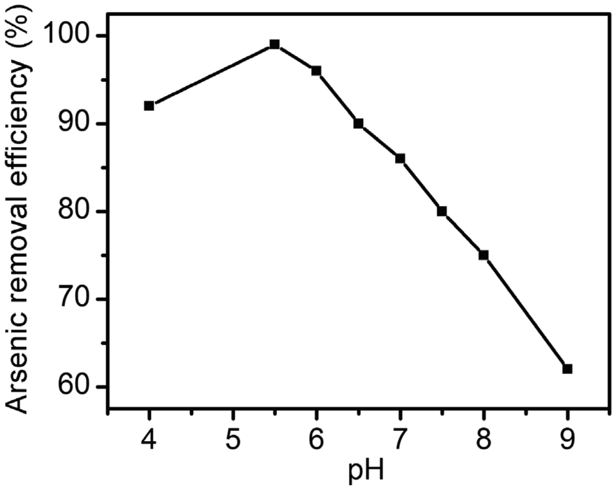

Fig. 4. The effect of solution pH on the adsorption of arsenic onto boehmite coated zeolite.

coated zeolite. When pH value of solution was more than 5.5, the removal efficiency for arsenic slightly decreased with the increase of pH value. The surface charge of modified zeolite was changed by deprotonation and protonation reactions of boehmite. Also As(V) was an oxyanion and the hydrochemical speciation of As(V) was affected by the pH value. As a result, adsorption of As(V) highly depends on the solution pH. Under acidic condition, surface charge became more positive, because of the protonation of the modified zeolite, which provided more adsorption sites for arsenic. However, in a strong acidic solution with pH below 5.5, As(V) competed with hydrogen ions for the adsorption onto modified zeolite which attributed to the decreased As(V) removal. It was clearly shown that arsenic could be effectively absorbed by boehmite coated zeolite in a wide pH range. With the increase of pH, the zeolite surface became negatively charged and electrostatic repulsion between zeolite and arsenic resulted in a decrease of adsorption.

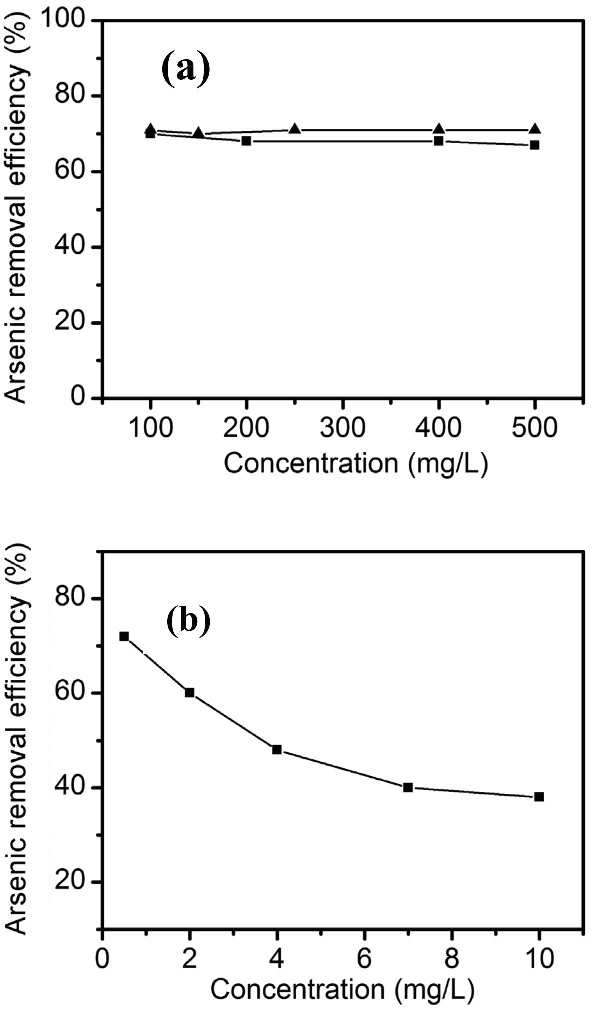

Fig. 5. The effect of sulfate (triangle), chloride (square) anion (a) and phosphate anion (b) on arsenic removal.

3.4. Influence of coexisting anion on arsenic sorption

Fig. 5 showed the influence of coexisting anions upon the adsorption capacity of As(V). The addition of chloride, sulfate ions hardly affected the As(V) adsorption, while the adsorption was significantly depressed by the addition of phosphate ion. The coexistence of phosphate decreased adsorption capacities of boehmite coated zeolite for arsenic, because arsenic ions competed with phosphate ions for the adsorption onto boehmite coated zeolite. The presence of phosphate reduced the adsorption efficiency of boehmite coated zeolite for arsenic from 75% to 38% with the increase of phosphate ion concentration from 0 to 10 mg/L in the parallel experiments. This result was ascribed to the similar chemical ligand structure in the adequate range of pH values between phosphate and arsenate [32].

3.5. Adsorption isotherm study

It is suggested that the As(V) adsorption mostly occurs at active sites on boehmite species deposited on the surface and/or in the cavity of modified zeolite by loading treatment.

The As(V) adsorption could be enhanced with increasing the amount of these active sites which is dependent on the effective surface area of the bound aluminum species. Concentration dependence of As(V) adsorption on boehmite modified zeolite is depicted in Fig. 6. The equilibrium data obtained from the adsorption of arsenic on boehmite coated zeolite over the different initial arsenic concentrations were correlated with the Langmuir monolayer isotherm model. The model is based on some assumptions which include metal ions were chemically adsorbed at a fixed number of well-defined sites, each site can hold only one ion, all sites are energetically equivalent, and there is no interaction between the ions. The Langmuir linearized isotherm is given by the following equation:

$$C_e/Q_e = b/Q_m + C_e/Q_m \tag{4}$$

where Q_e (mg/L) is milligrams of arsenic adsorbed per gram of adsorbent, C_e (mg/L) is arsenic concentration in equilibrium solutions, Q_m (mg/g) and b (mg/L) are Langmuir constants related to sorption capacity and sorption energy, respectively. A good linear plot is obtained by plotting C_e/Q_e against C_e for boehmite coated zeolite. Q_m values computed from slope of plot were 0.82 mg/g for boehmite coated zeolite.

Table 1 shows some natural adsorbents that are low cost and modified simply for arsenic removal. Compared with Fe-modified coal fly ash and chestnut shell, boehmite coated zeolite had a similar adsorption capacity but with the advantages of simple preparation and nil secondary pollution. Boehmite coated zeolite also exhibited higher adsorption ability than other natural adsorbents showed in Table 1.

3.6. Adsorption kinetics

Time dependence of As(V) adsorption on boehmite coated zeolite was presented in Fig. 7. These experiments were carried out to find out the equilibrium time of adsorption and adsorption kinetics. In the present system, the rate of As(V) removal was quite rapid. About 60% of the arsenic species could be removed within first 30 min. The adsorption equilibrium time for arsenic onto boehmite coated zeolite lay in the range of 60 min. Thus it indicates that the adsorption kinetic of As(V) on boehmite modified zeolite accomplished in two stages. The first stage was the

Table 1
Adsorption capacity of different adsorbents for arsenic removal

Adsorbent	Adsorption capacity (mg/g)	Reference
Granulated ferric oxide medium	0.35–1.63	[17]
Iron-modified alumina/silica oxide hydrate from coal fly ash	2.11	[20]
$FeCl_3$-modified chestnut shell	0.885	[25]
Wheat straw modified with sodium bicarbonate	0.12	[26]
Boehmite coated zeolite	0.82	This work

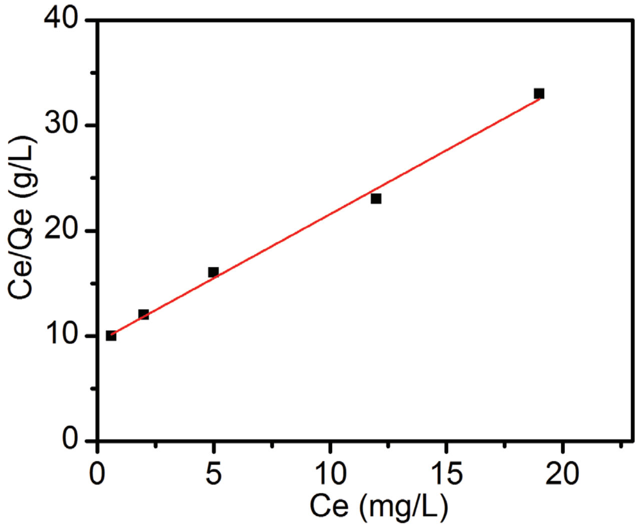

Fig. 6. Langmuir plots of arsenic adsorption onto boehmite coated zeolite ($R^2 = 0.9941$).

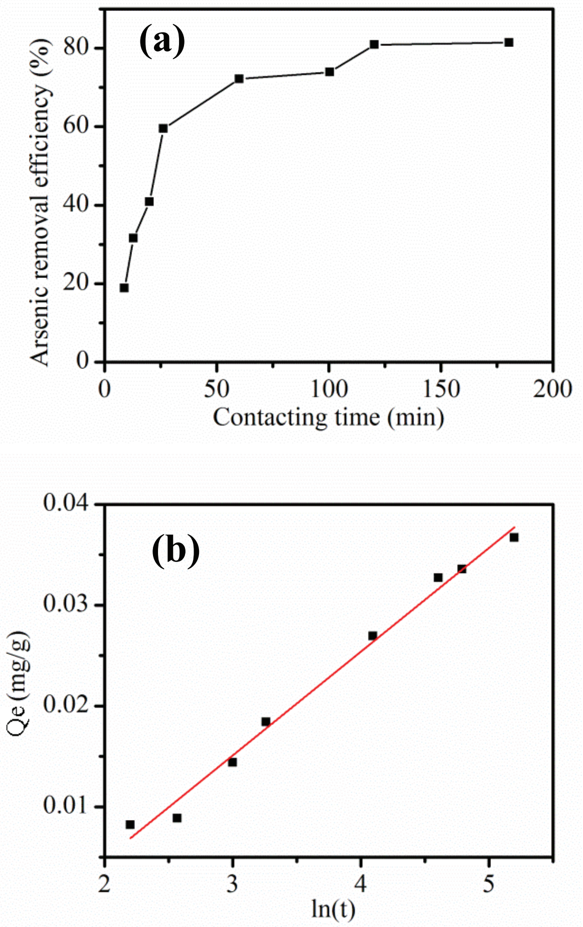

Fig. 7. Time dependence of arsenic ion adsorption onto boehmite coated zeolite. (a) Time courses and (b) kinetic study.

immediate uptake of arsenic within first 30 min which was followed by the steady stage of solute removal. Therefore, to elucidate the adsorption mechanism, an Elovich equation was used as the fitting kinetic model to the experimental results (Fig. 7(b)).

$$Q_e = a + b \times \ln(t) \tag{5}$$

where Q_e (mg/g) is the equilibrium amount of As(V) uptake; a is the initial adsorption rate, t (min) is the contact time, b is a constant. The fitting equation could be described as $Q_e = -0.0157 + 0.0103 \times \ln(t)$ ($R^2 = 0.9901$). It showed that the As(V) removal by boehmite coated zeolite was multi-processes such as surface exchange, surface diffusion, pore diffusion, and static electronic adsorption.

4. Conclusions

A new adsorbent for arsenic removal, boehmite coated zeolite, was prepared and characterized. As(V) adsorption onto boehmite coated zeolite followed the Elovich kinetic equation and the adsorption mode was of a Langmuir isothermal nature. In the batch experiments, arsenic was efficiently removed within 30 min. The adsorption of As(V) depended on the initial pH and favored in acidic and natural solutions. Phosphate, coexisting ion, competitively adsorbed onto boehmite coated zeolite with arsenic. The abundant boehmite coated zeolite adsorbent showed great adsorption capacity, reached to 0.82 mg/g, for the arsenic removal in a wide optimum pH range.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 21373032).

References

[1] B.K. Mandal, K.T. Suzuki, Arsenic round the world: a review, Talanta, 58 (2002) 201–235.

[2] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, Appl. Geochem., 17 (2002) 517–568.

[3] C.J. Chen, C.W. Chen, M.M. Wu, T.L. Kuo, Cancer potential in liver, lung, bladder and kidney due to ingested inorganic arsenic in drinking-water, Br. J. Cancer, 66 (1992) 888–892.

[4] W.R. Cullen, K.J. Reimer, Arsenic speciation in the environment, Chem. Rev., 89 (1989) 713–764.

[5] A.H. Smith, M. Goycolea, R. Haque, M.L. Biggs, Marked increase in bladder and lung cancer mortality in a region of Northern Chile due to arsenic in drinking water, Am. J. Epidemiol., 147 (1998) 660–669.

[6] S.C. Ying, B.D. Kocar, S.D. Griffis, S. Fendorf, Competitive microbially and Mn oxide mediated redox processes controlling arsenic speciation and partitioning, Environ. Sci. Technol., 45 (2011) 5572–5579.

[7] F.L. Sun, K.A. Osseo-Asare, Y.S. Chen, B.A. Dempsey, Reduction of As(V) to As(III) by commercial ZVI or As(0) with acid-treated ZVI, J. Hazard. Mater., 196 (2011) 311–317.

[8] K.A. Rittle, J.I. Drever, P.J.S. Colberg, Precipitation of arsenic during bacterial sulfate reduction, Geomicrobiol. J., 13 (1995) 1–11.

[9] D.B. Singh, G. Prasad, D.C. Rupainwar, Adsorption technique for the treatment of As(V)-rich effluents, Colloids Surf., A., 111 (1996) 49–56.

[10] R.E. Rivas, I. Lopez-Garcia, M. Hernandez-Cordoba, Speciation of very low amounts of arsenic and antimony in waters using dispersive liquid-liquid microextraction and electrothermal atomic absorption spectrometry, Spectrochim. Acta B., 64 (2009) 329–333.

[11] H. Yin, F. Liu, X.H. Feng, M.M. Liu, W.F. Tan, G.H. Qiu, Co^{2+}-exchange mechanism of birnessite and its application for the removal of Pb^{2+} and As(III), J. Hazard. Mater., 196 (2011) 318–326.

[12] Z.X. Wu, W. Li, P.A. Webley, D.Y. Zhao, General and controllable synthesis of novel mesoporous magnetic iron oxide@carbon encapsulates for efficient arsenic removal, Adv. Mater., 24 (2012) 485–491.

[13] J.A. Wilkie, J.G. Hering, Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes, Colloids Surf., A., 107 (1996) 97–110.

[14] M.N. Amin, S. Kaneco, T. Kitagawa, A. Begum, H. Katsumata, T. Suzuki, K. Ohta, Removal of arsenic in aqueous solutions by adsorption onto waste rice husk, Ind. Eng. Chem. Res., 45 (2006) 8105–8110.

[15] A. Ohki, K. Nakayachigo, K. Naka, S. Maeda, Adsorption of inorganic and organic arsenic compounds by aluminium-loaded coral limestone, Appl. Organomet. Chem., 10 (1996) 747–752.

[16] D. Sanchez-Rivera, O. Perales-Perez, F.R. Roman, Removal of inorganic arsenic oxyanions using Ca-Fe(III) alginate beads, Desal. Wat. Treat., 51 (2013) 2162–2169.

[17] E. Sazakli, S.V. Zouvelou, I. Kalavrouziotis, M. Leotsinidis, Arsenic and antimony removal from drinking water by adsorption on granular ferric oxide, Water Sci. Technol., 71 (2015) 622–629.

[18] H. Castillo-Michel, J.A. Hernandez-Viezcas, A. Servin, J.R. Peralta-Videa, J.L. Gardea-Torresdey, Arsenic localization and speciation in the root-soil interface of the desert plant *Prosopis juliflora-velutina*, Appl. Spectrosc., 66 (2012) 719–727.

[19] D. Srivastava, R.C. Vaishya, Treatment of arsenic (III) contaminated water by dynamically modified iron-coated sand (DMICS), Desal. Wat. Treat., 53 (2015) 2565–2577.

[20] K. Zhang, D. Zhang, K. Zhang, Arsenic removal from water using a novel amorphous adsorbent developed from coal fly ash, Water Sci. Technol., 73 (2016) 1954–1962.

[21] J. Ma, Z.L. Zhu, B. Chen, M.X. Yang, H.M. Zhou, C. Li, F. Yu, J.H. Chen, One-pot, large-scale synthesis of magnetic activated carbon nanotubes and their applications for arsenic removal, J. Mater. Chem. A, 1 (2013) 4662–4666.

[22] C.B. Gula, E.B. Simsek, D. Duranoglu, U. Beker, An experimental design approach for modeling As(V) adsorption from aqueous solution by activated carbon, Water Sci. Technol., 71 (2015) 203–210.

[23] Y.H. Kim, C.M. Kim, I.H. Choi, S. Rengaraj, J.H. Yi, Arsenic removal using mesoporous alumina prepared via a templating method, Environ. Sci. Technol., 38 (2004) 924–931.

[24] H.T. Fan, J. Li, M.M. Guo, X.L. Fan, D.S. Zhang, Z.J. Su, J. Wang, Removal of arsenic from ammoniacal etching waste liquor by 3-(2-aminoethylamino) propyltrimethoxysilane functionalized silica gel sorbent, Desal. Wat. Treat., 50 (2012) 51–58.

[25] S. Targan, V.N. Tirtom, Arsenic removal from aqueous system using modified chestnut shell, Desal. Wat. Treat., 56 (2015) 1029–1036.

[26] R. Ebrahimi, A. Maleki, B. Shahmoradi, H. Daraei, A.H. Mahvi, A.H. Barati, A. Eslami, Elimination of arsenic contamination from water using chemically modified wheat straw, Desal. Wat. Treat., 51 (2013) 2306–2316.

[27] A.A. Alswat, M. Bin Ahmad, T.A. Saleh, Zeolite modified with copper oxide and iron oxide for lead and arsenic adsorption from aqueous solutions, J. Water Supply Res. Technol. AQUA, 65 (2016) 465–479.

[28] J.B. Awuah, N.Y. Dzade, R. Tia, E. Adei, B. Kwakye-Awuah, C.R.A. Catlow, N.H. de Leeuw, A density functional theory study of arsenic immobilization by the Al(III)-modified zeolite clinoptilolite, Phys. Chem. Chem. Phys., 18 (2016) 11297–11305.

[29] H.M. Wilson, S.R. Juan, M.S. Juan, Z.M. Juan, Synthesis of lanthanum aluminate by reverse chemical precipitation using pseudoboehmite as alumina precursor, Appl. Radiat. Isot., 117 (2016) 96–99.

[30] R.T. Tettenhorst, Comparison of experimental and calculated X-ray-power diffraction data for boehmite, Clays Clay Miner., 36 (1988) 181–183.

[31] X. Krokidis, P. Raybaud, A.E. Gobichon, B. Rebours, P. Euzen, H. Toulhoat, Theoretical study of the dehydration process of boehmite to gamma-alumina, J. Phys. Chem. B, 105 (2001) 5121–5130.

[32] T. Tuutijärvi, E. Repo, R. Vahala, M. Sillanpää, G. Chen, Effect of competing anions on arsenate adsorption onto maghemite nanoparticles, Chin. J. Chem. Eng., 20 (2012) 505–514.