Adsorption of antimony(V) onto Mn(II)-enriched surfaces of manganese-oxide and Fe–Mn binary oxide

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HIGHLIGHTS

- K_2SO_3 improve Sb(V) sorbing onto FMBO and Mn-oxide with higher effect on Mn-oxide.
- Mn(IV) dissolution result in Mn^{2+} release and re-adsorption as outer-sphere complex.
- Mn^{2+} -enriched MnO_2 show higher ζ -potential and stronger affinity towards Sb(V).
- Sb(V) sorption onto Mn^{2+} -enriched MnO_2 substitute $-O-Mn$ and release Mn^{2+} .
- Mn(IV) dissolution improve surface $-O-H$ exposure and benefit Sb(V) adsorption.

GRAPHICAL ABSTRACT

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ABSTRACT

Manganese(IV) oxide [Mn(IV)] potentially oxidizes antimony(III) [Sb(III)] to antimony(V) [Sb(V)] and improves Sb removal by Fe–Mn binary oxide (FMBO) through an oxidation-adsorption mechanism. This study focused on the effect of Mn(IV) reductive dissolution by potassium sulfite (K_2SO_3) on Sb(V) adsorption onto manganese oxide (Mn-oxide) and FMBO. The maximum Sb(V) adsorption ($Q_{max,Sb(V)}$) increased from 1.0 to 1.1 $mmol\ g^{-1}$ for FMBO and from 0.4 to 0.6 $mmol\ g^{-1}$ for Mn-oxide after pretreatment with 10 $mmol\ L^{-1}$ K_2SO_3 . The addition of 2.5 $mmol\ L^{-1}$ Mn^{2+} also significantly improved Sb(V) adsorption, and the observed $Q_{max,Sb(V)}$ increased to 1.4 and 1.0 $mmol\ g^{-1}$ for FMBO and Mn-oxide, respectively, with pre-adsorbed Mn^{2+} . Neither K_2SO_3 nor Mn^{2+} addition had any effect on Sb(V) adsorption onto iron oxide (Fe-oxide). Mn^{2+} introduced by either Mn(IV) dissolution or addition tended to form outer-sphere surface complexes with hydroxyl groups on Mn-oxide surfaces ($\equiv MnOOH$). Mn^{2+} at 2.5 $mmol\ L^{-1}$ shifted the isoelectric point (pH_{iep}) from 7.5 to 10.2 for FMBO and from 4.8 to 9.2 for Mn-oxide and hence benefited Sb(V) adsorption. The adsorption of Sb(V) onto Mn^{2+} -enriched surfaces contributed to the release of Mn^{2+} , and the X-ray photoelectron spectra also indicated increased binding energy of Mn 2p_{3/2} after the adsorption of Sb(V) onto K_2SO_3 -pretreated FMBO and Mn-oxide. Sb(V) adsorption involved the formation of inner-sphere complexes and contributed to the release of Mn^{2+} . In the removal of Sb(III) by Mn-based oxides, the oxidation of Sb(III) to Sb(V) by Mn(IV) oxides had an effect; however, Mn(IV) dissolution and Mn^{2+} -enrichment also played an important role.

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1. Introduction

Antimony (Sb) is the ninth most mined metal in the world, with a global production of more than 1.0×10^5 tons each year. The industrial uses of Sb include flame retardants, catalysts for plastics synthesis, and alloys for ammunition (Montserrat et al., 2002; Krachler et al., 2001; Mitsunobu et al., 2010; Guo et al., 2009). Some Sb-related compounds are designated as priority pollutants by the US Environmental Protection Agency, the European Union, and China (Kang et al., 2003; Oorts et al., 2008). Currently, the maximum contamination level of Sb is 5 µg/L, as required in the newly issued National Drinking Water Standard in China (Ministry of Health of PR China, 2007).

Anthropogenic activities can result in serious Sb pollution, although typical dissolved Sb concentrations in unpolluted waters are below $1.0 \mu\text{g L}^{-1}$ (Montserrat et al., 2002). Sb concentrations as high as several milligrams per liter have been reported in some water bodies near mining areas (Tessier et al., 1979; Hung et al., 2009; Wang et al., 2011), with Sb(V) found to be the dominant species (Wang et al., 2011; He, 2007). After discharge, river sediments are an important sink for Sb immobilization, with Fe–Mn oxides the most important pool (Wang et al., 2011). Extended X-ray absorption fine structure (EXAFS) spectroscopy has also provided direct evidence of the strong association of Sb(V) with iron(III) oxyhydroxides in oxic soils and sediments (Scheinost et al., 2006; Ackermann et al., 2009). Sb(V), predominantly present as $\text{Sb}(\text{OH})_6^-$ in the natural pH range (Mitsunobu et al., 2010), may be stable over a wide redox range in soil (Mitsunobu et al., 2006). The release of Sb(V) is more significant than that of Sb(III), which is enhanced in anaerobic conditions.

In China, persistent Sb pollution in drinking water sources occurs due to point and non-point Sb pollution and the release of Sb from river sediments. Neutralized arsenic(III) is more difficult to remove than negative arsenic(V), and the oxidation of arsenic(III) to arsenic(V) improves arsenic removal greatly. However, Sb(V) is more difficult to remove by either coagulation or adsorption than Sb(III). Guo et al. (2009) reported that the removal of Sb(III) by coagulation was more pronounced than that of Sb(V), especially under basic pH conditions, presumably due to the higher solubility of Sb(V) (Kang et al., 2003). Sb(III) as a strong Lewis base also shows higher affinity to goethite than Sb(V) over a wide pH range (Leuz et al., 2006), and tends to form a bidentate inner-sphere complex on goethite surfaces (Scheinost et al., 2006). Oxidation processes such as prechlorination prior to coagulation and adsorption are not recommended in the removal of Sb(III).

Arsenic(V), phosphate, and Sb(V) strongly adsorb onto iron hydro(oxide) surfaces by forming inner-sphere complexes, with ligand-exchange being the dominant mechanism. Negatively-charged Mn hydro(oxide) shows lower efficiency than iron hydro(oxides) in terms of the removal of these protic acids. In previous studies we successfully developed a Fe–Mn binary oxide (FMBO) with more significant removal capability to As(III) and Sb(III) than iron oxide (Fe-oxide) and manganese oxide (Mn-oxide), and an oxidation and adsorption mechanism was proposed (Xu et al., 2011; Zhang et al., 2007). A recent X-ray absorption near edge structure (XANES) study indicated that Mn-oxide ($1.5 < x < 2$) within FMBO was responsible for As(III) oxidation, whereas Fe-oxide dominated in the adsorption of the formed As(V) (Zhang et al., 2014). At pH 3.0, FMBO achieved a maximum Sb(III) removal capacity as high as 1.76 mmol g^{-1} , whereas that of Fe-oxide and Mn-oxide was 0.83 and 0.81 mmol g^{-1} , respectively (Xu et al., 2011). The oxidization of Sb(III) to Sb(V) ought to inhibit Sb removal, according to previous studies (Guo et al., 2009; Leuz et al., 2006). The apparent discrepancy may be attributed to the Sb(III) concentrations used in our study, which were

much higher than those in other studies, i.e. several tens of milligrams per liter compared to several micrograms per liter. Sb(III) at high concentrations shows a remarkable reductive dissolution effect on Mn(IV) within Mn-oxide and FMBO, whose surface characteristics and removal behaviors tend to vary accordingly. In the removal of arsenic(III) by Mn-oxide, surface passivation, i.e., lowered oxidation capability towards As(III), was observed in stirred flow experiments, and several mechanisms such as the adsorption of As(V) and Mn^{2+} and the formation of Mn(III) were proposed (Lafferty et al., 2010a). To the best of our knowledge, however, studies investigating the effect of Mn(IV) dissolution and Mn(II) re-adsorption on adsorptive behaviors are rare.

Surface hydroxyl groups play an important role in the adsorption of oxo species such as As(V) and Sb(V), and the significance of surface hydroxyls in As(V) adsorption onto Fe–Ce bimetal oxide was confirmed by *ex situ* Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) (Zhang et al., 2005). *Ex situ* FTIR provides insightful information on the surface functional groups and structure of metal (hydr)oxides (Cornell and Schindler, 1980; Kung and McBride, 1991); however, this technique suffers from complicated sample preparation procedures and has difficulty quantifying rapid reactions at short time-scales (Sheals et al., 2003). Recently, *in situ* methods such as rapid X-ray absorption fine structure (Q-XAFS) spectroscopy and attenuated total reflection FTIR (ATR-FTIR) have received great attention and have been successfully used to probe the kinetics of fast interfacial reactions (Matthew et al., 2009; Parikh et al., 2008).

In this study, we prepared the adsorbents of Fe-oxide, Mn-oxide, and FMBO and aimed to: (1) compare the effects of potassium sulfite (K_2SO_3) pretreatment and the addition of extra Mn^{2+} on their removal capability towards Sb(V); (2) investigate the adsorption of Mn^{2+} onto Mn-oxide and FMBO and its release after adsorption of Sb(V); (3) characterize the changes in their surfaces by XPS and *in situ* ATR-FTIR analysis; and (4) elucidate the role of adsorbed Mn^{2+} in the adsorption of Sb(V) onto Mn^{2+} -enriched surfaces. This study advances understanding of the removal behaviors of Mn-based adsorbents towards reductive pollutants such as Sb(III).

2. Materials and methods

2.1. Materials and chemicals

FMBO, Fe-oxide, and Mn-oxide were prepared at $25 \pm 2^\circ\text{C}$ following the procedures described in our previous studies (Xu et al., 2011; Zhang et al., 2007, 2014). To prepare FMBO with a Fe/Mn molar ratio of 3:1, solutions of potassium permanganate (KMnO_4) and iron(II) sulfate (FeSO_4) were first prepared in 200 ml of deionized water. The obtained FeSO_4 solution was then slowly added into the KMnO_4 solution under vigorous magnetic stirring (300 rpm), and a NaOH solution at 5 M was also carefully added to keep the solution pH in the range of 7–8. The formed suspension was continuously stirred for 0.5 h, aged for 5 h, and then washed with deionized water three times. Finally, the suspension was filtered, freeze-dried, and dried in a drier at 60°C to a constant weight. The final dry materials were passed through a $<50 \mu\text{m}$ sieve and then kept in an air-tight container until use. The synthesis of iron oxide (Fe-oxide) and Mn-oxide followed similar methods except that different starting materials were used.

Potassium antimonite [$\text{KSb}(\text{OH})_6$] (Alfa Aesar Co., UK), potassium nitrate, nitrate acid, and potassium hydroxide were all of analytical grade. Sb(V) stock solution at 10 mmol L^{-1} was prepared by dissolving $\text{KSb}(\text{OH})_6$ in an appropriate amount of deionized water.

2.2. Experimental methods

Sb(V) adsorption isotherms were determined using batch tests in a 50-mL polypropylene centrifuge tube along with 40 mL of Sb(V) solution, with initial Sb(V) concentration varying from 0.1 to 1 mmol L⁻¹. In each test, 0.016 mg of adsorbent sample was added to a tube after adjusting the pH to the desired values by adding 0.1 M HCl and/or KOH. Ionic strength was maintained with 0.01 M KNO₃. The tubes were shaken on an end-over-end tumbler at 30 rpm for 24 h at 20 ± 1 °C, and solution pH was adjusted at intervals to achieve pH variation of below ±0.2. After the reaction, all samples were filtered by 0.45-μm cellulose acetate membranes and analyzed for Sb, Fe, and Mn concentrations.

For the adsorption of Sb(V) onto K₂SO₃ pretreated adsorbents, similar procedures were followed except that prior to the addition of Sb(V), 0.01 M K₂SO₃ solution was reacted with the adsorbents for 4 h. While investigating the effect of Mn²⁺ on Sb(V) adsorption, 2.5 mmol L⁻¹ Mn²⁺ solution was added 4 h prior to or simultaneously with Sb(V).

2.3. Analysis and characterization

2.3.1. Zeta potential (ζ-potential)

A ζ-potential analyzer (Zetasizer 2000, Malvern, UK) was used to analyze ζ-potential. The doses of the two adsorbents, i.e., FMBO and Mn-oxide, were about 200 mg L⁻¹, and background electrolyte was provided by 0.01 M KNO₃. The concentrations of Sb(V) and Mn²⁺ were 1 mmol L⁻¹.

2.3.2. X-ray photoelectron spectroscopy (XPS)

Selected samples were freeze-dried for XPS analysis. Chemical analysis of the sorbent surfaces was conducted by XPS (Kratos AXIS Ultra, UK), with a monochromatized Al Kα X-ray source (1486.7 eV) working at 150 W, 15 kV, and 10 mA with a base pressure of 3 × 10⁻⁸ Torr in the analytical chamber. For wide-scan spectra, an energy range of 0–1100 eV was used with a pass energy of 160 eV. High-resolution scans were conducted according to the peak being examined with a pass energy of 40 eV. The C 1s peak at 284.7 eV was used as an internal standard. The XPS results were collected in binding energy form and fit using Vision (PR2.1.3) and CasaXPS (2.3.12Dev7) software.

2.3.3. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra

To prepare an ATR sample, the adsorbents were added to deionized water or solution with the desired species [e.g., Sb(V), Mn²⁺] to yield a solids concentration of 50 g L⁻¹, and deionized water or background solution was also used as a reference. The ATR-FTIR spectra were recorded using a TENSOR 27 infrared spectrometer (Brucker Co., Germany) with a DLaTGS detector and a ZnSe horizontal ATR cell. Infrared spectra over the wave-number range of 4000–650 cm⁻¹ were obtained at room temperature by averaging 32 scans, with a resolution of 4 cm⁻¹. The spectra of the suspended particles were corrected by subtracting the reference spectrum from that of the slurry (sample). The cell remained in place throughout the collection of all of the single beam spectra, including the empty cell, references, and to-be-analyzed samples, to make sure that a constant transmittance and average angle of incidence was maintained.

2.3.4. Analysis of Sb, Fe, and Mn

Inductively coupled plasma optical emission spectroscopy (ICP-OES) (SCIEX Perkin–Elmer Elan mode 5000) was used to analyze the concentrations of Sb, Fe, and Mn, and samples were filtered through 0.45-μm glass fiber membranes prior to analysis.

3. Results and discussion

3.1. Effect of K₂SO₃ pretreatment on the adsorption of Sb(V)

Fig. 1 illustrates the adsorbed Sb(V) per gram of adsorbent, [Sb(V)]_{ads} (mmol g⁻¹), plotted against the equilibrium Sb(V) concentrations ([Sb(V)]_{equilibrium}) at pH 5.0 and 6.0. Among the K₂SO₃-pretreated FMBO, Fe-oxide, and Mn-oxide adsorbents, FMBO showed the highest removal efficiency towards Sb(V). The maximal removal capacity ($Q_{\max, \text{Sb(V)}}$), as indicated by the direct graphic maximal capacity and corresponding to the isotherm plateau, was 1.14, 0.83, and 0.64 mmol g⁻¹ for FMBO, Fe-oxide, and Mn-oxide, respectively, at pH 5.0. In our previous study, without K₂SO₃ pretreatment, the corresponding $Q_{\max, \text{Sb(V)}}$ was 1.05, 0.82, and 0.44 mmol g⁻¹, respectively (Xu et al., 2012). K₂SO₃ pretreatment improved the adsorption of Sb(V) onto FMBO and Mn-oxide, and a more remarkable effect was observed for Mn-oxide. Comparatively, the effect of K₂SO₃ on Sb(V) sorption onto Fe-oxide was slight. Elevating the pH to 6.0 contributed to a decrease in $Q_{\max, \text{Sb(V)}}$ by 14.0% for FMBO, 18.8% for Fe-oxide, and 14.8% for Mn-oxide. As for the adsorbents without K₂SO₃ pretreatment, the elevation of pH from 5.0 to 6.0 also decreased the [Sb(V)]_{ads} by 8.8% for FMBO, 15.4% for Fe-oxide, and 40.7% for Mn-oxide ([Sb(V)]₀ = 0.5 mmol L⁻¹, adsorbent dose = 400 mg L⁻¹, ion strength = 0.01 mmol L⁻¹) (Xu et al., 2012). The pretreatment of Mn-oxide by K₂SO₃ seemed to buffer the adverse effect of elevated pH on Sb(V) adsorption.

3.2. Re-adsorption and release of Mn²⁺ involved in K₂SO₃ pretreatment

K₂SO₃ hardly reacted with Fe-oxide, whereas it showed a reductive dissolution effect towards the Mn(IV) oxide within FMBO and Mn-oxide. Fig. S1 illustrates the concentrations of released Mn²⁺ plotted with increasing K₂SO₃ concentrations from 1 to 10 mmol L⁻¹ in these two systems. K₂SO₃ contributed to the release of Mn²⁺ from FMBO and Mn-oxide, and a critical K₂SO₃ concentration was observed, i.e. 6 mmol L⁻¹, below which Mn²⁺ concentrations were lower than the detection limit of elemental Mn (0.04 mg L⁻¹). At 10 mmol L⁻¹ K₂SO₃, the released Mn²⁺ concentrations were as high as 10.8 mg L⁻¹ for FMBO and 21.7 mg L⁻¹ for MnO₂.

The reductive dissolution effect of K₂SO₃ towards Mn(IV) contributed to the formation of Mn²⁺ (Eq. (1)). Furthermore, the formed Mn²⁺ tended to re-adsorb onto the Mn(IV) oxide surfaces by forming outer-sphere surface complexes, e.g., ≡Mn–O–O–Mn⁺ and ≡Mn–O–O–Mn–O–O–Mn≡, with the

Fig. 1. Adsorption of Sb(V) onto K₂SO₃-pretreated adsorbents of FMBO, Fe-oxide, and Mn-oxide at pH 5.0 ± 0.1 or 6.0 ± 0.1. (Experimental conditions: adsorbents doses = 400 mg/L, K₂SO₃ = 10 mmol/L).

surface hydroxyl groups ($\equiv\text{MnO}-\text{OH}$) therein (Eqs. (2) and (3)). As for FMBO, Mn(IV) oxide rather than iron oxide dominated in the adsorption of Mn^{2+} . This was supported by the zero charge points (pH_{ZPC}), which were 8.5, 4.8, and 7.5 for Fe-oxide, Mn-oxide, and FMBO, respectively. The adsorption of Mn^{2+} onto positively-charged Fe-oxide was assumed to be insignificant. In comparison to FMBO, Mn-oxide had more active surface sites towards K_2SO_3 , and the observed Mn^{2+} concentration was higher in the presence of excess K_2SO_3 .

Birnessite includes two types of reactive sites, i.e., vacancy sites and edge sites (Drits et al., 1997; Silvester et al., 1997). The formed Mn^{2+} tends to primarily adsorb onto the vacancy sites, and after their occupation, onto edge sites (Lafferty et al., 2010b). By comparison, oxo species of arsenic and antimony mainly adsorb at edge sites (Tournassat et al., 2002). Additionally, the adsorption of Mn^{2+} onto Mn(IV) oxide contributes to the formation of Mn(III) via comproportionation between adsorbed Mn^{2+} and Mn(IV) (Eq. (4)) (Lafferty et al., 2010b). At low K_2SO_3 concentrations, the formed Mn^{2+} was low, and the surface sites on Mn-oxide were sufficient for Mn^{2+} adsorption. At high K_2SO_3 concentrations above 6 mmol L^{-1} , these sites were consumed and Mn^{2+} appeared in the solution accordingly (Fig. S1). K_2SO_3 concentrations of 10 mmol L^{-1} resulted in significant Mn(IV) dissolution, Mn(II) adsorption, and the formation of Mn(II)-saturated surfaces for FMBO and Mn-oxide.

The interactions between Mn(IV) oxide and K_2SO_3 also formed sulfate in addition to Mn(II). However, sulfate showed little effect on the adsorption of Sb(V) onto these two adsorbents even at the high concentration of 10 mmol L^{-1} (Xu et al., 2012). The observed positive effect of K_2SO_3 on Sb(V) adsorption was attributed to Mn(II) rather than sulfate.

3.3. Release of adsorbed Mn^{2+} after adsorption of Sb(V)

At the same doses, the elemental Mn content in Mn-oxide was nearly four times that in FMBO, as indicated by stoichiometric calculations. In comparison to FMBO, Mn-oxide showed more sites available for K_2SO_3 oxidation and Mn^{2+} adsorption, and the adsorbed Mn^{2+} on Mn-oxide surfaces was assumed to be higher than that on FMBO surfaces. The adsorbed Mn^{2+} may affect the behaviors of FMBO and Mn-oxide towards antimony. The heterogeneous oxidation of As(III) by manganese oxide and the adsorption of Mn^{2+} on manganese oxide has been investigated before (Lafferty et al., 2010a,b). First, Mn^{2+} sorption decreased the oxidative reactivity greatly, owing to the formation of Mn(III) via Mn(II)/(IV) comproportionation reactions (Lafferty et al., 2010b). This effect also resulted in the passivation of the adsorbents' surfaces by physically blocking the sites available for oxidation and adsorption (Lafferty et al., 2010a). Additionally, the adsorbed Mn^{2+} formed ternary Mn–As(V) complexes with As(V) and enhanced As(V) adsorption thereafter (Lafferty et al., 2010a). Furthermore, at high As(V) concentrations the adsorbed Mn^{2+} also tended to form protonated manganese arsenate precipitates on the Mn(IV) oxide surfaces (Lafferty et al., 2010a). In this study, these positive effect of Mn^{2+} on Sb(V) adsorption may also occur through

the formation of surface complexes with Sb(V) or Mn–Sb(V) precipitates, although further study is required to confirm this.

In the adsorption of Sb(V) onto Mn^{2+} -saturated surfaces, Sb(V) and Mn^{2+} competed for sorption sites, and the adsorbed Mn^{2+} at edge sites was expected to be released from the surfaces accordingly. In the Mn-oxide adsorption system, Mn^{2+} release showed two stages with increasing $[\text{Sb(V)}]_{\text{ads}}$ (Fig. 2). In the first stage, the aqueous Mn^{2+} concentration, i.e., released Mn^{2+} , was low and independent of $[\text{Sb(V)}]_{\text{ads}}$. In the second stage, aqueous Mn^{2+} increased with increasing $[\text{Sb(V)}]_{\text{ads}}$. Quantitatively, the concentrations of released Mn^{2+} were below 0.01 mg L^{-1} at $<0.11 \text{ mmol g}^{-1}$ $[\text{Sb(V)}]_{\text{ads}}$ at pH 5.0, but increased to 0.10 mg L^{-1} at 0.76 mmol g^{-1} $[\text{Sb(V)}]_{\text{ads}}$. Similar trends were observed at pH 6.0, except that the release of Mn^{2+} was more significant. Additionally, at pH 6.0 the Mn^{2+} concentrations plotted against $[\text{Sb(V)}]_{\text{ads}}$ showed a plateau, and Mn^{2+} release showed little change for $[\text{Sb(V)}]_{\text{ads}}$ above 0.26 mmol g^{-1} . As(V) was reported to adsorb primarily onto edge sites rather than vacancy sites within $\delta\text{-MnO}_2$ (Tournassat et al., 2002). With characteristics similar to As(V), Sb(V) was assumed to primarily occupy edge sites. At low $[\text{Sb(V)}]_{\text{ads}}$, the substitution of adsorbed Mn^{2+} by Sb(V) was slight. At elevated $[\text{Sb(V)}]_{\text{ads}}$, the available edge sites were consumed, competition for vacancy sites occurred, and the release of Mn^{2+} was observed. Sb(V) adsorption also facilitated the detachment and release of adsorbed Mn^{2+} from FMBO, and at pH 5.0 the elevation of $[\text{Sb(V)}]_{\text{ads}}$ from 0.015 to 0.57 mmol g^{-1} led to an increase in Mn^{2+} concentration from 0.04 to 0.12 mg L^{-1} accordingly. Interestingly, Mn^{2+} release occurred even at $[\text{Sb(V)}]_{\text{ads}}$ as low as $0.006 \text{ mmol g}^{-1}$, indicating that FMBO had many fewer edge sites available for Sb(V) adsorption than did Mn-oxide. These edge sites may have been occupied by iron oxide while preparing FMBO, and the vacancy sites were inferred to dominate on manganese oxide surfaces within FMBO. At $[\text{Sb(V)}]_{\text{ads}}$ of above 0.26 mmol g^{-1} , the released Mn^{2+} also showed a plateau, which may correspond to the complete substitution of Mn^{2+} on vacancy sites. These results implied that Mn^{2+} and Sb(V) occupied different sites on the surfaces, and it was inferred that Mn^{2+} bound more strongly on vacancy sites than on edge sites.

Macroscopic adsorption data, i.e., adsorption of Sb(V) onto FMBO and Mn-oxide with elevated ionic strength over a wide pH range, also illustrated the differences between the behaviors of Mn^{2+} and Sb(V) on the surfaces of FMBO and Mn-oxide (Xu et al., 2012). The adsorption of Sb(V) onto Mn-oxide was slightly affected by ionic strength in the pH range 3–5 and increased with higher ionic strength at pH 6–9, while ionic strength showed little effect on Sb(V) sorption onto FMBO over a wide pH range of 3–9. These results indicated the formation of inner-sphere complexes in the

Fig. 2. The release of Mn(II) after the adsorption of Sb(V) onto K_2SO_3 -pretreated Mn-oxide and FMBO at pH 5.0 ± 0.1 and 6.0 ± 0.1 (Experimental conditions: adsorbents doses = 400 mg/L).

adsorption of Sb(V) onto these two adsorbents. By comparison, Mn^{2+} primarily formed outer-sphere surface complexes on manganese oxide surfaces (Liu et al., 2009). In the adsorption of Sb(V) onto FMBO and Mn-oxide with adsorbed Mn^{2+} , the substitution of $-\text{O}-\text{Mn}$ groups within $\equiv\text{Mn}-\text{O}-\text{O}-\text{Mn}$ by Sb(V) occurred and contributed to the release of Mn^{2+} into solution (Eq. (5)). At low $[\text{Sb(V)}]_{\text{ads}}$, the substitution of $-\text{O}-\text{Mn}$ by Sb(V) dominated in Sb(V) adsorption. At high $[\text{Sb(V)}]_{\text{ads}}$, the release of Mn^{2+} showed a plateau and was independent of $[\text{Sb(V)}]_{\text{ads}}$, owing to the complete consumption of $-\text{O}-\text{Mn}$ groups. The adsorption of Sb(V) was achieved by the formation of inner sphere complexes and the replacement of the surface hydroxyl groups on FMBO and Mn-oxide surfaces, with the reactions simply expressed by Eqs. (6) and (7).

3.4. Effect of Mn^{2+} adsorption on Sb(V) removal

To further illustrate the role of Mn^{2+} on Sb(V) removal, 2.5 mmol L^{-1} Mn^{2+} was respectively introduced 4 h prior to and simultaneously with Sb(V), and its effects on Sb(V) adsorption onto FMBO and Mn-oxide were investigated (Fig. 3a). The pre-adsorbed

Fig. 3. Adsorption of (a) Sb(V) and (b) Mn^{2+} onto FMBO and Mn-oxide in the presence of 2.5 mmol/L of extra-dosed Mn^{2+} at pH 5.0 ± 0.1 (Experimental conditions: adsorbents doses = 400 mg/L; Mn^{2+} was introduced 4-h prior to Sb(V) (blank symbol) and simultaneously with Sb(V) (black symbols); the blue symbols indicate the control systems without introducing Mn^{2+}).

Mn^{2+} significantly improved Sb(V) adsorption, and at pH 5.0 the observed $Q_{\text{max,Sb(V)}}$ increased from 1.0 to 1.4 mmol g^{-1} for FMBO and from 0.4 to 1.0 mmol g^{-1} for Mn-oxide, respectively. When Mn^{2+} and Sb(V) were simultaneously introduced, Mn^{2+} also benefited Sb(V) adsorption, except that the observed $Q_{\text{max,Sb(V)}}$ was slightly lower. The adsorption of Sb(V) onto Mn^{2+} -occupied FMBO and Mn-oxide also decreased with elevated pH from 5.0 to 6.0; however, the extent was less than that for the original adsorbents.

The additional Mn^{2+} underwent comproportionation with Mn(IV) to form Mn(III) reactive sites, and the newly formed sites were available for the adsorption of arsenic (Lafferty et al., 2010a). By comparison, the addition of 2.5 mmol L^{-1} Mn^{2+} showed a more significant positive effect on Sb(V) adsorption than that of 10 mmol L^{-1} K_2SO_3 . In the K_2SO_3 -reduction system, the re-adsorbed Mn^{2+} blocked Mn(IV) oxide surfaces and inhibited the dissolution of Mn(IV) oxide even in the presence of excess K_2SO_3 (Fig. S1), and the observed maximum Mn^{2+} concentrations were much lower than 2.5 mmol L^{-1} thereafter. In addition to this effect, the dissolution of Mn(IV) oxide reduced the number of sites available for Sb(V) adsorption.

The adsorption of Mn^{2+} onto FMBO and Mn-oxide over a wide $[\text{Sb(V)}]_{\text{ads}}$ range, as expressed by $[\text{Mn}^{2+}]_{\text{ads}}$, is shown in Fig. 3b. The observed $[\text{Mn}^{2+}]_{\text{ads}}$ in the Mn-oxide adsorbent system was higher than that in the FMBO adsorbent system. When Mn^{2+} was introduced prior to Sb(V), the $[\text{Mn}^{2+}]_{\text{ads}}$ was 0.43 mmol g^{-1} for FMBO and 0.82 mmol g^{-1} for Mn-oxide at a low $[\text{Sb(V)}]_{\text{ads}}$ of about 0.15 mmol g^{-1} . At an elevated $[\text{Sb(V)}]_{\text{ads}}$ of approximately 1.0 mmol g^{-1} , $[\text{Mn}^{2+}]_{\text{ads}}$ decreased to 0.37 mmol g^{-1} for FMBO and 0.54 mmol g^{-1} for Mn-oxide. These results confirmed that Mn-oxide showed more sites available for Mn^{2+} adsorption, which was in accordance with the results in Fig. S1. When Mn^{2+} and Sb(V) were simultaneously added, the adsorption of Mn^{2+} onto FMBO and Mn-oxide also occurred, except that the observed $[\text{Mn}^{2+}]_{\text{ads}}$ was lower. This may be related to Mn^{2+} having a less positive effect on Sb(V) adsorption in these simultaneously-dosed systems.

Additionally, the extent of $[\text{Mn}^{2+}]_{\text{ads}}$ decrease with elevated $[\text{Sb(V)}]_{\text{ads}}$ in the Mn-oxide adsorbent system was more significant than that in the FMBO adsorbent system. This further indicated that the competition between Sb(V) and Mn^{2+} towards vacancy sites on Mn-oxide surfaces was more significant than that on FMBO surfaces.

3.5. ζ -potential variation after adsorbing Sb(V) and Mn^{2+}

Regardless of whether it was introduced by K_2SO_3 pretreatment or by addition to the solution, Mn^{2+} improved Sb(V) adsorption onto FMBO and Mn-oxide. The beneficial effect of Mn^{2+} may be primarily attributed to its effect on the surface charge of FMBO and Mn-oxide. The additional Mn^{2+} increased the oxides' ζ -potentials over a wide pH range, from 3 to 12, and a more significant pH_{iep} shift was observed for Mn-oxide. Quantitatively, the pH_{iep} of FMBO increased from 7.5 to 10.2 and that of Mn-oxide increased from 4.8 to 9.2 after the introduction of 2.5 mmol L^{-1} Mn^{2+} (Fig. 4). By comparison, the adsorption of Sb(V) decreased the pH_{iep} values, which were 3.2 for FMBO and 3.0 for Mn-oxide. The remarkable shift in pH_{iep} indicated the occurrence of specific adsorption and the formation of surface complexes in the adsorption of Mn^{2+} and Sb(V) (Zhang et al., 2009; Hsia et al., 1994). The elevated ζ -potential due to Mn^{2+} enrichment benefited the adsorption of negatively-charged Sb(OH)_6^- , which was the main Sb(V) species over a wide pH range of 3–9. The positive electrostatic effect of Mn^{2+} on the adsorption of arsenic and phosphate has been reported before (Zhang et al., 2007, 2009; Stumm and Morgan, 1996). Mn^{2+} contributed to a more significant ζ -potential increase for Mn-oxide, and the more remarkable effect on Sb(V) adsorption

Fig. 4. Effects of Sb(V) and Mn^{2+} adsorption on the ζ -potential variation of FMBO and MnO_2 over a wide pH range (Experimental conditions: Background electrolyte = 10 mmol/L KNO_3 ; adsorbents doses = 200 mg/L; Mn^{2+} = 2.5 mmol/L; Mn^{2+} was introduced 4-h prior to Sb(V) and simultaneously with Sb(V)).

was observed thereafter. Besides the electrostatic effect, the adsorbed Mn^{2+} and the formed Mn(III) also played an important role. Lafferty et al. (2010a) reported the positive effect of newly formed Mn^{2+} , through reactions between As(III) and Mn(IV) oxide, on As(V) adsorption, and attributed it to the formation of $\text{Mn}^{\text{II}}\text{—As}^{\text{V}}$ complexes and the presence of Mn^{III} reactive sites.

3.6. XPS characterization of the sorbents after Sb(V) adsorption

The XPS spectra of elemental Fe 2p, Mn 2p_{3/2}, and Sb 3d_{3/2} on FMBO, Fe-oxide, and Mn-oxide after adsorbing Sb(V) are illustrated in Fig. S2. The Fe 2p_{3/2} peaks for FMBO and Fe-oxide respectively showed the binding energies of 711.8 and 711.9 eV, and the chemical valence of Fe was inferred to be +III in view of the typical peak shape of the Fe 2p spectra. Prior to adsorbing Sb(V), the Mn 2p_{3/2} within FMBO and Mn-oxide showed a binding energy of 642.5 eV, which was consistent with a chemical valence of +IV for Mn (Zhang et al., 2007). The binding energy of Mn 2p_{3/2} barely changed after the adsorption of Sb(V), indicating negligible variation in its chemical valence. The binding energy of Sb 3d_{3/2} on the three adsorbents was 540.1 eV, which corresponded to the chemical valence of +V for Sb species (Delobel et al., 1983). These results indicated that oxidation and reduction reactions scarcely occurred in the adsorption of Sb(V) onto these three adsorbents. Our previous study indicated that after the adsorption of Sb(III), the binding energy of Mn 2p_{3/2} decreased from 642.5 eV to 641.3 eV for FMBO and to 642.3 eV for Mn-oxide (Leuz et al., 2006), which indicated the reduction of Mn(IV) oxide and the re-adsorption of Mn(II) onto its surfaces. Additionally, the binding energy of Sb 3d_{3/2} was elevated to 539.9 and 540.1 eV for FMBO and Mn-oxide, respectively.

K_2SO_3 pretreatment contributed to the reductive dissolution of Mn(IV) oxides into Mn^{2+} , decreasing the intensity of the Mn2p spectrum by 55% and shifting the binding energy from 642.6 to

642.3 eV (Zhang et al., 2007). The formed Mn^{2+} tended to re-adsorb onto FMBO and Mn-oxide surfaces by forming surface complexes and resulted in Mn^{2+} -enriched surfaces. In addition, the elemental ratios of Fe—Mn on FMBO surfaces increased from 2.84:1 to 5.82:1 after K_2SO_3 pretreatment (Zhang et al., 2007), and this effect benefited the adsorption of Sb(V) thereafter. To further clarify the effect of K_2SO_3 pretreatment, 400 mg L⁻¹ of FMBO and Mn-oxide were respectively pretreated by K_2SO_3 (10 mmol L⁻¹), and then Sb(V) at different concentrations of 0.1, 0.5, and 1.0 mmol L⁻¹ was dosed for 24 h. The obtained samples were centrifuged and freeze-dried for XPS analysis. Table 1 illustrates the atomic ratios of Fe, Mn, Sb, and O and the binding energies of Sb 3d_{3/2}, Fe 2p_{3/2}, and Mn 2p_{3/2}, and Figs. S3 and S4 show the XPS spectra of Fe 2p_{3/2}, Mn 2p_{3/2}, and Sb 3d_{3/2} on FMBO and Mn-oxide surfaces. After adsorbing Sb(V), the binding energy of Fe 2p_{3/2} was near 710.8 eV, and its peak shape showed little variation at different Sb(V) concentrations, whereas the intensity of the peak decreased greatly. This result indicated the presence of strong interactions between Sb(V) and Fe atoms (Smichowski et al., 1998), while the Fe chemical valence barely changed, remaining at +III. The binding energy of Mn 2p_{3/2} on FMBO increased from 641.8 to 642.0 eV with elevated Sb(V) concentrations from 0.1 to 1.0 mmol L⁻¹. The Mn 2p peak at lower binding energy was related to the lower oxidation state, and the binding energies of Mn 2p_{3/2} in MnO, Mn_3O_4 , Mn_2O_3 , and MnO_2 were 641.0, 641.5, 641.9, and 642.6 eV, respectively (Smichowski et al., 1998; Castro and Polzonetti, 1989). Sb(V) cannot oxidize Mn(II), which was confirmed by the lack of variation in Sb 3d_{3/2} binding energy after adsorption. The elevated binding energy of Mn 2p_{3/2} was attributed to the release of adsorbed Mn^{2+} after the adsorption of Sb(V), through the abovementioned inner-sphere complex formation (Eq. (5)), rather than the oxidation of Mn(II) to that at a higher oxidation state. The lowered Mn atom content also supported the involvement of Mn(II) release in Sb(V) adsorption. Similar trends were also observed in the adsorption of Sb(V) onto K_2SO_3 -pretreated Mn-oxide, and the binding energy of Mn 2p_{3/2} increased from 642.1 to 642.3 eV whereas the Mn content decreased from 37.2% to 34.5%.

The adsorbed Sb showed a binding energy of 540.0 eV for Sb 3d_{3/2}, and the chemical valence of Sb was +V on the FMBO and Mn-oxide surfaces. With increasing Sb(V) concentration from 0.1 to 1.0 mmol L⁻¹, the atom content of Fe and Mn on the FMBO surfaces decreased from 32.2% to 28.1% and from 9.7% to 8.0%, respectively. The Sb atom content increased from 0.49% to 4.08% due to the coverage of Sb(V) on the available sites. In the Mn-oxide adsorbent system, the extent of Sb atom content increase and Mn atom content decrease was lower than that in the FMBO adsorbent

Table 1

XPS results of the K_2SO_3 -pretreated FMBO and Mn-oxide ($[\text{K}_2\text{SO}_3]_0 = 10$ mmol/L) with adsorbed Sb(V) ($[\text{Sb(V)}]_0 = 0.1, 0.5, \text{ and } 1.0$ mmol/L) (adsorbents doses = 400 mg/L, pH = 5.0 ± 0.1).

Sample	Composition (at.%)			Binding energy (eV)			
	Fe(t)	Mn(t)	O(t)	Sb(t)	Sb 3d _{3/2}	Fe 2p _{3/2}	Mn 2p _{3/2}
FMBO (0) Zhang et al. (2014)	18.2	6.4	75.4	/	/	711.0	642.6
FMBO* (0) Zhang et al. (2014)	19.8	3.4	76.8	/	/	711.0	642.3
FMBO* (0.1)	32.2	9.7	57.2	0.49	539.9	710.8	641.8
FMBO* (0.5)	31.3	8.40	58.5	2.4	540.0	710.9	641.9
FMBO* (1.0)	28.1	8.0	59.6	4.08	540.0	710.8	642.0
Mn-oxide* (0.1)	N	37.2	61.2	0.47	539.9	N	642.1
Mn-oxide* (0.5)	N	36.6	59.2	1.07	540.0	N	642.2
Mn-oxide* (1.0)	N	34.5	61.4	2.4	540.0	N	642.3

FMBO*: K_2SO_3 -pretreated FMBO; Mn-oxide*: K_2SO_3 -pretreated Mn-oxide.

system, which was in agreement with its lower capability in terms of Sb(V) adsorption.

3.7. ATR-FTIR of FMBO, Fe-oxide, and Mn-oxide after Sb(V) and Mn^{2+} adsorption

In situ ATR-FTIR probes mineral/liquid interfaces and provides valuable information on interfacial reactions, oxidation/reduction, and kinetic mechanisms (Parikh et al., 2008). ATR-FTIR spectra of the original and K_2SO_3 -pretreated adsorbents and those after adsorbing Sb(V) and Mn^{2+} were respectively collected and are illustrated in Fig. 5. The peaks at frequencies near 1634 cm^{-1} were assigned to the hydroxyl groups of physisorbed water molecules on the adsorbents. The original FMBO exhibited a strong peak at 1103 cm^{-1} , which was rather weak on Fe-oxide and Mn-oxide surfaces. K_2SO_3 pretreatment greatly increased the intensity of this peak at 1103 cm^{-1} , and a more significant increase was observed with prolonged contact time from 0.1 to 1.0 h. This peak might be attributed to the stretching vibration of interfacial hydroxyl groups such as $\equiv\text{Fe}-\text{O}-\text{OH}$ and $\equiv\text{Mn}-\text{O}-\text{OH}$ within FMBO. It was noted that Fe-oxide showed a weak peak at this frequency (Fig. 5c), and it was inferred that the $\equiv\text{Mn}-\text{O}-\text{OH}$ group contributed more than $\equiv\text{Fe}-\text{O}-\text{OH}$ to this peak. The increased intensity after K_2SO_3 pretreatment implied that Mn(IV) dissolution improved the exposure of these hydroxyl groups, and this effect was beneficial to the adsorption of Sb(V). Mn^{2+} adsorption decreased the intensity of this peak, which was attributed to the consumption of $\equiv\text{Mn}-\text{O}-\text{OH}$ rather than $\equiv\text{Fe}-\text{O}-\text{OH}$. The interaction between Mn^{2+} and $\equiv\text{Fe}-\text{O}-\text{OH}$ was insignificant, as indicated by the slight variation in this peak at 1103 cm^{-1} after

introducing Mn^{2+} into the original Fe-oxide (Fig. 5c). Interestingly, this peak was barely observed in the original MnO_2 , whereas it appeared in K_2SO_3 -pretreated Mn-oxide. K_2SO_3 pretreatment, with subsequent Mn(IV) dissolution, strengthened the exposure of $\equiv\text{Mn}-\text{O}-\text{OH}$, and increased the intensity of the peak at 1103 cm^{-1} accordingly.

In addition, the adsorption of Mn^{2+} onto the original Mn-oxide also contributed to the appearance of this peak, which was attributed to the formation of Mn(III) reactive sites after Mn^{2+} adsorption and its conproportionation with Mn(IV) (Lafferty et al., 2010b). Further study is required to illustrate the dominant reactions involved to clarify the changes in the Mn-oxide lattice and surfaces. In the Fe-oxide adsorbent system, the introduction of K_2SO_3 might have affected and contributed to the appearance of a broad band at 1100 cm^{-1} ; however, the intensity was rather weak. The adsorption of Sb(V) onto FMBO and Mn-oxide consumed these hydroxyl groups by the formation of inner-sphere complexes, as expressed by Eqs. (6) and (7), and a decrease in the intensity of this peak was observed. Additionally, two new peaks at 1245 and 990 cm^{-1} appeared after K_2SO_3 pretreatment on FMBO and Mn-oxide, respectively. In the Fe-oxide adsorbent system, a new broad band at 937 cm^{-1} was also observed after introducing K_2SO_3 . These peaks might be indicative of adsorbed SO_3^{2-} and/or SO_4^{2-} , the substitution of which by Sb(V) contributed to the disappearance of these peaks.

3.8. Mechanism of Mn^{2+} improvement of Sb(V) adsorption onto FMBO and Mn-oxide

As shown by XRD analysis (Fig. S5), the Mn-oxide prepared in this study showed two weak peaks at 2θ of 37.3° and 66.7° ($\text{Cu K}\alpha$), which corresponded to the XRD pattern of $\delta\text{-MnO}_2$. Although it is expressed as MnO_2 , the average oxidation state of Mn is near to rather than equal to 4.0 owing to the sorption of small amounts of $Mn^{II/III}$ at vacancy sites (Lafferty et al., 2010b; Drits et al., 2007). XANES analysis in our recent study also indicated the mixed valence state of Mn species as +III and +IV for the Mn atoms within Mn-oxide; and Mn-oxide may be denoted as MnO_x ($1.5 < x < 2$) and FMBO as $\text{FeOOH}-MnO_x$ (Zhang et al., 2014). This was confirmed by the release of Mn^{2+} at 0.08 mg L^{-1} after the adsorption of Sb(V) ($[\text{Sb(V)}]_0 = 1.0\text{ mmol L}^{-1}$) onto the original FMBO surface. XRD analysis of FMBO indicated that these two peaks within Mn-oxide weakened greatly and shifted to lower 2θ . This implied the inhibited crystallization of Mn oxide in the preparation of FMBO, which showed lower crystallinity thereafter. Amorphous FMBO showed higher BET surface area ($231\text{ m}^2\text{ g}^{-1}$) than Mn-oxide having higher crystallinity ($117\text{ m}^2\text{ g}^{-1}$). Additionally, Fe-oxide showed a higher affinity towards Sb(V) than Mn-oxide did (Xu et al., 2012), and these effects enabled FMBO to show higher Sb(V) removal efficiency than Mn-oxide.

Whether introduced by K_2SO_3 -reduction or addition to the solution, Mn^{2+} was re-adsorbed onto Mn(IV) oxide and significantly affected the surface character and adsorptive behavior towards Sb(V) thereafter. Fig. 6 illustrates the dominant role of Mn^{2+} in the adsorption of Sb(V) onto FMBO and Mn-oxide. The introduced Mn^{2+} tended to form outer-sphere surface complexes ($\equiv\text{Mn}-\text{O}-\text{O}-\text{Mn}$) by substituting for the hydroxyl groups on Mn(IV) oxide surfaces. This effect shifted the pH_{iep} to the higher pH range, benefiting Sb(V) adsorption by decreasing electrostatic repulsion. Additionally, $-\text{O}-\text{Mn}$ was easier than $-\text{O}-\text{H}$ to be replaced by Sb(V), and the formation of inner-sphere complexes of $\equiv\text{Mn}-\text{O}-\text{Sb(V)}$ was favored accordingly. Furthermore, Mn(IV) oxide dissolution by K_2SO_3 enhanced the exposure of $-\text{O}-\text{H}$ and/or $-\text{O}-\text{Mn}$ groups available for Sb(V) adsorption. Besides these effects, the adsorbed Mn^{2+} potentially formed a $\text{Mn}-\text{Sb(V)}$ precipitate on adsorbent surfaces in cases with high Sb(V) concentrations.

Fig. 5. ATR-FTIR spectra of original FMBO, Mn-oxide, and Fe-oxide, and those after pretreated by K_2SO_3 (100 mmol/L) for 0.1 and 1 h, and those with adsorbed Sb(V) ($[\text{Sb(V)}]_0 = 20\text{ mmol/L}$) and Mn^{2+} ($[\text{Mn}^{2+}]_0 = 100\text{ mmol/L}$) (Experimental conditions: adsorbents doses = 50 g/L ; $\text{pH} = 6.0 \pm 0.2$).

Fig. 6. Proposed dominant reactions and the roles of Mn^{2+} involved in the adsorption of Sb(V) onto FMBO and MnO_2 .

Cadmium ion was reported to improve arsenate adsorption on goethite at high initial arsenate concentration, owing to the occurrence of co-precipitation reaction between cadmium and arsenate on goethite surfaces (Jiang et al., 2013). The formation of Mn(III) by comproportionation between adsorbed Mn^{2+} and Mn(IV) may have also shown beneficial effects; however, further study will be required to quantify this effect on Sb(V) adsorption.

4. Conclusions

K_2SO_3 pretreatment improved the adsorption of Sb(V) onto FMBO and Mn-oxide, with a more significant positive effect observed for Mn-oxide. K_2SO_3 showed a reductive dissolution effect towards Mn(IV) oxide, and the released Mn^{2+} tended to re-adsorb onto its surfaces by forming outer-sphere complexes. The introduction of Mn^{2+} , either by Mn(IV) dissolution or extra addition, increased the ζ -potential over a wide pH range and benefited Sb(V) adsorption thereafter. The formation of inner-sphere complexes was dominant in the adsorption of Sb(V), and Sb(V) substitution for the $-\text{O}-\text{Mn}$ group within the $\equiv\text{O}-\text{O}-\text{Mn}$ surface occurred in Mn^{2+} -saturated surfaces. The XPS spectra indicated the occurrence of Mn(IV) dissolution and Mn^{2+} re-adsorption after K_2SO_3 pretreatment. The release of adsorbed- Mn^{2+} occurred after Sb(V) adsorption, owing to its substituting for the $-\text{O}-\text{Mn}$ group.

ATR-FTIR spectra implied that Mn(IV) dissolution improved the exposure of surface hydroxyl groups to benefit the adsorption of Sb(V). In the removal of As(III) and Sb(III) by Mn-based oxides, i.e., Mn-oxide and FMBO, the oxidation of neutral +III species to negative +V species had a significant effect; however, this study indicates that the reductive dissolution of Mn(IV) oxide and the re-adsorption of Mn^{2+} also played an important role. The effects of to-be-treated adsorbates on adsorbent characteristics should be well evaluated in adsorbent design.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2015.07.039>.

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