Simultaneous removal of Cd(II) and Sb(V) by Fe–Mn binary oxide: Positive effects of Cd(II) on Sb(V) adsorption

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HIGHLIGHTS

- Fe–Mn binary oxide achieves the simultaneous removal of Cd(II) and Sb(V).
- Cd(II) at above 0.25 mmol/L improves Sb(V) adsorption onto FMBO.
- Cd(II) improves more significant Sb(V) adsorption than Ca^{2+} and Mn^{2+} .
- Sb(V) adsorption decreases whereas Cd(II) adsorption increases with elevated pH.
- The increased ζ -potential and Cd(II)–Sb(V) precipitation favors Sb(V) adsorption.

GRAPHICAL ABSTRACT

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ABSTRACT

The coexistence of cadmium ion (Cd(II)) and antimonate (Sb(V)) creates the need for their simultaneous removal. This study aims to investigate the effects of positively-charged Cd(II) on the removal of negative Sb(V) ions by Fe–Mn binary oxide (FMBO) and associated mechanisms. The maximum Sb(V) adsorption density ($Q_{\text{max,Sb(V)}}$) increased from 1.02 to 1.32 and 2.01 mmol/g in the presence of Cd(II) at 0.25 and 0.50 mmol/L. Cd^{2+} exhibited a more significant positive effect than both calcium ion (Ca^{2+}) and manganese ion (Mn^{2+}). Cd^{2+} showed higher affinity towards FMBO and increased its ζ -potential more significantly compared to Ca^{2+} and Mn^{2+} . The simultaneous adsorption of Sb(V) and Cd(II) onto FMBO can be achieved over a wide initial pH (pH_i) range from 2 to 9, and $Q_{\text{Sb(V)}}$ decreases whereas $Q_{\text{Cd(II)}}$ increases with elevated pH_i . Their combined values, as expressed by $Q_{\text{Sb(V)+Cd(II)}}$, amount to about 2 mmol/g and vary slightly in the pH_i range 4–9. FTIR and XPS spectra indicate the significant synergistic effect of Cd(II) on Sb(V) adsorption onto FMBO, and that little chemical valence transformation occurs. These results may be valuable for the treatment of wastewater with coexisting heavy metals such as Cd(II) and Sb(V).

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1. Introduction

Recently antimony (Sb) pollution has received great concern due to its environmental toxicity and health risk, and Sb has been

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considered a priority pollutant by the United States Environmental Protection Agency (USEPA) [1] and the European Union (EU) [2]. Sb pollution in the environment is mainly the result of anthropogenic activities such as mining, smelting, and metallurgy, and the production of flame retardants, semiconductors and so on [3,4]. China has the most abundant Sb reserves in the world, and produces approximately 84.0% of the world's supply [5]. The large-scale extraction and utilization of Sb-related minerals has led to serious Sb pollution in some areas [6,7]. Even more serious, the Sb in tailing heaps, waters, and sediments is often observed to coexist with other heavy metals such as cadmium (Cd) [7,8]. For example, in Xikuangshan (XKS), which is well known as the “World Capital of Sb”, the wide occurrence of simultaneous Cd and Sb pollution was reported due to the coexistence of Cd in Sb-containing ores [7]. Some cities in Guangxi province in China are also threatened by widespread pollution by heavy metals, among which Sb and Cd are the most abundant [9]. The coexistence of heavy metals might pose a higher risk to human health and ecological safety than when they are present separately. Additionally, the coexisted heavy metals may also show different removal behavior as compared to that in single-existing system. Unfortunately, studies focusing on the simultaneous removal of several coexisting heavy metals such as Cd and Sb are rare.

Sb(III) and Sb(V) are the dominant Sb species in natural environments, and Sb(V) mainly exists in oxic surface waters, whereas Sb(III) dominates in anoxic conditions such as underground water and sediment [3,10]. The species of Sb plays an important role in its treatability. The transformation of more toxic Sb(III) to less toxic Sb(V) by chemical or biogeochemical oxidation [11–13] is valuable to reduce its toxicity toward the environment [14,15]. Unfortunately, the conversion of Sb(III) to Sb(V) could not only contribute to Sb species mobilization in soils [16] but also increase the difficulty of removing Sb from the engineering point-of-view [17]. Guo et al. compared the removal efficiency of Sb(III) to that of Sb(V) using coagulation with ferric chloride, and effective Sb(III) removal was observed over a wide pH range from 4 to 10, whereas significant Sb(V) removal could be achieved at pH below 6 [17]. Our previous study developed a novel adsorbent of Fe–Mn binary oxides (FMBO) for the removal of heavy metals such as arsenic, Sb, and Cd²⁺ [18–20], and FMBO may be practically suitable to achieve the simultaneous removal of Sb and Cd²⁺. The adsorption of positive Cd²⁺ onto FMBO was improved at elevated pH whereas that of Sb was more significant at lower pH [19,20]. Moreover, the adsorbed Cd²⁺ may change the character of the FMBO surface greatly, and affect the adsorptive behaviors of Sb accordingly. However, few studies have investigated this before, to the best of our knowledge.

On the basis of these considerations, this study first aimed to evaluate the effect of Cd²⁺ on the removal of Sb(V) by FMBO, and the effects of two other cations, manganese ion (Mn²⁺) and calcium ion (Ca²⁺), were also investigated for comparison. Next, the effects of these cations on the interfacial characteristics of FMBO were characterized by zeta potential, FTIR spectra, and X-ray photoelectron spectroscopy (XPS). Finally, the dominant mechanism by which Cd²⁺ affects the adsorption of Sb(V) by FMBO is proposed. It is noted that the heterogeneous oxidation of Sb(III) to Sb(V) occurs on the FMBO surface; consequently the adsorptive behaviors of Sb(III) were not investigated herein.

2. Materials and methods

2.1. Materials and chemicals

FMBO with a Fe/Mn molar ratio of 3:1 was prepared by the stoichiometric reaction between iron(II) sulfate (FeSO₄) and potassium permanganate (KMnO₄) as described in our previous study

[18,19]. The stock solutions of Sb(V), Cd²⁺, Mn²⁺, and Ca²⁺ were prepared by dissolving potassium pyroantimonate [KSb(OH)₆], cadmium nitrate [Cd(NO₃)₂], manganese sulfate (MnSO₄), and calcium nitrate [Ca(NO₃)₂] in deionized water, respectively. Modeling analysis by the Visual MINTEQ software indicates that Sb(OH)₆[−] is the dominant Sb(V) species over a wide pH range from 4 to 12 (Fig. S1).

2.2. Batch adsorption experiments

2.2.1. Adsorption kinetics

Adsorption kinetics experiments were performed in glass beakers at room temperature. Sb(V) stock solution was added to obtain the desired [Sb(V)]₀ of 0.5 mmol/L, and the ionic strength was maintained at 0.01 mol/L potassium nitrate (KNO₃). While investigating the effect of divalent cations, i.e., Cd²⁺, Mn²⁺, and Ca²⁺, on Sb(V) adsorption, their stock solutions were respectively dosed to achieve initial concentrations of 0.2 mmol/L. While investigating the effects of Cd²⁺ at different concentrations on Sb(V) adsorption, different amounts of Cd²⁺ stock solution were added to achieve [Cd²⁺]₀ in the range from 0.02 to 2.0 mmol/L. Initial pH (pH_i) was adjusted to 5.0 ± 0.1 by HNO₃ and/or KOH solutions. Next, 200 mg FMBO was added and the suspension was rapidly mixed by a magnetic stirrer, and the pH was adjusted at intervals during the adsorption process. Aliquots (5 mL) were taken from the suspension at reaction times of 0, 0.05, 0.1, 0.167, 0.25, 0.333, 0.5, 1, 2, 3, 4, 5, 7, 9, 11, 24, 36, and 48 h. All the samples were filtered by 0.45-μm cellulose acetate membranes and then kept at 4 °C before analyzing the concentrations of Sb(V) and Cd²⁺, Mn²⁺, or Ca²⁺. The obtained suspensions were freeze-dried and kept air-tight in darkness for FTIR analysis.

2.2.2. Adsorption isotherm

Sb(V) adsorption isotherms were determined using batch tests in a 50-mL polypropylene centrifuge tube along with 40-mL solution spiked with suitable amounts of the stock solutions of Sb(V) and Cd²⁺ to achieve their desired concentrations. [Sb(V)]₀ varied from 0.1 to 2.0 mmol/L and the [Cd²⁺]₀ was designed to be 0, 0.025, 0.25, 0.5, and 1.0 mmol/L, respectively. Ionic strength was also provided by 0.01 mol/L KNO₃ and pH was adjusted to 5.0 ± 0.1 by HNO₃ and/or KOH solutions. In each test, 0.016 mg FMBO was added to a tube, and then the tubes were shaken on an end-over-end tumbler at 30 rpm for 24 h at 20 ± 1 °C, and solution pH was also carefully adjusted at intervals to achieve pH variation less than ±0.2. After the reaction, all samples were filtered by 0.45-μm cellulose acetate membranes and analyzed for Sb, Fe, and Mn concentrations.

While investigating the effects of Cd(II) at different concentrations on the pH variation during Sb(V) adsorption on FMBO, similar procedures were used except that pH adjustment was not performed after pH_i was adjusted to 5.0 ± 0.1.

2.2.3. pH effects

While investigating the effects of pH on Sb(V) and Cd(II) adsorption in the coexisting system, pH_i was adjusted to 2.0–9.0, and the [Sb(V)]₀ and [Cd(II)]₀ was controlled at 0.5 and 0.2 mmol/L. The tubes were shaken on an end-over-end tumbler at 30 rpm at 20 ± 1 °C and pH adjustment was not performed. After 24-h reaction, the equilibrium pH was measured, and the samples were filtered and stored before analysis.

2.3. Analysis and characterization

2.3.1. Zeta potential (ζ-potential)

The ζ-potential of FMBO was determined with a ζ-potential analyzer (Zetasizer 2000, Malvern, UK). The stock solutions of Sb(V), Cd²⁺, Mn²⁺, and Ca²⁺ were added in glass vessels to achieve desired

Fig. 1. Effects of Cd(II) at different concentrations on the adsorption kinetics of Sb(V) on FMBO ([Sb(V)]₀ = 0.5 mmol/L, FMBO = 200 mg/L, pH 5.0 ± 0.1).

concentrations, and pH_i was adjusted to be in the range from 2 to 12. After dosing FMBO at 200 mg/L, the tubes were shaken at 30 rpm for 4 h prior to ζ-potential analysis, and the equilibrium pH was also measured.

2.3.2. FTIR

FTIR spectra were collected on a Nicolet 5700 spectrometer using transmission mode. Samples were ground with KBr (Spectral Grade) in an agate mortar. A fixed amount of sample (~1% W:W) in KBr was used to prepare the pellet.

2.3.3. XPS

Samples were freeze-dried before X-ray photoelectron spectroscopy (XPS) analysis by an XPS (Kratos AXIS Ultra, UK) with a mono-chromatized AlKα X-ray source (1486.7 eV). An energy range of 0–1100 eV was used with pass energy of 160 eV for wide-scan spectra, and the high-resolution scans were conducted according to the peak being examined with pass energy of 40 eV. The C 1s peak at 284.7 eV was used as an internal standard calibration peak. The XPS data were converted into VAMAS file format and imported into the software of Vision (PR2.1.3) and CasaXPS (2.3.12Dev7) for manipulation and curve-fitting.

2.3.4. Concentrations of Sb, Cd, and Mn

The concentrations of Sb, Cd, and Mn were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (SCIEX PerkinElmer Elan mode 5000), and the detection limit was determined to be 0.04, 0.0005, and 0.003 μg/mL for Sb, Cd, and Mn, respectively.

3. Results and discussion

3.1. Effects of Cd²⁺ on the adsorptive behaviors of Sb(V) onto FMBO

3.1.1. Adsorption kinetics

Fig. 1 illustrates the positive effect of Cd²⁺ at different concentrations from 0.02 to 2.0 mmol/L on the adsorption kinetics of Sb(V) onto FMBO. The maximum adsorption capacity (Q_{max}), as indicated by pseudo-second-order modeling, was determined to be 1.33 mmol/g in the absence of Cd²⁺. Cd²⁺ at 0.02, 0.2, and 2.0 mmol/L contributed to the elevated Q_{max} values of 1.50, 1.55, and 1.79 mmol/g accordingly. Additionally, the adsorption of Sb(V) on FMBO was observed to be rapid, and the 4-h contact time achieved over 75% of the Q_{max} regardless of the presence of Cd(II) or not. The adsorption of Sb(V) on FMBO may be divided into two steps of rapid adsorption and slow adsorption. Without Cd(II)-present,

Fig. 2. Effects of Cd(II) at different concentrations on the adsorption isotherms for Sb(V) by FMBO (FMBO = 200 mg/L, pH 5.0 ± 0.1).

FMBO achieved 75.2% of the Q_{max} within the initial 2-h contact time. Comparatively, the prolonged contact time from 2 to 48 h only achieved about 25% of the Q_{max}. Similar trends were also observed in the presence of Cd(II) at different concentrations.

To better compare the adsorption kinetics in these systems, three kinetic models, including the pseudo-first-order model, pseudo-second-order model, and Elovich model, were used to fit the observed adsorption data, and the fitted parameters are shown in Table 1. In the absence of Cd(II), the pseudo-second-order model can best describe the adsorption of Sb(V) onto FMBO (R² = 0.97), and the involvement of chemisorption as the dominant mechanism was inferred accordingly. In the presence of Cd(II), the Elovich model showed the highest R² values and was best able to describe the adsorption kinetics of Sb(V) among these models. This implied the involvement of multilayer adsorption and the occurrence of heterosphere diffusion reactions after the introduction of Cd(II). The positive effect of Cd²⁺ on Sb(V) adsorption onto FMBO may also be quantified by the q_{max} values as obtained by Pseudo-first-order and Pseudo-second-order modeling, which showed higher q_{max} values in Cd(II)-containing systems than that in the absence of Cd²⁺ (Table 1).

3.1.2. Adsorption isotherms

Fig. 2 illustrates the adsorption isotherms for the adsorption of Sb(V) onto FMBO with the Cd(II) concentrations ranging from 0 to 1.0 mmol/L, and the fitted constants are presented in Table 2. Cd(II) at low concentration of 0.025 mmol/L showed little effect on the removal of Sb(V) by FMBO; however, its beneficial effect was observed at elevated Cd(II) concentrations of above 0.25 mmol/L. Quantitatively, the maximum Sb(V) adsorption density (Q_{max,Sb(V)}), as being indicated by the direct graphic maximum capacity, was observed to be 1.02 mmol/g in the absence of Cd(II), and Cd(II) at 0.5 mmol/L contributed to significant Q_{max,Sb(V)} increase to as high as 2.01 mmol/g. A more remarkable improvement on Sb(V) adsorption was observed at further elevated Cd(II) concentrations, i.e., 0.5 mmol/L, and the adsorption isotherm plateau could hardly be achieved at relatively low equilibrium Sb(V) concentrations of below 0.6 mmol/L. The formation of Cd(II)–Sb(V) precipitates also contributed to the removal of Sb(V). To evaluate this effect on Sb(V) removal, Cd(II) solution over a wide concentration range from 0.1 to 4.0 mmol/L was dosed into 0.5 mmol/L Sb(V) solution for 2-h reaction, and then the residual concentrations of Sb(V) and Cd(II) in the filtrates were analyzed. The results indicated that residual Sb(V) concentrations showed little variation even in Cd(II) concentrations as high as 4.0 mmol/L. The significantly improved Sb(V) removal at Cd(II) concentrations above 0.5 mmol/L was attributed to its beneficial effect on Sb(V) adsorption rather than the formation

Table 1

The kinetic model parameters for the adsorption of Sb(V) on FMBO at different initial Cd(II) concentrations at pH 5.0 ± 0.1.

[Cd ²⁺] ₀ (mmol/L)	Pseudo-first-order equation $q = q_{\max} - \exp(\ln(q_{\max}) - k \times t)$			Pseudo-second-order equation $q = q_{\max} - q_{\max} / (k \times q_{\max} \times t + 1)$			Elovich $y = a + k \times \ln(t)$	
	R ²	q _{max} (mmol/g)	k (mmol/g h)	R ²	q _{max} (mmol/g)	k	R ²	k
0	0.92	1.23	2.52	0.97	1.33	2.34	0.94	0.19
0.02	0.83	1.22	2.44	0.92	1.31	2.37	0.98	0.17
0.2	0.85	1.27	2.73	0.94	1.37	2.46	0.99	0.18
2.0	0.68	1.44	4.64	0.81	1.52	4.51	0.93	0.17

Table 2

Langmuir and Freundlich isotherm constants for Sb(V) adsorption by FMBO at different initial Cd(II) concentrations at pH 5.0 ± 0.1.

[Cd(II)] ₀ (mmol/L)	Langmuir model $Q = Q_{\max} \times (K_L/c + 1)^{-1}$			Freundlich model $q = K_F \times c^{1/m}$		
	R ²	K _L (L/mg)	Q _{max} (mmol/g)	R ²	K _F	m
0	0.85	0.035	1.02	0.96	1.134	4.06
0.025	0.82	0.027	1.02	0.91	1.103	5.35
0.25	0.88	0.014	1.32	0.95	1.507	5.24
0.5	0.88	0.034	2.01	0.97	2.466	3.46
1.0	0.87	0.109	3.18	0.96	3.716	2.51

Fig. 3. Effects of different divalent cations at 0.2 mmol/L on the adsorption kinetics of Sb(V) on FMBO ([Sb(V)]₀ = 0.5 mmol/L, FMBO = 200 mg/L, pH 5.0 ± 0.1). **Fig. 4.** Effects of these divalent cations on the ζ-potential of FMBO over a wide pH range from 2 to 9 (FMBO = 200 mg/L).

of Cd(II)–Sb(V) precipitates. Additionally, our previous study indicated that Sb(III) was more easily removed by FMBO than Sb(V), and the $Q_{\max, Sb}$ was observed to be 1.76 mmol Sb(III)/g and 1.05 mmol Sb(V)/g, respectively [19]. This study indicates that Sb(V) adsorption onto FMBO can be improved by divalent cations such as Cd²⁺.

The Freundlich model showed higher R^2 values and was better than the Langmuir model at fitting the adsorption isotherms of Sb(V) on FMBO (Table 2).

The Langmuir model was developed on the assumption that adsorption occurs on homogeneous surfaces, and is ineffective to describe the adsorption behavior of Sb(V) onto heterogeneous FMBO surfaces. The higher R^2 values obtained with Freundlich modeling inferred that FMBO provided heterogeneous surface sites with different energies available for the adsorption of Sb(V). SEM/EDX analysis indicated that FMBO surfaces are heterogeneous with a surface elemental ratio of iron to manganese of close to 3:1, and the analysis of pore volume and pore diameter also supported the presence of porous and heterogeneous surfaces for FMBO. Additionally, Cd(II) tends to form surface complexes with FMBO surfaces [20], and this effect further complicate the FMBO surfaces accordingly.

3.1.3. Comparison with other divalent cations

Fig. 3 compares the effects of three divalent cations, i.e., Cd²⁺, Ca²⁺, and Mn²⁺, on the adsorption of Sb(V) onto FMBO at pH 5.0. The

observed $Q_{\max, Sb(V)}$ was 1.41 mmol/g in the absence of these cations. After the introduction of 0.2 mmol/L of Cd²⁺, Ca²⁺, and Mn²⁺, the $Q_{\max, Sb(V)}$ was observed to be 1.59, 1.40, and 1.45 mmol/g, respectively. Ca²⁺ showed no effect whereas Mn²⁺ slightly improved the adsorption of Sb(V) by FMBO. Comparatively, Cd²⁺ showed much more beneficial effects than both Ca²⁺ and Mn²⁺ did. The formation of insoluble precipitates between Sb(V) and these cations was also evaluated, and insoluble precipitates rarely occurred even at concentrations of as high as 4.0 mmol/L (Fig. S2). In this study, the concentrations of Sb(V) and these cations were much lower than the water solubility of their precipitates, and complexation between Sb(V) and these ions is rather weak and may be ignored accordingly.

The ζ-potential of FMBO decreased with elevated pH, and the isoelectric point (pH_{iep}) was determined to be near to 5.7 [21]. These divalent cations tend to compress the diffuse electrical double layer of FMBO. Besides this effect, the interactions between these cations and the FMBO surface (≡S–OH), e.g., ion exchange and surface complexation reactions, also contribute to the increase of the surface potential [22]. As shown in Fig. 4, these divalent cations at 0.2 mmol/L contributed to the increase of ζ-potential over a wide pH range from 4 to 9, and a more significant increase was observed for Cd²⁺. The pH_{iep} shifted to 6.9 in the presence of Cd²⁺, and to 6.2 and 6.1 after the introduction of Mn²⁺ and Ca²⁺, respectively. Over a wide range of cation concentrations from 0.02 to 0.8 mmol/L, Cd²⁺

also showed remarkably higher ability to increase the ζ -potential than the other two cations (Fig. S3).

The ionic radii of Cd^{2+} , Ca^{2+} , and Mn^{2+} are 0.97, 0.99, and 0.91 Å, and the radii of their hydrous cations follow the sequence of $\text{Mn}^{2+} > \text{Cd}^{2+} > \text{Ca}^{2+}$. Hydrous cations with lower radius show more significant ability to compress the double-layer of FMBO than those with higher radius, and more remarkable ζ -potential increase was observed accordingly. This effect contributed to the higher efficacy of Cd^{2+} than Mn^{2+} in terms of increasing the ζ -potential of FMBO. Compared to Ca^{2+} , with similar ionic radius, Cd^{2+} showed priority with respect to increasing the ζ -potential. To explain this phenomenon, the adsorption density of these cations onto FMBO was compared, and $Q_{\text{Cd}^{2+}}$ was significantly higher than $Q_{\text{Ca}^{2+}}$ over a wide range of their initial concentrations from 0.2 to 1.0 mmol/L (Fig. S4). This implied that Cd^{2+} reacted more significantly with FMBO surfaces (=S-OH) than Ca^{2+} did, and further studies are required to explain this difference. The adsorption of Sb(V) onto Cd^{2+} -enriched surfaces was more significant than that onto Ca^{2+} -enriched surfaces. Over wide ranges of pH (from 3.0 to 9.0) and Cd(II) concentrations (from 0.035 to 3.5 mmol/L), the adsorption density of Sb(V) onto FMBO ($Q_{\text{Sb(V)}}$) was observed to increase with elevated ζ -potential (Fig. S5). The elevated ζ -potential played an important role in Cd(II) enhancing the adsorption of Sb(V) onto FMBO.

3.2. Simultaneous adsorption of Sb(V) and Cd(II) onto FMBO

Fig. 5 illustrates the adsorption density of Sb(V) ($Q_{\text{Sb(V)}}$) and Cd(II) ($Q_{\text{Cd(II)}}$) over a wide pH range from 2 to 9. Note that pH was not adjusted during adsorption, and equilibrium pH (pH_e) was measured after 24-h. The pH_{iep} of pure FMBO was determined to be close to 5.7 [21], and in the presence of Cd(II) and Sb(V), pH_{iep} shifted to elevated pH of nearly 7.0 (Fig. 4). pH_e tended to approach pH_{iep} over a wide pH range. Quantitatively, pH_e was above pH_i at $\text{pH}_i < 6.4$ whereas at $\text{pH}_i > 6.4$, pH_e shifted to lower values than pH_i . FMBO surfaces, as being expressed by =S-OH , show a pH-buffering effect through protonation (Eq. (1)) and deprotonation reactions (Eq. (2)), and pH_e approached pH_{iep} over the wide pH_i range from 2 to 9.

Fig. 5. The adsorption of Sb(V) and Cd(II) in their co-existing system over a wide initial pH range from 2 to 9 (FMBO = 200 mg/L; $[\text{Sb(V)}]_0 = 0.5 \text{ mmol/L}$; $[\text{Cd(II)}]_0 = 0.2 \text{ mmol/L}$).

The adsorption of positively-charged Cd(II) increased whereas that of negative Sb(V) ions decreased with elevated pH_i , and electrostatic attraction played a determining role in the adsorption of these two chemicals. This was in accordance with our previous studies on the adsorption of Sb(V) and Cd(II) onto FMBO in the single component systems [19,20]. The combined values of $Q_{\text{Sb(V)}}$ and $Q_{\text{Cd(II)}}$, as expressed by $Q_{\text{Sb(V)}+ \text{Cd(II)}}$, varied little and were close to 2.0 mmol/g for pH_i from 4 to 9. At lowered pH_i of 2 and 3, $Q_{\text{Sb(V)}}$ increased remarkably and $Q_{\text{Sb(V)}+ \text{Cd(II)}}$ was observed to be as high as 2.47 and 2.62 mmol/g accordingly. This result is practically valuable to optimize the treatment of source waters with different ratios of Sb(V) to Cd(II), and it is inferred that pH adjustment is a feasible strategy to achieve the simultaneous removal of Sb(V) and Cd(II) by FMBO.

Fig. 6 illustrates the adsorption density of Sb(V) and Cd(II) in single-component and coexisting systems with elevated equilibrium concentrations of Sb(V) and Cd(II), respectively. $Q_{\text{Sb(V)}}$ in the coexisting system was slightly higher than that in the single-component system, and this indicated the positive effect of Cd(II) on Sb(V) adsorption. Comparatively, Sb(V) showed an adverse effect, and $Q_{\text{Cd(II)}}$ in the coexisting system was slightly lower than that in the single-component system. As for source waters with different ratios of Sb(V) to Cd(II), FMBO can successfully achieve the

Fig. 6. The adsorption density of Sb(V) and Cd(II) in single and coexisting systems with different ratios of Sb(V) to Cd(II) (FMBO = 200 mg/L; a- $[\text{Cd(II)}]_0 = 0.2 \text{ mmol/L}$, b- $[\text{Sb(V)}]_0 = 0.5 \text{ mmol/L}$).

Fig. 7. Effects of Cd(II) at different concentrations on the pH variation during Sb(V) adsorption on FMBO (pH_i = 5.0 ± 0.1, FMBO = 200 mg/L).

simultaneous removal of these two toxic elements as observed from the $Q_{Sb(V)+Cd(II)}$ in different systems.

3.3. Proposed mechanisms of Cd²⁺ improving Sb(V) adsorption onto FMBO

3.3.1. pH variation

Cd(II) had an effect on pH variation and the adsorption of Sb(V) thereafter. In the absence of Cd(II), solution pH increased from pH_i of 5.0 to pH_e of 7.4 (Fig. 7). The elevated pH caused the deprotonation of the FMBO surface and weakened its affinity towards negative Sb(V) ions. Cd(II) at 0.25 and 2.5 mmol/L contributed to the decrease of pH_e to 6.7–6.1. This was ascribed to the formation of outer-sphere complexes between Cd(II) and the FMBO surface and the substitution Cd²⁺ for H⁺ of surface hydroxyl groups (Eq. (3)). The lowered pH inhibited the adsorption of Cd(II) whereas it improved that of Sb(V) (Fig. 5).

3.3.2. FTIR spectra

Fig. 8 illustrates the FTIR spectra of FMBO with adsorbed Cd²⁺ and Sb(V) in single-component and coexisting systems, and spectra of FMBO, K₂Sb(OH)₆, and Cd–Sb(V) precipitate are also shown. The band at 1630 cm^{−1} was assigned to the deformation of water molecules, and this indicated the presence of physisorbed water on these samples. The intense peak at 1386 cm^{−1} was ascribed to the vibration of NO₃[−], the sources of which included the NaNO₃ background electrolyte and the HNO₃ used for pH adjustment.

FMBO showed three typical peaks at 1130, 1052, and 976 cm^{−1}. These peaks corresponded to the bending vibration of the surface hydroxyl groups associated with Fe and Mn oxide, and were the characteristic infrared peaks of FMBO [18,19]. The peak at 1052 cm^{−1} was attributed to the hydroxyl group associated with Fe rather than Mn, as indicated by our previous study [19]. The adsorption of Cd²⁺ and/or Sb(V) weakened these peaks to a large extent, and the peaks at 1130 and 976 cm^{−1} even disappeared accordingly. The hydroxyl groups associated with both Fe and Mn were inferred to participate in the adsorption of Cd²⁺ and Sb(V).

K₂Sb(OH)₆ exhibited three peaks at 689, 588, and 472 cm^{−1}, which may be assigned to the stretching vibration of Sb(V)–O [19], and these peaks can also be observed in the Cd–Sb(V) precipitate. The peak at 472 cm^{−1} showed a slight blue shift to 445 cm^{−1}, and this indicated the formation of Cd–Sb(V) complexes within the Cd–Sb(V) precipitate. The adsorbed Sb(V) in FMBO–Sb(V) and FMBO–Sb(V)–Cd also showed these peaks related to the Sb(V)–O groups. FMBO–Sb(V)–Cd showed more significant peaks than FMBO–Sb(V) did, and this demonstrated the positive effect of Cd²⁺

Fig. 8. FTIR spectra of FMBO, FMBO–Sb(V), FMBO–Cd, FMBO–Cd–Sb(V), Cd–Sb(V) precipitates, and K₂Sb(OH)₆. ([Sb(V)]₀ = 0.5 mmol/L, [Cd(II)]₀ = 0.2 mmol/L; FMBO = 200 mg/L, pH 5.0 ± 0.1).

on Sb(V) adsorption. The intensity of the peak at 689 cm^{−1} was lowest among these three peaks, which might be ascribed to the weakened absorption of the group after its being adsorbed. By comparison, Cd–Sb(V) precipitate with more Sb(V) content showed more intense peaks than either FMBO–Sb(V) or FMBO–Sb(V)–Cd. The introduction of Cd²⁺ contributed to the appearance of two new peaks at 1086 and 879 cm^{−1} for the samples of FMBO–Sb(V)–Cd, FMBO–Cd, and Sb(V)–Cd, and they were attributed to the bending vibration of Cd–O. Additionally, another specific peak at 830 cm^{−1} can only be observed in FMBO–Sb(V)–Cd, which might be ascribed to the Sb–O–Cd stretching vibration.

3.3.3. XPS characterization

The surface elemental composition of FMBO with adsorbed Sb(V) in the presence of Cd²⁺, Mn²⁺, and Ca²⁺ was analyzed by XPS analysis, and results are shown in Table 3. The ratio of Fe to Mn ($R_{\text{Fe:Mn}}$) was close to 3:1 for the original FMBO [18], and then increased to 3.83:1 owing to the release of Mn²⁺. The elemental Mn within FMBO showed the mixed chemical valence of +IV and +III, and the existence of Mn₂O₃ due to the disproportionation reactions between Mn²⁺ and MnO₂ [23]. The adsorption of Sb(V) was achieved by the formation of inner-sphere complexes, and the substitution of –O–Mn groups on the FMBO surface played an important role [24]. In the presence of divalent cations, they tended to form surface complexes with Mn oxide (Eq. (3)), and the enrichment of these cations contributed the increase of $R_{\text{Fe:Mn}}$ to 4.48:1, 4.43:1, and 4.27:1 due to the presence of Cd²⁺, Mn²⁺, and Ca²⁺, respectively. The atomic ratios of Sb increased due to the introduction of these cations with Cd²⁺ exhibiting the most significant improvement, and the highest ratio of Sb was observed accordingly. The XPS spectra of Fe 2p_{3/2}, Mn 2p_{3/2}, Sb 3d_{5/2}, and Sb 3d_{3/2} on the surface of FMBO obtained in different systems are illustrated in Fig. S6, and the chemical valences of Fe, Mn, and Sb were determined accordingly.

The binding energy (BE) of Fe 2p_{3/2} in these samples ranged from 711.0 to 711.2 eV, and the peak shape showed the typical

Table 3

XPS results of FMBO after the adsorption of Sb(V) with the co-existence of Cd^{2+} , Mn^{2+} , and Ca^{2+} ($[\text{Sb(V)}]_0 = 0.5 \text{ mmol/L}$, $[\text{Cd}^{2+}]_0 = [\text{Mn}^{2+}]_0 = [\text{Ca}^{2+}]_0 = 0.2 \text{ mmol/L}$, FMBO = 200 mg/L, pH 5.0 ± 0.1).

Sample	Atomic ratios (%)					Binding energy (eV)				FWHM (eV)	
	Fe(t)	Mn(t)	O(t)	Sb	Cd	Mn 2p _{3/2}	Sb 3d _{5/2}	3d _{3/2}	Fe 2p _{3/2}	Sb	Mn
FMBO–Sb(V)	24.57	6.41	48.77	2.15	N	642.5	540.2	531	711.1	1.34	2.82
FMBO–Cd–Sb(V)	20.72	4.63	51.44	3.99	0.74	642.5	540.2	531	711.1	1.37	3.16
FMBO–Mn–Sb(V)	21.45	4.84	52.1	3.85	N	642.3	540.2	531	711	1.35	3.08
FMBO–Ca–Sb(V)	20.45	4.79	51.26	3.8	N	642.5	540.2	531	711.2	1.37	2.89

Fe(III) signals of Fe2p_{3/2} spectra. This indicated that the chemical valence of Fe showed little variation. After the adsorption of Sb(V), the BE of Mn 2p_{3/2} was determined to be 642.5 eV and was close to that of the original FMBO (642.6 eV) [18]. The presence of Cd^{2+} and Ca^{2+} had little effect on the BE of Mn 2p_{3/2}, whereas in case of Mn^{2+} addition, the BE of Mn 2p_{3/2} decreased to 642.3 eV due to the adsorption of Mn^{2+} . The observed BE of Sb in different samples were the same at 540.2 eV for Sb3d_{5/2} and 531.0 eV for Sb3d_{3/2}, and this indicated that Sb(V) dominated in these samples and showed no variation in chemical valence. These results indicated that oxidation and reduction reactions rarely occurred in the adsorption of Sb(V) onto FMBO. Additionally, the results showed that these divalent cations increased the intensity of Sb3d_{3/2}, and the fact that Cd^{2+} showed the most significant improvement was in accordance with previous results.

3.3.4. Dominant mechanisms

The adsorption of negative Sb(V) ions onto the FMBO surface may first be attributed to the electrostatic interaction. The adsorption of Sb(V) lowered the surface charge, whereas the divalent cations such as Cd^{2+} contributed to the elevation of surface charge and benefited Sb(V) adsorption thereafter. However, this effect cannot fully explain the observed remarkably positive effect of Cd^{2+} on Sb(V) adsorption at $[\text{Cd(II)}]_{\text{equilibrium}}$ at above 0.5 mmol/L, in case of which the $Q_{\text{max,Sb(V)}}$ can hardly be determined from the direct graphic maximal capacity (Fig. 2). It is noted that Cd(II) cannot directly form Sb(V) precipitates to contribute to the removal of Sb(V) at their experimental concentrations (Fig. S2). However, in the adsorption of Sb(V) onto Cd(II)-enriched surfaces, the formation of Cd(II)–Sb(V) precipitates may occur and improve the Sb(V) adsorption. Jiang et al. has investigated the co-adsorption and co-precipitation behaviors of arsenate and cadmium on goethite, and it is observed that arsenate shows positive effects on the adsorption of Cd over a wide range of initial Cd concentrations; however, the improved arsenate adsorption can only be observed at its high initial concentration when the co-precipitation reaction occurs [25]. Bothe and Brown, also reported Ca-induced enhancement of As(V) sorption, and the formation of CaHAsO_4 and $\text{Ca}_3(\text{AsO}_4)_2$ precipitates was proposed [26]. Hu et al. also reported the formation of $\text{Cd}_3(\text{AsO}_4)_2$ between Cd(II) and As(V) [27]. To evaluate this effect in Sb(V) adsorption, the adsorption density of these cations onto FMBO at pH 5.0 and 7.5 was investigated, and Cd(II) showed the highest adsorption density among these cations (Fig. S8). The formation of Cd(II)–Sb(V) precipitates on the FMBO surface, as expressed by $-\text{Cd} \cdots \text{Sb(V)}$ in (Eq. 4), is proposed to occur, and further study is required to provide direct information on these species. This effect contributed to its higher efficacy in the improvement of Sb(V) adsorption than either Ca^{2+} or Mn^{2+} .

4. Conclusions

From an engineering point-of-view, most heavy metal wastewaterers include many toxic elements rather than one species. For wastewater with coexisting Cd(II) and Sb(V), their simultaneous removal can be achieved by adsorption onto FMBO over a wide pH range from 2 to 12. The adsorption of Sb(V) decreases whereas that of Cd(II) increases with elevated pH, and $Q_{\text{Sb(V)} + \text{Cd(II)}}$ is close to 2 mmol/g in the pH range 4–9. pH optimization is a feasible strategy to achieve their simultaneous removal on the basis of the ratios of Cd(II) to Sb(V). Besides this, Cd(II) shows a positive effect on the adsorption of Sb(V) by FMBO, and more significant improvement is observed in comparison with either Ca^{2+} or Mn^{2+} . The pH_{iep} of FMBO shifts from 5.7 to 6.9, 6.2, and 6.1 in the presence of Cd^{2+} , Mn^{2+} , and Ca^{2+} at 0.2 mmol/L, respectively. Hydrous Cd^{2+} has a smaller ionic radius and thus more significant ability to compress the double-layer of FMBO than hydrous Mn^{2+} . Compared to Ca^{2+} with similar ionic radius, the adsorption density of Cd^{2+} is much higher than that of Ca^{2+} , and the formation of Cd–Sb(V) precipitates on the FMBO surface also occurs. The improved adsorption of Sb(V) onto FMBO is due to the increased ζ -potential and the enrichment of Cd^{2+} on its surface.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2015.08.020>.

References

- [1] USEPA, Antimony an Environmental and Health Effects Assessment, 1984.
- [2] USEPA, Water Related Fate of the 129 Priority Pollutants, 1 (1979).
- [3] M. Filella, N. Belzile, Y.W. Chen, *Earth-Sci. Rev.* 57 (2002) 125.
- [4] K.A. Herbst, G. Rose, K. Hanusch, H. Schumann, H.U. Wolf, *Ullmann's Encyclopedia Ind. Chem.* 3 (1985) 55.
- [5] M.C. He, X.Q. Wang, F.C. Wu, *Sci. Total Environ.* 421 (2012) 41.
- [6] P.M. Ashley, D. Craw, B.P. Graham, D.A. Chappell, *J. Geochem. Explor.* 77 (2003) 1.
- [7] M.C. He, *Environ. Geochem. Health* 29 (2007) 209.
- [8] X.J. Guo, K.P. Wang, M.C. He, *J. Environ. Sci. China* 26 (2014) 1549.
- [9] S. Fu, C.Y. Wei, *J. Soil Sediment* 13 (2013) 106.
- [10] M. Filella, N. Belzile, Y.W. Chen, *Earth-Sci. Rev.* 59 (2002) 265.
- [11] J.M. Skeaff, R. Beaudoin, R.P. Wang, B. Joyce, *Integr. Environ. Assess. Manag.* 9 (2013) 98.
- [12] A.K. Leuz, J.H. Stephan, W. Beranhard, C.A. Johnson, *Environ. Sci. Technol.* 40 (2006) 2565.

- [13] J. Li, W. Qian, S.Z. Zhang, D. Qin, G.J. Wang, *Int. Biodeter. Biodegr.* 76 (2013) 76.
- [14] N. Belzile, Y. Chen, Z. Wang, *Chem. Geol.* 174 (2001) 379.
- [15] A.K. Leuz, H. Monch, C.A. Johnson, *Environ. Sci. Technol.* 40 (2006) 7277.
- [16] S.C. Wilson, P.V. Lockwood, P.M. Ashley, M. Tighe, *Environ. Pollut.* 158 (2010) 1169.
- [17] X.J. Guo, Z. Wu, M.C. He, *Water Res.* 43 (2009) 4327.
- [18] G.S. Zhang, J.H. Qu, H.J. Liu, R.P. Liu, G.T. Li, *Environ. Sci. Technol.* 41 (2007) 4613.
- [19] W. Xu, H.J. Wang, R.P. Liu, X. Zhao, J.H. Qu, *J. Colloid Interface Sci.* 363 (2011) 320.
- [20] W. Xu, H.C. Lan, H.J. Wang, H.M. Liu, J.H. Qu, *Front. Environ. Sci. Eng. China* 8 (2011) 58.
- [21] G.S. Zhang, J.H. Qu, H.J. Liu, R.P. Liu, R.C. Wu, *Water Res.* 41 (2007) 1921.
- [22] J.A. Davis, D.B. Kent, Surface Complexation Modeling in Aqueous Geochemistry, in: M.F. Hochella Jr., A.F. White (eds.), *Mineral-water Interface Geochemistry*, Mineralogical Society of America. *Reviews in Mineralogy* 23 (1990) 177.
- [23] G.S. Zhang, F.D. Liu, H.J. Liu, J.H. Qu, R.P. Liu, *Environ. Sci. Technol.* 48 (2014) 10316.
- [24] R.P. Liu, W., Xu, Z., He, H.C., Lan, H.J., Liu, J.H., Qu, P. Tista, *Chemosphere*, <http://authors.elsevier.com/authorforms/CHEM16354/5207a7be7d60ec1ce302eb73c4838df0>, in press.
- [25] W. Jiang, J.T. Lv, L. Luo, K. Yang, Y.F. Lin, F.B. Hu, J. Zhang, S.Z. Zhang, *J. Hazard. Mater.* 262 (2013) 55.
- [26] J.V. Bothe, P.W. Brown, *Environ. Sci. Technol.* 33 (1999) 3806.
- [27] S. Hu, M.Q. Nie, J.S. Lu, C.Y. Jing, *Environ. Chem.* 30 (2011).