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Practical performance and its efficiency of arsenic removal from groundwater using Fe-Mn binary oxide

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Abstract

A treatment unit packed by granular adsorbent of Fe-Mn binary oxide incorporated into diatomite (FMBO(1:1)-diatomite) was studied to remove arsenic from anaerobic groundwater without any pre-treatment or post-treatment. The raw anaerobic groundwater containing 35–45 μg/L of arsenic was collected from suburb of Beijing. Arsenic(III) constituted roughly 60%–80% of the total arsenic content. Approximately 7,000 bed volumes (ratio of effluent volume to adsorbent volume) treated water with arsenic concentration below 10 μg/L were produced in the operation period of four months. The regeneration of FMBO(1:1)-diatomite had been operated for 15 times. In the first stage, the regeneration process significantly improved the adsorption capacity of FMBO(1:1)-diatomite. With increased loading amount of Fe-Mn binary oxide, the adsorption capacity for arsenic decreased 20%–40%. Iron and manganese in anaerobic groundwater were oxidized and adsorptive filtrated by FMBO(1:1)-diatomite efficiently. The final concentrations of iron and manganese in effluents were nearly zero. The continued safe performance of the treatment units proved that adsorbent FMBO(1:1)-diatomite had high oxidation ability and exhibited strong adsorptive filtration.

Key words: arsenic; groundwater; adsorption; filtration; Fe(II); Mn(II)

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Introduction

Groundwater resources are being increasingly exploited for drinking water because of its high quality. However, groundwater contamination by arsenic is a major public concern in many regions of the world. There are many reports of arsenic contamination in Bangladesh (Halim et al., 2009), India (Mukherjee and Fryar, 2008), Vietnam (Berg et al., 2001), China (Guo et al., 2008), and Argentina (Bundschuh et al., 2004). In these areas, millions of people are at risk of developing cancer due to chronic arsenic poisoning.

Arsenic exists in groundwater predominantly as inorganic arsenite (As(III)) and arsenate (As(V)) (Ferguson and Garvis, 1972), depending primarily on pH and redox conditions. According to the reports, As(III) is the dominant form in anaerobic groundwater, and being more toxic than As(V) (Smedley and Kinniburgh, 2002). As(III) is neutral charge in the pH range of 4–9, and As(V) is negatively charge (Wolthers et al., 2005). Therefore, As(III) is more difficult to be removed from water than As(V) because of the lack of electrostatic attraction on the solid.

Various treatment methods such as precipitation, membrane filtration, reverse osmosis, and adsorption have so far been adopted to remove arsenic (Meng et al., 2001; Guo et al., 2007; Walker et al., 2008). The precipitation technique is generally low cost, but it is not suitable for small water facilities, and less effective for As(III) removal without pre-oxidation of As(III) to As(V). The demonstrated membranes processes including membrane filtration and reverse osmosis, are expensive and also require an oxidizing agent to achieve a higher arsenic removal rate. However, the oxidizing agents are normally harmful to membranes. The adsorptive filtration technology is currently applied in developing countries (Leupin et al., 2005). This technology presents several advantages towards conventional technologies, including less amounts of toxic sludge, low-cost, and application of full-scale or small-scale treatment units for low-level arsenic removal (Katsoyiannis and Zouboulis, 2002).

In our previous study, Fe-Mn binary oxide exhibited high oxidation and adsorption efficiency for arsenic (Zhang et al., 2007a). Diatomite, as a result of its extremely lightweight and highly porous, has been put in industrial application as filtration media for water treatment (Wu et al., 2005). As a granular adsorbent, Fe-Mn binary oxide

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incorporated into diatomite (FMBO-diatomite) can be used to remove arsenic by adsorptive filtration technology, and can be regenerated consecutively in fixed-bed column.

Generally, iron and manganese are typical unwanted constituents in groundwater, because they can impart a metallic taste to the water. Moreover, the growth of iron and manganese bacteria can be supported by high concentration of iron and manganese. Although these bacteria are not considered a health risk, they can cause clogging or restriction of pipes, pumps, and other water-system parts by precipitation of metal hydroxides (Onganer and Temur, 1998). Thus, the filtration method can effectively remove iron and manganese from water.

The objective of this study is to present the application of FMBO(1:1)-diatomite for removing arsenic (35–45 μg/L) from anaerobic groundwater through the adsorptive filtration technology. It represents a case study, which is an application in real raw anaerobic groundwater in long-term operation. The location of the treatment unit is in Beijing suburb which is an arsenic affected area and where As(III) comprises the main arsenic species in the groundwater with the present of relatively high concentration of phosphorus. Fe(II) and Mn(II) also existed as the main reducing substances in the groundwater. The removal of arsenic along with phosphorus, iron, and manganese, have been investigated.

1 Materials and methods

1.1 Description of the treatment unit

The column consisted of a clear glass column (30 mm internal diameter and 400 mm long), with the adsorbent FMBO-diatomite supported by glass beads at the bottom. The FMBO-diatomite was prepared according to the following method: (1) immerge plain diatomite (0.25–0.35 mm) into the solution of ferrous sulfate, potassium permanganate and manganese chloride (analytical grade, Beijing Chemical Reagents Co., China) in a 500-mL glass beaker; (2) adjust the pH of suspension to 5.0; (3) rinse the solid with deionized water three times, and stored in polyethylene bottle for filling into column. In order to obtain a high efficiency of arsenic adsorption in anaerobic groundwater, the molar ratio of Fe to Mn in Fe-Mn binary oxide should be optimized. Before starting the runs, the FMBO-diatomite bed (240 mm in height, 58 g in weight) was rinsed by pumping water up flow through the column. The procedure was stopped when no air bubble existed inside of the bed. Raw groundwater was pumped through the FMBO-diatomite bed in down-flow mode. The flow rate was 17 mL/min (about 1.44 $m^3/(m^2 \cdot hr)$), and 1 bed volume (BV) of effluent was 0.17 L. When the arsenic concentration in effluent reached 10 μg/L (the maximum contaminant level of arsenic in drinking water of the standard in China), the regeneration was performed in up-flow mode by injecting the solution of 12 mmol/L potassium permanganate, 30 mmol/L ferrous sulfate and 18 mmol/L manganese chloride. Subsequently, treated water flowed at a mount of 5–10 BVs. Finally, the treatment unit can be set back into operation.

1.2 Sampling and analytical determinations

The raw groundwater and treatment unit effluent samples were filtered through a 0.45-μm membrane, and analyzed for arsenic, phosphorus, iron, and manganese concentrations. Unfiltered, not acidified samples were collected for the groundwater quality measurements, such as temperature, pH, and turbidity.

Exhausted FMBO-diatomite were dried and tested through the toxicity characteristic leaching procedure (TCLP) (USEPA, 1990). About 10.0 g of samples extracted in 200 mL of leachate which contained 0.1 mol/L acetic acid and 0.064 mol/L NaOH with pH of 4.93 in capped glass conical flasks. The leachant-to-solid ratio was 20. After being shaken at 30 r/min for 18 hr, the extraction solutions were filtered through 0.45 μm membrane filters, and analyzed for arsenic, iron, and manganese.

The dissolved oxygen (DO), pH, oxidation reduction potential (ORP) and electrical conductivity (EC) were measured by multi parameters portable instruments (HACH Sension, USA). Turbidity was determined using a turbidimeter (2100P, Hach Co., USA). Chemical oxygen demand (COD) was measured by a COD analyzer (HACH DRB200 and DR/2800, USA). Total organic carbon (TOC) was measured by a TOC analyzer (Jena multi N/C 3000, Germany). Alkalinity was measured by automatic potentiometric titrator (716 DMS, Metrohm Co., Switzerland). The surface morphology of diatomite and FMBO-diatomite were examined by scanning electron microscopy (SEM) (S-3000N, Hitachi Co., Japan).

Inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 2000, PerkinElmer Co., USA) was used to determine the concentration of major elements, e.g., arsenic, phosphorus, iron, and manganese. Hydride generation atomic fluorescence spectrometry (HG-AFS) (Beijing Beifenruili Analytic Instrument Co., China) was used to evaluate As(III) concentrations.

2 Results and discussion

2.1 Groundwater characterization and the adjustment of operation parameters

A field-based investigation had been carried out on arsenic contaminated groundwater in Beijing suburb. According to the result of this investigation, a typical well was chosen as raw groundwater source because of its typical anaerobic characteristics. The geochemical characteristics of the raw groundwater are shown in Table 1. After directly pumping, the raw groundwater was relatively anoxic with DO about 2.11 mg/L, and had low ORP (8.8 mV). In this reducing condition, the concentration of iron and manganese were slightly over the current Chinese standards for drinking water (GB 5749–2006) and existing mainly as dissoluble Fe(II) and Mn(II) (Hiemstra and Van Riemsdijk, 2007). Total arsenic (As(tot)) concentration of 44.7 μg/L was greatly higher than the maximum contaminant level of Chinese Drinking Water Standard (10 μg/L). Major arsenic

Table 1 Characteristics of the groundwater collected in suburb of Beijing on Match 2007

Item	Value	Item	Value
Well depth (m)	50	Mg (mg/L)	16
Temp. (°C)	14	P (mg/L)	1.21
DO (mg/L)	2.11	S (mg/L)	1.9
EC (μS/cm)	530	Cl (mg/L)	9.8
COD (mg/L)	8	K (mg/L)	0.57
pH	7.4	Ca (mg/L)	28
Turbidity (NTU)	0.7	Mn (mg/L)	0.151
ORP (mV)	8.8	Fe (mg/L)	0.257
Alkalinity (mg/L)	305	As(tot) (mg/L)	0.0447
TOC (mg/L)	2.84	As(III) (mg/L)	0.0366

species was present in the form of As(III) (As(III)/As(tot) was 80%), which is in consistency with the observed groundwater reducing conditions.

Fe-Mn binary oxide had high oxidation ability for As(III) (Zhang et al., 2007b). It is indicated that manganese dioxide oxidized As(III) to As(V), and iron oxide was dominant to adsorb As(V). In this study, the molar ratio of Fe to Mn in FMBO-diatomite was optimized firstly. The present of phosphorus, which did not constitute a problem for the drinking water quality, can adversely affect arsenic removal efficiency, because phosphorus competes with arsenic for the available sorption sites on iron oxides (Su and Puls, 2003). Therefore, the removal of phosphorus was also concerned.

As shown in Fig. 1a, the adsorbent FMBO-diatomite exhibited the best performance in arsenic removal at Fe to Mn molar ratio 1:1, with the effluent arsenic concentration of 10 μg/L and a breakthrough at 450 BVs. The increase proportion of manganese oxides in Fe-Mn binary oxide can enhance the arsenic removal efficiency in anaerobic groundwater. Meanwhile, the phosphorus removal did not reflect any difference (Fig. 1b). It can be explained by that the oxidation ability of Fe-Mn binary oxide may be consumed partly by other reducing substances in anaerobic groundwater, i.e., Fe(II), Mn(II), nature organic matter, and nitrite.

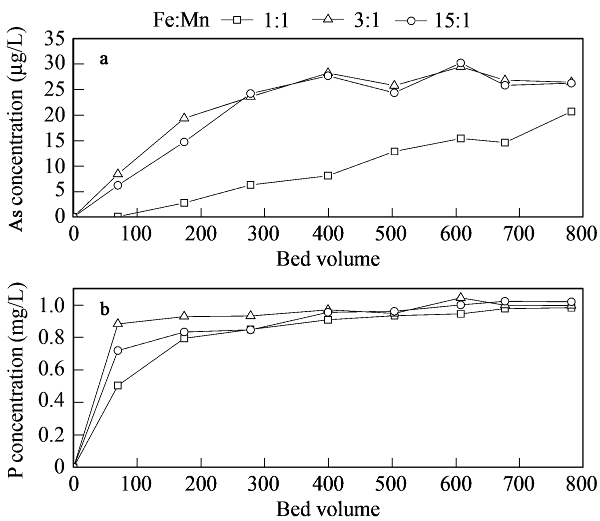

Fig. 1 Effect of Fe to Mn molar ratio on arsenic (a) and phosphorus (b) adsorption. Empty bed contact time (EBCT): 10 min; 1 bed volume = 0.17 L.

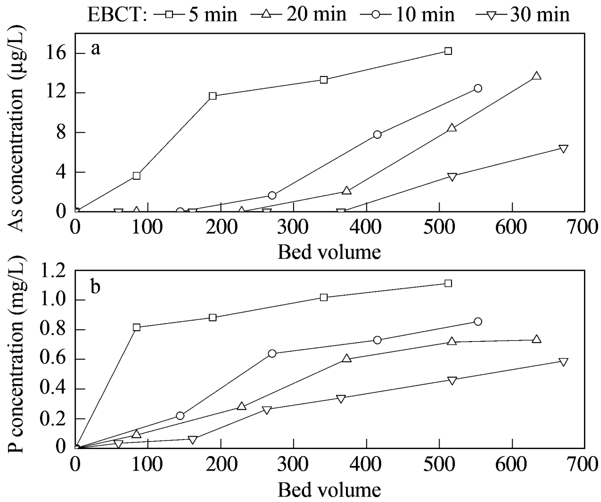

Fig. 2 Effect of EBCT on arsenic (a) and phosphorus (b) adsorption. 1 bed volume = 0.17 L.

As shown in Fig. 2, empty bed contact time (EBCT) shows a strong influence on both arsenic and phosphorus adsorption by FMBO(1:1)-diatomite. The breakthrough effluent volumes increased obviously with the increase of EBCT, attributing to low intra-particle diffusion of adsorbate into the pores of the adsorbent (Singh and Pant, 2006). The limit arsenic concentration of 10 μg/L in effluent can not be reached when effluent volume was more than 700 BVs at the longest EBCT of 30 min. The breakthrough of 10 μg/L arsenic took place at 180, 450, and 550 BVs for the EBCT of 5, 10, and 20 min, respectively. EBCT of 10 min can ensure an enough water supply quality and can be considered as a cost-effective operational condition. Therefore, in the subsequent treatment unit, FMBO (1:1)-diatomite and EBCT 10 min were used.

2.2 Performance of treatment unit to remove arsenic

The treatment unit was operated for approximately 4 months with 7000 BVs of raw anaerobic groundwater. Consecutive regenerations were carried out every 6–8 day. Figure 3b shows the history of arsenic concentrations in both raw groundwater and the treated water. Total arsenic concentrations in raw groundwater varied from 35 to 45 μg/L with 60%–80% of As(III). During the rainy season, the level of arsenic increased slightly. Due to the presence of phosphorus, the adsorption capability of FMBO(1:1)-diatomite for arsenic removal was limited. The volume of treated water containing arsenic below 10 μg/L was about 1173 L per 0.17 L of FMBO(1:1)-diatomite. No As(III) was detected in effluents. It is supposed that As(III) in raw groundwater was oxidized completely by the oxides on the surface of FMBO(1:1)-diatomite without air sparging or pre-oxidation.

The breakthrough bed volumes of FMBO(1:1)-diatomite varied during the whole treatment process (Fig. 3c). As the regeneration time increased in the first stage, the breakthrough bed volumes increased significantly because of the high Fe-Mn binary oxide loading. After the fourth regeneration, the breakthrough bed volumes showed the dramatic decrease trend. The similar phenomenon had

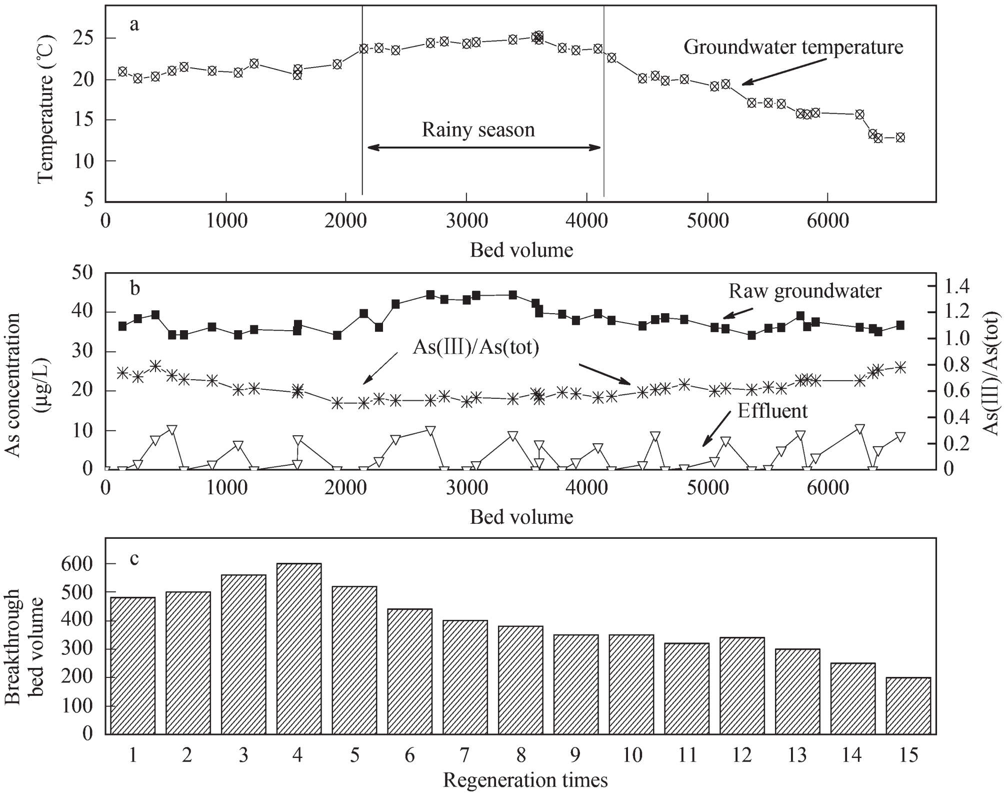

Fig. 3 History of temperature (a), and arsenic concentrations of (b) in groundwater and effluent from FMBO(1:1)-diatomite column over 15 consecutive cycles, and breakthrough bed volumes (c). EBCT: 10 min; 1 bed volume = 0.17 L.

also been observed by Zhang et al. (2008), who indicated that adsorbents with a further increase of hydrated ferric oxide loadings may result in a decrease of the adsorption capacity due to the pore-block effect and the inaccessibility of active adsorption sites. After regeneration 6–7 times, the adsorption capacity of FMBO(1:1)-diatomite had little change. It indicated that the arsenic adsorption efficiency did not depend on the pore structure of FMBO(1:1)-diatomite in the later stage. Being benefited from the extreme porosity of diatomite, large amount of Fe-Mn binary oxide can be incorporated into the pores, and finally covered the surface of diatomite completely. Compared to the virgin diatomite, the exhausted FMBO(1:1)-diatomite was a granular solid with much less pores (Fig. 4).

2.3 Removal of iron and manganese

The quality of groundwater was improved greatly by the treatment unit. Treatment reduced iron by 98%, manganese by 100%, phosphorus by 50%–90%, and turbidity by 50%–70% (Fig. 5). The pH values of effluent were in the range of 6.8–7.8. Phosphorus removal was attributed to the adsorption of FMBO(1:1)-diatomite. However, iron and manganese removal reflected the high efficiency of adsorptive filtration. Oxidation ability of Fe-Mn binary oxide will immediately lead to a transformation of Fe(II) into Fe(III), because the oxidation rate of Fe(II) is much higher than As(III) (Sarkar et al., 2005). The oxidized iron and manganese can be efficiently adsorbed and filtrated by FMBO(1:1)-diatomite. The concentrations of iron

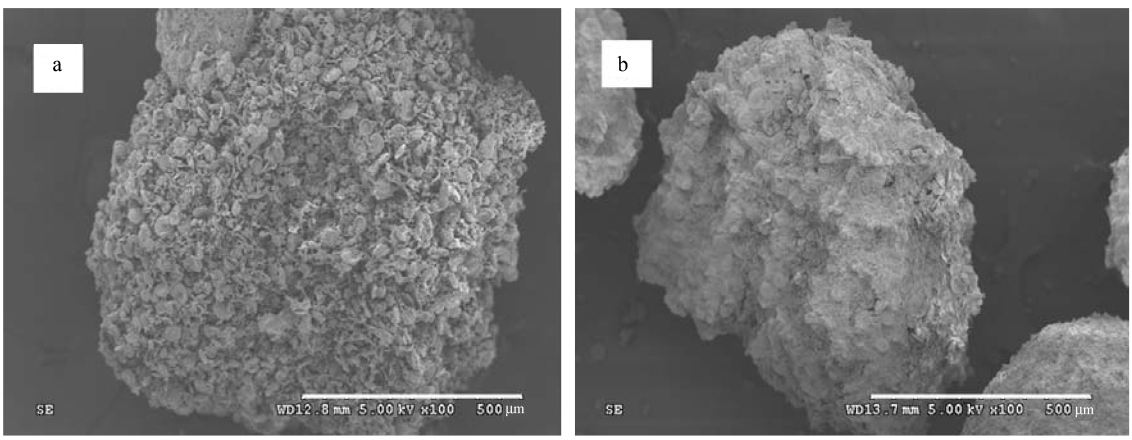

Fig. 4 SEM images of virgin (a) and exhausted (b) FMBO(1:1)-diatomite.

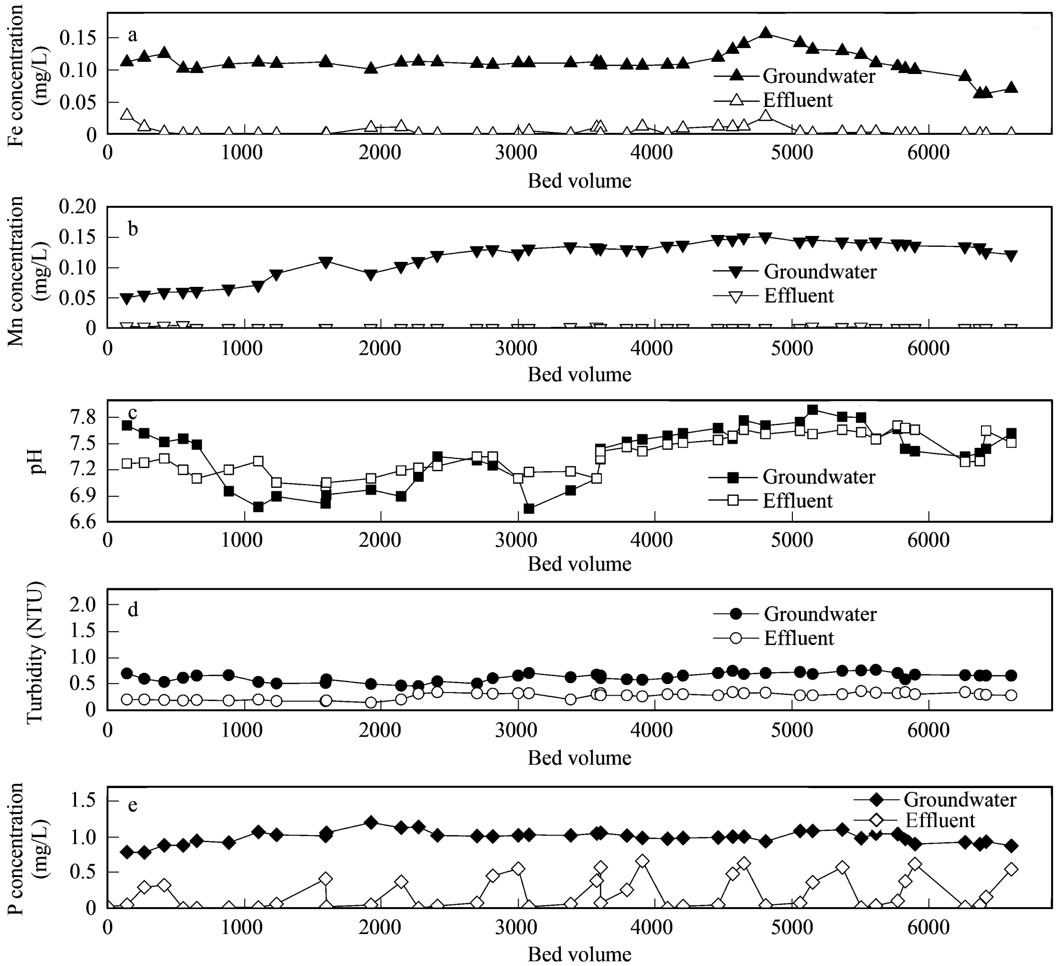

Fig. 5 History of Fe concentration (a), Mn concentration (b), pH (c), turbidity (d), and P concentration (e) in groundwater and effluents.

and manganese of effluents were nearly zero, and were independent of the FMBO(1:1)-diatomite consecutive regeneration. Only a small amount of iron and manganese flocculation was observed during the backwashing process. It is indicated that the adsorption played the main role in iron and manganese removal.

2.4 Leachability of adsorbed arsenic

The TCLP was used to evaluate the leachability of the arsenic adsorbed and to estimate the toxicity of the exhausted FMBO(1:1)-diatomite to the environment. Results showed that the arsenic released did not exceed 1.0 mg/L, which is well below the EPA regulatory limit of 5 mg/L for arsenic. Along the leaching of exhausted FMBO(1:1)-diatomite, the maximum dissolution concentrations of iron and manganese were 3.02 mg/L and 0.96 mg/L, respectively, which were far less than that of loaded Fe-Mn binary oxide. It suggests that the exhausted FMBO(1:1)-diatomite was not hazardous, and can be discharged in landfill deposits.

3 Conclusions

In the present study, the results of treatment unit indicated that FMBO(1:1)-diatomite was highly effective in removing arsenic (35–45 μg/L) from reducing groundwater at pH 6.8–7.8. High adsorption capacity and suitable Fe-Mn ratio of FMBO(1:1)-diatomite were beneficial for this high efficiency. With an increase loading amount of Fe-Mn binary oxide, the breakthrough bed volumes increased firstly and then decreased. After 15 times generation, the treated water with arsenic concentrations below 10 μg/L was 7000 BVs by 58 g (0.17 L) FMBO(1:1)-diatomite. Without any oxidants or accessional unit, the quality of treated water was stable and up to standards of drinking water.

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