Fe–Mn binary oxide incorporated into diatomite as an adsorbent for arsenite removal: Preparation and evaluation

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ABSTRACT

Fe–Mn binary oxide incorporated into diatomite (FMBO-diatomite) was prepared by a simple coating method, and exhibited high oxidation and adsorption ability for arsenite [As(III)]. After being incorporated by Fe–Mn binary oxide, the surface area of diatomite increased 36%, and the pore volume increased five times. The pH_{zpc} of FMBO-diatomite was determined to be 8.1. These characteristics are responsible for the increased As(III) adsorption efficiency. The adsorption equilibria of As(III) on FMBO-diatomite were described well by a Langmuir isotherm model due to the homogeneous distribution of Fe–Mn binary oxide on a diatomite surface. As(III) was oxidized into As(V), and then adsorbed by FMBO-diatomite. The oxidation and adsorption efficiencies for As(III) depended deeply on the pH of solution. When the pH was raised to 8.1, the As(III) adsorption efficiency of FMBO-diatomite was almost equal to the As(III) oxidation efficiency. Silicate and phosphate had negative effects on As(III) adsorption. Also the influence of silicate and phosphate with the pH variation was different.

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1. Introduction

Arsenic, as a carcinogenic substance, is present mostly as arsenite [As(III)] and arsenate [As(V)] in natural water [1]. As(III) is more mobile and toxic than As(V) [2,3]. Therefore, efficient removal of As(III) is more desired.

Being different from other arsenic removal techniques, adsorption seems to be a promising route to effectively and economically remove As(III) with metal-oxide adsorbents [4,5]. Among these adsorbents, Fe–Mn-based adsorbents have played a dominant role in the removal of As(III). A low-cost ferruginous manganese ore can remove As(III) from groundwater without any preoxidation [6]. Mn-substituted iron oxyhydroxide was prepared by the oxidation of ferrous carbonate, and exhibited high removal efficiency for As(III) [7]. However, applications of these Fe–Mn-based adsorbents were complicated in large-scale treatments. Ferruginous manganese ore had low adsorption capacity, because the ore crystal has a small amount of adsorption sites. Mn-substituted iron oxyhydroxide had low hydraulic conductivity, because this adsorbent was an amorphous material.

As a porous supporting material, diatomite has various good characteristics, i.e., high permeability, high porosity, and low bulk density [8]. In water treatment, diatomite was modified by Mn oxides to increase the surface area for adsorbing lead and dye [9,10]. Fe (25%)-diatomite exhibited high adsorption speed for arsenic

[11], due to the well-dispersed hydrous ferric oxide on the diatomite.

In this study, Fe–Mn binary oxide was incorporated into diatomite (FMBO-diatomite) by a simple coating method. After being dried, the granular FMBO-diatomite was used as an adsorbent in the removal of As(III). The strong oxidation and adsorption abilities of FMBO-diatomite were determined through batch equilibration experiments. Effects of temperature, pH, and coexisting anions on the As(III) adsorption efficiency were also studied.

2. Material and methods

2.1. Materials

All chemicals were analytical grade from Beijing Chemical Reagents Company. Stock solutions of As(III) were prepared by dissolving NaAsO₂ with deionized water. The NaNO₃, HNO₃, and NaOH solutions, used in the titration experiments, were prepared with ultrapure water. Other chemicals and reagents were dissolved or diluted by deionized water. The glassware was cleaned by washing with tap water, soaked with 10% HNO₃ for at least 24 h, and finally rinsed with deionized water for three times.

Diatomite, from Changbai Mountain in China, mainly consists of silicon dioxide ($\geq 85\%$, w/w). The diatomite was washed with tap water to remove fines and other adhered impurities and then dried at 60 °C for 24 h. The dried diatomite was sieved to a uniform size of 0.25–0.35 mm, and stored in polyethylene bottles.

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2.2. Incorporation of Fe–Mn binary oxide into diatomite

A precursor of Fe–Mn binary oxide was prepared by 150 mL solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.075 mol/L) and KMnO_4 (0.025 mol/L). The following procedure was developed to incorporate Fe–Mn binary oxide precursor into pores of diatomite as homogeneously as possible: (1) Place 50 g of dried diatomite into 75 mL solution of FeSO_4 (0.075 mol/L). (2) Add 75 mL solution of KMnO_4 (0.025 mol/L) and NaOH (0.1 mol/L) into the above solution. (3) Stir the suspension liquid gently for 30 min at pH of 4.5–5.0. (4) Separate the solids from the suspension and dry the solids at 60 °C for 12 h. A homogeneous load of Fe–Mn binary oxide was judged by observing the change of deep brown color distribution on the diatomite. The adsorbent FMBO-diatomite, deep brown grain (size of 0.25–0.35 mm), was prepared and stored in polyethylene bottles for the subsequent experiments.

2.3. Adsorbent characterization

The surface morphologies of diatomite and FMBO-diatomite were examined by scanning electron microscopy (SEM) (S-3000 N, Hitachi Co., Japan) with energy-dispersive X-ray analysis (EDX) (EDAX Co., USA). FTIR spectra were collected on a Nicolet 5700 FTIR spectrophotometer (Nicolet Co., USA) using a transmission model. Samples for FTIR determination were ground with spectral grade KBr in an agate mortar. IR spectra of diatomite and FMBO-diatomite were obtained as dry samples in KBr pellets corresponding to 5 mg of sample in approximately 100 mg of spectral grade KBr. All IR measurements were carried out at room temperature. Both the second derivative and the deconvoluted spectra were used to determine the number of overlapping bands. Then, Gaussian profile fitting was performed to reveal the assemblage of multiple bands using the Jandel PeakFit software (PeakFit-Jandel Scientific Software, San Rafael, CA).

The specific surface area and average pore size distribution of diatomite and FMBO-diatomite were measured by the nitrogen adsorption–desorption isotherm method using the accelerated surface area and porosimetry (ASAP 2000, Micromeritics Co., USA). The amount of Fe and Mn in 1.0 g FMBO-diatomite was determined by digesting via 40 mL 98% nitric acid. The acidic solution was filtered through a 0.45- μm membrane filter and analyzed for Fe and Mn concentration. Potentiometric titrations of FMBO-diatomite were conducted using an automatic potentiometric titrator (716 DMS, Metrohm Co., Switzerland) at 25 °C in 0.1, 0.01, and 0.001 mol/L NaNO_3 solutions, respectively. The prepared suspensions (solid concentration 1.0 g/L) were equilibrated at the desired ionic strength for 24 h. In the whole titration procedure, two steps were performed. The suspensions were acidified to pH 2.5 in acidimetric titration first, and then back titrated to the alkaline region in alkalimetric titration, purging with N_2 gas to minimize CO_2 contamination. The titrants were 0.05 mol/L NaOH and 0.05 mol/L HNO_3 .

2.4. Batch adsorption experiments

The isotherm experiments were conducted to evaluate adsorption capacities of As(III) at constant temperatures of 10, 25, 35, and 45 °C with a pH of 5.0 or 7.0. The other adsorption conditions were 1.0 g/L FMBO-diatomite, initial As(III) concentration of 0.05–5.0 mg/L, and 24 h equilibrium time.

To investigate the influence of initial pH (2.0–11.0) on the oxidation and adsorption efficiency for As(III), the experiments were performed with 1.0 g/L FMBO-diatomite and 1.0 mg/L As(III) solutions for 6.0 h of equilibrium time at 25 °C.

The effects of common coexisting anions in water, i.e., carbonate, sulfate, fluoride, nitrate, silicate, and phosphate, were investi-

gated by adding a defined amount (1.0 g/L) of FMBO-diatomite into one solution which contained 1.0 mmol/L of the coexisting anions and 1.0 mg/L of As(III). The vessels were shaken for 6.0 h at 25 °C. The solution pH values were adjusted to 3.5, 6.0, and 9.0.

All batch solutions were sampled and filtered through 0.45- μm membrane filter, and then analyzed for arsenic [As(tot)] and As(III). The analysis of As(III) was finished within 30 min in order to avoid air oxidation.

2.5. Analytical methods

Inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 2000, PerkinElmer Co., USA) was used for As(tot), Fe, and Mn concentrations. Hydride generation atomic fluorescence spectrometry (HG-AFS) (Beijing Beifenruili Analytic Instrument Co., China) was used for As(III) concentrations. The pH of solution was adjusted by adding 0.1 mol/L HNO_3 or 0.1 mol/L NaOH , and was measured with a pH meter (Model 720A, Orion Co., USA).

2.6. Quality assurance

In order to ascertain reliability, accuracy, and reproducibility of the experiment data, the batch adsorption experiments were replicated twice and experimental blanks were run in parallel. Sample blanks were analyzed for the correction of background effect on instrument response. For analytical calibration standard, solutions with arsenic concentrations ranging from 0 to 5.0 mg/L were employed on ICP-OES. Calibration curves between 0 and 0.5 mg/L As(III) were prepared for HG-AFS. The limits of determinations on ICP-OES and HG-AFS were 0.040 and 0.0005 mg/L, respectively. Precision of the parallel measurements was $\pm 5\%$ RSD (relative standard deviation). The software Origin 7.5 was used to deal with all experiment data in this study.

3. Results and discussion

3.1. Characterization of FMBO-diatomite

3.1.1. SEM with EDX analysis

The morphologies of diatomite and FMBO-diatomite are displayed in Fig. 1. Many pores can be seen on the surface of diatomite (Fig. 1a). After being incorporated, the surface of diatomite was covered by Fe–Mn binary oxide, and a porous structure can still be observed (Fig. 1b), which is beneficial for the As(III) adsorption. Compared to amorphous Fe–Mn binary oxide described in our previous work [12], FMBO-diatomite exhibited higher mechanical strength and higher water permeability. As shown in the EDX elemental analysis (Fig. 1c and d), silicon was the main element in diatomite and FMBO-diatomite. The chemical composition of FMBO-diatomite showed that the elemental molar ratio of Fe to Mn was 3:1, the same as that of the preparation precursor.

3.1.2. FTIR spectroscopy fitting

The FTIR spectra of diatomite and FMBO-diatomite are presented in Fig. 2. The overlapping bands were fitted via the Peakfit software. Fitting correlation coefficients (r^2) of diatomite and FMBO-diatomite FTIR spectra are 0.9452 and 0.9486, respectively. In Fig. 2a, the resolved band positions are illustrated at approximately 1280, 1200, 1090, 990, 790, 615, and 475 cm^{-1} (Fig. 2a), which are attributed to the infrared characteristic peaks of diatomite [13]. When diatomite was loaded by Fe–Mn binary oxide, the intensities of these bands decreased (Fig. 2b). Compared to diatomite, three new bands at 1378, 711, and 535 cm^{-1} were observed in FTIR spectra of FMBO-diatomite. The vibration at 535 cm^{-1} may be attributed to either the asymmetric Fe–O

Fig. 1. SEM images and EDX analysis: (a) diatomite (magnification 2500 $\times$), (b) FBMO-diatomite (magnification 5000 $\times$), (c) EDX of diatomite, (d) EDX of FBMO-diatomite.

Fig. 2. Partial FTIR spectra and curve fitting of (a) diatomite ($r^2 = 0.9452$) and (b) FBMO-diatomite ($r^2 = 0.9486$).

stretching bond or the Mn–O vibration bonding [14,15]. The characteristic peak at 1378 cm^{-1} indicates the O–H bending vibrations combined with Mn atoms [15]. The peak at 711 cm^{-1} was not an infrared characteristic peak of iron oxides and manganese oxides. Kwon et al. [16] affirmed that the peak at 710 cm^{-1} was the Fe–O–Si band when γ -FeOOH particles were incorporated with silicate ions. As a supporting material, diatomite mainly consisted of silicon dioxide. In the preparation of FBMO-diatomite, the diatomite was directly immersed into the FeSO_4 solution. It is suggested that the peak at 711 cm^{-1} in Fig. 2b can be assigned to the vibration of the Fe–O–Si bond. These results also indicated that a strong surface complex was formed between Fe–Mn binary oxide and diatomite

instead of a simple physical mixture, which is described in Fig. 3. The surface complex can enhance the granulated adsorbent strength [17], and contribute to the high stability of FBMO-diatomite.

3.1.3. BET surface area analysis

The adsorption efficiency depended on surface area, surface charge, and pore volume of the adsorbent [18]. After being incorporated by a small amount of Fe–Mn binary oxide which had a high surface area [12], the surface area of diatomite increased 36% and the porosity was improved significantly (see Table 1). The improved surface characteristics can enhance the As(III) adsorption efficiency, which will be exhibited subsequently.

3.1.4. Potentiometric titrations

It is known that the interface of FBMO-diatomite plays an important role in the adsorption process. The quality and the quantity of the surface charges were determined via potentiometric titration analysis. The surface charge (σ_H) was calculated using [19]

$$\sigma = \frac{(C_A - C_B + [\text{OH}^-] - [\text{H}^+]) F}{a s} \quad (1)$$

In this equation, σ is the surface charge (C/m^2); C_A is the added acid concentration (mol/L); C_B is the added base concentration (mol/L); $[\text{OH}^-]$ is the hydroxyl ion concentration (mol/L); $[\text{H}^+]$ is the proton concentration (mol/L); a is the solid concentration (g/L); F is the Faraday constant (96,500 C/mol); and s represents the specific surface area (m^2/g).

Fig. 3. Schematic bonding for Fe–Mn binary oxide with silicon hydroxyl.

Table 1

The physical characterization of diatomite and FMBO-diatomite.

Sample	Surface area (m ² /g)	Pore volume (mL/g)	Average pore diameter (Å)	Fe and Mn content (mg/g)
Diatomite	11.09	0.005	18.13	0.00
FMBO-diatomite	15.04	0.025	67.96	11.87

The calculated surface charges of FMBO-diatomite are shown in Fig. 4. The zero point of charge (pH_{zpc}) of FMBO-diatomite is identified as the common intersection point of three titration curves recorded at different ionic strengths. It is determined to be 8.1. By contrast, the pH_{zpc} of diatomite was typically below pH 3.0 because of a permanent structural negative charge caused by Si-OH [20].

3.2. Effect of the temperature on As(III) adsorption isotherms

The adsorption isotherms, which take into account the effects of equilibrium concentration on the adsorption capacity under different temperatures at pH 5.0 and 7.0, are shown in Fig. 5. The Langmuir isotherm model is used to evaluate the experimental results. In Eq. (2), $q_{\max}$ and b represent the maximum adsorption capacity (mg/g) and the affinity between the adsorbent and the adsorbate, respectively. In addition, q_e is the amount of adsorbate adsorption on the adsorbent (mg/g), and C_e is the equilibrium concentration in the solution (mg/L). These parameters and r^2 are shown in Table 2.

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (2)$$

From Table 2, r^2 values are found to be 0.851–0.982. Being different from Fe–Mn binary oxide [12], the adsorption behavior of FMBO-diatomite was described well by the Langmuir isotherm model, which assumes monolayer adsorption onto a homogeneous surface with a finite number of identical sites [21]. It is suggested that Fe–Mn binary oxide dispersed well on the diatomite as a layer of adsorption sites. In addition, it can be seen from Fig. 5 that the amount of adsorption increases with the initial concentration of As(III) and temperature, and finally reaches saturation.

Specially, at 25 °C and pH 5.0, the maximum As(III) adsorption capacity of FMBO-diatomite was 1.76 mg/g. Judging from the amount of Fe and Mn incorporated into diatomite (11.9 mg Fe and Mn/g FMBO-diatomite), the maximum adsorption capacity

Fig. 4. The surface charge of FMBO-diatomite as a function of pH at different ionic strengths (solid concentration 1.0 g/L, 25 °C, equilibrium time 24 h, N₂ gas blow off).

Fig. 5. As(III) adsorption isotherms on FMBO-diatomite at (a) pH 5.0 and (b) pH 7.0 (solid concentration 1.0 g/L, and equilibrium time 24 h).

Table 2

The Langmuir isotherms parameters of As(III) adsorption by FMBO-diatomite at pH 5.0 and 7.0.

Temperature (°C)	pH 5.0			pH 7.0		
	$q_{\max}$ (mg/g)	b	r^2	$q_{\max}$ (mg/g)	b	r^2
10	1.51	2.91	0.851	1.16	2.67	0.938
25	1.76	4.87	0.922	1.68	5.62	0.986
35	1.66	8.94	0.982	1.64	5.21	0.970
45	2.06	11.67	0.964	1.84	8.08	0.959

can also be calculated to be about 147.9 mg As(III)/g Fe and Mn, which was higher than that of Fe–Mn binary oxide [12]. The increased adsorption capacity is attributed to the effective utilization of Fe–Mn binary oxide. The obtained maximum adsorption capacity of FMBO-diatomite is compared with those obtained using other low-cost and natural adsorbents in Table 3. These results suggested that FMBO-diatomite loaded with a small amount of Fe–Mn binary oxide was more effective for As(III) removal than other Fe–Mn-based adsorbents.

3.3. Effect of pH on As(III) adsorption

The effect of the initial solution pH (2.0–11.0) on As(III) removal is illustrated in Fig. 6. The concentrations of As(tot) and As(III) in the solution were analyzed simultaneously, and As(V) was calculated by the difference. Increased As(III) and As(tot) concentrations with the pH in solutions reflected that the oxidation and adsorption efficiencies of As(III) decreased. In the pH range of 2.0–11.0, the As(III) oxidation efficiency was higher than the adsorption efficiency. It is proved that As(III) was oxidized to As(V), and then the As(V) was adsorbed onto FMBO-diatomite. The manganese dioxide in Fe–Mn binary oxide may play an important role in the As(III) oxidation [23].

The oxidation of As(III) to As(V) undoubtedly promoted the adsorption efficiency, because As(V) species are negatively charged and As(III) exists mainly as a neutral molecule in natural water [3]. Decreasing adsorption efficiency with increasing pH may reflect the declining surface charge of FMBO-diatomite. It is explained that the adsorption behavior was dominated by electrostatic attraction [22].

Table 3

Maximum As(III) adsorption capacities of some adsorbents.

Adsorbent	Max. As(III) adsorption capacity (mg/g)	pH	Temp. (°C)	Con. range (mg/L)	Model used to calculate adsorption capacity
FMBO-diatomite (11.87 mg Fe and Mn)	1.68	7.0	25	0.05–5.0	Langmuir
Ferruginous manganese ore [6]	0.5367	6.3	–	–	Langmuir
Natural siderite [26]	1.04	~7.0	20	0.25–2.0	Langmuir
Iron oxide-coated sand [27]	0.998	~7.0	25	0.7–13.5	Langmuir

Fig. 6. Effect of initial solution pH on As(III) adsorption by FMBO-diatomite (25 °C, solid concentration 1.0 g/L, initial As(III) concentration 1.0 mg/L, and equilibrium time 6.0 h).

The lowest residual As(V) concentration was found around pH 8.1 which was the pH_{zpc} of FMBO-diatomite. Singh et al. [28] observed that specific adsorption caused an increase of adsorption capacity for As(V) on hematite and feldspar at pH_{zpc} . In this study, the adsorption efficiency was almost equal to the oxidation efficiency when the pH was raised to pH_{zpc} . It is assumed that the specific adsorption is another important mechanism for As(III) removal by FMBO-diatomite.

3.4. Influence of the coexisting anions

The influences of coexisting anions, carbonate, sulfate, fluoride, nitrate, silicate, and phosphate on As(III) adsorption at pH 3.5, 6.0, and 9.0 are shown in Fig. 7. It is found that carbonate, sulfate, fluoride, and nitrate had little positive effect on As(III) adsorption. With the addition of these anions, the ionic strength of the solution was increased, which may be responsible for the increase of the adsorption efficiency. The increased ionic strength could make the double layer more compressed and the electrostatic potential that contributed to adsorption became more positive, thus enhancing the adsorption capacity [24]. On the contrary, the presence of silicate and phosphate showed a significantly negative influence on As(III) adsorption. Similar results were reported by Su and Puls [25] and they explained that silicate and phosphate can compete with As(III) for similar adsorption sites. In the case of As(III) adsorption onto FMBO-diatomite, the negative influence of silicate increased with an increase of pH. With the presence of phosphate, As(III) had slightly higher adsorptive affinity on FMBO-diatomite in alkaline solution than in acid solution. The adsorption efficiency of phosphate onto FMBO-diatomite decreased when the pH was raised. It is clear that the adsorption of phosphate on FMBO-diatomite depends more deeply on the pH of solution than the adsorption of As(III).

Fig. 7. Effects of coexisting anions on As(III) removal at pH 3.5, 6.0, and 9.0 (25 °C, solid concentration 1.0 g/L, initial As(III) concentration 1.0 mg/L, coexisting anions concentration 1.0 mmol/L, and equilibrium time 6.0 h).

4. Conclusions

Fe–Mn binary oxide has been homogeneously incorporated into diatomite and exhibited high As(III) removal efficiency. The oxidation of As(III) can significantly enhance the As(III) removal efficiency and reduce the As(III) toxicity. Acid solution and high temperature are advantageous to oxidize and adsorb As(III). Electrostatic attraction and specific adsorption were the two major forces during the As(III) adsorption process. Being different from other coexisting anions, the presence of silicate and phosphate has negative effects on the As(III) adsorption. With the increase of pH, the negative influence of silicate was enhanced, while the competition ability of phosphate for the adsorption sites was weakened. Because of the high oxidation ability and adsorption capacity for As(III), FMBO-diatomite can be filled into fixed beds for large-scale water treatments, in order to remove As(III) with low concentration from water rapidly and effectively.

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