Novel Composite Adsorbents Preparation through *In Situ* Coating and Embedded Regeneration for the Simultaneous Removal of As(III) and As(V) from Drinking Water

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Abstract: This study investigated the effectiveness and mechanisms of a novel composite adsorbent, prepared through in situ coating and regenerated through in situ embedding with Fe-Mn binary oxides onto porous diatomite (FMBO-DE), for the simultaneous removal of As(III) and As(V) from drinking water.

FMBO-DE was prepared in situ by interactions between equivalent amount of KMnO₄ and FeSO₄ (3:1) with suspended porous diatomite. Zeta potential analysis showed the zero point of charge was pH 7.0, slightly higher than Fe-Mn binary oxides (pH 6.1). No X-ray diffraction peaks were observed, confirming that FMBO-DE was amorphous; SEM/EDX analysis showed the surface elemental ratio of Fe to Mn was 3:1, indicating that ferric and manganese oxides were evenly homogeneous in Fe-Mn binary oxides.

Kinetics studies showed As was quickly removed by FMBO, up to 80% of equilibrium capacity within initial 60 minutes. Additionally, it exhibited strong potential for removing both As(III) and As(V), with maximum adsorption capacities as high as 350 mgAs(III)/g FMBO and 200 mgAs(V)/g FMBO, respectively. It was noteworthy that FMBO showed higher potential of removing As(III) than As(V).

Continuous column tests demonstrated significant removal of both As(III) and As(V). At an initial As concentration of 100 µg L⁻¹ and empty bed contact time of 5 min, freshly prepared FMBO-DE could treat 3000 bed volume (BV) of As(III) and 2000 BV of As(V) and the effluent As concentration was consistently below 10 µg L⁻¹. The in situ embedded regeneration processes obviously increased the capability of removing As from water. After three regenerations, the adsorbing potential was as high as 4500 BV of As(III) and 3100 BV of As(V), respectively.

Keywords: *in situ* coating; embedded regeneration; composite adsorbents; arsenic

INTRODUCTION

Arsenic has been receiving world attention in the past several decades due to its toxicity and carcinogenicity (WHO, 1993; USEPA, 2001). In China, the newly issued National Drinking Water Standard requires that the MCLs level of arsenic being lower than 10 µg·L⁻¹ (PRCMH and PRCSA, 2007).

The objectives of this study were to: i) develop novel adsorbents with oxidizing ability for the simultaneous removal of both As(III) and As(V) without oxidants addition; ii) investigate

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the main characteristics of the novel adsorbents; iii) evaluate the capability of removing arsenic (As(III) and As(V)) and the mechanisms involved in these processes.

METHODOLOGY

Generally, the novel adsorbent (FMBO-DE) was prepared through *in situ* coating the active components of ferric and manganese binary oxides (FMBO) onto porous diatomite (DE), and was regenerated through *in situ* embedding active species onto the surfaces with adsorbed arsenic. The SEM image of FMBO-DE was presented in Figure 1. Noteworthy, the freshly prepared and regenerated FMBO-DE was directly employed as adsorbents for arsenic removal without further aging and drying.

Figure 1: SEM image of FMBO-DE grain ((a) $\times 100$, (b) $\times 5000$)

RESULTS AND CONCLUSIONS

Characterization of composite adsorbents

Zeta potential analysis. The zeta potential of FMBO-DE generally decreased with elevated pH, showing the isoelectric point (pH_{iep}) of pH7.0. The zeta potential of FMBO showed similar trends to that of FMBO-DE, except that the pH_{iep} was slightly lower to be at pH6.1. The surface potential of FMBO-DE was mainly determined with that of FMBO, rather than that of diatomite.

XRD characterization of FMBO. No obvious peaks were observed by X-ray diffraction (XRD) analysis for FMBO, which confirming that the adsorbents prepared through the procedures noted above was amorphous. The *in situ* prepared amorphous adsorbents exhibited high surface area and much surface hydroxyl groups, which was of critically importance for arsenic adsorption (Zhang, G.S. *et al.*, 2007a).

SEM/EDX analysis. SEM/EDX analysis indicated that Si, O and C were the main elements for plain diatomite (Figure 2a). FMBO-DE showed obvious peaks of elemental Fe and Mn, demonstrated the presence of ferric oxides and manganese oxides on the surface (Figure 2b). Additionally, it was observed that the surface elemental ratio of Fe to Mn was 3:1 for FMBO-DE, indicating that ferric oxides and manganese oxides were evenly homogeneous.

Arsenic removal potential evaluation and environmental effects

Arsenic removal kinetics. Kinetics studies showed that both As(III) and As(V) was quickly removed by FMBO-DE, and the removing capacity reached to 80% of equilibrium capacity within the initial 60 minutes.

Figure 2: Energy dispersive X-ray analysis of (a) plain diatomite, (b) FMBO-DE

Adsorption capacity for As(III) and As(V). Adsorption isotherms analysis demonstrated that FMBO-DE exhibited strong potential of removing both As(III) and As(V). The maximum adsorption capacities were as high as 350 mgAs(III)/g FMBO and 200 mgAs(V)/g FMBO as Fe and Mn, respectively. It was interestingly observed that FMBO-DE showed remarkably higher potential of removing As(III) than As(V). Our research group has reported similar results for FMBO, which had been aged and dried before employed as adsorbents for arsenic removal, and the mechanisms involved in these processes had also been well investigated (Zhang, G.S. *et al.*, 2007a; Zhang, G.S. *et al.*, 2007b).

Effects of pH on arsenic removal. FMBO-DE exhibited good potential of removing As(III) and As(V) in relatively high pH ranges of pH4.0~8.0, showing maximal adsorption capability as near pH5.5 for both As(III) and As(V). The elevated pH led to more negatively charged surfaces, which inhibiting the interaction between FMBO surfaces and anionic arsenic species.

Effects of coexistent ions on arsenic removal. The effects of coexistent ions as carbonate, phosphate, sulphate, nitrate, silicate, chloride ion, fluoride ion, calcium ion, and magnesium ion on arsenic removal had been investigated at ion concentration of 1.0mmol·L⁻¹. Phosphate and silicate showed significant inhibiting effects of decreasing removal potential for As(III) and As(V). Carbonate also slightly decreased arsenic adsorption onto FMBO-DE. Other coexistent species had negligible effects on arsenic removal with FMBO-DE. These results were in accordance with what had been noted before (Liu *et al.*, 2007; Meng *et al.*, 2000). Additionally, more remarkable side effects were observed at more acidic pH3.6 than at near neutral pH of pH6.0 for both phosphate and silicate.

Bench scale column tests for arsenic removal and adsorbents regeneration

Continuous column tests also demonstrated the strong capacity of removing both As(III) and As(V) (Figure 3). At the initial arsenic concentration of 100µg L⁻¹ and empty bed contact time (EBCT) of 5 min, the freshly-prepared FMBO-DE can respectively treat 3000 bed volume (BV) of As(III) and 2000 BV of As(V) to achieve the effluent arsenic concentration being consistently below 10µg L⁻¹. Moreover, the *in situ* embedded regeneration processes would not decrease, but obviously increased the capability of removing both As(III) and As(V) from water. After repeating 3 circles of arsenic adsorption and adsorbents regeneration, the adsorbing potential increased to as high as 4500 BV of As(III) and 3100 BV of As(V), respectively.

Figure 3: Arsenite (a) and arsenate (b) breakthrough curves for FMBO-DE column regenerated through *in situ* embedding (pH=7.0, [As]₀=100 μg L⁻¹, EBCT=5 min)

Furthermore, it was demonstrated that the higher capability of removing arsenic was ascribed to higher BET surface areas and more Fe-Mn binary oxides coated after *in situ* embedded regeneration (Table 1).

Table 1: Summary of the characteristics of FMO-DE packed in column A and plain Porous diatomite

sample	Surface area (m ² g ⁻¹)	Pore volume (mL g ⁻¹)	Average pore diameter (Å)	Fe and Mn content (mg g ⁻¹)
Plain DE	7.0866	0.0050	18.1292	0.0
cA-I	8.6632	0.0126	58.2454	10.58
cA -II	10.7284	0.0149	61.5657	16.40
cA -III	12.5079	0.0206	65.7307	22.61
cA -IV	16.2295	0.0209	69.5322	29.74

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