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## Efficient removal of Pb(II) ions using manganese oxides: the role of crystal structure

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Manganese oxides have been proven to be promising adsorbents to capture Pb(II) from wastewaters. In nature, MnO<sub>2</sub> can be found in different crystalline structures, while the effect of crystal structure on their adsorption performance remains unclear. In this study, five manganese oxides with different crystallographic phases,  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ -MnO<sub>2</sub> were prepared and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), N<sub>2</sub> adsorption–desorption, Fourier transform infrared (FT-IR) spectroscopy and zeta potential measurements. The adsorptive removal of aqueous Pb(II) was investigated using these manganese oxides as adsorbents. The results showed that the adsorption capacities of manganese oxides for Pb(II) varied with BET surface area and crystalline structure, following the order of  $\delta$ -MnO<sub>2</sub> >  $\alpha$ -MnO<sub>2</sub> >  $\lambda$ -MnO<sub>2</sub> >  $\gamma$ -MnO<sub>2</sub> >  $\beta$ -MnO<sub>2</sub>.  $\delta$ -MnO<sub>2</sub> displayed the highest capacity for Pb(II), and the adsorption was scarcely influenced by the presence of the coexisting Na<sup>+</sup> cation. The surface complexation model was used to describe the Pb(II) adsorption on the MnO<sub>2</sub> adsorbents. In a column adsorption test  $\delta$ -MnO<sub>2</sub> was capable of continuously treating 25 000 bed volumes synthetic wastewater stream with an influent concentration of 20 mg L<sup>-1</sup> Pb(II) and an effluent concentration below 0.5 mg L<sup>-1</sup>. This work indicates that  $\delta$ -MnO<sub>2</sub> has great potential to be used as an effective adsorbent for Pb(II) removal.

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### 1. Introduction

Water pollution by Pb(II) is a serious environmental problem. Wastewaters from various industrial activities usually contain considerable amounts of Pb(II) which can be a severe threat to public health.<sup>1</sup> Toxicity studies have demonstrated that Pb(II) can be accumulated in human body because of its high volatility and non-biodegradability, causing neurological, reproductive and immunological pathologies.<sup>2,3</sup> Therefore, a simple and cost-effective treatment technique to remove Pb(II) from the environment is recognized as a top priority by the World Health Organization (WHO).<sup>4</sup>

Adsorption is considered as an effective and economic technology to remove Pb(II) from water prior to its discharge into the natural environment. A variety of materials have been explored for adsorptive removal of Pb(II) from water, including carbon materials,<sup>5</sup> clay minerals<sup>6,7</sup> and metal oxides (*e.g.* Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>),<sup>8</sup> and MnO<sub>2</sub> was found to be the one of the most active species for Pb(II) removal.<sup>9</sup> Wang *et al.*<sup>10</sup> prepared layered birnessite type MnO<sub>2</sub> and found that the adsorbent was effective for the removal of Pb(II) at pH 4.5. In parallel,

Maliyekkal *et al.* synthesized cellulose–manganese oxide hybrid material for adsorptive removal of Pb(II) in water.<sup>11</sup> It should be emphasized that manganese oxides are suitable for Pb(II) adsorption because of the high specific surface area, low isoelectric point (IEP) and negatively charged surface over a wide pH range.<sup>12</sup> Tonkin *et al.*<sup>13</sup> reported that Pb(II) could be effectively adsorbed on  $\delta$ -MnO<sub>2</sub> within the pH range of 2–9. Moreover, manganese oxides have attracted special attention because of their outstanding structural flexibility, low-cost and environmental friendliness, which have been widely applied in adsorbents,<sup>9</sup> catalysts<sup>14</sup> and cathodes.<sup>15</sup>

Manganese oxides are widely used in adsorption of removing Pb(II) from aqueous solutions. However, according to some recent studies, the adsorption affinity of MnO<sub>2</sub> towards Pb(II) was highly related to the structures and surface properties of MnO<sub>2</sub>. Luo *et al.*<sup>16</sup> studied adsorptive removal of lithium by 3D-MnO<sub>2</sub> from wastewater and found that 3D-MnO<sub>2</sub> with high degree of porosity and large pores exhibited a higher adsorption capacity than 1D-MnO<sub>2</sub>. Kozlova *et al.*<sup>17</sup> prepared complex manganese oxides with different sizes of structural tunnels, and concluded that the tunnel size was the determining factor for the sorption of heavy metal cations. In addition, Korshin *et al.*<sup>18</sup> and Abdullah *et al.*<sup>19</sup> found that heavy metal ions could be complexed at different adsorption sites on birnessite and  $\alpha$ -MnO<sub>2</sub> using EXAFS spectroscopy. Wang *et al.*<sup>10</sup> studied the adsorption mechanisms of Pb(II) onto varied birnessite type

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MnO<sub>2</sub> and found that the adsorption capacities were largely controlled by the Mn average oxidation states and type of sorption sites on the MnO<sub>2</sub> surface. Notably, MnO<sub>2</sub> exists in five main crystallographic forms in nature:  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ - types, as the basic structure unit, [MnO<sub>6</sub>] octahedron, links in different conditions.<sup>20</sup> The crystalline structures are generally believed to be responsible for their chemical and physical properties.<sup>21</sup> The influence of crystal forms on MnO<sub>2</sub> catalytic performance has been extensively studied.<sup>22,23</sup> Different crystallographic MnO<sub>2</sub> materials were also prepared for pollutants adsorption, and MnO<sub>2</sub> adsorbents showed varying adsorption performance depending on the surface area and crystalline structure. Zhang *et al.* investigated the effect of the crystallographic structure of MnO<sub>2</sub> on Li<sup>+</sup> adsorption, and found that MnO<sub>2</sub> ion sieve with  $\lambda$ -crystallographic structure exhibited higher capacity for Li(I) selective adsorption.<sup>24</sup> Kanungo and Parida prepared MnO<sub>2</sub> adsorbents with different crystallographic forms ( $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -MnO<sub>2</sub>), and adsorption of Cu(II) on those adsorbents were studied. They found the layered  $\delta$ -MnO<sub>2</sub> showed the highest adsorption capacity and the adsorption capacity was directly related to BET surface area.<sup>25</sup> To gain a better understanding of the effect of MnO<sub>2</sub> structure on adsorption behaviors, the adsorption comparison of Pb(II) on  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ -MnO<sub>2</sub> were made in our experiments. However, to the best of our knowledge, no attempt has been made.

In this study,  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ -MnO<sub>2</sub> were prepared and characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR), N<sub>2</sub> adsorption/desorption and zeta potential measurements. The adsorption properties of the adsorbents toward Pb(II) in aqueous solution were systematically examined for adsorption capacity and effect of water chemistry. The influence of crystal forms of MnO<sub>2</sub> on their adsorption performance was investigated in conjunction with important physicochemical parameters. Column adsorption tests were also carried out to elucidate the applicability of  $\delta$ -MnO<sub>2</sub> in Pb(II) removal from synthetic wastewater effluent.

## 2. Experimental section

### 2.1 Materials and reagents

Chemicals used in the experiments were of analytical grade and were used without further purification. All chemicals including manganese sulfate (MnSO<sub>4</sub>·H<sub>2</sub>O), ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), potassium permanganate (KMnO<sub>4</sub>), lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>), sodium nitrate (NaNO<sub>3</sub>), magnesium nitrate (Mg(NO<sub>3</sub>)<sub>2</sub>), calcium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>) were purchased from Nanjing Chemical Reagents Co., Ltd. Stock solutions of Pb(II) was prepared by dissolving appropriate amount of Pb(NO<sub>3</sub>)<sub>2</sub> in deionized (DI) water.

### 2.2 Preparation of manganese oxides

The  $\alpha$ -MnO<sub>2</sub>,  $\beta$ -MnO<sub>2</sub>, and  $\gamma$ -MnO<sub>2</sub> were prepared by the hydrothermal method according to the literature.<sup>20</sup> In brief, 2.4 g of MnSO<sub>4</sub>·H<sub>2</sub>O and appropriate amount of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5.3 g for  $\alpha$ -MnO<sub>2</sub>, and 3.7 g for  $\beta$ -MnO<sub>2</sub> and  $\gamma$ -MnO<sub>2</sub>) were put

into DI water at room temperature to form a homogeneous solution, which was then transferred into a 40 mL Teflon-lined stainless steel autoclave and heated for 12 h. The hydrothermal temperature was set at 90 °C for  $\gamma$ -MnO<sub>2</sub>, and 140 °C for  $\alpha$ -MnO<sub>2</sub> and  $\beta$ -MnO<sub>2</sub>. After the reaction was completed, the resulting solid product was filtered and washed with DI water, drying at 110 °C for 12 h.

To prepare  $\delta$ -MnO<sub>2</sub>, 1.8 g of KMnO<sub>4</sub> was dissolved in 100 mL DI water, then 30 mL H<sub>2</sub>O<sub>2</sub> (30%) was added dropwise to the solution under fast stirring. The solution pH was kept at 7.0 ± 0.2 using 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and/or KOH. After continuously stirring for another 30 min, the suspension was aged at room temperature for 3 h. Then the aged precipitate was filtered and washed with DI water and dried at 110 °C for 12 h.

The  $\lambda$ -MnO<sub>2</sub> was prepared using LiMn<sub>2</sub>O<sub>4</sub> as the precursor. Four grams of KMnO<sub>4</sub>, 1.5 g of NaCl and 4.5 g of LiCl were grinded thoroughly and transferred to ceramic crucible, followed by a heat-treatment at 600 °C for 5 h.<sup>26</sup> The resulting solid product was added in 200 mL 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> solution under fast stirring for 12 h. After the acid treatment, the suspension was filtered and the solid product was washed with DI water and dried at 110 °C for 12 h.

### 2.3 Characterization of manganese oxides

Powder XRD patterns of the samples were collected on a Rigaku D/max-RA powder diffraction meter with Cu K $\alpha$  radiation (Rigaku, Japan). TEM images of the samples were collected on a Hitachi H-800 transmission electron microscope (Hitachi, Japan). The specific surface areas of the adsorbents were measured by N<sub>2</sub> adsorption/desorption after pretreated at 200 °C under vacuum (1.33 Pa) for 4 h on a Micromeritics ASAP 2020 analyzer (Micromeritics ASAP 2020, USA) at -196 °C (77 K) and were calculated by the Brunauer–Emmett–Teller (BET) method. FT-IR spectra of the samples were recorded on a Nicolet Nexus 870 FT-IR spectrometer (Nicolet, USA) with the KBr pellet technique. An XPS spectrometer (Perkin Elmer PHI 550 ESCA/SAM, USA) equipped with a monochromatized Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV) and a hemispherical electron analyzer was used to analyze the surface properties of the samples. The C 1s peak (284.6 eV) was used for the calibration of binding energy values. Surface zeta potentials ( $\zeta$ ) of the materials were measured using a zeta potential analyzer (Zeta PALS, Brookhaven Instruments Co., USA). Briefly, 0.01 g of materials were dispersed in 100 mL of 1 mmol L<sup>-1</sup> NaCl with varied pH adjusted using 0.1 mol L<sup>-1</sup> HCl or NaOH, and the suspension was allowed to settle for 24 h before zeta-potential measurement.

### 2.4 Adsorption kinetics

To examine the adsorption kinetic of Pb(II) to the adsorbent, 0.25 g of adsorbent was added into a 500 mL round-bottom flasks containing 500 mL of Pb(II) solution with varied initial concentrations under vigorous magnetic stirring. The initial Pb(II) concentrations were 45.0 mg L<sup>-1</sup> for  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\lambda$ -MnO<sub>2</sub>, and 150.0 mg L<sup>-1</sup> for  $\delta$ -MnO<sub>2</sub>. The samples were taken from the flasks at preset time intervals and the adsorbent was removed



by fast filtration. The concentration of Pb(II) in the filtrate was determined by AAS, and the adsorption amount was calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where  $q_t$  ( $\text{mg g}^{-1}$ ) is the adsorption amount at time  $t$ ,  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration of Pb(II) in solution,  $C_t$  ( $\text{mg L}^{-1}$ ) is Pb(II) concentration at time  $t$ ,  $V$  (L) is the solution volume, and  $M$  (g) is the mass of the adsorbent.

## 2.5 Adsorption isotherms

Adsorption isotherms of Pb(II) on the adsorbents were obtained from batch experiments by placing 20.0 mg of adsorbent in 40 mL polytetrafluoroethylene-lined screw cap glass tubules receiving 40 mL of  $\text{Pb}(\text{NO}_3)_2$  aqueous solutions with varied initial concentrations. The pH of the aqueous solutions was adjusted to  $4.0 \pm 0.2$  using  $0.1 \text{ mol L}^{-1}$   $\text{HNO}_3$  or  $\text{NaOH}$ . Then, the samples were shaken at room temperature for 24 h in an orbital shaker. The time period was sufficient to reach apparent adsorption equilibrium based on preliminarily determined adsorption kinetics. After shaking, the sample was filtrated using a  $0.45 \mu\text{m}$  filter, and Pb(II) concentration in the filtrate determined by AAS. The adsorbed amount of Pb(II) at equilibrium was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are the adsorbed concentration and aqueous concentration of Pb(II) at equilibrium, respectively,  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial Pb(II) concentration,  $V$  (L) is the solution volume, and  $M$  (g) is the adsorbent mass.

The impact of ionic strength and pH on Pb(II) adsorption was tested in the presence of  $\text{NaNO}_3$  solutions with varied concentrations (0.001, 0.01, and  $0.10 \text{ mol L}^{-1}$ ) in a pH range of 2.5–10.0. The initial Pb(II) concentrations were  $45.0 \text{ mg L}^{-1}$  for  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\lambda$ - $\text{MnO}_2$ , and  $150.0 \text{ mg L}^{-1}$  for  $\delta$ - $\text{MnO}_2$ . The initial pH of Pb(II) solution was adjusted using  $0.1 \text{ mol L}^{-1}$   $\text{HNO}_3$  or  $\text{NaOH}$ , and the pH of all samples was measured after adsorption equilibrium. All adsorption experiments were conducted in duplicate.

## 2.6 Fixed-bed column adsorption

The experiments of column adsorption were carried out in a polyethylene column (1.78 mm internal diameter, 130 mm in length) equipped at room temperature. The wet  $\delta$ - $\text{MnO}_2$  (bed volume = 2.0 mL,  $M = 3.27 \text{ g}$ ) or silica sand was packed within the columns before operation. A control of only silica sand was also tested and the results revealed that the silica sand did not adsorb Pb(II) (data not shown). A synthetic influent solution containing Pb(II) ( $20.0 \text{ mg L}^{-1}$ ), Na(I) ( $100.0 \text{ mg L}^{-1}$ ), Mg(II) ( $100.0 \text{ mg L}^{-1}$ ) and Ca(II) ( $150.0 \text{ mg L}^{-1}$ ) was pumped upflow through the column at flow rate of  $15.0 \text{ mL h}^{-1}$  using a Lange-580 pump (Baoding, China). The effluent was collected regularly by a BSZ-100 programmable fraction collector (Shanghai, China) and measured by AAS. As for the regeneration test,

a mixed solution containing  $0.1 \text{ mol L}^{-1}$   $\text{HNO}_3$  and 5 wt%  $\text{Ca}(\text{NO}_3)_2$  was used as the regenerant and the flow rate was  $7.5 \text{ mL h}^{-1}$ .

# 3. Results and discussion

## 3.1 Characterization of adsorbents

The XRD patterns of varied  $\text{MnO}_2$  adsorbents are compiled in Fig. 1. For  $\alpha$ - $\text{MnO}_2$ , diffraction peaks were identified with  $2\theta$  at  $22.5^\circ$ ,  $28.7^\circ$ ,  $37.5^\circ$ ,  $42.0^\circ$ ,  $49.9^\circ$ ,  $56.6^\circ$ ,  $59.9^\circ$ ,  $65.3^\circ$  and  $68.9^\circ$ , indicative of the presence of manganese oxide with a tetragonal structure.<sup>20</sup> As for  $\beta$ - $\text{MnO}_2$ , diffraction peaks were observed with  $2\theta$  at  $28.6^\circ$ ,  $37.3^\circ$ ,  $40.9^\circ$ ,  $42.8^\circ$ ,  $46.1^\circ$ ,  $56.7^\circ$ ,  $59.3^\circ$  and  $64.9^\circ$ , assigned to rutile structure.<sup>20</sup> The XRD pattern of  $\gamma$ - $\text{MnO}_2$  displayed four distinct diffraction peaks at  $22.2^\circ$ ,  $37.6^\circ$ ,  $42.5^\circ$  and  $56.2^\circ$ , corresponding to manganese oxide resulted from a random intergrowth of blocks of the rutile-type structural units within the Ramsdellite structure.<sup>20</sup> Two low intensity and broad diffraction peaks at  $37.0^\circ$  and  $67.5^\circ$  were observed for  $\delta$ - $\text{MnO}_2$ , characteristic of hexagonal randomly-stacked and single phased birnessite-type  $\text{MnO}_2$ .<sup>27</sup> The diffraction peaks of  $\lambda$ - $\text{MnO}_2$  were identified with  $2\theta$  at  $36.5^\circ$ ,  $38.2^\circ$ ,  $44.4^\circ$ ,  $48.8^\circ$ ,  $58.9^\circ$ ,  $64.6^\circ$ ,  $65.6^\circ$  and  $67.9^\circ$ , indicative of cubic spinel structure for  $\lambda$ - $\text{MnO}_2$ .<sup>26</sup> The XRD results clearly revealed the successful preparation of varied  $\text{MnO}_2$  crystallographic forms.

The TEM images of the five  $\text{MnO}_2$  adsorbents are compared in Fig. 2.  $\alpha$ - $\text{MnO}_2$  (Fig. 2a) was shown to be ribbon-like nanowires with diameters around 10 nm and lengths ranging between 0.06 and  $0.4 \mu\text{m}$ .  $\beta$ - $\text{MnO}_2$  (Fig. 2b) and  $\gamma$ - $\text{MnO}_2$  (Fig. 2c) were observed to be nanorods with average diameters of 100 and 20 nm, respectively. As for  $\delta$ - $\text{MnO}_2$  (Fig. 2d), the layered structure was clearly identified, which was commonly formed by  $\text{MnO}_2$  nanosheets organizing in layer-by-layer structure for multilayer systems. The  $\lambda$ - $\text{MnO}_2$  (Fig. 2e) had a cubic structure with a size about 20 nm, which was consistent with the XRD results. The BET surface areas were 97.5, 14.2, 71.4, 270.8 and 36.6 for  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ - $\text{MnO}_2$ , respectively. The  $\delta$ - $\text{MnO}_2$  with a layered structure exhibited a highest BET surface area, which was likely because the layer spacing of  $\delta$ - $\text{MnO}_2$  was large enough

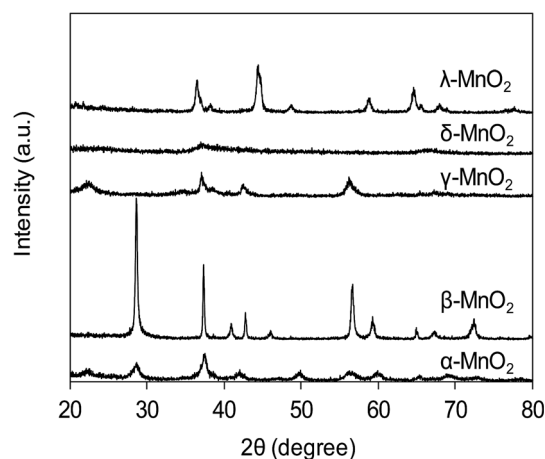


Fig. 1 XRD patterns of synthetic  $\text{MnO}_2$  samples.



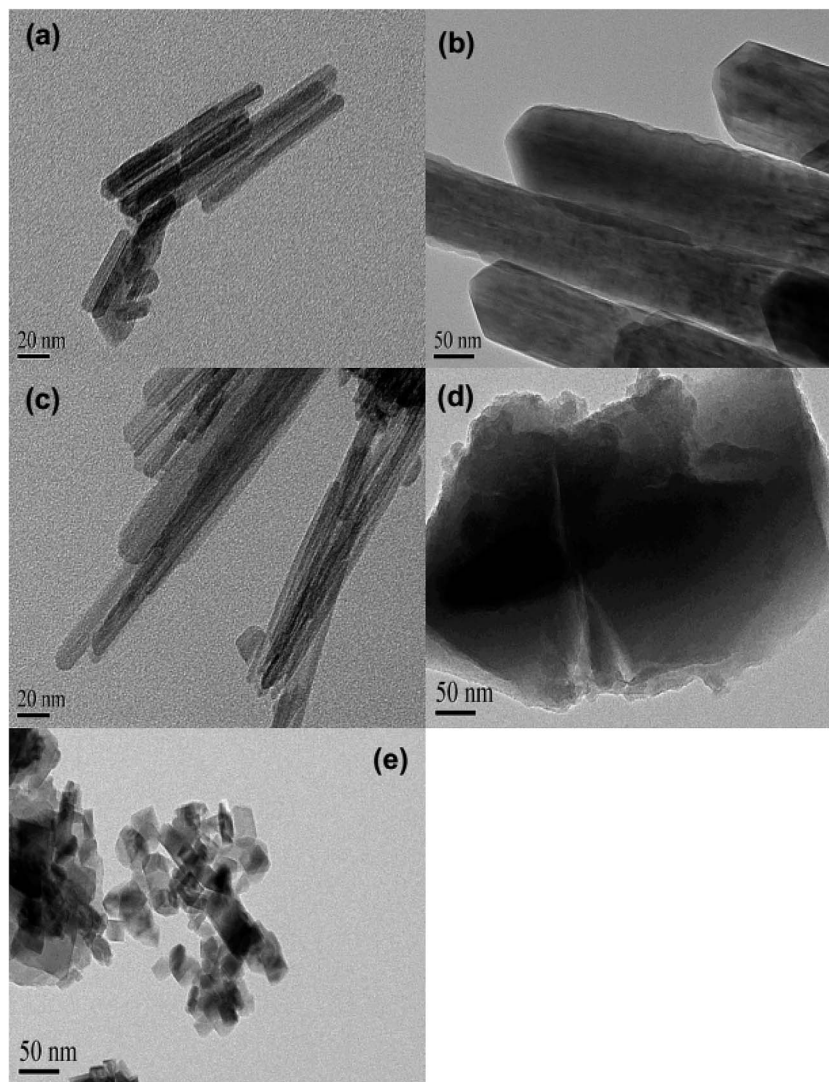


Fig. 2 TEM images of (a)  $\alpha$ -MnO<sub>2</sub>, (b)  $\beta$ -MnO<sub>2</sub>, (c)  $\gamma$ -MnO<sub>2</sub>, (d)  $\delta$ -MnO<sub>2</sub>, and (e)  $\lambda$ -MnO<sub>2</sub>.

to host N<sub>2</sub> molecules. As for  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\lambda$ -MnO<sub>2</sub>, N<sub>2</sub> molecules were mainly adsorbed on the external surface.<sup>23</sup>

The XPS spectra of the adsorbents in the Mn 2p<sub>3/2</sub> and O 1s regions are compared in Fig. 3a and b, respectively. As can be seen in Fig. 3a, the Mn 2p<sub>3/2</sub> spectrums were asymmetrical and could be divided into three peaks at 639.9, 641.2 and 642.2 eV, assigned to Mn<sup>2+</sup>, Mn<sup>3+</sup> and Mn<sup>4+</sup>, respectively.<sup>10,28</sup> To obtain the relative quantity of Mn<sup>2+</sup>, Mn<sup>3+</sup> and Mn<sup>4+</sup> in the adsorbents, the Mn 2p<sub>3/2</sub> spectrums were fitted according to the literature,<sup>10,29</sup> and the fitting results are listed in Table 1. The content of Mn<sup>3+</sup> in  $\alpha$ - and  $\beta$ -MnO<sub>2</sub> were higher than others. According to literature, the higher Mn<sup>3+</sup> content led to fewer cationic vacancies because the Mn<sup>3+</sup> site binding might involve additional complexes when compared to Mn<sup>4+</sup>.<sup>10</sup> The O 1s spectrums (Fig. 3b) of the adsorbents were highly asymmetrical and were divided into two peaks at 528.6–529.0 eV and 530.9–531.0 eV, assigned to oxygen containing species of lattice oxygen and adsorbed oxygen, respectively.<sup>30</sup> The contents of lattice oxygen and adsorbed oxygen in the adsorbents are listed in Table 1. As

for  $\delta$ -MnO<sub>2</sub>, the content of adsorbed oxygen was the highest among the adsorbents, revealing an abundance of surface hydroxyl groups.

The functional groups on MnO<sub>2</sub> surface were studied by FT-IR, and the FT-IR spectra of the adsorbents are compiled in Fig. 4. The broad band appearing at around 3400 cm<sup>-1</sup> was assigned to O–H stretching and the band at 1610 cm<sup>-1</sup> was attributed to O–H bending vibration.<sup>31</sup> For all MnO<sub>2</sub> adsorbents, the characteristic bands at 400–800 cm<sup>-1</sup> were observed, corresponding to the Mn–O lattice vibration.<sup>27</sup> For the layered  $\delta$ -MnO<sub>2</sub> and cubic spinel  $\lambda$ -MnO<sub>2</sub>, the bands around 416, 441 and 512 cm<sup>-1</sup> were recorded, which is in good agreement with reported FT-IR characteristic bands in literature.<sup>27</sup> However, as for the tunnel  $\alpha$ -,  $\beta$ - and  $\gamma$ -MnO<sub>2</sub> the position of those characteristic bands displayed some obvious changes. A weak band around 711 cm<sup>-1</sup> was observed, corresponding to the manganese oxides with tunnel structure.<sup>32,33</sup> Additionally, the band at 1106 cm<sup>-1</sup> was also recorded in the FT-IR spectra of  $\alpha$ - and  $\gamma$ -MnO<sub>2</sub>, characteristic of the vibration of the Mn<sup>3+</sup>–O bond.<sup>27</sup>



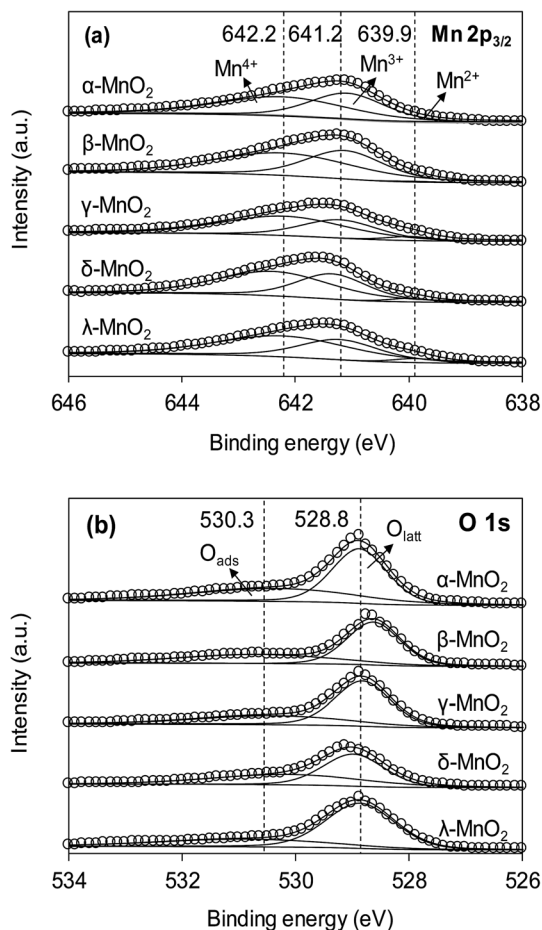


Fig. 3 (a) Mn  $2p_{3/2}$  and (b) O  $1s$  XPS spectra of different  $MnO_2$  adsorbents.

This observation suggests that some  $Mn^{3+}$  occupies the  $Mn^{4+}$  sites in the frameworks of  $\alpha$ - and  $\gamma$ - $MnO_2$ . These results implied that the crystal structure of  $MnO_2$  played a key role in affecting the Mn–O lattice vibration as well as the nature of surface hydroxyl groups.

Surface zeta potentials of the varied crystallographic  $MnO_2$  as a function of solution pH are compared in Fig. 5. Within the test pH range, surface zeta potentials of all adsorbents monotonically decreased due to the continuous deprotonation effect

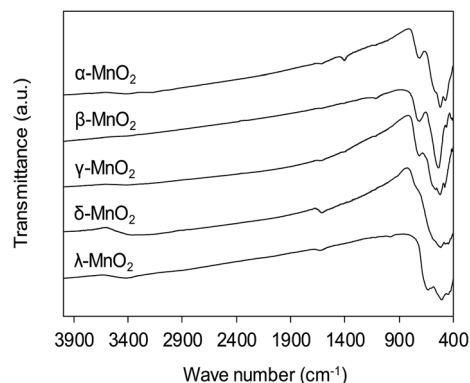


Fig. 4 FT-IR spectra of  $MnO_2$  adsorbents with different crystallographic forms.

of surface hydroxyl groups. The isoelectric points (IEP) of  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ - $MnO_2$  were found to be 2.4, 2.4, 2.0, 1.3 and 2.6, respectively, similar to those reported in literatures.<sup>12,21,26,34</sup> Additionally, negative surface zeta potentials were observed on the five adsorbents over a wide pH range, suggesting the potential for adsorptive removal of Pb(II) in water. Notably, much lower  $\zeta$  potential was observed in  $\delta$ - $MnO_2$  than in others in the test pH range of 1.0–6.0.

### 3.2 Adsorption kinetics

Fig. 6a compares the kinetics of Pb(II) adsorption onto the five  $MnO_2$  adsorbents. It was shown that the adsorption of Pb(II) on  $MnO_2$  adsorbents were very fast. The Pb(II) adsorption amounts increased sharply within 20 min and reached equilibrium at about 150 min. The kinetic data were fitted using the pseudo-second-order kinetic model as follow:<sup>21</sup>

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (3)$$

where  $q_e$  ( $mg\ g^{-1}$ ) and  $q_t$  ( $mg\ g^{-1}$ ) are the adsorbed amount at equilibrium and time  $t$  (min), respectively, and  $k$  ( $g\ mg^{-1}\ min^{-1}$ ) is the pseudo-second-order rate constant. Fig. 6b displays the linear fitting plots of Pb(II) adsorption on the adsorbents to the pseudo-second-order kinetics. The fitting parameters are summarized in Table 2. High correlation coefficients ( $R^2 > 0.99$ ) and the consistency of calculated  $q_{cal}$  values with experimental data indicated

Table 1 The results of XPS Mn  $2p_{3/2}$  and O  $1s$  multiplets peak fitting

Sorbents	Mn <sup>4+</sup>			Mn <sup>3+</sup>			Mn <sup>2+</sup>			O <sub>latt</sub>			O <sub>ads</sub>		
	BE <sup>a</sup> (eV)	FWHM <sup>b</sup> (eV)	At. <sup>c</sup> (%)	BE (eV)	FWHM (eV)	At. (%)	BE (eV)	FWHM (eV)	At. (%)	BE (eV)	FWHM (eV)	At. (%)	BE (eV)	FWHM (eV)	At. (%)
$\alpha$ - $MnO_2$	642.22	2.72	56.1	641.08	1.57	43.9	639.02	1.18	0.0	528.62	1.10	61.7	530.67	3.29	38.3
$\beta$ - $MnO_2$	642.21	2.93	58.3	641.13	1.62	41.1	639.91	0.91	0.6	528.87	1.15	58.9	530.31	3.40	41.1
$\gamma$ - $MnO_2$	642.18	2.64	60.1	641.21	1.61	35.2	639.96	0.96	4.7	528.82	1.15	64.0	530.37	3.17	36.0
$\delta$ - $MnO_2$	642.29	2.38	58.9	641.35	1.46	38.1	639.99	0.85	3.0	528.97	1.26	55.7	530.10	3.20	44.3
$\lambda$ - $MnO_2$	642.21	2.78	60.5	641.22	1.63	35.6	639.87	0.90	3.9	528.86	1.43	71.0	530.86	3.53	29.0

<sup>a</sup> Binding energy. <sup>b</sup> The FWHM of all peaks were constrained. <sup>c</sup> At. represents the percentage of the contribution for each peak to the total number of counts under the Mn  $2p_{3/2}$  or O  $1s$  peak, and all peaks modeled as 70% Gaussian–30% Lorentzian.



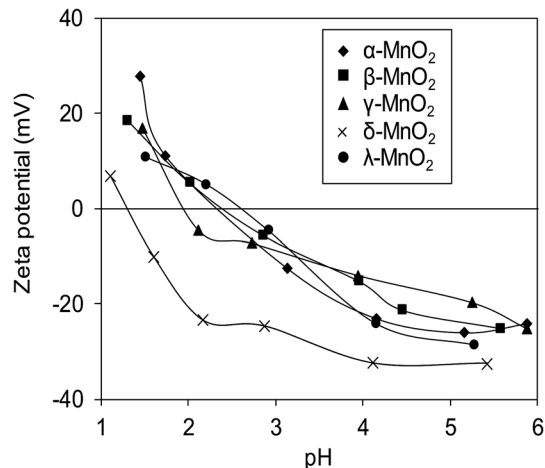


Fig. 5 Zeta potential of different MnO<sub>2</sub> adsorbents as a function of pH.

that Pb(II) uptake onto the adsorbents could be described by the pseudo-second-order kinetic model and were controlled by chemisorption rather than mass transport.<sup>21</sup> The adsorption rates of Pb(II) adsorption on the adsorbents were in the order of  $\gamma\text{-MnO}_2 > \alpha\text{-MnO}_2 > \beta\text{-MnO}_2 > \lambda\text{-MnO}_2 > \delta\text{-MnO}_2$ , reflecting a lower adsorption kinetic on layered MnO<sub>2</sub> adsorbent.

To further verify the controlling mechanism involved in the adsorption process, Weber–Morris model was used to fit the kinetic adsorption data. The model is expressed as follows:<sup>21</sup>

$$q_t = k_i t^{1/2} + C_i \quad (4)$$

where  $k_i$  ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) is the intraparticle diffusion rate constant, and  $C_i$  is the intercept.

Fig. 6c presents the plots of  $q_t$  versus  $t^{1/2}$  for adsorption of Pb(II) onto the five adsorbents, and the fitting parameters are listed in Table 2. The  $q_t$ – $t^{1/2}$  relations clearly exhibited multilinearity, reflecting that the adsorption process appeared to be controlled by more than one step. According to Weber–Morris model, the adsorption process is only controlled by intraparticle diffusion when  $C_i = 0$ . For  $\delta\text{-MnO}_2$ , the  $q_t$ – $t^{1/2}$  plots consisted of three linear portions, and the first linear portion did not pass through the origin, suggesting the involvement of external diffusion.<sup>21</sup> Therefore, the first linear portion was attributed to the fast lead adsorption onto  $\delta\text{-MnO}_2$  external surface and the second one was indicative of Pb(II) diffusion into the interlayer space of the adsorbent, and the third one was characteristic of the final equilibrium step. Notably, the majority of Pb(II) adsorption onto  $\delta\text{-MnO}_2$  was observed in second linear portion and the intraparticle diffusion was slower than the external surface diffusion. In contrast, the Weber–Morris plots of  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\lambda$ -MnO<sub>2</sub> consisted of two linear portions, in which the first linear portion was Pb(II) diffusion to the sorbents external surfaces and the second one was the final equilibrium stage.

### 3.3 Adsorption isotherms

The adsorption isotherms of Pb(II) onto various MnO<sub>2</sub> adsorbents are compared in Fig. 7a. For  $\delta\text{-MnO}_2$ , Pb(II) adsorption

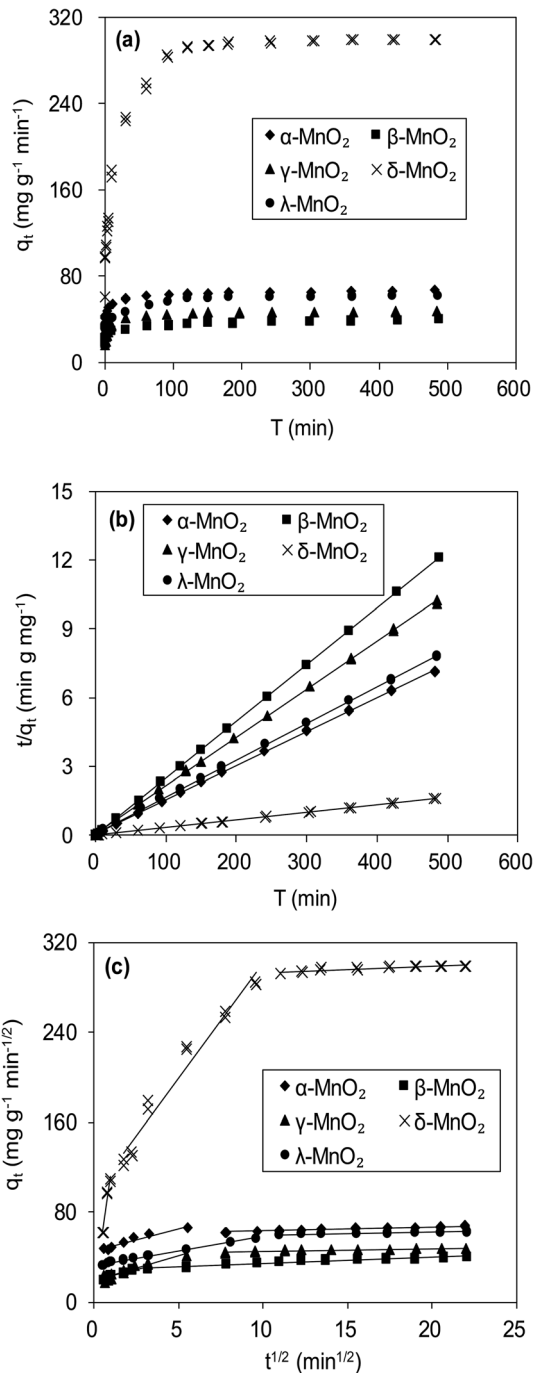


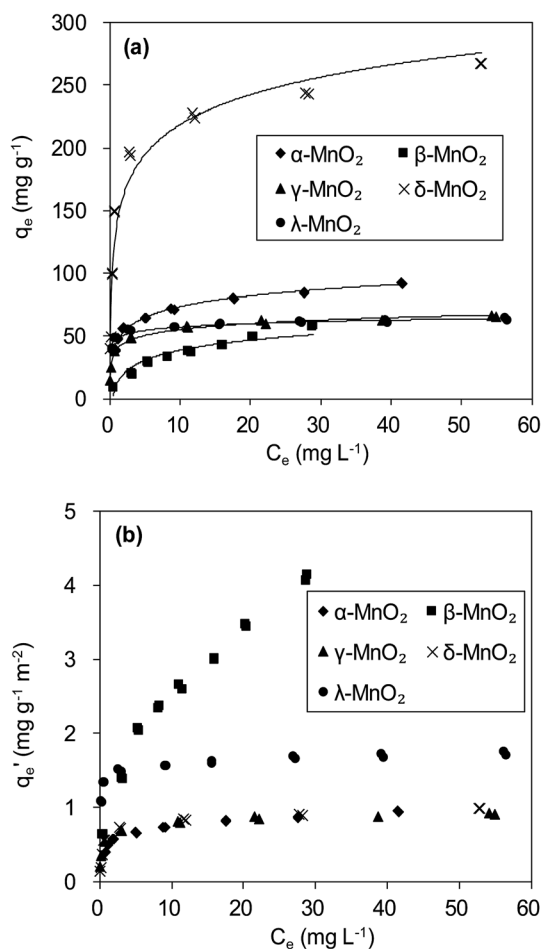
Fig. 6 (a) Time resolved Pb(II) adsorption on MnO<sub>2</sub> adsorbents, and fitting of Pb(II) adsorption kinetics using (b) pseudo second-order model and (c) Weber–Morris model. The initial Pb(II) concentrations were 45.0  $\text{mg L}^{-1}$  for  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\lambda$ -MnO<sub>2</sub>, and 150.0  $\text{mg L}^{-1}$  for  $\delta$ -MnO<sub>2</sub>.

amount was 242.6  $\text{mg g}^{-1}$  at an equilibrium concentration of 28.2  $\text{mg L}^{-1}$ , which was significantly larger than that for  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\lambda$ -MnO<sub>2</sub> (84.4, 58.9, 62.1 and 61.9  $\text{mg g}^{-1}$ , respectively). To analyze the adsorption behavior of the adsorbents, the adsorption isotherms were further modeled using Langmuir and Freundlich models. The Langmuir isotherm model is expressed as follows:



Table 2 Fitting parameters of Pb(II) adsorption kinetics to MnO<sub>2</sub> adsorbents using pseudo second-order and Weber–Morris model

Sorbents	$q_{\text{exp}}$ , mg g <sup>-1</sup>	Pseudo second-order			Weber–Morris model					
		$k$ , mg g <sup>-1</sup> min <sup>-1</sup>	$q_{\text{cal}}$ , mg g <sup>-1</sup>	$R^2$	$k_1$ , mg g <sup>-1</sup> min <sup>-1/2</sup>	$C_1$	$R^2$	$k_2$ , mg g <sup>-1</sup> min <sup>-1/2</sup>	$C_2$	$R^2$
$\alpha$ -MnO <sub>2</sub>	67.6	$4.40 \times 10^{-3}$	67.1	0.99	3.63	40.75	0.94			
$\beta$ -MnO <sub>2</sub>	40.3	$3.42 \times 10^{-3}$	39.7	0.99	3.78	18.82	0.85			
$\gamma$ -MnO <sub>2</sub>	47.9	$5.94 \times 10^{-3}$	47.6	0.99	4.44	18.42	0.90			
$\delta$ -MnO <sub>2</sub>	299.2	$6.07 \times 10^{-4}$	303.0	0.99	36.67	1.65	0.92	20.51	97.27	0.96
$\lambda$ -MnO <sub>2</sub>	62.4	$3.31 \times 10^{-3}$	62.5	0.99	2.59	32.33	0.99			

Fig. 7 (a) Pb(II) adsorption isotherms and (b) BET surface area normalized Pb(II) adsorption isotherms on MnO<sub>2</sub> adsorbents.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (5)$$

where  $q_m$  (mg g<sup>-1</sup>) is the maximum adsorption capacity, and  $b$  (L mg<sup>-1</sup>) is the Langmuir equilibrium constant.

The Freundlich isotherm model can be described as:

$$\log q_e = \log K_f + \frac{1}{n} \log(C_e) \quad (6)$$

where  $K_f$  is Freundlich coefficient that characterizes the adsorption capacity of the adsorbent, and  $n$  is the linearity index which reflects the intensity of adsorption.

The fitting parameters are summarized in Table 3. High correlation coefficients ( $R^2$ ) were achieved for the Langmuir and Freundlich models, indicating that Pb(II) adsorption onto the adsorbents could be well described by these two models. The maximum adsorption capacity  $q_m$  value and Freundlich coefficient  $K_f$  value for  $\delta$ -MnO<sub>2</sub> were both higher in comparison with the other MnO<sub>2</sub>, confirming the largest adsorption capacity of  $\delta$ -MnO<sub>2</sub>. This can be explained by different BET surface area of the five MnO<sub>2</sub> adsorbents. Among the five MnO<sub>2</sub> adsorbents,  $\delta$ -MnO<sub>2</sub> exhibited the largest BET surface area with abundant hydroxyl groups as observed in XPS and FT-IR spectra.<sup>30</sup> Compared with the other three MnO<sub>2</sub> adsorbents,  $\gamma$ - and  $\lambda$ -MnO<sub>2</sub> had larger  $b$  values in Langmuir model, suggesting their high affinity for Pb(II). This is likely due to the high contents of Mn<sup>4+</sup> in  $\gamma$ - and  $\lambda$ -MnO<sub>2</sub>. The charge imbalance on Mn<sup>4+</sup> sites is much higher than on Mn<sup>3+</sup> and Mn<sup>2+</sup> sites and the former sites exhibit higher affinity for metal binding. Thus, structural forms of MnO<sub>2</sub> had great impact on its Pb(II) adsorption performance.

The interaction of Pb(II) with surface hydroxyl groups was confirmed by the XPS results of MnO<sub>2</sub> after Pb(II) adsorption. Fig. 8 displays the XPS spectra of Pb 4f and O 1s of the MnO<sub>2</sub> after Pb(II) adsorption. The MnO<sub>2</sub> adsorbents displayed two peaks with Pb 4f<sub>7/2</sub> and Pb 4f<sub>5/2</sub> derived from spin-orbit splitting. The binding energy of Pb 4f<sub>7/2</sub> core level was observed at around 138.6 eV, reflecting the orthorhombic PbO compound and no hydroxides or carbonates precipitation of Pb during adsorption.<sup>21</sup> As for O 1s spectra, after Pb(II) adsorption the ratio of O<sub>ads</sub> decreased in all MnO<sub>2</sub> adsorbents. This was likely due to the complexation interactions between surface -OH and Pb(II). The increase of O<sub>latt</sub> ratio in Pb(II)-loaded MnO<sub>2</sub> was attributed to the formation of Pb–O–Mn bond and the higher binding energy of O 1s in Pb(II)-loaded MnO<sub>2</sub> confirmed the covalent of Pb–O–Mn linkage.

More insight into the structural properties of the adsorbents with varied crystallographic forms could be gained by comparing the surface area normalized adsorption isotherms, and the results are shown in Fig. 7b. Among the tested adsorbents, the normalized adsorption capacity of  $\beta$ -MnO<sub>2</sub> was much higher. This could be well explained by the interface reaction mechanism inferred from adsorbate–adsorbent polyhedral linkage. Previous studies found that the [MnO<sub>6</sub>] octahedral structure units of the manganese dioxide were connected with the edge and double-corner linkages, and concluded that Pb(II) was adsorbed at double-corner-sharing (DCS) and double-edge-



Table 3 Parameters of Langmuir and Freundlich isotherm model for the adsorption of Pb(II) onto sorbents

Sorbents	Langmuir model			Freundlich model		
	$b$ (L g <sup>-1</sup> )	$q_m$ (mg g <sup>-1</sup> )	$R^2$	$K_f$ (mg <sup>1-n</sup> L <sup>-1</sup> g <sup>-1</sup> )	$n$	$R^2$
$\alpha$ -MnO <sub>2</sub>	1.08	84.0	0.97	45.4	5.08	0.96
$\beta$ -MnO <sub>2</sub>	0.55	42.4	0.93	12.5	2.20	0.99
$\gamma$ -MnO <sub>2</sub>	12.93	51.6	0.92	34.6	5.35	0.94
$\delta$ -MnO <sub>2</sub>	3.57	200.0	0.92	112.2	3.68	0.87
$\lambda$ -MnO <sub>2</sub>	6.92	60.2	0.96	47.5	13.02	0.91

sharing (DES) sites.<sup>35</sup> Notably,  $\beta$ - and  $\lambda$ -MnO<sub>2</sub> is composed of single strands of edge-sharing [MnO<sub>6</sub>] octahedral with 1 × 1 tunnels, while  $\alpha$ - and  $\gamma$ -MnO<sub>2</sub> are constructed from the chains of 2 × 2, 1 × 1 and 1 × 2 tunnels, respectively.<sup>20,36</sup> Thus, more DCS and DES adsorption sites per unit area were observed on  $\beta$ - and  $\lambda$ -MnO<sub>2</sub> surfaces, making them showed higher surface area normalized adsorption capacities of Pb(II). Additionally,  $\delta$ -MnO<sub>2</sub> exhibited nearly identical normalized adsorption capacity to that of  $\alpha$ - and  $\gamma$ -MnO<sub>2</sub>. These results further implied that crystal structure confinement effect was the main factor that affected the adsorption capacity.

The  $q_m$  value for  $\delta$ -MnO<sub>2</sub> (200.0 mg g<sup>-1</sup>) synthesized in this study was also markedly larger than the values reported for

many other adsorbents such as coconut shell carbon (26.5 mg g<sup>-1</sup>),<sup>37</sup> amino-functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (76.7 mg g<sup>-1</sup>),<sup>38</sup> montmorillonite (158.5 mg g<sup>-1</sup>)<sup>7</sup> and nanoscale organo-functionalized SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (183.0 mg g<sup>-1</sup>).<sup>39</sup> Hence, the  $\delta$ -MnO<sub>2</sub> exhibited a significantly higher adsorption capacity than these other adsorbents. Additionally, the synthesis cost of  $\delta$ -MnO<sub>2</sub> was much less than amino-functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, which was feasible for industrial Pb(II) recycling.

### 3.4 Effect of pH and ionic strength

The effects of pH and ionic strength on Pb(II) adsorption to the adsorbents were examined, and the results are presented in Fig. 9. For the five adsorbents, Pb(II) adsorption was significantly affected by the solution pH, which increased continuously in the experimental pH range of 2.5–5.5. It should be noted that Pb(II) would precipitate under high pH (e.g. pH > 7.0) conditions. The effect of pH on Pb(II) adsorption on MnO<sub>2</sub> could be well explained by the electrostatic interaction mechanism. Because surface hydroxyl groups were the adsorption sites, the impact of solution pH on Pb(II) adsorption predominantly depending on the protonation–deprotonation transition of surface hydroxyl groups.<sup>13,21</sup> The results of zeta potential showed that the isoelectric points (IEP) of  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ -MnO<sub>2</sub> were found to be 2.4, 2.4, 2.0, 1.3 and 2.6, respectively, indicated that MnO<sub>2</sub> was negatively charged at pH values above the IEP and electrostatic attractive interaction was expected at high pH, resulting in increased Pb(II) adsorption. When the solution pH values below IEP, MnO<sub>2</sub> was positively charged and repulsive interaction occurred at low pH between Pb(II) and MnO<sub>2</sub>, thus displaying lowered Pb(II) adsorption. The  $\zeta$  potential analysis showed that MnO<sub>2</sub> surface became more negative charged with increasing solution pH, which would enhance the attraction of Pb(II). The nearly negligible Pb(II) adsorption on the sorbents at pH 2.0 suggested that the saturated adsorbent could be regenerated under acidic conditions.

In NaNO<sub>3</sub> solutions, the formation of aqueous Pb(II) complexes with NO<sub>3</sub><sup>-</sup> and OH<sup>-</sup> species might affect the Pb(II) adsorption on MnO<sub>2</sub> as reported in previous work.<sup>41</sup> The aqueous speciation reactions of Pb(II) with the electrolyte anions (OH<sup>-</sup> and NO<sub>3</sub><sup>-</sup>) were described as follows:<sup>40,41</sup>

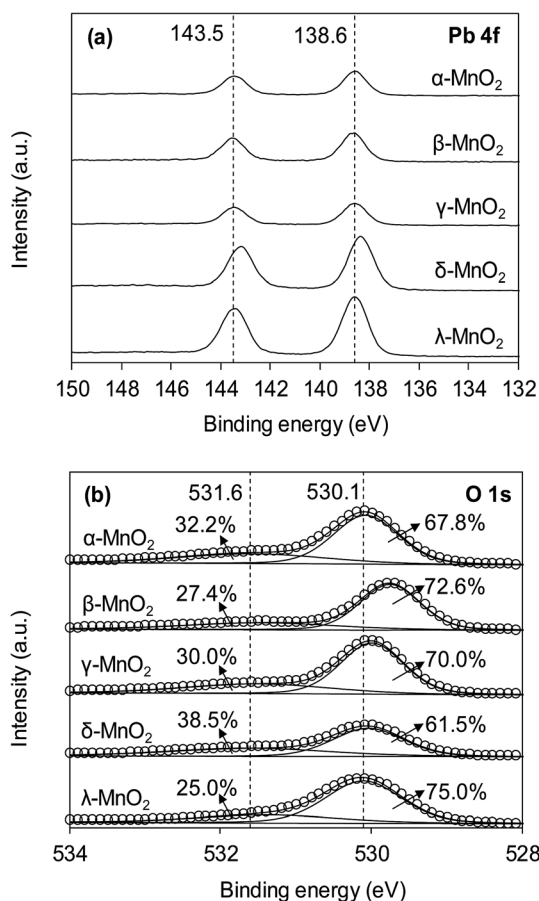
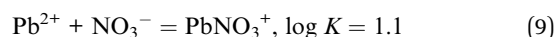
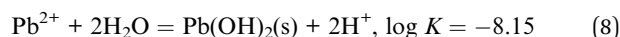


Fig. 8 (a) Pb 4f and (b) O 1s XPS spectra of MnO<sub>2</sub> adsorbents after Pb(II) adsorption.





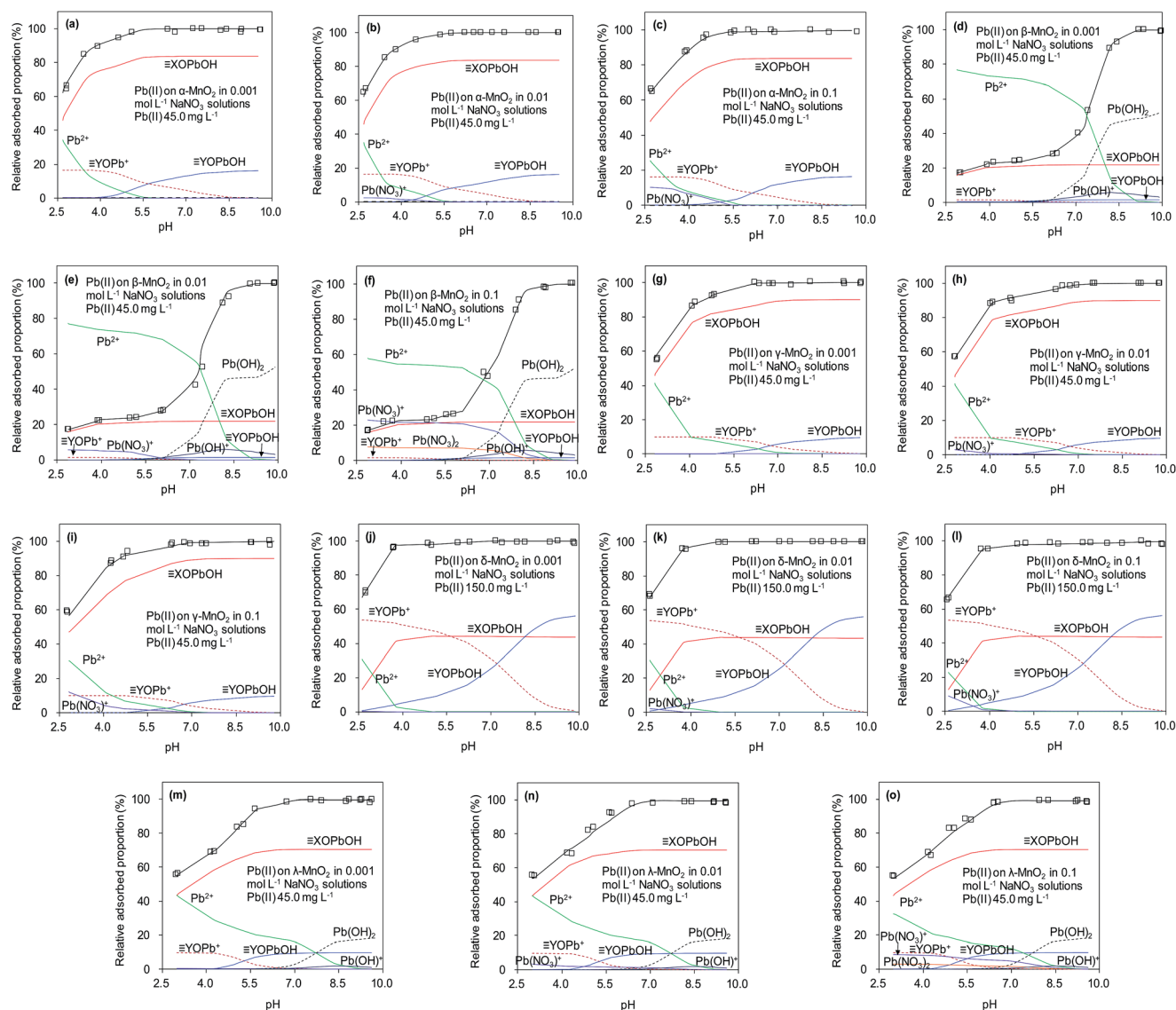
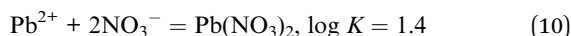


Fig. 9 Surface binding species for Pb(II) adsorbed on the five MnO<sub>2</sub> adsorbents at different solution pH and ionic strengths.



The equilibrium protonation constants and complexation constants with OH<sup>-</sup> and NO<sub>3</sub><sup>-</sup> were calculated at the ionic strength of 0.01 mol L<sup>-1</sup> NaNO<sub>3</sub>, and these constants were also used for the higher ionic strengths. The predicted aqueous complexation of Pb(II) in 0.001, 0.01 and 0.1 mol L<sup>-1</sup> NaNO<sub>3</sub> solutions was performed using the computer program FITEQL 3.2, and the results are shown in Fig. 9. The amount of Pb(OH)<sup>+</sup> species increased with the solution pH, while the amount of PbNO<sub>3</sub><sup>+</sup> species increased with ionic strength. According to the literature, the increase of ionic strength facilitated the formation of the Pb(NO<sub>3</sub>)<sup>+</sup> and Pb(NO<sub>3</sub>)<sub>2</sub> species,<sup>40</sup> whose amounts increased at higher ionic strength at low pH conditions (<5.0). Moreover, the stability of aqueous Pb(II) complexes was enhanced at high ionic strength, which might suppress the adsorption of Pb(II) on the adsorbents. However, due to the high

adsorption capacity of α-, γ-, δ- and λ-MnO<sub>2</sub>, the PbNO<sub>3</sub><sup>+</sup> and Pb(OH)<sup>+</sup> species could also be adsorbed on the negative charged MnO<sub>2</sub> in the tested pH range, suggesting the negligible effect of speciation on Pb(II) adsorption onto α-, γ- and δ-MnO<sub>2</sub>. As for β- and λ-MnO<sub>2</sub>, the poor Pb(II) adsorption capacity within the pH range of 2.5–5.0 implied that a large amount of PbNO<sub>3</sub><sup>+</sup> and Pb(OH)<sup>+</sup> complexes remained in the solutions. The residual PbNO<sub>3</sub><sup>+</sup> and Pb(OH)<sup>+</sup> complexes would precipitate at high pH conditions (>6.0), which was in line with the results of pH effect. Additionally, the observed effect of ionic strength on Pb(II) adsorption on MnO<sub>2</sub> was negligible over the pH range of 2–10, indicating that Pb(II) was adsorbed predominantly *via* inner-sphere complexation. Similar results were also observed by Al Degs *et al.*<sup>42</sup> and Han *et al.*<sup>43</sup> This could be ascribed to the fact that the five MnO<sub>2</sub> adsorbents possessed excellent adsorption selectivity for Pb(II) under the interference of Na(I). Moreover, δ-MnO<sub>2</sub> exhibited a high adsorption capacity of Pb(II) with



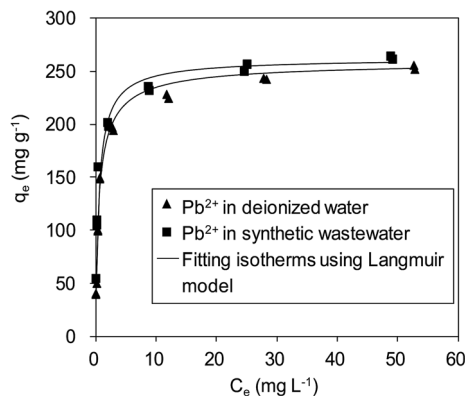


Fig. 10 Adsorption isotherms of Pb(II) on  $\delta$ -MnO<sub>2</sub> in a synthetic wastewater containing 100 mg L<sup>-1</sup> of Na(I), 100 mg L<sup>-1</sup> Mg(II) and 150 mg L<sup>-1</sup> Ca(II).

outstanding selectivity under high ionic strength, indicating a promising potential for Pb(II) adsorptive removal from wastewaters.

To verify the efficiency of using  $\delta$ -MnO<sub>2</sub> to remove Pb(II) from real wastewater, Pb(II) adsorption on  $\delta$ -MnO<sub>2</sub> in a synthetic wastewater containing Na(I) (100.0 mg L<sup>-1</sup>), Mg(II) (100.0 mg L<sup>-1</sup>) and Ca(II) (150.0 mg L<sup>-1</sup>) was studied, and the results are shown in Fig. 10. It is shown that Pb(II) adsorption on the  $\delta$ -MnO<sub>2</sub> adsorbent slightly increased with the co-existing ions in synthetic wastewater at pH 4.0, further indicating that Pb(II) adsorption was mainly driven by the strong inner-sphere complexation interactions between Pb(II) and the hydroxyl groups on  $\delta$ -MnO<sub>2</sub>.<sup>21</sup> The observed effects of coexisting alkaline/earth metal ions on Pb(II) adsorption to  $\delta$ -MnO<sub>2</sub> in synthetic wastewater clarified the validity of using  $\delta$ -MnO<sub>2</sub> as an efficient adsorbent for Pb(II) removal from actual wastewater.

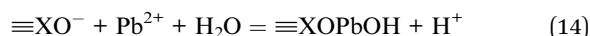
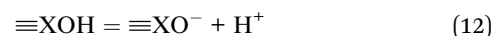
### 3.5 Modeling the adsorption of Pb(II) onto MnO<sub>2</sub>

A number of previous researchers have used the diffuse double layer surface complexation model (SCM) to predict the adsorption of Pb(II) on manganese oxides at different ionic strengths.<sup>44,45</sup> The SCM assumes that only surface complexation occurs on the charged surfaces, consistent with the adsorption mechanism of Pb(II) adsorption to the five MnO<sub>2</sub> adsorbents. Thus, the SCM was chosen to be used in this study to describe the adsorption of Pb(II) to the surface sites on the five MnO<sub>2</sub> adsorbents. The determination of surface equilibrium constants from experimental data was performed using the

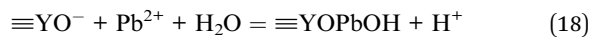
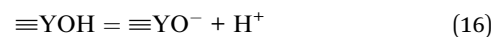
computer program FITEQL 3.2. The surface hydroxyl groups, including DCS and DES sites, at the five MnO<sub>2</sub> adsorbents surface were determined according to the literature,<sup>44</sup> and the results are listed in Table 4. The content of hydroxyl groups on  $\delta$ -MnO<sub>2</sub> was observed to be much higher than those of other MnO<sub>2</sub> adsorbents, which resulted from its largest BET surface area. Manganese oxides with a larger BET surface area possessed more site vacancies, resulting in more surface hydroxyl groups. These results suggested that the BET surface area was the predominant factor affecting the content of hydroxyl groups on manganese oxides.

A two-site model is employed to describe the reactions at manganese oxides surface, and the following reactions were used in FITEQL 3.2 to model Pb(II) adsorption on the five MnO<sub>2</sub> adsorbents surface.

On the DCS sites:



On the DES sites:



The FITEQL failed to simulate the surface species on the five MnO<sub>2</sub> adsorbents because the species  $\equiv\text{XOH}_2^+$  did not exist below the IEP of MnO<sub>2</sub>.<sup>42</sup> The zeta potential analysis showed that the IEP values of the five MnO<sub>2</sub> adsorbents were all below tested solution pH, suggesting that the  $\equiv\text{XOH}_2^+$  and  $\equiv\text{XOPb}^+$  would not be significant species in the present study. Thus, the reaction  $\equiv\text{XOH}_2^+ + \text{Pb}^{2+} = \equiv\text{XOPb}^+ + 2\text{H}^+$  was ignored in this study. All the parameters used to simulate the acid-base chemistry of the five MnO<sub>2</sub> adsorbents are summarized in Table 4.

Fig. 9 presents predicted the surface binding species for Pb(II) adsorbed onto the five MnO<sub>2</sub> adsorbents in 0.001, 0.01 and 0.1 mol L<sup>-1</sup> NaNO<sub>3</sub>. It is apparent that the fitted curves

Table 4 Parameters for modeling the acid-base surface chemistry of MnO<sub>2</sub> adsorbents

Sorbents	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	$\equiv\text{XOH}$ (mmol g <sup>-1</sup> )	$\equiv\text{YOH}$ (mmol g <sup>-1</sup> )	$\log K_{\equiv\text{XO}^-}$	$\log K_{\equiv\text{YO}^-}$	$\log K_{\equiv\text{YOH}_2^+}$
$\alpha$ -MnO <sub>2</sub>	97.5	0.1996	0.0355	-0.86	-1.45	4.35
$\beta$ -MnO <sub>2</sub>	14.2	0.0477	0.0333	-1.24	-1.91	4.61
$\gamma$ -MnO <sub>2</sub>	71.4	0.1993	0.0214	-1.25	-2.67	4.71
$\delta$ -MnO <sub>2</sub>	270.8	0.7093	0.4090	-1.76	-4.52	2.57
$\lambda$ -MnO <sub>2</sub>	36.6	0.1528	0.0208	-1.44	-1.28	4.28



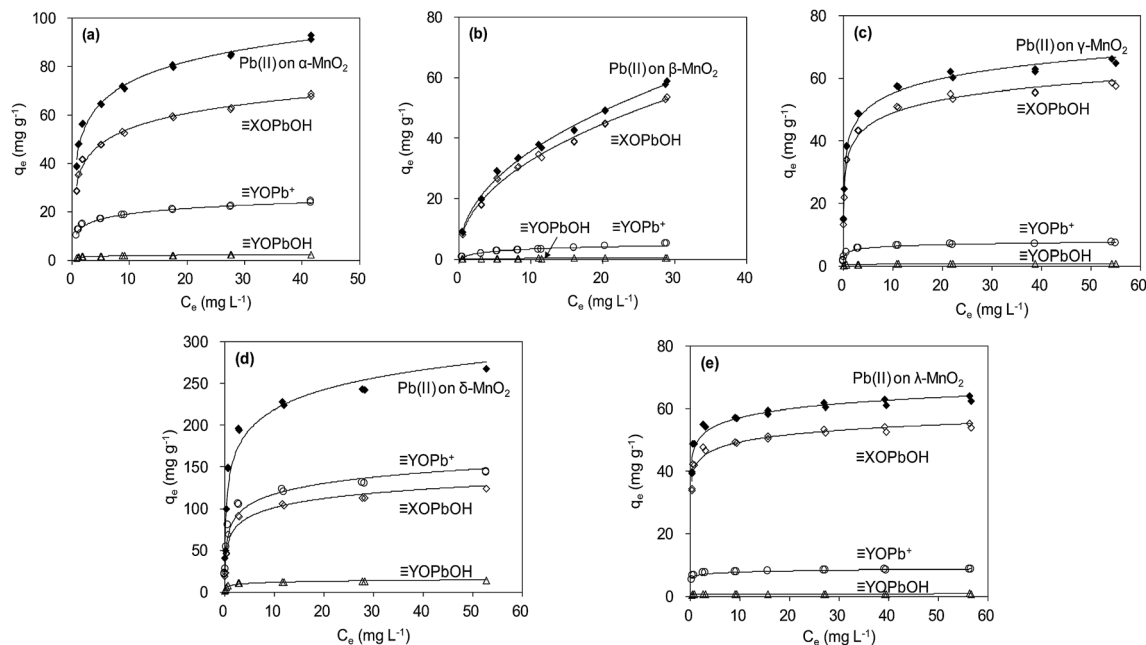


Fig. 11 Modeling Pb(II) adsorption isotherms using diffuse double layer surface complexation model (SCM).

provided a close description of Pb(II) adsorption on the five MnO<sub>2</sub> adsorbents over the tested pH range. Within the pH range of 2.5–10.0, ≡XOPbOH was the predominant species on α-, β-, γ- and λ-MnO<sub>2</sub> surfaces, while ≡YOPb<sup>+</sup> made insignificant contributions to adsorption at acidic to neutral pH conditions. The ≡YOPb<sup>+</sup> species decreased with the increase of solution pH, probably because the OH<sup>-</sup> species increased at higher pH conditions and would bind to the ≡YOPb<sup>+</sup>, resulting in the increase of ≡YOPbOH species on α-, β-, γ- and λ-MnO<sub>2</sub> surfaces. For δ-MnO<sub>2</sub>, ≡YOPb<sup>+</sup> was the predominant species over the pH range of 2.5–5.8, likely due to the large amount of ≡YOH groups on the layered structural surfaces. Notably, Pb(OH)<sub>2</sub> species appeared on the surface of β- and λ-MnO<sub>2</sub> at high pH conditions, suggesting the Pb(II) had precipitated. This is conceivably attributed to the insufficient hydroxyl groups on β- and λ-MnO<sub>2</sub> surfaces for Pb(II) adsorption.

The adsorption isotherm data were reproduced by using parameters estimated from SCM, and the results are shown in Fig. 11. According to the fitting results from SCM, Pb(OH)<sup>+</sup> and Pb(OH)<sub>2</sub> precipitate did not present at low pH conditions (<6.0) (Fig. 9). The aqueous Pb(II) species were Pb<sup>2+</sup> and Pb(NO<sub>3</sub>)<sup>+</sup>. For α-, β-, γ- and λ-MnO<sub>2</sub>, ≡XOPbOH was the dominant species contributing to Pb(II) adsorption at the tested Pb(II) concentration in deionized water. This is likely due to the high Pb(II) concentration in the adsorption isotherm experiment. Similar results were also reported by Uiyama and Fukushi.<sup>41</sup> As for δ-MnO<sub>2</sub>, prediction of surface speciation showed that the ≡YOPb<sup>+</sup> was the dominant species at various Pb(II) concentrations. The difference of dominant surface speciation between δ-MnO<sub>2</sub> and other MnO<sub>2</sub> adsorbents was possibly attributed to the high content of DES adsorption sites and high cation exchange capacity on layered manganese oxides.

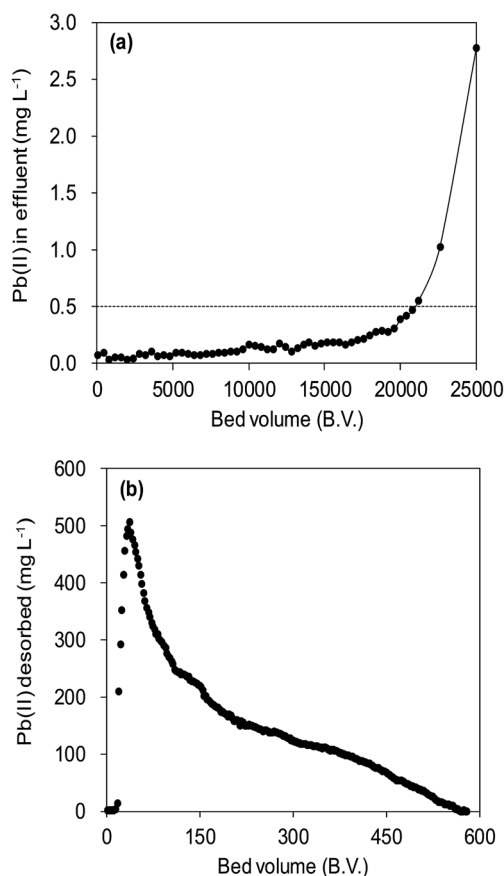


Fig. 12 Fixed-bed column adsorption and regeneration test. (a) Pb(II) removal from a synthetic wastewater by a column bed packed with δ-MnO<sub>2</sub>. Influent Pb(II) was 20 mg L<sup>-1</sup> with 100 mg L<sup>-1</sup> of Na(I), 100 mg L<sup>-1</sup> Mg(II), and 150 mg L<sup>-1</sup> Ca(II), and the flow rate was 15.0 mL h<sup>-1</sup>. (b) Regeneration of Pb(II) preloaded δ-MnO<sub>2</sub> using a mix solution containing 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and 5% (wt) Ca(NO<sub>3</sub>)<sub>2</sub>, and the flow rate was 7.5 mL h<sup>-1</sup>.



Table 5 Estimated parameters of Thomas and Yoon–Nelson models for the sorption of Pb(II) by the  $\delta$ -MnO<sub>2</sub> packed column

$C_0$ (mg L <sup>-1</sup> )	Flow rate (mL h <sup>-1</sup> )	Thomas model			Yoon–Nelson model		
		$k_T$ (L mg <sup>-1</sup> h <sup>-1</sup> )	$Q_m$ (mg g <sup>-1</sup> )	$R^2$	$k_{YN}$ (min <sup>-1</sup> )	$\tau$	$R^2$
20.0	15.0	$4.26 \times 10^{-5}$	$6.27 \times 10^5$	0.82	$8.52 \times 10^{-4}$	$7.32 \times 10^3$	0.82

### 3.6 Fixed-bed adsorption

Fig. 12a illustrated an effluent history of  $\delta$ -MnO<sub>2</sub> fixed-bed column adsorption experiment, which was carried out to evaluate the sorbent applicability in wastewater treatment. The breakthrough point was set as 0.5 mg L<sup>-1</sup> for Pb(II), as the regulated maximum concentration level by the mining industry emission standard of China.<sup>46</sup> The sorbent exhibited a breakthrough at the point of  $\sim$ 25 000 bed volume (BV) under the experimental conditions, indicated that Pb(II) could be efficiently removed by  $\delta$ -MnO<sub>2</sub> till the significant breakthrough occurs. The column adsorption behavior of Pb(II) on  $\delta$ -MnO<sub>2</sub> could be further quantified by the Thomas model and Yoon–Nelson model. The Thomas model can be expressed as follows:<sup>47</sup>

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_T Q_m M}{F} - k_T C_0 t \quad (19)$$

The Yoon–Nelson model is given in eqn (20).<sup>48</sup>

$$\ln \frac{C}{C_0 - C} = k_{YN} t - \tau k_{YN} \quad (20)$$

where  $C_0$  is influent Pb(II) concentration (mg L<sup>-1</sup>),  $C$  is effluent Pb(II) concentration (mg L<sup>-1</sup>) at time  $t$  (h),  $k_T$  (L mg<sup>-1</sup> h<sup>-1</sup>) and  $k_{YN}$  (min<sup>-1</sup>) are the kinetic constants of Thomas model and Yoon–Nelson model, respectively,  $Q_m$  is the maximum solid-phase concentration of the solute (mg g<sup>-1</sup>),  $M$  is the sorbents packed in the column (g),  $F$  is the flow rate (mL h<sup>-1</sup>), and  $\tau$  is the time required for 50% adsorbate breakthrough (h).

The fitting parameters of experimental data are summarized in Table 5. From the regression coefficients it could be concluded that the Thomas and Yoon–Nelson models fitted the experimental data accurately. As was not observed in the present study, the column breakthrough capacity was estimated using the Thomas model according to the literature.<sup>48</sup> The Pb(II) adsorption capacity at the breakthrough point was  $6.27 \times 10^5$  mg g<sup>-1</sup>, which was much higher than the values reported for hydrous Zr(IV) oxide-based nanocomposite (319.4 mg g<sup>-1</sup>) and polyacrylamide-hydrated ferric oxide hybrid material (211.4 mg g<sup>-1</sup>).<sup>48,49</sup> Considering the structure of  $\delta$ -MnO<sub>2</sub>, the higher adsorption capacity was likely due to the capillary condensation, which was used advantageously as universal functionalization strategy in nanoparticle thin films assembled layer-by-layer.<sup>49</sup> The value of  $\tau$  was as large as  $7.32 \times 10^3$  h, also remarkably larger than the reported values.<sup>50,51</sup> These results indicate that  $\delta$ -MnO<sub>2</sub> is highly effective for removal of Pb(II) from water in both batch and fixed-bed mode. Notably, the synthetic method of  $\delta$ -MnO<sub>2</sub> in this study was simple, economic, environmentally friendly, and was suitable for large-

scale production. Therefore,  $\delta$ -MnO<sub>2</sub> could be applied as a cost-effective adsorbent for the adsorptive removal of Pb(II) from wastewater.

The suppressed adsorption of Pb(II) on  $\delta$ -MnO<sub>2</sub> observed at low pH implied that acidic treatment was a feasible approach to regenerating the Pb(II)-loaded adsorbent. The mixed regenerant of 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and 5 wt% wt Ca(NO<sub>3</sub>)<sub>2</sub> was used for the exhausted  $\delta$ -MnO<sub>2</sub> column regeneration at room temperature, and the results are showed in Fig. 12b. The cumulative desorption efficiency was around 20%, and about 80% of Pb(II) preloaded by  $\delta$ -MnO<sub>2</sub> could not be effectively desorbed by the regeneration solution. Such low desorption ratio suggested that the adsorption sites of  $\delta$ -MnO<sub>2</sub> were irreversible and could not be reused. Li *et al.*<sup>35</sup> and Pan *et al.*<sup>52</sup> investigated the adsorption sites of  $\delta$ -MnO<sub>2</sub> by EXAFS and found two distinct sites of  $\delta$ -MnO<sub>2</sub> for heavy metal ions adsorption. They concluded that the edge-linkage inner-sphere complexation were irreversible, while the corner-linkage mode was reversible. Additionally, the ionic strengths effects proved surface complexes were formed by Pb(II) and surface adsorption sites. Thus, we suggested that the edge-linkage inner-sphere complexes were responsible for the irreversible Pb(II) adsorption by  $\delta$ -MnO<sub>2</sub>. Moreover, the ability of  $\delta$ -MnO<sub>2</sub> fixed-bed column to efficiently remove Pb(II) from synthetic wastewaters makes it a good system for large-scale application.

## 4. Conclusions

In this work, we investigated the adsorption behavior of Pb(II) on five manganese oxides with different crystallographic phases.  $\delta$ -MnO<sub>2</sub> showed the highest adsorption capacity due to its high BET surface area and layered structure which was fully accessible for Pb(II). Additionally, the large interlayer spacing and high amount of surface chemisorbed oxygen enhanced the Pb(II) adsorption on  $\delta$ -MnO<sub>2</sub>. On the contrary, adsorption capacities of porous  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\lambda$ -MnO<sub>2</sub> were constrained by the low efficiency of pores and Pb(II) was mainly adsorbed on the external surfaces. The adsorption kinetics of Pb(II) on MnO<sub>2</sub> adsorbents followed the pseudo-second-order model, and the adsorption of  $\delta$ -MnO<sub>2</sub> was no affected by coexisting cations in water. The hydroxyl groups on the MnO<sub>2</sub> surface undergo pH dependent inner-sphere surface complexation reactions. The predominant species on  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\lambda$ -MnO<sub>2</sub> surfaces was  $\equiv$ XOPbOH, while the  $\equiv$ YOPb<sup>+</sup> species was the predominant species on  $\delta$ -MnO<sub>2</sub> surface over the pH range of 2.5–5.8. Column test verified the high working adsorption capacity and durability of  $\delta$ -MnO<sub>2</sub> and therefore highlighted its promising potential as an effective adsorbent for the removal of heavy metal ions in water.



## Conflicts of interest

There are no conflicts of interest to declare.

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