



## Synergistic adsorption of Cd(II) and As(V) on birnessite under electrochemical control

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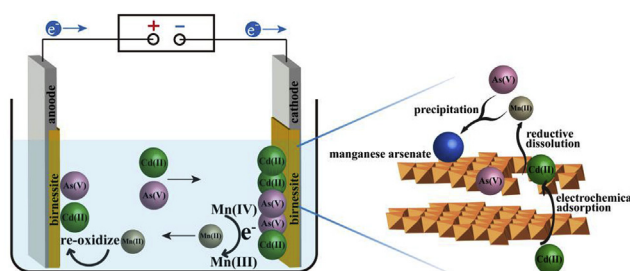
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### HIGHLIGHTS

- Cd(II) and As(V) could be synergistically removed by electrochemical adsorption.
- The removal capacities of 239.7 (Cd(II)) and 149.5 (As(V)) mg g<sup>-1</sup> were achieved.
- Electrochemical redox of birnessite plays a key role in Cd(II) and As(V) removal.
- Coexisting Cd(II) enhances electrochemical adsorption of As(V) on birnessite.
- Voltages above 0.9 V have a negative effect on Cd(II) removal by birnessite.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Manganese oxides are potentially used for the electrochemical removal of heavy metals from wastewater. However, little is known about the performance and mechanism of simultaneous electroadsorption for multiple heavy metals, especially for coexisting anions and cations. In this work, birnessite-type manganese oxide was used for the electrochemical adsorption of coexisting Cd(II) cations and As(V) anions with a symmetrical electrode system, and the effects of the concentrations of coexisting metal ions and applied voltage were investigated. The results indicated that both the Cd(II) and As(V) adsorption capacity of birnessite increased in a mixed solution containing Cd(II) cations and As(V) anions, compared with that in single heavy metal solution. This synergistic effect was mainly ascribed to the formation of manganese arsenate precipitate and the reduction dissolution of birnessite on the cathode and the re-oxidation of Mn(II) with subsequently increased fresh adsorption sites on the anode. The electrochemical adsorption capacity for As(V) increased from 52.7 to 88.0 and 496.0 mmol kg<sup>-1</sup> with increasing Cd(II) concentration from 0.1 to 1.5 mM, respectively, in the mixed solution containing 0.5 mM As(V). The removal efficiency of heavy metals increased first and then decreased with increasing voltage from 0 to 1.2 V. Under the optimum condition at 0.6 V for 12 h, the electrochemical adsorption capacity increased

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with increasing Cd(II) and As(V) concentrations and the highest capacity reached 2132.0 mmol kg<sup>-1</sup> for Cd(II) and 1996.0 mmol kg<sup>-1</sup> for As(V). This work provides a facile technique for the treatment of wastewaters containing metal anions and cations.

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## 1. Introduction

Toxic heavy metals including cadmium and arsenic have been largely discharged into the environment due to rapid industrialization (Resongles et al., 2014). Therefore, the separation and removal of heavy metals from wastewaters are critical for ecological health and resource recovery. Many methods, including adsorption, chemical precipitation and ion-exchange, have been developed to remove heavy metals from aqueous solution (Fu and Wang, 2011). Adsorption is recognized as a promising method for its advantage of high efficiency and simple operation. Easily prepared and low-cost adsorbents such as activated carbons, clay minerals and metal oxides are popular in the development of adsorption materials (Mohan and Pittman, 2007). Among these available adsorbents, manganese oxides are promising candidates due to the abundant natural resources (Hua et al., 2012; Wang et al., 2012).

Despite of their high theoretical adsorption capacity and selectivity for heavy metals, manganese oxides are easily agglomerated due to their small particle size and often exhibit some undesirable performance in actual wastewater treatment (Hua et al., 2012). Some strategies have been developed to improve the adsorption capacity of manganese oxides, such as compositing with porous materials and doping with cations (Yin et al., 2015; Zhu and Li, 2015). Although these methods have been proved to be effective, the preparation processes are relatively complicated with high costs. Therefore, it is necessary to enhance the adsorption capacity of manganese oxides via some cheap and simple alternative approaches. The presence of Mn<sup>3+</sup>/Mn<sup>4+</sup> redox couple contributes to the high redox activity of manganese oxides, which can change the chemical state of heavy metals with variable valence such as chromium, arsenic, and uranium and affect the adsorption capacity of manganese oxides for these heavy metals (Landrot et al., 2012; Wang et al., 2013; Hou et al., 2017). The reduction of MnO<sub>2</sub> by Mn<sup>2+</sup> also facilitates its adsorption for Ni<sup>2+</sup> and Zn<sup>2+</sup> (Lefkowitz and Elzinga, 2015, 2017). The manganese dioxide generated in situ from the reduction of KMnO<sub>4</sub> showed excellent adsorption capacity for Pb<sup>2+</sup> (8616.8 mmol kg<sup>-1</sup>) (Qin et al., 2011). In addition, the reduction of MnO<sub>2</sub> by Mn(II) facilitates the adsorption of As(V) (Manning et al., 2002). Therefore, adjusting the redox state of manganese oxides through some easy and economic methods is a promising way to improve their heavy metal adsorption capacity.

Electrochemical technologies are characterized by high efficiency and eco-friendliness, and great progress has been made in the application of such technologies in wastewater treatment during the latest two decades (Zhang et al., 2013). As super-capacitor electrode materials, manganese oxides can be electrochemically reduced and oxidized (Wei et al., 2011). The adsorption of alkali metals including Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> on MnO<sub>2</sub> can be enhanced by electrochemically controlled redox (Byles et al., 2018a, 2018b), due to that metal ions are adsorbed or intercalated to balance the negative charge of manganese oxides during the electrochemical reduction (Athouël et al., 2008). Our recent work has revealed that the adsorption capacity of birnessite for heavy metals including Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup> and As(III,V) could also be remarkably improved by adjusting the chemical composition of birnessite with electrochemical methods (Liu et al., 2017, 2019; Yang et al., 2018).

These studies are mainly focused on the removal of single heavy metal ions in a reaction system. However, there are usually multiple types of heavy metals in actual wastewaters (Jiang et al., 2013; Liu et al., 2015; Yoon et al., 2017). The coexisting heavy metals may interplay with each other, which affects the corresponding adsorption capacities and behaviors, especially for co-existing cations and anions (Power et al., 2005; Villalobos et al., 2014). The electrochemical adsorption process for the removal of coexisting heavy metals needs extensive studies, which would expand the application of manganese oxides in complicated wastewater systems.

Cd(II) and As(V) are usually found to coexist in acid mine drainage and industrial wastewaters (Yan et al., 2016; Yoon et al., 2017). The maximum concentrations allowed for Cd<sup>2+</sup> and As(V) are 5 and 10 µg L<sup>-1</sup> in drinking water, respectively, as set by the World Health Organization (WHO, 2011). Among various manganese oxides, birnessite is a good candidate for the removal of Cd<sup>2+</sup> and As(III,V) due to its high adsorption capacity and redox reactivity (Manning et al., 2002). Previous studies have shown that the isothermal adsorption capacity of birnessite for single Cd<sup>2+</sup> and As(V) is 1119.1 and 204.6 mmol kg<sup>-1</sup>, respectively (Singh et al., 2010; Peng et al., 2016), and the adsorption capacity could be further enhanced by changing its chemical composition with electrochemically controlled redox reactions (Peng et al., 2016; Liu et al., 2019). However, the competitive or cooperative adsorption mechanism for coexisting Cd<sup>2+</sup> and As(V) on birnessite under electrochemical reactions is still elusive.

In this work, the electrochemical removal of coexisting Cd<sup>2+</sup> and As(V) was investigated using birnessite, and the effect of the concentrations of the coexisting metal ions and cell voltage were also studied. The intermediates were characterized by X-ray diffractometer (XRD), field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS) to elucidate the electrochemical adsorption mechanism.

## 2. Materials and methods

### 2.1. Chemicals and materials

The chemical reagents used in this work were of analytical grade. Manganese sulfate (MnSO<sub>4</sub>·H<sub>2</sub>O), potassium permanganate (KMnO<sub>4</sub>), and potassium sulfate (K<sub>2</sub>SO<sub>4</sub>) were used to synthesize birnessite. Di-sodium hydrogen arsenate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O) and cadmium sulfate (CdSO<sub>4</sub>·3H<sub>2</sub>O) were used to prepare the mixed solution containing As(V) and Cd<sup>2+</sup>. The initial pH of the solution was adjusted to 5.0 using 0.1 M H<sub>2</sub>SO<sub>4</sub> solutions. Manganese oxide was synthesized by the microwave-hydrothermal method (Supporting Information, S1) according to a previous study (Ming et al., 2012), and characterized to be single-phase birnessite (Fig. S1).

### 2.2. Electrochemical adsorption experiments

The electrochemical adsorptions were conducted at room temperature in a 100-mL glass cell containing 30 mL of heavy metal-

containing solution. The electrolytic cell consisted of two-sided birnessite electrodes, and the voltages between the two electrodes were controlled by a battery testing system, and the electrode potential values were measured against the saturated calomel electrode (SCE) by an electrochemical workstation (CHI660E). The preparation method of birnessite electrodes was described in [Supporting Information \(SII\)](#), and birnessite mass was controlled at 10 mg on each electrode. To simply compare the electrochemical adsorption rate for coexisting As(V) and Cd<sup>2+</sup>, adsorption reactions were performed for 3–18 h in a mixed solution containing 0.5 mM Cd<sup>2+</sup> and As(V) (Cd<sup>2+</sup>/As(III) = 1). In order to study the effect of heavy metal concentration on electrochemical adsorption capacity, 0.5–2.5 mM mixed solution of Cd<sup>2+</sup> and As(V) (Cd<sup>2+</sup>/As(III) = 1) was prepared for the adsorption reactions. The cycle performance of the birnessite electrode was tested by periodically reversing the cell voltage. The cell voltage was controlled at 0.6 V for all the above experiments.

The effect of voltage on the adsorption was further investigated. The electrochemical adsorptions were conducted in single and mixed solutions at 0–1.2 V for 12 h. The concentrations of Cd<sup>2+</sup> or As(V) were both 0.5 mM. To investigate the effect of coexisting Cd<sup>2+</sup> on the electrochemical adsorption of As(V), adsorption experiments were performed at 0.6 V in mixed solutions (Cd<sup>2+</sup> (0.1–1.5 mM) or Na<sup>+</sup> (1.0–3.5 mM) and 0.5 mM As(V)) for 12 h. The effect of concentrations of coexisting As(V) on the removal of Cd<sup>2+</sup> was also investigated by the same approach. The electrochemical adsorption capacity of birnessite for heavy metals was calculated by Eq. S1 ([Supporting Information, SIII](#)).

### 2.3. Chemical analysis and characterization

To measure the contents of Cd<sup>2+</sup> and As adsorbed on birnessite, the birnessite electrodes after electrochemical adsorption were acid digested with HCl and HNO<sub>3</sub> (3:1) at 190 °C for 40 min by microwave digestion (CEM Mars 6), followed by the addition of 5 mL 0.01 M hydrochloric acid hydroxylamine (NH<sub>2</sub>OH·HCl) solution to fully dissolve the birnessite coated on electrodes. The concentration of As(V) in the solution was determined by a molybdenum blue method ([Qiu et al., 2017](#)) on an ultraviolet–visible spectrophotometer (UV-1800, Shanghai Mapada Instruments Co., Ltd., China). The concentration of As(III) was measured on an atomic fluorescence spectrophotometer (AFS9700, Beijing Haiguang Instrument Co., Ltd) using 1.5% HCl and 1.5% KBH<sub>4</sub> solution ([Xu et al., 2014](#)). The concentration of total As was the sum of As(III) and As(V) concentration. Dissolved Cd<sup>2+</sup> and

Mn<sup>2+</sup> were quantified by atomic absorption spectroscopy (AAS, Varina AAS240FS).

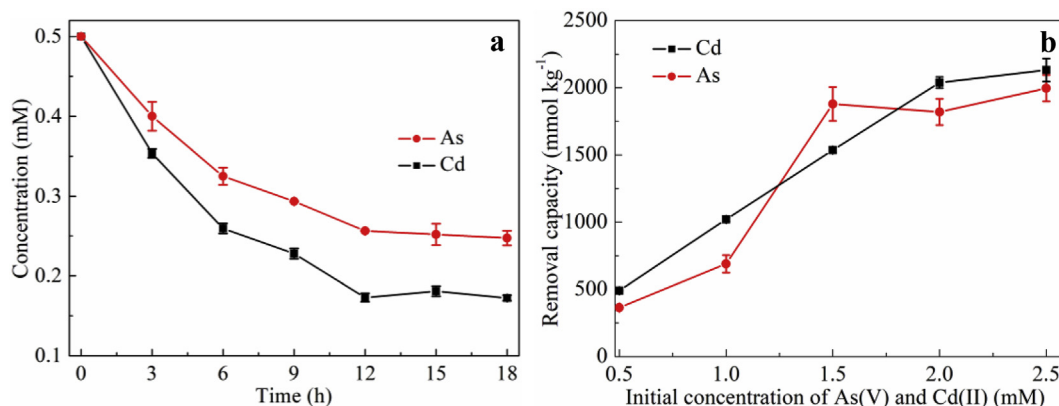
The structure of birnessite was identified by XRD (Bruker D8 Advance diffractometer with Cu K $\alpha$ ) at a scan rate of 2° min<sup>-1</sup>. The synthesized birnessite and intermediates in the adsorption process were characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet 8700), FESEM (Hitachi, SU8000), high-resolution transmission electron microscope (HRTEM, FEI, Talos F200C), and XAS. The Mn average oxidation state (AOS) in birnessite could be determined by Combo method from Mn K-edge XANES spectra ([Manceau et al., 2012](#)). The detailed collection and analysis of XAS were presented in the [Supporting Information \(SIV\)](#). The chemical composition of birnessite electrodes after electrochemical adsorption was also analyzed by XPS (VG Multilb 2000, Thermo Electron Corporation) with Mg K $\alpha$  X-ray.

## 3. Results

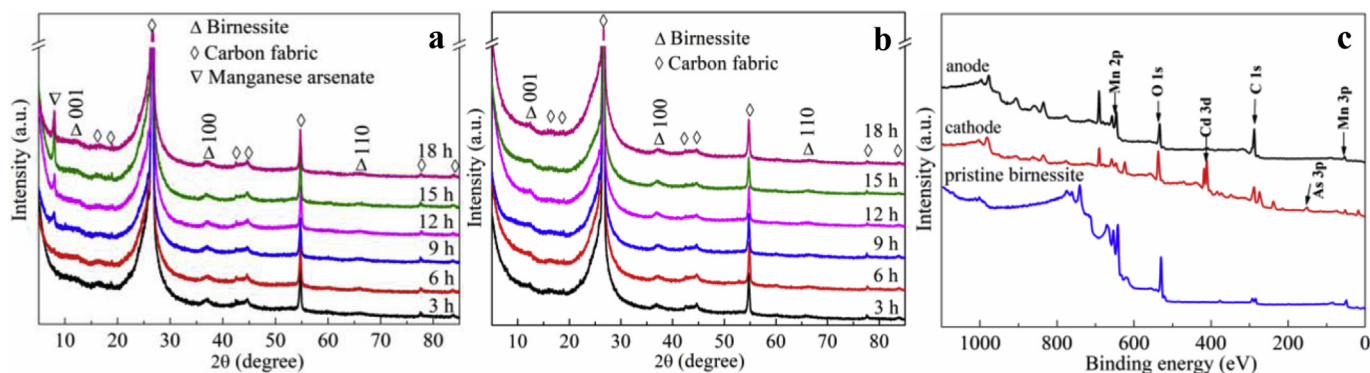
### 3.1. Electrochemical adsorption of Cd(II) and As(V)

The electrochemical adsorption of coexisting Cd<sup>2+</sup> and As(V) on birnessite was conducted in a symmetrical two-electrode system at 0.6 V. The variation in concentrations of heavy metals in mixed solution containing 0.5 mM Cd<sup>2+</sup> and As(V) at different time indicated that the best removal time was 12 h ([Fig. 1a](#)). Neither Cd<sup>2+</sup> nor As(V) was electrochemically adsorbed on the blank electrode (without birnessite) after 12 h of reaction, suggesting that the birnessite on the electrode was responsible for the heavy metal adsorption. The removal efficiency increased with increasing heavy metal concentrations within 0.5–2.5 mM and reached equilibrium at 2.5 mM ([Fig. 1b](#)), and the maximum electrochemical adsorption capacity for Cd<sup>2+</sup> and As(V) respectively reached 2132.0 and 1996.0 mmol kg<sup>-1</sup>, which were remarkably higher than those reported from the isothermal adsorption of birnessite for Cd<sup>2+</sup> and As(V) (1119.1 and 204.6 mmol kg<sup>-1</sup>, respectively) ([Singh et al., 2010](#); [Peng et al., 2016](#)).

The adsorption of heavy metals on birnessite is usually followed by the release of Mn<sup>2+</sup> ([Liu et al., 2017](#)). In this work, the concentration of released Mn<sup>2+</sup> slowly increased from 0.07 to 0.10 mM within 3–18 h ([Fig. S2a](#)), and rose from 0.10 to 0.51 mM when the initial heavy metal concentration was increased from 0.5 to 2.5 mM ([Fig. S2c](#)). The content of released Mn<sup>2+</sup> was positively correlated with the heavy metal adsorption capacity. In addition, a small amount of dissolved As(III) (less than 3% of the initial As(V) concentration) was detected after the reaction ([Figs. S2b and d](#)), which



**Fig. 1.** Concentrations of heavy metals in the mixed solution containing 0.5 mM Cd<sup>2+</sup> and As(V) after electrochemical adsorption at different time (a) and the removal capacities for Cd<sup>2+</sup> and As(V) after 12 h of reaction in the mixed solution with different initial concentrations at 0.6 V (b).

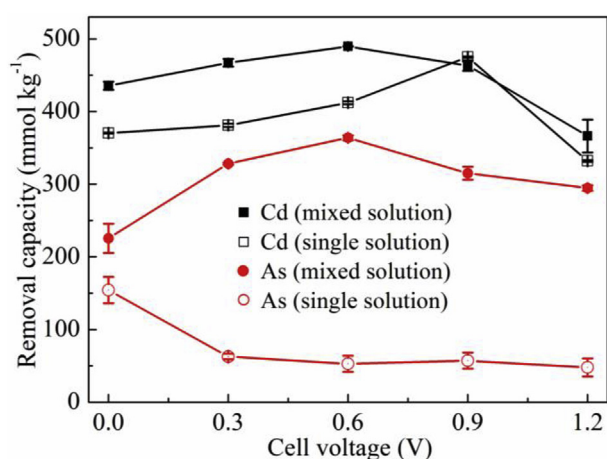


**Fig. 2.** XRD patterns of the birnessite cathode (a) and anode (b) after electrochemical adsorption at different time, and XPS spectra (c) of the pristine birnessite, cathode and anode after electrochemical adsorption for 12 h at 0.6 V in 0.5 mM mixed solution of  $\text{Cd}^{2+}$  and  $\text{As(V)}$ .

might have little effect on  $\text{As(V)}$  adsorption. The generation of  $\text{As(III)}$  was due to the electrochemical reduction of  $\text{As(V)}$  on the cathode.

The changes in the crystal structure and chemical composition of birnessite were analyzed after electrochemical reaction in a mixed solution containing  $\text{Cd}^{2+}$  and  $\text{As(V)}$  of 0.5 mM. As shown by the XRD patterns, new diffraction peaks corresponding to manganese arsenate [ $\text{Mn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ ] (Dias et al., 2008) appeared on the cathode and the intensity increased with reaction time (Fig. 2a), but no other new phase was detected on the anode (Fig. 2b). The formation of manganese arsenate on the cathode was likely attributed to the precipitation of  $\text{As(V)}$  and released  $\text{Mn}^{2+}$ . As shown in Fig. 2c, two absorption peaks of Cd 3d and As 3p could be observed in the XPS spectrum of the cathode after reaction for 12 h; while only one weak peak of Cd 3d was found in the spectrum of the anode, indicating that the birnessite cathode plays a critical role in the removal of both  $\text{Cd}^{2+}$  and  $\text{As(V)}$ .

The electrochemical adsorption experiments were continuously performed in the mixed solutions of 0.5 mM  $\text{Cd}^{2+}$  and  $\text{As(V)}$  to test the cycle performance of the birnessite electrode (Fig. S3). The removal capacity for heavy metals decreased with the cycle number. After eight cycles of continuous use, about 29% ( $139.6 \text{ mmol kg}^{-1}$ ) and 20% ( $73.1 \text{ mmol kg}^{-1}$ ) of the initial  $\text{Cd}^{2+}$  and  $\text{As(V)}$  removal capacities were retained. These results suggested that the surface precipitation of manganese arsenate is not conducive to the continuous use performance.



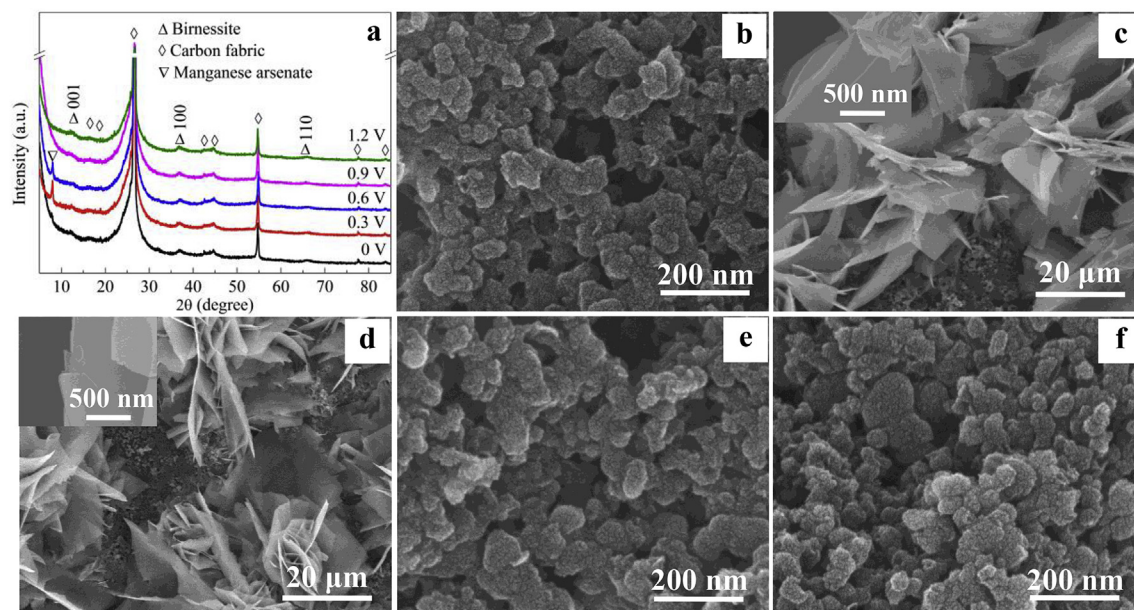
**Fig. 3.** Removal capacities of  $\text{Cd}^{2+}$  and  $\text{As(V)}$  from 0.5 mM  $\text{Cd}^{2+}$  solution,  $\text{As(V)}$  solution, and mixed solution of  $\text{Cd}^{2+}$  and  $\text{As(V)}$  at different cell voltages.

### 3.2. Effect of cell voltage

The applied cell voltage could affect the electrochemical redox of birnessite and the electromigration of heavy metal ions (Peng et al., 2016), and thereby affect the removal performance. After electrochemical reaction in mixed solution of  $\text{Cd}^{2+}$  and  $\text{As(V)}$ , the electrochemical adsorption capacities of heavy metals first increased and then decreased with increasing voltages, and the highest capacity was obtained at 0.6 V (Fig. 3). The variation of the adsorption capacity of  $\text{Cd}^{2+}$  with the change in voltage in single  $\text{Cd}^{2+}$  solution was similar to that in mixed solution. However, the single  $\text{As(V)}$  adsorption capacity was  $154.2 \text{ mmol kg}^{-1}$  at 0 V and decreased to about  $52.0 \text{ mmol kg}^{-1}$  at voltage above 0.3 V. The decrease in electrochemical adsorption capacity of single  $\text{As(V)}$  may be ascribed to the electrostatic repulsion between the cathode and anionic  $\text{As(V)}$ .

The adsorption performance at 0.6 V in mixed solution was further compared with that in single heavy metal solution. The electrochemical adsorption capacity of  $\text{Cd}^{2+}$  and  $\text{As(V)}$  in single solution system reached  $412.3$  and  $52.7 \text{ mmol kg}^{-1}$ , and that in the mixed solution system reached  $489.7$  and  $363.9 \text{ mmol kg}^{-1}$ , respectively, indicating the synergistic adsorption of  $\text{Cd}^{2+}$  and  $\text{As(V)}$ . Fig. S4 and Table S1 present the fitting curves and results of Mn K-edge XANES spectra of birnessite after reaction at 0.6 V. The Mn AOS in the cathode decreased from 3.82 to about 3.72 after electrochemical adsorption in both single  $\text{Cd}^{2+}$  solution and mixed solution of  $\text{Cd}^{2+}$  and  $\text{As(V)}$ , and that of the birnessite cathode in single  $\text{As(V)}$  solution and all birnessite anodes showed no obvious changes, indicating that birnessite on the cathodes was reduced during the electrochemical adsorption in  $\text{Cd(II)}$ -containing solution. To quantify the contribution of the birnessite cathode and anode to heavy metal removal, the contents of  $\text{Cd}^{2+}$  and  $\text{As(V)}$  adsorbed on birnessite electrodes were determined. After adsorption at 0.6 V in single and mixed solutions, the molar ratio of  $\text{As(V)}$  on the cathode to that on the anode was 0.98 and 2.18, and the molar ratio was 2.39 and 2.36 for  $\text{Cd}^{2+}$ , respectively. These results indicated that  $\text{Cd}^{2+}$  tends to be adsorbed on the cathode and the electrochemical adsorption of  $\text{As(V)}$  on the cathode was remarkably enhanced by the presence of  $\text{Cd}^{2+}$ .

Fig. 4a and S5 present the XRD patterns of the birnessite electrodes after electrochemical adsorption at 0–1.2 V. Manganese arsenate could only be formed on the cathodes after electrochemical adsorption at 0.3 and 0.6 V in a mixed solution of  $\text{Cd}^{2+}$  and  $\text{As(V)}$ , and no new compounds were generated in other cases. The changes in the micromorphology of birnessite were investigated by SEM. The flower-like microspheres of birnessite disappeared (Fig. 4 and S6), indicating the dissolution of birnessite



**Fig. 4.** XRD patterns (a) and SEM images of the cathodes after electrochemical adsorption in 0.5 mM mixed solution of  $\text{Cd}^{2+}$  and  $\text{As(V)}$  at cell voltages of 0 V (b), 0.3 V (c), 0.6 V (d), 0.9 V (e) and 1.2 V (f) for 12 h.

during the electrochemical reaction. In addition, some plate-like precipitates with dimensions of about 20  $\mu\text{m}$  appeared on the cathodes after electrochemical adsorption at 0.3 and 0.6 V (Fig. 4c and d). The newly formed precipitates were inferred as manganese arsenate according to the XRD results (Fig. 4a).

### 3.3. Effect of the concentrations of coexisting heavy metals on the adsorption

To better understand the positive effect of coexisting  $\text{Cd}^{2+}$  on the removal of  $\text{As(V)}$ , electrochemical adsorptions were conducted in mixed solutions of 0.5 mM  $\text{As(V)}$  and various concentrations of  $\text{Cd}^{2+}$  or  $\text{Na}^+$  at 0.6 V for 12 h. In the mixed solution of  $\text{Cd}^{2+}$  (0–1.5 mM) and  $\text{As(V)}$ , the  $\text{As(V)}$  adsorption capacity increased with increasing  $\text{Cd}^{2+}$  concentration, and reached the maximum (496.0  $\text{mmol kg}^{-1}$ ) when the initial  $\text{Cd}^{2+}$  concentration was 1.5 mM (Fig. 5a). After adsorption in the mixed solution of  $\text{Na}^+$  (1.0–3.5 mM) and  $\text{As(V)}$ , the electrochemical adsorption capacity for  $\text{As(V)}$  showed little change and stayed steady at about 55.0  $\text{mmol kg}^{-1}$  (Fig. 5b), which was close to that in single  $\text{As(V)}$  adsorption (52.0  $\text{mmol kg}^{-1}$ ) (Fig. 3). These results indicated that the electrochemical adsorption capacity for  $\text{As(V)}$  could be remarkably improved in the presence of heavy metal  $\text{Cd}^{2+}$ , while hardly affected by alkali metal  $\text{Na}^+$ .

The cathodes were characterized by XRD (Fig. 5c). The peak intensity of manganese arsenate increased with increasing  $\text{Cd}^{2+}$  concentration, indicating that the presence of more  $\text{Cd}^{2+}$  facilitated the formation of manganese arsenate, which was further confirmed by the SEM images (Fig. S7). However, no manganese arsenate was generated after electrochemical adsorption in the mixed solution of  $\text{Na}^+$  and  $\text{As(V)}$  (Fig. 5d).

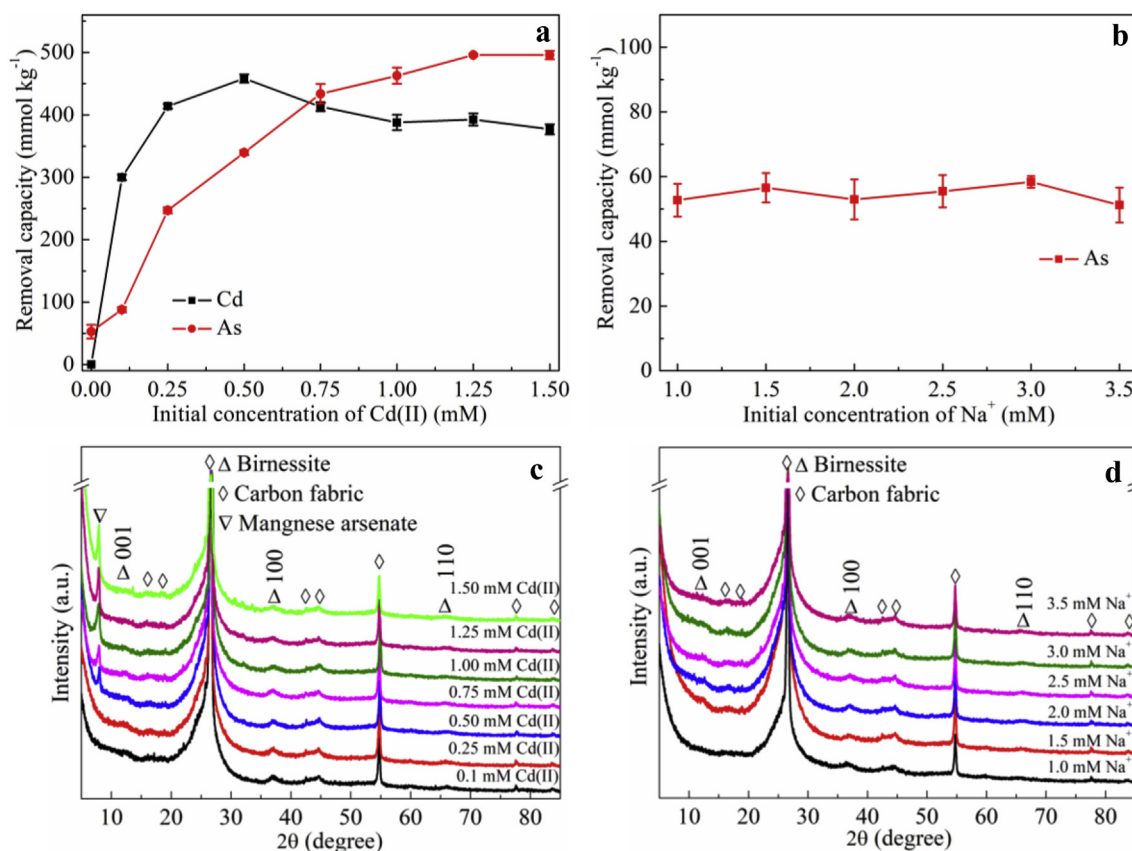
The effect of the concentration of coexisting  $\text{As(V)}$  on the removal of  $\text{Cd}^{2+}$  was also investigated (Fig. S8). The removal capacity for  $\text{Cd}^{2+}$  in a single solution was 412.3  $\text{mmol kg}^{-1}$ , and increased to 491.9  $\text{mmol kg}^{-1}$  in the presence of 0.25 mM  $\text{As(V)}$ . However, further increasing the  $\text{As(V)}$  concentration did not further enhance the removal capacity for  $\text{Cd}^{2+}$ , indicating that the coexisting  $\text{As(V)}$  has less influence on the removal capacity for  $\text{Cd}^{2+}$ .

## 4. Discussion

### 4.1. Mechanism of electrochemical co-adsorption of $\text{Cd(II)}$ and $\text{As(V)}$

The adsorption capacities for  $\text{Cd}^{2+}$  and  $\text{As(V)}$  at 0 V in the mixed solution were respectively 17.6% and 46.2% higher than those in single metal solutions (Fig. 3), suggesting the occurrence of synergistic adsorption of  $\text{Cd}^{2+}$  and  $\text{As(V)}$  during inorganic adsorption. The inorganic adsorption of coexisting  $\text{Cd}^{2+}$  and  $\text{As(V)}$  on birnessite may involve several interaction mechanisms. The adsorption of  $\text{Cd}^{2+}$  might compensate the negative surface charge of birnessite to decrease its electrostatic repulsion against  $\text{As(V)}$ . The  $\text{As(V)}$  anions are easily adsorbed by positively charged materials like iron oxides, while its adsorption on negatively charged manganese oxides is rather limited (Zhang et al., 2009, 2014), and the increase in surface charge due to cation adsorption facilitates  $\text{As(V)}$  adsorption. For example,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  pre-adsorbed on birnessite promote  $\text{As(V)}$  removal (Villalobos et al., 2014). The adsorption of coexisting  $\text{Cd}^{2+}$  might decrease the electrostatic repulsion between  $\text{As(V)}$  and birnessite, allowing the adsorption of more  $\text{As(V)}$ . In addition,  $\text{Cd}^{2+}$  and  $\text{As(V)}$  might form complex on birnessite. Some coexisting heavy metals cannot directly form precipitates in the solution, but coprecipitation occurs on the surface of adsorbent. As reported, the formation of ternary  $\text{Cd(II)-As(V)-goethite}$  complex facilitates  $\text{Cd}^{2+}$  adsorption (Jiang et al., 2013).  $\text{Sb(V)}$  adsorption on Fe–Mn binary oxide could also be enhanced by the co-precipitation of  $\text{Cd}^{2+}$  and  $\text{Sb(V)}$  on mineral surface (Liu et al., 2015). In this study, the possible  $\text{Cd(II)-As(V)}$  precipitates need to be further characterized and clarified in future studies.

When cell voltage was controlled at 0.6 V, higher adsorption capacity for  $\text{Cd}^{2+}$  could be achieved in both single and mixed solutions compared with that at 0 V (Fig. 3). In an electrostatically driven adsorption process, heavy metal ions are attracted by oppositely charged electrodes (Ahualli et al., 2017), and the electroadsorption capacity is positively correlated with the applied voltage (Fan et al., 2016). In this study, the adsorption capacity for  $\text{Cd}^{2+}$  first increased and then decreased with increasing voltage



**Fig. 5.** Removal capacities of heavy metals (a, b) and the corresponding XRD patterns of the cathodes (c, d) after electrochemical adsorption in the mixed solution of 0.5 mM As(V) and different initial concentrations of Cd<sup>2+</sup> or Na<sup>+</sup> at 0.6 V for 12 h.

(Fig. 3), suggesting that electrostatic adsorption is not mainly responsible for Cd<sup>2+</sup> removal. In fact, the electrochemical redox reactions of birnessite would occur under electric field, which promotes the adsorption of heavy metals (Yang et al., 2018). The results of Zn<sup>2+</sup> and Ni<sup>2+</sup> adsorption on birnessite by constant potential electrolysis have confirmed that electrochemical reduction of birnessite plays a crucial role in heavy metal removal (Liu et al., 2017). The enhancement of heavy metal removal capacity was mainly ascribed to the adsorption of cations for balancing the negative charge on birnessite during the electrochemical reduction of Mn(IV) to Mn(III) (Athouël et al., 2008). After electrochemical adsorption reaction in Cd(II)-containing solutions, the Mn AOS of the birnessite cathode decreased (Table S1) with the accumulation of Cd<sup>2+</sup> on the cathode (Fig. 2c), indicating that the electrochemical reduction facilitates the adsorption of Cd<sup>2+</sup> on the cathode.

In the presence of Cd<sup>2+</sup>, the electrochemical adsorption capacity for As(V) was remarkably increased (Fig. 3). The birnessite cathodes were coated by manganese arsenate after electrochemical adsorption in mixed solution of Cd<sup>2+</sup> and As(V) (Fig. 2a). During the oxidation of As(III) by birnessite, the formation of manganese arsenate facilitates the removal of As(V) (Tournassat et al., 2002; Dias et al., 2008). However, the production of manganese arsenate requires sufficient Mn<sup>2+</sup> to generate high thermodynamic driving force (Dias et al., 2008). After electrochemical reaction in single As(V) solution, the birnessite on the cathode could not be electrochemically reduced (Table S1). Therefore, the concentration of released Mn<sup>2+</sup> (0.04 mM) (Fig. S9) was insufficient to produce enough manganese arsenate. Our previous work has revealed that the electrochemical adsorption of Cd<sup>2+</sup> on birnessite involves the reduction of birnessite coupled with the release of Mn<sup>2+</sup> (Peng

et al., 2016). The increase in released Mn<sup>2+</sup> concentration is due to the strong inhibitory effect of the adsorbed heavy metal on the re-oxidation of Mn (Peng et al., 2016; Yang et al., 2018). After the electrochemical adsorption in Cd(II)-containing solution, the birnessite on the cathode was electrochemically reduced (Table S1), accelerating the release of Mn<sup>2+</sup> (Fig. S10a). Thus, As(V) could be removed through forming manganese arsenate with Mn<sup>2+</sup> generated from the birnessite cathode during the electrochemical adsorption in the mixed solution of Cd<sup>2+</sup> and As(V).

The decrease in particle size and disappearance of flower-like microspheres of birnessite suggested the dissolution of birnessite (Fig. 4). The presence of As(III) can also promote As(V) adsorption during the adsorption of As on birnessite (Manning et al., 2002; Tani et al., 2004). The total As adsorption capacity of birnessite is higher in As(III) solution than in As(V) solution (Hou et al., 2017). This higher adsorption capacity is partly due to the reductive dissolution of birnessite after reaction with As(III), exposing more edge sites for As(V) adsorption (Villalobos et al., 2014). In this study, the coexisting Cd<sup>2+</sup> could also lead to the reductive dissolution of birnessite on the cathode during electrochemical adsorption, which contributed to enhanced As(V) adsorption.

After electrochemical adsorption in the mixed solution of Cd<sup>2+</sup> and As(V) at 0.6 V, the ratio of As on the birnessite cathode to that on the anode was 2.18, and the adsorption capacity of As(V) was 363.9 mmol kg<sup>-1</sup>. Thus, the As(V) adsorption capacity of the birnessite anode was calculated to be 114.4 mmol kg<sup>-1</sup>, which was higher than that from single As(V) solution at 0.6 V (52.7 mmol kg<sup>-1</sup>). This result suggests that coexisting Cd<sup>2+</sup> also promotes the adsorption of As(V) on the birnessite anode. The anode at high potential may initiate the electrochemical oxidation

of birnessite or dissolved  $\text{Mn}^{2+}$ , and  $\text{Mn}^{2+}$  could be oxidized by birnessite to form new adsorption sites for As (Lafferty et al., 2010). In this work, dissolved  $\text{Mn}^{2+}$  cations were diffused to the anode and subsequently oxidized on the birnessite anode. This reaction process may be confirmed by the formation of small-sized birnessite on the anode after electrochemical reaction (Fig. S6). Therefore,  $\text{Mn}^{2+}$  released from the birnessite cathode can not only form manganese arsenate with As(V) on the birnessite cathode, but also be re-oxidized, generating new As(V) adsorption sites on the birnessite anode in the electrochemical adsorption processes of  $\text{Cd}^{2+}$ .

#### 4.2. Effect of cell voltage

The adsorption capacity of  $\text{Cd}^{2+}$  in a mixed solution first increased and then declined with increasing voltage (Fig. 3). During the electrochemical adsorption of  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  by birnessite using constant potential electrolysis, the electrochemical reduction of birnessite at appropriate potentials is conducive to the adsorption of heavy metals; however, a relatively low reduction potential would lead to the reduction of birnessite to manganese oxides with low adsorption activity like  $\text{Mn}_3\text{O}_4$  (Liu et al., 2017). Therefore, the heavy metal adsorption capacity first increased and then decreased with decreasing potential from 0.2 to  $-0.2$  V (vs. SCE) (Liu et al., 2017). In this work, with increasing applied cell voltage within 0–1.2 V, the reduction current continuously increased (Fig. S11a), and the potential of the birnessite cathode declined from 0.37 to  $-0.09$  V (vs. SCE) (Fig. S11e). The  $\text{Cd}^{2+}$  adsorption could be promoted by the electrochemical reduction of birnessite at relatively low cell voltages (below 0.9 V); however, when the cell voltage was increased to be higher than 0.9 V, the potential of the cathode was lower than 0 V (vs. SCE), leading to the further reduction of birnessite and a decrease in adsorption ability. In previous studies, some electrochemical adsorptions of manganese oxides for cations were conducted at the cell voltage of 1.2 V (Zhao et al., 2017; Byles et al., 2018a, 2018b). The present work indicated that decreasing the applied cell voltage may achieve better adsorption performance.

As for As(V), its electrochemical removal was promoted by the electrochemical adsorption of  $\text{Cd}^{2+}$  (Figs. 3 and 5a). At relatively low voltages, the increase in cell voltage would result in higher adsorption efficiencies for  $\text{Cd}^{2+}$  and higher concentration of released  $\text{Mn}^{2+}$ , which contributed to the formation of manganese arsenate, the generation of As(V) adsorption sites on the birnessite cathode, and the re-oxidation of  $\text{Mn}^{2+}$  to newly formed birnessite on the birnessite anode. With the application of higher cell voltages (0.9 V or above), the electrochemical adsorption capacity of  $\text{Cd}^{2+}$  decreased, which decreased the reductive dissolution of birnessite and the corresponding As(V) removal. During the oxidation of As(III) by birnessite, the precipitation reaction for the formation of manganese arsenate could be suppressed by the addition of excessive As(III), because excess reductant is not beneficial to the reductive release of  $\text{Mn}^{2+}$  (Dias et al., 2008). In this work, a low concentration of released  $\text{Mn}^{2+}$  (0.05 mM) was observed with the applied voltages no lower than 0.9 V (Fig. S9), inhibiting the formation of manganese arsenate on the cathode (Fig. 4). Therefore, the reductive dissolution of birnessite was promoted at low cell voltages (0–0.6 V), and suppressed at high cell voltages (0.9–1.2 V) during the electrochemical adsorption of  $\text{Cd}^{2+}$ , resulting in first an increase and then a decrease in As(V) removal capacity with increasing voltage (Fig. 3).

## 5. Conclusions

In summary,  $\text{Cd}^{2+}$  and As(V) could be synergistically removed from aqueous solutions through adsorption by birnessite at certain

cell voltage. The enhancement of  $\text{Cd}^{2+}$  adsorption can be mainly attributed to the electrochemical reduction of birnessite on the cathode. The enhanced As(V) removal could be ascribed to the surface precipitation of As(V) and  $\text{Mn}^{2+}$  released from the birnessite cathode in the  $\text{Cd}^{2+}$  adsorption process, as well as changes in the surface micromorphology of birnessite during the reductive dissolution and re-oxidation of birnessite. The simultaneous removal of  $\text{Cd}^{2+}$  and As(V) can be achieved over a wide range of voltage from 0 to 1.2 V, and the electrochemical adsorption capacity first increases and then decreases with increasing voltage. The highest adsorption capacity could reach  $2132.0 \text{ mmol kg}^{-1}$  for  $\text{Cd}^{2+}$  and  $1996.0 \text{ mmol kg}^{-1}$  for As(V) at 0.6 V for 12 h. This work provides a new technique for the treatment of real wastewaters, and expands the understanding of the electrochemical adsorption mechanism of manganese oxides in heavy metal-containing wastewaters.

## CRedit authorship contribution statement

**Xiong Yang:** Conceptualization, Writing - original draft, Visualization. **Qichuan Peng:** Investigation. **Lihu Liu:** Methodology, Formal analysis, Validation. **Wenfeng Tan:** Software. **Guohong Qiu:** Writing - review & editing, Supervision. **Chengshuai Liu:** Resources. **Zhi Dang:** Project administration.

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## Appendix A. Supplementary data

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