**RESEARCH ARTICLE** 



# **Removal of arsenic(III,V) by a granular Mn-oxide-doped Al oxide adsorbent: surface characterization and performance**

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Abstract In order to remove arsenic (As) from contaminated water, granular Mn-oxide-doped Al oxide (GMAO) was fabricated using the compression method with the addition of organic binder. The analysis results of XRD, SEM, and BET indicated that GMAO was microporous with a large specific surface area of 54.26  $m^{2/}g$ , and it was formed through the aggregation of massive Al/Mn oxide nanoparticles with an amorphous pattern. EDX, mapping, FTIR, and XPS results showed the uniform distribution of Al/Mn elements and numerous hydroxyl groups on the adsorbent surface. Compression tests indicated a satisfactory mechanical strength of GMAO. Batch adsorption results showed that As(V) adsorption achieved equilibrium faster than As(III), whereas the maximum adsorption capacity of As(III) estimated from the Langmuir isotherm at 25 °C (48.52 mg/g) was greater than that of As(V) (37.94 mg/g). The As removal efficiency could be maintained in a wide pH range of 3~8. The presence of phosphate posed a significant adverse effect on As adsorption due to the competition mechanisms. In contrast, Ca2+ and Mg2+ could favor As adsorption via cationbridge involvement. A regeneration method was developed by using sodium hydroxide solution for As elution from saturated adsorbents, which permitted GMAO to keep over 75% of its As adsorption capacity even after five adsorption-

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regeneration cycles. Column experiments showed that the breakthrough volumes for the treatment of As(III)-spiked and As(V)-spiked water (As concentration =  $100 \mu g/L$ ) were 2224 and 1952, respectively. Overall, GMAO is a potential adsorbent for effectively removing As from As-contaminated groundwater in filter application.

Keywords Arsenic · Adsorption · Granular adsorbent · Manganese oxide · Aluminum oxide

## Introduction

Arsenic (As) contamination, which is mainly caused by geochemical processes or anthropogenic activities, is ubiquitous in groundwater around the world (Mandal and Suzuki 2002; Smedley and Kinniburgh 2002). As is classified as one of the most toxic and carcinogenic chemical elements and thus exerts a significant impact on drinking water security (Hughes 2002). In the aqueous environment, As predominantly exists in the inorganic forms of arsenite [As(III)] and arsenate [As(V)], and As(III) is more toxic and more mobile than As(V) (Smedley and Kinniburgh 2002; Hughes 2002). According to the World Health Organization (WHO) guidelines, the concentration of As in drinking water should be less than 10 µg/L (World Health Organization 2008). Therefore, to minimize the adverse impacts of As pollution, it is of crucial importance to develop feasible and economical technologies for the removal of excess As from drinking water.

Compared with other water treatment technologies, the adsorption process is an efficient and economical method with respect to removing As from drinking water, and many researches have been conducted on the development of advanced adsorbents for As removal (Jadhav et al. 2015; Mohan and Pittman 2007). New types of adsorbents attracting

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much attention in recent years, such as grapheme-based materials, were used to remove As from aqueous solution. For example, Yoon et al. used magnetite-graphene oxide and magnetite-reduced graphene oxide composite for the adsorption of As(III) and As(V) (Yoon et al. 2016). Roy et al. synthesized europium-doped magnetic graphene oxide and investigated its performance for the removal of As(III) and As(V) (Roy et al. 2016). On the other hand, the by-product or waste materials were also utilized for the removal of As. Ociński used water treatment residuals containing iron and manganese oxides for arsenic removal from water (Ociński et al. 2016). Imvim et al. studied the removal of As(III) and As(V) from wastewater by using cationic polymer-modified waste tyre rubber (Imyim et al. 2016). It is noted that metal oxide nanoparticles, which have extremely high surface areas and plenty of hydroxyl groups, can exhibit remarkable adsorption capacities and play a significant role in the researches concerning As removal (Lata and Samadder 2016).

In recent years, many researchers used metal composite materials (containing two or more metals) as adsorbents to remove As from contaminated water. The results showed that the composite metal oxides can not only inherit the advantages of parent oxides but also show a synergistic effect of higher adsorption capacity than that of individual metal oxides (Lata and Samadder 2016). Various composite metal oxides have been synthesized and evaluated for As removal, such as Fe-Ce (Zhang et al. 2005), Fe-Ti (Gupta and Ghosh 2009), Fe-La (Zhang et al. 2014), Fe-Zr (Ren et al. 2011), Fe-Cr (Basu and Ghosh 2011), Fe-Mn (Zhang et al. 2007; Wen et al. 2017), Zr-Mn (Zhang et al. 2013a), Fe-Cu (Peng et al. 2016; Zhang et al. 2013b), Ce-Ti (Li et al. 2010), Mn-Co (Yin et al. 2011), and Al-Mn (Wu et al. 2012) binary oxides. The introduction of some transition metals can remarkably improve the capabilities of bare Fe or Al oxides for removing As. Peng et al. synthesized magnetic Fe<sub>3</sub>O<sub>4</sub>@Cu(OH)<sub>2</sub> composites for As(V) removal and obtained a satisfactory adsorption performance (Peng et al. 2016). They stated that the coating of  $Cu(OH)_2$  can greatly improve the arsenic adsorption capacity of bare magnetic particles, and the mechanism for As(V) adsorption was attributed to -OH groups and electrostatic attraction. Zhang et al. developed Fe-Cu binary oxide via a facile co-precipitation method, and this novel adsorbent could exhibit a great adsorption capacity for both As(V) and As(III) (Zhang et al. 2013b). Moreover, some metal composite sorbents are characterized by their oxidative activity during the adsorption of As(III). The Mn-oxide-containing composites can oxidize As(III) to As(V) successfully and thereby enhancing the adsorption of As (Zhang et al. 2007; Wen et al. 2017; Zhang et al. 2013a; Wu et al. 2012). These results showed that metal composite materials can combine the adsorption characteristics and the extraordinary properties of different metal oxides, such as large surface areas, uniformly distributed micropores, and the presence of functional groups on the surface.

The above-mentioned researches provided useful information on the improvement of As removal from polluted water by using metal composite nanoparticles. However, most of these adsorbents cannot be directly used in practical engineering processes due to their insufficient mechanical strength and propensity to aggregate, which inevitably leads to extremely high pressure drop and poor hydraulic properties in fixed-bed or other flow-through systems (Lata and Samadder 2016; Santhosh et al. 2016; Tan et al. 2016). To solve this problem, it is required to immobilize powdered adsorbents in a granular form. The methods for immobilization mainly include coating, loading, impregnation, or entrapment of active components in/on certain carriers (Dou et al. 2011). To prepare granular adsorbents, coating and loading (or impregnating) active components to a carrier can be easily realized and has been tried extensively in previous studies (Wang et al. 2014, 2016; Kumar et al. 2016; Zhu et al. 2016; Dutta et al. 2015). Some researchers have incorporated Fe-Mn binary oxide into granular carriers such as diatomite and polystyrene anion exchanger (Chang et al. 2009; Li et al. 2012a, b). The resultant sorbents showed a satisfactory hydraulic property and a relatively good arsenic sorption performance. However, the engineering applications of these adsorbents are restricted by several drawbacks such as limited active components, low stability, and poor durability (Zhang et al. 2010). Hence, a compact granule method is recommended to overcome these drawbacks. This method can fabricate small-sized particles from powdered materials without a carrier core and has been successfully applied in the preparation of particles for food or pharmaceutical production on a mass scale (Mangwandi et al. 2016; Hong et al. 2013; Dou et al. 2013; Chen et al. 2011; Zhao et al. 2014).

In previous studies, we prepared a composite adsorbent of Mn-oxide-doped Al oxide (MODAO) for As(III)/As(V) removal. The introduction of Mn oxide can not only improve the performance of Al oxides for As(III) removal but also enhance the adsorption of As(V) (Wu et al. 2012; Liu et al. 2015). However, this powdered adsorbent cannot be used in column reactors, not to mention in engineering application. Therefore, in consideration of the treatment of practical Aspolluted water, a granular Mn-doped Al oxide adsorbent (GMAO) was prepared via the compression method by using cross-linked polyacrylamide (PAM) as the binder. In this study, a granulation method (with an optimal mass ratio of MODAO powder/binder and an optimum drying temperature) was used to prepare a suitable granular adsorbent, namely GMAO, for the removal of As(III) and As(V). Several surface characterization methods were used to explore the physicochemical properties of this adsorbent. Batch experiments were conducted to evaluate the performance of the optimized GMAO for As removal from synthesized As-contaminated water. The data for adsorption isotherms and kinetics were fitted with different isotherm and kinetic models to calculate

the corresponding parameters, which are in relation with the adsorption rate and adsorption capacity of As. We also investigated the effects of water quality parameters on the removal of As, including solution pH and coexisting ions. Moreover, a desorption study was performed by using alkali solutions as an effective eluent. Furthermore, dynamic experiments were carried out to assess the performance of GMAO-packed columns for removing As from simulated As-spiked water.

# Materials and methods

#### Materials

All chemicals are of analytical grade and used without further purification. All solutions were prepared with deionized water. The glass vessels used in the experiments were soaked in a 1% nitric acid (HNO<sub>3</sub>) solution and rinsed several times with deionized water before use. The stock solutions of As(III) and As(V) were prepared with sodium arsenite (NaAsO<sub>2</sub>) and sodium arsenate (NaHAsO<sub>4</sub>·7H<sub>2</sub>O). Sodium nitrate (NaNO<sub>3</sub>) was used to maintain the constant ionic strength of solutions (0.01 M NaNO<sub>3</sub>). Sodium hydroxide (NaOH) and HNO<sub>3</sub> solutions were used to adjust solution pH. The arsenic working solutions were freshly prepared by diluting the arsenic stock solutions with deionized water.

# The preparation of GMAO

The preparation of MODAO powders was conducted according to a method as described in our previous studies (Wu et al. 2012; Liu et al. 2015). To prepare GMAO, first of all, MODAO was smashed and sieved, and the particles less than 300  $\mu$ m were selected and used for the next step. Subsequently, MODAO powders were mixed with PAM solution (the mass ratio of MODAO/PAM was about 19:1) and then compressed into tablets (d = 3 mm) by using a tablet compression machine. After that, these tablets were dried in an oven at T = 60 °C for 12 h, cooled to room temperature, and finally stored for the following experiments. Figure 1 shows the schematic diagram of the preparation process.

#### Adsorption experiments for As removal by GMAO

For all the batch experiments, 0.05 g adsorbent was added into 150-mL flasks containing 50 mL of As solution, which were shaken in an orbit shaker at 170 rpm for 24 h at  $T = 25 \pm 0.5$  °C. In the adsorption isotherm experiments, the concentrations of As(III) and As(V) ranged from 0.1 to 1.6 mM. NaOH and HNO<sub>3</sub> solutions were added as needed to maintain the solution pH to approximately 7.0. The samples were collected after 24 h of contact and filtered with a 0.45-µm polycarbonate filter membrane. In the adsorption

kinetic experiments, the initial concentrations of As(V) and As(III) were 0.2 mM (initial pH = 7.0). The samples were obtained at designed time intervals from different flasks and filtered with 0.45 µm membranes. In the pH effect experiments, the solutions of 0.1 M HCl and 0.1 M NaOH were used for the preadjustment of initial solution pH ranging from 3.0 to 12.0 (initial As = 0.2 mM). In addition, various anions (chloride, sulfate, carbonate, phosphate, and silicate; 2~4 mM) and cations (calcium  $(Ca^{2+})$  and magnesium  $(Mg^{2+})$ ; 2~10 mM) were employed to investigate the influences of coexisting ions on As removal. To evaluate the reuse performance of GMAO, the saturated adsorbent was soaked with alkaline solutions (0.2 M NaOH) as an eluent and reused in five consecutive cycles for the removal of As from solutions  $(C_{0-As} = 5 \text{ mg/L})$ . Rapid small-scale column (RSSC) tests were also carried out to evaluate the performance of GMAO for As removal in dynamic reactors. A glass column with a 3cm inner diameter was packed with 212 cm<sup>3</sup> of adsorbent (about 100 g). The height of the adsorbent was approximately 30 cm. To ensure a good hydraulic condition, a layer of 1 cm cotton and a layer of 6 cm small glass beads were positioned in the column at both the top and the bottom of the GMAO layer. A peristaltic pump (Lange-580, China) was used to maintain a constant flow rate of 14.13 mL/min, resulting in an empty bed contact time (EBCT) of 15 min.

#### Analytical and characterization methods

Total arsenic [As(T) = As(V) + As(III)] and As(III) concentrations were determined using spectroscopy equipment (AF-610A, Beijing Ruili Analytical Instrument Co., Ltd., China) on the basis of hydride generation atomic fluorescence (HG-AFS). The total concentrations of Al and Mn were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (SCIEX Perkin-Elmer Elan mode 5000). Total organic carbon (TOC) contents were analyzed by using a TOC analyzer (Shimadzu Corporation, Kyoto, Japan). Prior to analysis, the aqueous samples (10 mL for each one) were acidified by adding 0.1 mL of HNO<sub>3</sub> and stored in acid-washed glassware vessels.

The surface area was measured by the BET method with a Micrometritics ASAP 2000 surface area analyzer (Micrometritics Co., USA). X-ray diffraction (XRD) analysis was carried out on a D/Max-3A diffractometer (Rigaku Co., Japan) by using Ni-filtered copper K $\alpha$ 1 radiation. A particle strength meter (0–200 N, KQ-2, Jiangyan, China) was used to measure the compressive strength of GMAO. In addition, a field emission scanning electron microscope combined with energy-dispersive X-ray spectroscopy (Quanta FEG 250, FEI Ltd., USA) was used to obtain its surface characteristics. FTIR spectra were obtained by using a Nicolet 5700 FTIR spectrophotometer (Nicolet Co., USA) with a transmission model. Samples containing 10 mg of the adsorbent were ground



together with 250 mg of spectral grade potassium bromide (KBr) in an agate mortar. XPS data were collected by using an ESCA-lab-220i-XL spectrometer (Shimadzu, Japan) with monochromatic Al K $\alpha$  radiation (1486.4 eV). A zeta potential analyzer (Zetasizer 2000, Malvern, UK) was used to analyze the zeta potential of GMAO samples. To evaluate the weight loss ratio of GMAO after adsorption, 0.05 g adsorbent was added into 150 mL flasks containing 50 mL of NaNO<sub>3</sub> solution (NaNO<sub>3</sub> = 0.01 M, pH = 6.0~9.0), and these flasks were shaken in an orbit shaker at 170 rpm for 24 h at  $T = 25 \pm 0.5$  °C. After that, the solid samples were filtered, dried, and reweighted.

The weight loss ratio ( $\eta$ ) of GMAO after the adsorption processes was calculated as Eq. (1):

$$\eta = \frac{m_2}{m_1} \times 100\%$$
 (1)

where  $\eta$  is the weight loss ratio of GMAO;  $m_1$  and  $m_2$  are the weight of fresh GMAO and used GMAO, respectively.

#### Theory

In order to investigate the potential rate-controlling step of the adsorption process, the kinetics data were fitted with different kinetic models, which were respectively presented in the following equations (Ho and Mckay 1998a, b; Sparks 1989; Weber and Morris 1963):

$$q_t = q_e \left( 1 - e^{-k_1 t} \right) \text{ pseudo-first-order model}$$
(2)

$$q_t = \frac{k_2 q_e^{-2} t}{1 + k_2 q_e t} \quad psuedo-second-order \ model \tag{3}$$

$$\ln q_t = \ln(kq_e) + \frac{1}{m} \ln t \quad power \ model \tag{4}$$

$$q_t = k_{id^{0.5}} + C$$
 intraparticle diffusion model (5)

where *t* is the contact time of adsorption experiment (h);  $q_e$  (mg/g) and  $q_t$  (mg/g) are the adsorption capacity at equilibrium and at any time *t*, respectively;  $k_1$  (1/h),  $k_2$  (g/mg·h),  $kq_e$ ,  $k_{id}$  (mg/g h<sup>0.5</sup>), *m*, and *C* are the rate constants for these models, respectively.

To provide quantitative information for the isotherms, these data were fitted with the following four isotherm models (Langmuir 1918; Freundlich 1906; Gimbert et al. 2008; Sips 1948; Casas et al. 2012), and the calculated parameters for these isotherm models are listed in Table 2.

$$q_{\rm e} = \frac{q_{\rm m}bC_{\rm e}}{1+bC_{\rm e}} \quad Langmuir \ model \tag{6}$$

*b* is the Langmuir constant (L/mg) related to the affinity of the binding sites;  $q_{\rm m}$  is the maximum monolayer adsorption capacity (mg/g).

$$q_{\rm e} = K_{\rm F} \log C_{\rm e}^{\frac{1}{n_{\rm F}}} \quad Freundlich \ model \tag{7}$$

where  $K_{\rm F}$  is the Freundlich constant or capacity factor (mg/g); *n* is the heterogeneity factor related to adsorption intensity.

$$q_{\rm e} = \frac{RT \ln(K_{\rm T} C_{\rm e})}{b_{\rm T}} \quad Temkin \ model \tag{8}$$

where *R* is the gas constant, *T* is the absolute temperature in Kelvin,  $b_T$  is the constant related to the heat of adsorption, and  $K_T$  is the Temkin isotherm constant.

$$q_{\rm e} = \frac{q_{\rm S}K_{\rm S}C_{\rm e}^{n_{\rm S}}}{1 + K_{\rm S}C_{\rm e}^{n_{\rm S}}} \quad Sips \ model \tag{9}$$

where  $K_{\rm S}$  (L/mg) is the median association constant,  $n_{\rm S}$  is the heterogeneity factor, and  $q_{\rm S}$  is the maximum monolayer adsorption capacity (mg/g).

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$$q_{\rm e} = \frac{q_{\rm H} C_{\rm e}^{n_{\rm H}}}{K_{\rm H} + C_{\rm e}^{n_{\rm H}}} \quad Hill \ model \tag{10}$$

where  $q_{\rm H}$  (mg/g) is the monolayer adsorbed quantity,  $n_{\rm H}$  is the number of molecules per site, and  $K_{\rm H}$  is a Hill isotherm constant.

The fitting of experimental data with different equilibrium or kinetic models was carried out by using the software of MATLAB (R2013b).

#### **Results and discussion**

## Surface characterization

It can be seen from the photo of GMAO that this granular adsorbent has a regular shape and an even thickness (Fig. 1). Figure 2a illustrates an amorphous X-ray diffraction pattern of

Fig. 2 Surface characterizations of GMAO adsorbent (a XRD spectrum of GMAO; b XPS all-scan spectrum of GMAO; c FTIR spectrum of GMAO; d zeta potential values of GMAO at different pH conditions; e N<sub>2</sub> adsorption-desorption isotherms of GMAO; f compressional behavior of GMAO under different compression powers)





decreased with the increased solution pH, and the pH<sub>PZC</sub> value of GMAO was around 8.3. Figure 2e illustrates the nitrogen adsorption isotherm curve of GMAO. A plateau in the adsorption curve started from the relative pressure of  $P/P_0 = 0.20$ , and the adsorption entered into a sharp increase at the relative pressure of  $P/P_0 = 0.85$ . Based on BDDT classification, the adsorption isotherms followed the type II isotherm (Brunauer et al. 1940). This result indicated the appearance of capillary condensation in a mesoporous adsorbent material during the multilayer adsorption (Fletcher et al. 2005). Additionally, according to the BET method, GMAO showed a specific surface area of 54.26 m<sup>2</sup>/g, a pore volume of 0.31 mL/g, and a mean pore diameter of 515.5°A. The compressive strength illustrated in Fig. 2f was as high as 300 N, indicating that the amount of stabilizer was sufficient for binding the nanoparticles of MODAO and GMAO exhibited a considerable mechanical strength. Furthermore, the weight loss ratio of GMAO after adsorption was less than 0.5% in the pH range of 6.0~9.0, implying a reliable stability for use.

The SEM image showed regular characteristics and a compact structure of GMAO (Fig. 3a). In addition, the surface of GMAO was comprised of massive small aggregates that adhered together. The EDS result illustrated the large amounts of Al and Mn on the surface of GMAO (Fig. 3b). The occurrence of C and S was also observed, which might originate from the content of PAM and sulfate used in the preparation process. The elemental mapping analysis is shown in Fig. 3c, d, which indicated that the elements of Al and Mn were uniformly distributed on the selected surface of GMAO. The aforementioned characterization results revealed that GMAO is inherently heterogeneous and represents a defined combination of chemically and structurally different constituent materials. This combination produces a synergistic effect and aggregate properties that are different from those of its constituents (Ranđelović et al. 2012).

## Kinetic and isotherm studies

Adsorption kinetic experiments were conducted to examine the adsorption rate of As(III) and As(V) at T = 25 °C. Figure 4 shows the variations of As adsorption amounts as a function of contact time. It could be seen that the adsorption



**Fig. 3** SEM/EDX patterns of GMAO adsorbent (**a** SEM image of the GMAO surface; **b** the elemental adequate spectrum of GMAO; **c** mapping mode image of Al distribution in the section plane of GMAO; **d** mapping mode image of Mn distribution in the section plane of GMAO)



Fig. 4 Kinetic curves for As(III)/As(V) adsorption onto GMAO

equilibrium was reached after 48 h for both As(III) and As(V). This equilibrium time was longer than that of As adsorption onto Al-Mn binary oxide powders. This phenomenon may be due to the slower mass transfer rate at the surface of particulate adsorbents than that of powdered adsorbents. Oi et al. fabricated Fe-Mn binary oxide-impregnated chitosan bead for the adsorption of As(III) and As(V), and they also found that the equilibrium time of As adsorption for this adsorbent was longer than that for Fe–Mn binary oxide powders (Qi et al. 2015). Obviously, the powdered adsorbents with a smaller particle size are more favorable than particulate adsorbents for fast arsenic adsorption. In spite of this, the equilibrium time of As adsorption onto GMAO was much shorter than that of some other particulate adsorbents, such as hydrous iron oxide-impregnated alginate beads (148 h) (Sigdel et al. 2016). Consequently, all other batch sorption experiments were carried out for 48 h, ensuring that the sorption equilibrium was reached.

The results of the kinetic analysis are summarized in Table 1. According to  $R^2$  values, the pseudo-second-order model ( $R^2 = 0.998$  for As(III) and 0.983 for As(V)) and the power model ( $R^2 = 0.983$  for As(III) and 0.988 for As(V)) should be the better-fit models. The presice description of kinetic data with the pseudo-second-order model suggested that the adsorption of As(III)/As(V) by GMAO in water is a chemisorption process, and this finding was consistent with As adsorption studies using different types of adsorbents (Qi et al. 2015; Ntim and Mitra 2012; Li et al. 2012a, b). The chemisorption occurring between

**Table 1** Parameters of kmodels for fitting kineticAs(III)/As(V) adsorption

GMAO

As and GMAO may be attributed to the complexation reaction. which has been proposed in our previous studies (Wu et al. 2012; Liu et al. 2015). In addition, the accuracy of the power model was in accordance with the moderately heterogeneous surfaces of GMAO, which could exhibit different activation energies for the chemisorption on its surfaces (Ho and McKay 1999). The kinetic data were also fitted with the intraparticle diffusion model. Figure 4 illustrates that the fitting curves (a plot of solute sorbed against square root of contact time) for both As(III) and As(V) kinetic data could be divided into two portions. As the straight lines did not pass through the origin point, the intraparticle diffusion played an important role but was not the only rate-controlling step for the sorption of As(III) or As(V). In addition to intraparticle diffusion effects, As(III)/ As(V) adsorption may be also affected by diffusional effects outside the solid phase and the interactions between As(III)/ As(V) and the active sites onto GMAO surfaces.

Adsorption isotherm curves, which play a significant role in evaluating the practical applicability of an adsorbent, can illustrate the relationship between the equilibrium amount of adsorbate adsorbed onto the adsorbent and its residual concentration in the solution. The positive relationship between  $q_e$ and  $C_e$  is graphically shown in Fig. 5, in which the adsorption capacity finally flattens to the value of an equilibrium saturation point. The equilibrium data were fitted with different adsorption isotherm models, and the corresponding parameters were listed in Table 2.

The Langmuir isotherm model assumes that the adsorption process happens on a homogeneous sorbent surface composed of a finite number of identical sites with equal sorption activation energies (Gimbert et al. 2008). The equilibrium data for As adsorption in most previous studies may not be explicitly expressed in this form. However, many researchers preferred to use the parameter  $q_{\rm m}$  calculated by the Langmuir model to represent the maximum sorption capacity for As(III) or As(V) (Kumar et al. 2014). In this study, the Langmuir  $q_{\rm m}$  values for As(III) and As(V) were calculated as 48.52 and 37.94 mg/g, respectively (Table 2). To compare the maximum adsorption capacities of As(III)/As(V) between GMAO and some other adsorbents, their  $q_{\rm m}$  values are listed in Table 3. It is interesting to observe that the  $q_{\rm m}$  values of GMAO for As(III) and As(V) were higher than those of other adsorbents, indicating that GMAO has an advantage in As adsorption capacities. The Freundlich model is an empirical equation which describes a simple relation between the adsorbed amount and the

inetic data of	Adsorbate	Pseudo-first-order model			Pseudo-sec	Power model				
on		$q_{\rm e} ({\rm mg/g})$	<i>k</i> <sub>1</sub> (1/h)	$R^2$	$q_{\rm e} ({\rm mg/g})$	$k_2$ (g/mg·h)	$R^2$	k·q <sub>e</sub>	k∙q <sub>e</sub> m	
	As(III) As(V)	14.16 12.68	0.035 0.042	0.998 0.955	20.11 16.04	0.027 0.041	0.998 0.983	0.96 1.50	0.63 0.49	0.983 0.988



Fig. 5 Isotherm curves for As(III)/As(V) adsorption onto GMAO

equilibrium concentration. It also can reflect not only the heterogeneity of the surface but the different interactions between the molecules existing in the adsorbed layer. This isotherm model could also fit the data fairly well ( $R^2 = 0.96$  and 0.99), thereby indicating that the adsorption of As(III)/As(V) onto GMAO is a chemisorption process. The Freundlich constants,  $K_{\rm F}$  and  $1/n_{\rm F}$ , are 4.81 mg $^{1-1/n}L^{1/n}/g$  and 0.49 for As(III) and 1.55 mg $^{1-1/n}L^{1/n}/g$ g and 0.66 for As(V), respectively. Being similar to  $q_{\rm m}$ ,  $K_{\rm F}$  is a comparative measure of the total adsorption capacity under specified conditions. The  $K_{\rm F}$  values were in agreement with the finding that GMAO exhibited a greater capacity for As(III) than for As(V). The values of  $1/n_{\rm F}$  were less than unity, indicating that As(III) or As(V) could be favorably adsorbed by GMAO (Belhachemi and Addoun 2011). The Temkin isotherm model, which is also an empirical equation and can be used to describe adsorption of various adsorbates in chemisorption systems, is often used to explore the energy distribution of the sorption process (Samarghandi et al. 2009). The constants  $K_{\rm T}$ and  $b_{\rm T}$  were 0.436 and 0.237 J/mmol for As(III) and 0.326 and 0.410 J/mmol for As(V), respectively. The Sips isotherm model, which is a combination of the Langmuir and Freundlich isotherm models, is expected to describe the adsorption system at a heterogeneous surface (Casas et al. 2012). The  $R^2$  values (0.981 and 0.977) indicated that the Sips model could also describe the isotherm data very well for both As(III) and As(V) adsorption. For the Sips isotherm model, the constant  $K_{\rm S}$  (L/mg) represents the energy of adsorption. If the value of  $n_{\rm S}$  is closer to 1 or even equal to 1, the Sips model equation will approach the Langmuir model. When the value of  $K_{\rm S}$  becomes closer to 0, the Sips model will approach the Freundlich model. The constants  $K_{\rm S}$  and  $n_{\rm S}$  were 0.027 L/mg and 1.258 for As(III) and 0.017 L/ mg and 1.052 for As(V), respectively. The parameter  $n_{\rm S}$ , which could be regarded as the parameter characterizing the system heterogeneity, is usually greater than unity, and therefore, the larger is this parameter, the more heterogeneous is the system. Thus, it is indicated that this adsorbent has active sites with different binding energies, and the adsorption of As(III) or As(V) takes place on a heterogeneous surface (Foo and Hameed 2010; Umpleby et al. 2004). The  $q_{\rm S}$  values calculated by the Sips model ( $q_{S-As(III)} = 41.78 \text{ mg/g}, q_{S-As(V)} = 32.69 \text{ mg/}$ g) could correspond to the adsorbed As concentrations obtained experimentally and might be more realistic than that estimated by the Langmuir model. The Hill equation was postulated to describe the binding of different species onto homogeneous substrates. The model assumes that adsorption is a cooperative phenomenon, with the ligand-binding ability at one site on the macromolecule, and may influence different binding sites on the same macromolecule (Ringot et al. 2007). The constants  $K_{\rm H}$  and  $n_{\rm H}$  were 37.04 and 1.258 for As(III) and 58.82 and 1.052 for As(V), respectively. The  $q_{\rm H}$  values were determined to be 41.78 mg/g for As(III) and 32.69 mg/g for As(V), respectively. However, considering the applicability of the Sips and Hill models under different conditions, we supposed that the former one should be more suitable for As adsorption onto GMAO.

#### The influences of pH and coexisting ions

The existing literature reported that the changes in the solution pH can noticeably affect the adsorption of As(V) and As(III) by Al (hydr)oxides (Masue et al. 2007). Thus, we investigated the pH effects on As adsorption. In aqueous solutions, the predominant As species are negatively charged As(V) species  $(H_2AsO_4^- \text{ and or } HAsO_4^{2^-})$  and uncharged As(III) species (As(OH)<sub>3</sub>) at pH 3~9 (Smedley and Kinniburgh 2002). Arai et al. (2001) found that the solution pH posed different influences on the adsorption of As(III) and As(V) by pure Al oxides. The adsorption amounts of As(V) onto Al oxides

Table 2 Parameters of isotherm models for fitting the isotherm data of As(III)/As(V) adsorption on GMAO

Adsorbates Langmuir model			Freundlich model			Sips model			Temkin model			Hill model					
	$q_{ m m}$ (mg/g)	b (L/g)	R <sup>2</sup>	$ \begin{array}{c} K_{\rm F} \\ ({\rm mg}^{1-1/n} \\ {\rm L}^{1/n}/{\rm g}) \end{array} $	$1/n_{\rm F}$	R <sup>2</sup>	Ks (L/mg)	qs (mg/g)	n <sub>S</sub>	R <sup>2</sup>	K <sub>T</sub>	b <sub>T</sub> (J/mmol)	R <sup>2</sup>	<i>q</i> <sub>Н</sub> (mg/g)	K <sub>H</sub>	n <sub>H</sub>	<i>R</i> <sup>2</sup>
As(III) As(V)	48.52 37.94	0.042 0.016	0.988 0.990	4.812 1.554	0.486 0.602	0.960 0.994	0.027 0.017	41.78 32.69	1.258 1.052	0.981 0.977	0.436 0.326	0.237 0.410	0.962 0.902	41.78 32.69	37.04 58.82	1.258 1.052	0.981 0.977

Adsorbents	Maximum ad	sorption capacity (mg/g)	рН	References	
	As(V)	As(III)			
Magnetic nanoparticle-impregnated chitosan beads	35.7	35.3	6.8	Wang et al. (2014)	
Macroporous anion exchanger-supported Fe-Mn binary oxide	13.2	44.9	$7.0\pm0.1$	Li et al. (2012a, b)	
Granular Fe-Ce oxide adsorbent	20.1	N.A.	5.0	Zhang et al. (2010)	
Irregular shape granules of schwertmannite	31.7	N.A.	7.0	Dou et al. (2013)	
Modified granular natural siderite	N.A.	9.4	7.3	Zhao et al. (2014)	
Iron-impregnated biochar	2.16	N.A.	$5.8\pm0.2$	Hu et al. (2015)	
Nickel boride nanoparticle-coated resin	17.8	23.4	6.0	Çiftçi and Henden (2015)	
Zinc peroxide-functionalized synthetic graphite	19.1	18.8	6.5	Uppal et al. (2016)	
Granular Mn-oxide-doped Al oxides	37.94	48.52	7.0	This study	

Table 3 Maximum adsorption capacities of GMAO and other granular adsorbents

increased with pH increasing from 3 to 5 and then decreased as pH increased from 5 to 10. In contrast, the uptake of As(III) by Al oxides was kept increasing with the elevated pH and reached the plateau at a pH of 8.5, and the further increase of pH led to the decrease in As(III) removal. However, in our study, the curves for As(V) and As(III) adsorption amounts exhibited a similar trend as a function of pH change. Figure 6a shows that the adsorption amounts of both As(III) and As(V) were regardless of pH in the range of 3~7, and then dropped as the solution pH increased from 7 to 10. As the pH<sub>PZC</sub> value of GMAO was around 8.0, its surface was positively charged at pH < 8.0 and negatively charged at pH > 8.0 due to the protonated and deprotonated reactions. Because As(V) mainly exists as the species of H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup> in the pH range of 6.0~9.0 (Smedley and Kinniburgh 2002), the consistently weakened capability of GMAO for As(V) adsorption from pH 7.0 to 9.0 could not be attributed to the electrostatic repulsion effects. A similar phenomenon was also observed by Han and coworkers in their research concerning on the removal of As(V) by  $Al_2O_3$  (Han et al. 2013). When the solution pH was increased from 6.0 to 10.0, more OH<sup>-</sup> would compete with  $H_2AsO_4^{-}/HAsO_4^{2-}$  in binding at the active sites on the surface of GMAO. This may explain the decrease in As(V) adsorption amounts at high pH conditions. In addition, the deprotonated reactions at a higher pH could bring adverse effects on the ion exchange between H<sub>2</sub>AsO<sub>4</sub><sup>-/</sup>/HAsO<sub>4</sub><sup>2-</sup> and OH<sup>-</sup>, and this also accounted for the inhibition of As(V) removal.

Figure 6b illustrates the residual concentrations of As(III) and As(V) at different pH conditions after the removal of As(III) by GMAO. The existence of As(V) indicated that the transformation of As species occurred in the process of As(III) removal. The residual As(V) concentrations dropped consistently as pH increased from 3 to 10. Considering the decreased As(V) uptake at a higher pH, this result suggested that the oxidation of As(III) was inhibited due to the elevated pH value. That is to say, the oxidative reactivity of GMAO was suppressed at high pH conditions. Driehaus et al. (1995) stated that the pH change has no influence (pH 5~10) on the oxidation of As(III) by pure Mn oxides. The different oxidative capability of GMAO from that of Mn oxides may be attributed to the interaction between Al and Mn oxides, which could make the oxidation system become more complex. On the other hand, the residual As(III) concentrations were elevated consistently with increased pH. This phenomenon seemed to be different from the results for As(III) adsorption onto pure Al oxides, in which the As(III) removal was promoted with an increasing pH until the solution pH reached 8 or 9. Because the As(V) removal by GMAO was improved at a lower pH, the decreased As(III) uptake at the same condition could be attributed to the competition between As(V) and As(III) for the active sites onto adsorbent surfaces. Kanematsu et al. (2013) reported that As(III) adsorption can be strongly reduced at acidic to neutral pH conditions in the presence of As(V) due to the strong suppression of the two inner-sphere bidentate surface complexes. In addition, it has been proved that As(III) surface complex speciation would be changed significantly in the presence of As(V) (Jang and Dempsey 2008). Hence, the decline in the As(III) removal at high pH conditions could be explained by two reasons: (1) the inhibition of As(III) oxidation caused by the reduction of oxidative capability of GMAO and (2) the depression of As(V) capture due to the strengthened competition between As(V) and OH<sup>-</sup>. According to the aforementioned results, though the pH change posed a similar effect on the removal of As(III) and As(V) by GMAO, the removal mechanisms for As(III) and As(V) were quite different. Furthermore, it is shown in Fig. 6c that the residual concentrations of Al and Mn ions were at extremely low levels in the pH range of 4~10, and a slight release of Al and Mn ions occurred in acidic conditions (pH = 3). Meanwhile, TOC was never detected in the solution from pH 3 to 9 (data not shown). It means that no organic



Fig. 6 Effect of solution pH on As(III)/As(V) removal by GMAO (a As adsorption amounts for As(III)/As(V) removal; b As speciation distributions for the residual As after As(III) removal by GMAO; c the concentrations of released Al and Mn ions)

matter was released from this adsorbent. Hence, GMAO can be used in a wide pH range without side effect or second pollution.

Due to the complexity of natural water contents, the coexisting anions (such as chloride ion, sulfate, carbonate, silicate, and phosphate) and cations (such as  $Ca^{2+}$  and  $Mg^{2+}$ ) are generally present in underground water and may interfere with the removal of As(III)/As(V) by GMAO through competitive adsorptions. Herein, we examined the effects of these coexisting anions/cations at different concentrations (2~4 mM and 2~10 mM) on the removal of As, and the results were demonstrated in Fig. 7a, b. The presence of chloride, carbonate, sulfate, and silicate anions at a concentration (2 mM) 10

times higher than that of arsenic (0.2 mM) did not exhibit an obvious interfering effect on As(III) removal. By contrast, an obvious decrease in the adsorption amounts of As(V) was observed in the presence of sulfate and silicate anions, even at low concentrations. Noticeably, phosphate exhibited a more significant effect on the removal of As(III) and As(V). The decreased arsenic adsorption capacity of GMAO in the presence of phosphate/sulfate should be due to the competition between arsenic and the coexisting anions for the active sites onto this adsorbent. It is noted that phosphate exhibited the most fiercely interfering effect among these anions. It means that phosphate could form a more stable binding with the active sites onto GMAO surfaces, which could be attributed to its similar chemical structure with that of arsenate. Arco-Lazaro et al. (2016) reported that the strong competition between phosphate and As for adsorption sites could result in the monolayer adsorption of arsenic, and the competition occurred mainly at low As equilibrium concentrations. Stachowicz and Hiemstra (2008) stated that phosphate may have a more significant effect on the removal of As(V) than that of As(III) due to a different electrostatic interaction. However, the As(III) adsorption by GMAO responded more strongly to the change in phosphate concentration in comparison with As(V) adsorption. One explanation is that the phosphate would not only occupy the adsorption sites for As but also suppress the reactivity of Mn oxides. Hence, the presence of phosphate can pose a dual inhibition effect on the removal of As(III).

On the other hand, the existence of calcium or magnesium cations (from 2 to 10 mM) was beneficial to the adsorption of As(III) and As(V) (Fig. 7c, d). Guan et al. (2009) reported that the presence of  $Ca^{2+}$  ion could promote the adsorption of As(V) in the neutral or alkaline conditions. They explained that the calcium–arsenate hydroxide precipitates formed after the addition of calcium salt into an alkaline solution. In addition,  $Ca^{2+}$  ions could compress the double layer and make the internal pores more accessible, enhancing the adsorption of arsenic accordingly. Magnesium ion has similar chemical behaviors with calcium ion, and its beneficial effects on As removal could also be attributed to cation-bridging interactions.

#### **Regeneration and reusability**

In order to assess the cost-effectiveness of this adsorbent, desorption and regeneration studies on saturated GMAO were also carried out. Several different eluents were used to desorb As(III)-reacted or As(V)-reacted GMAO samples, respectively. Generally, alkaline solutions can be used for the regeneration of adsorbents, and the As desorption mechanism is expected to be the displacement of anions with hydroxyl ions (Chen et al. 2015). The NaOH solution was found to be the best eluent in this study, and the optimum concentration was 0.2 M (data not shown). Moreover, arsenic adsorption/



Fig. 7 Effects of coexisting ions on As(III)/As(V) removal by GMAO (a As adsorption amounts for As(III) removal in the presence of different anions; **b** As adsorption amounts for As(V) removal in the presence of

desorption cycles were studied to estimate the adsorbent lifetime. Figure 8 shows that the As desorption ratios for As(III)reacted samples were maintained in the range of 93.4~81.6% from the first to the fourth regeneration time. The As uptake decreased from 4.15 to 3.53 mg/g and then to 3.28 mg/g in the third and fifth time for use, which means that GMAO can be used for at least three cycles of As(III) adsorption without significant changes in adsorption capacities (less than 15% loss). Similar results were achieved for As(V)-reacted samples. The percentages of As desorbed from the As-loaded adsorbent were in the range of 91.4~80.4% in the four regeneration times, and the As(V) uptake of GMAO decreased slightly after each cycle and 76.8% of the initial adsorption capacity could be maintained after five adsorption/desorption cycles. Chen et al. (2015) investigated the regeneration of several iron-based adsorptive media used for removing arsenic from groundwater, and found that the restored arsenic removal efficiencies ranged from a low of 30% to a high of 95%. They pointed it out that if an adsorbent can be regenerated and reused with little loss of removal capacity and no major particle degradation, regeneration can be used as an economical option for the operation of the adsorptive media



different anions; **c** As adsorption amounts for As(III) removal in the presence of Ca/Mg cations; **d** As adsorption amounts for As(V) removal in the presence of Ca/Mg cations)

process. Hence, the regeneration results indicated that GMAO can be regenerated and reused for the adsorption process despite some loss of As adsorption capacity. Overall, GMAO is an efficient and renewable adsorbent for the removal of As(III)/As(V) from water.

#### **Column studies**

To further investigate the applicability of GMAO in water treatment processes, a small-scale column experiment was conducted to remove As(V)/As(III) from simulated underground water. The water quality parameters were selected as follows: As(III)/As(V) = 100 µg/L, KCl = 20 mg/L, NaNO<sub>3</sub> = 10 mg/L, Na<sub>2</sub>SO<sub>4</sub> = 20 mg/L, CaCl<sub>2</sub> = 10 mg/L, MgSO<sub>4</sub> = 10 mg/L, pH = 7.7~8.3. According to the drinking water standards of the WHO, the maximum concentration level (MCL) for As is 10 µg/L. As shown in Fig. 9, the column for As(V) removal treated over 1952 BV of 100 µg/L As(V) solutions before the drinking water standard (10 µg/L As) was broken through. This result indicated that the breakthrough time for As(V) removal ( $t_{b-As(V)}$ ) was 488 h. On the other hand, for the treatment of As(III)-spiked water, the As



Fig. 8 Regeneration performances of GMAO in the removal of a As(III) and b As(V)

concentration in the effluent surpassed 10 µg/L after a bed volume of 2224 was treated by the column  $(t_{b-})$  $A_{s(III)} = 556$  h). The mass balance calculations indicated that the total concentrations for As(V) and As(III) loaded onto the packed GMAO were 407.6 and 464.4 µg/g, respectively. In contrast to the batch adsorption results, similar As loads were observed in columns for the removal of As(III) and As(V). This phenomenon may be attributed to the shortened reaction time in the column experiments, which might bring side effects on the oxidation of As(III) and thus inhibited the removal of As(tot). Therefore, efforts need be made to further optimize GMAO in the future study. In order to ensure the requirement of adsorbent reuse in dynamic experiments, the in-situ regeneration of the adsorption column was carried out as follows: At first, a peristaltic pump was used for pumping 5 L of regenerant (0.2 M NaOH), which flowed through the column at 7.0 mL/min. After that, the column was washed with tap water and deionized water for three times, respectively. Finally, the residual solution in the column was discharged and the column was air-dried for use. In the regeneration cycle, a decrease in breakthrough bed volumes was observed for the treatment of both As(III)-spiked and As(V)-spiked water. Though there was a loss in the adsorption capacity of GMAO after the in situ regeneration, more than 1500 bed volumes of



Fig. 9 Breakthrough curves for As removal from simulated As(III)/ As(V)-spiked groundwater by using GMAO-packed columns

As(III/V)-spiked water could still be successfully treated by the GMAO-packed column. Hence, the elution method with 0.2 M NaOH solution can be used efficiently for GMAO regeneration in the continuous treatment of As-contaminated water. Furthermore, the concentrations of Al (below 0.2 mg/L) and Mn (below 0.1 mg/L) in the effluent could completely meet the drinking water safety standards promulgated by the WHO. This result suggested that GMAO can be a promising candidate for removing As(V) and As(III) from underground water.

# Conclusions

This study demonstrated that the granular Mn-oxide-doped Al oxide adsorbent could be prepared via a compression method. This material could exhibit a great potential for the removal of As(III) and As(V) because of its reasonably good physiochemical characteristics, such as a large surface area, considerable stability, and numerous hydroxyl groups on the surface. The adsorption kinetics followed the pseudo-second-order and the power kinetic models, which indicated that the removal of As is a chemisorption process on heterogeneous surfaces. The Langmuir maximum capacities for As(III) and As(V) were calculated to be 48.52 and 37.94 mg/g at pH 7.0, respectively, thereby indicating a satisfactory performance of GMAO compared with that of other granular adsorbents reported previously. The adsorption efficiencies of both As(III) and As(V) could be maintained in a wide pH range of 3~8 and were depressed at higher pH conditions. Some anions, especially phosphate, could cause side effects on the removal of As(III) and As(V) by GMAO due to the competition for active sites. By contrast, the coexistence of  $Ca^{2+}$  and  $Mg^{2+}$  could promote As adsorption through the cation-bridge involvement. In addition, the original adsorption capacity of GMAO

could be retained as 79.0 and 76.8% after 5 cycles of reuse for As(III) and As(V) removal, respectively. Furthermore, a small-scale column experiment for the treatment of Assiked water demonstrated that GMAO is a promising adsorbent for practical drinking water treatment.

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