Full length article

Removal of aqueous Pb(II) by adsorption on Al$_2$O$_3$-pillared layered MnO$_2$

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**A B S T R A C T**

In the present study, Al$_2$O$_3$-pillared layered MnO$_2$ (p-MnO$_2$) was synthesized using δ-MnO$_2$ as precursor and Pb(II) adsorption on p-MnO$_2$ and δ-MnO$_2$ was investigated. To clarify the adsorption mechanism, Al$_2$O$_3$ was also prepared as an additional sorbent. The adsorbents were characterized by X-ray fluorescence analysis, powder X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy and N$_2$ adsorption–desorption. Results showed that in comparison with pristine δ-MnO$_2$, Al$_2$O$_3$ pillaring led to increased BET surface area of 166.3 m$^2$ g$^{-1}$ and enlarged basal spacing of 0.85 nm. Accordingly, p-MnO$_2$ exhibited a higher adsorption capacity of Pb(II) than δ-MnO$_2$. The adsorption isotherms of Pb(II) on δ-MnO$_2$ and Al$_2$O$_3$ pillar fitted well to the Freundlich model, while the adsorption isotherm of Pb(II) on p-MnO$_2$ could be well described using a dual-adsorption model, attributed to Pb(II) adsorption on both δ-MnO$_2$ and Al$_2$O$_3$. Additionally, Pb(II) adsorption on δ-MnO$_2$ and p-MnO$_2$ followed the pseudo second-order kinetics, and a lower adsorption rate was observed on p-MnO$_2$ than δ-MnO$_2$. The Pb(II) adsorption capacity of p-MnO$_2$ increased with solution pH and co-existing cation concentration, and the presence of dissolved humic acid (10.2 mg L$^{-1}$) did not markedly impact Pb(II) adsorption. p-MnO$_2$ also displayed good adsorption capacities for aqueous Cu(II) and Cd(II). Findings in this study indicate that p-MnO$_2$ could be used as a highly effective adsorbent for heavy metal ions removal in water.

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1. Introduction

The removal of toxic heavy metals from water is of critical importance due to their high toxicity and severe environmental risks [1,2]. Adsorption is considered as one of the most cost competitive and efficient techniques to remove heavy metals from industrial wastewater [3,4]. However, exploring and developing adsorbents with high adsorption capacity and stable treatment efficiency for heavy metals are still considerably challenging.

Manganese oxides with varied morphologies (e.g., clusters, nanowires, spinel, layered and perovskite structures) have been widely explored as effective sorbents in removing heavy metal ions from water [5,6]. Particularly, Puppa et al. found that δ-MnO$_2$ consisting of lamellar close packing of [MnO$_6$] octahedral was efficient adsorbent for Pb(II) removal from water [7]. In parallel, Tonkin et al. and Wang et al. concluded that δ-MnO$_2$ with firm structure and good stability exhibited high adsorption capacities for heavy metals [8,9]. Notably, δ-MnO$_2$ is layered structured, and heavy metal ions are normally adsorbed on the external surface of δ-MnO$_2$ because the layer spacing is too small to host hydrated heavy metal ions [10]. Hence, Pb(II) adsorption on δ-MnO$_2$ is expected to be substantially suppressed due to the inaccessibility of the adsorption sites located in the interlayer of δ-MnO$_2$.

Exfoliation and pillaring are commonly used methods to increase the layer spacing aiming at effective exposure of active sites located in the interlayer of δ-MnO$_2$ [11–13]. For example, colloidal nanosheets of MnO$_2$ with a crystallographic thickness of subnanometer have been successfully obtained by exfoliation/pillaring using tetramethylammonium hydroxide (TMAOH) as the delamination and organic pillaring agent [14]. Similarly, ordered layer manganese oxides with large layer spacings and high specific surface areas exhibited much higher catalytic activities as compared with biotite [15]. Notably, monolayer and organic component pillared manganese oxides are very unstable and thus susceptible to aggregation into 3-dimensional or multilayer crystallites, leading to decreased specific surface area and blocking of
interlayer adsorption sites [16]. Pillaring of layered MnO₂ with inorganic oxides as rigid pillars provides an effective method to prepare stable MnO₂ materials with open interlayer spacings [14]. Various inorganic oxides, such as SiO₂, Ni(OH)₂, and TiO₂ have been introduced into the interlayer space of layered manganese oxides as pillars to modify their structures and properties [17–19]. For example, Zhou et al. found that layered manganese oxides upon Al₂O₃pillaring treatment had an expanded basal spacing of 0.73 nm and a good network pore structure, high mechanic strength and stability against high temperature treatment [15]. Although for catalytic reactions pillaring commonly led to enhanced catalytic activities, few studies have been carried out to investigate adsorption on pillared MnO₂ thus far.

In this study, we successfully synthesized Al₂O₃ pillared layered MnO₂ (p-MnO₂) using δ-MnO₂ as the precursor and [Al₁₃O₄(OH)₂₄(H₂O)₁₂]³⁺ (Keggin ion) as the pillaring agent. The structural characteristics of p-MnO₂ were characterized by XRD, TEM, XPS and XRF. The adsorption of Pb(II) on the adsorbents was investigated and the adsorption mechanism was discussed.

2. Materials and methods

2.1. Materials and reagents

All chemicals used in the experiments were of analytical grade and were used without further purification. Stock solutions of inorganic salts were prepared by dissolving appropriate amount of NaCl, CaCl₂ and Pb(NO₃)₂ in deionized (DI) water. Humic acid (HA) stock solution was prepared using the method previously reported [20]. Briefly, 150 g of humic acid (Sigma-Aldrich) was dissolved in 21 of DI water at room temperature under stirring, which was then filtered through a 0.22 μm cellulose acetate membrane. The concentration of HA (mg L⁻¹ as DOC) was measured by a total organic carbon analyzer (TOC, Shimadzu TOC-VCSH).

2.2. Preparation of organic amine pillared MnO₂

The layered precursor, δ-MnO₂, was prepared according to a previously reported method with slight modifications [21]. A mixture of 1 g K₂CO₃ and 5 g MnO₂ was carefully ground and heated at 750 °C in air for 30 h. Potassium ions were extracted from δ-MnO₂ (2 g) using a 500 mL of 0.5 mol L⁻¹ (NH₄)₂S₂O₈ aqueous solution at 60 °C for 7 h, then the solid was filtered, washed with DI and dried at 70 °C. To prepare organic amine intercalated MnO₂ with an enlarged interlayer spacing, 1.0 g of ion exchanged δ-MnO₂ with cation exchange capacity (CEC) measured to be 28.2 cmol kg⁻¹ was suspended in 250 mL of 0.35 mol L⁻¹ tetrathylammonium hydroxide (TMAOH) aqueous solution under stirring at room temperature for 10 days [14]. The sample was collected by centrifugation and repeated washing. The intercalated MnO₂ was abbreviated as TMAOH-MnO₂.

2.3. Preparation of Al₁₃ Keggin ion

Al₁₃ polyoxocation was prepared by dropwise addition of 200 ml of 0.2 mol L⁻¹ NaOH to 80 ml of 0.2 mol L⁻¹ Al(NO₃)₃ solution under magnetic stirring [16]. The molar ratio of OH/Al was controlled at 2.5, and the concentration of Al₁₃ Keggin ions was 4.4 × 10⁻³ mol L⁻¹. The resulting solution was aged overnight at room temperature.

2.4. Preparation of Al₂O₃ pillared MnO₂

1.5 g of as-prepared TMAOH-MnO₂ was suspended in 200 ml of aged Al₁₃ polyoxocation solution at Al₁₃ Keggin ion/Ce of MnO₂ ratio of 2.0 under strong mechanical stirring at room temperature for 30 days. The solid product was collected by filtration and washed with distilled water, and then dried at 70 °C for 24 h. The Al₁₃ Keggin ion intercalated MnO₂ was abbreviated as Al₁₃-MnO₂. Al₂O₃ pillared MnO₂ (denoted as p-MnO₂) was obtained by heating Al₁₃-MnO₂ in air at 300 °C for 3 h. The concrete preparation process of Al₂O₃-pillared layered MnO₂ was shown in Scheme 1.

2.5. Characterizations

Transmission electron microscopy (TEM) images of the samples were collected on a Hitachi H-800 transmission electron microscope. The contents of MnO₂ and Al₂O₃ in the sorbents were determined with a Thermo Electron ARL9800XP X-ray fluorescence (XRF) spectrometer. The Brunauer-Emmett-Teller (BET) surface areas of the materials were measured by N₂ adsorption-desorption on a Micrometrics ASAP 2020 analyzer at −196 °C. Powder XRD patterns of the samples were collected on a Rigaku D/max-RA powder diffraction meter. X-ray photoelectron spectra (XPS) analysis was performed on a Perkin Elmer PHI 550 ESCA/SAM equipped with a monochromatized AlKα X-ray source (hv = 1486.6 eV) and a hemispherical electron analyzer. C 1s photoelectron peak was used for calibration and fixed at binding energy (BE) equal to 284.6 eV.

2.6. Batch adsorption experiments

To examine the influence of contact time on Pb(II) uptake by p-MnO₂, 0.25 g adsorbent was added into a 500 ml round-bottom flasks containing 500 mL of Pb(II) aqueous solution under strong magnetic stirring. The solution pH was maintained at 4.0 ± 0.2 during the test. The samples were taken from the flasks at preset time intervals and the adsorbents were removed by fast filtration. The Pb(II) concentrations in the filtrates were determined by atomic

![Scheme 1](image)

Scheme 1. Preparation process of Al₂O₃-pillared layered manganese oxides.
absorption spectrophotometry (AAS). The Pb(II) adsorption amount was calculated according to the following equation:

\[ q_t = \frac{(C_0 - C_t)V}{M} \]  

(1)

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

Adsorption isotherm of Pb(II) on the sorbents was determined by placing 20 mg adsorbents in 40-ml of glass vials with polytetrafluoroethylene-lined screw caps receiving 40 ml of Pb(NO\(_3\))\(_2\) aqueous solutions with varied initial concentrations. pH of solutions was controlled to 4.0 ± 0.2 with 0.1 mol L\(^{-1}\) HCl or NaOH solution. After the samples were shaken to equilibrium at 25 °C for 24 h, the suspensions were filtered using 0.22 μm filters.

The equilibrium adsorption amount of Pb(II) was calculated according to the equation:

\[ q_e = \frac{(C_0 - C_e)V}{M} \]  

(2)

where \( q_e \) is the equilibrium adsorption amount (mg g\(^{-1}\)), \( C_0 \) (mg L\(^{-1}\)) is the initial concentration of Pb(II), \( C_e \) (mg L\(^{-1}\)) is the equi-
The equilibrium concentration of Pb(II), \( V \) (L) is the total volume of Pb(II) solution and \( M \) (g) is the mass of adsorbent.

To evaluate the adsorption property of the sorbents for other heavy metal ions, adsorption isotherms of Cu(II) and Cd(II) on p-MnO\(_2\) and \( \delta \)-MnO\(_2\) were measured from batch adsorption tests with the same procedure used for Pb(II).

The influence of pH on Pb(II) adsorption on p-MnO\(_2\) and \( \delta \)-MnO\(_2\) was studied in a pH range of 2.0–10.0. The pH values were adjusted using 0.1 mol L\(^{-1}\) HCl and NaOH solutions. The effect of background electrolyte on Pb(II) adsorption on p-MnO\(_2\) was tested in the presence of NaCl and CaCl\(_2\) solutions at ionic strength ranging from 0 to 0.2 mol L\(^{-1}\) at 25 °C. The impact of dissolved humic acid on Pb(II) adsorption was tested by comparing the adsorption isotherms of Pb(II) with and without dissolved humic acid at pH 4.0.

### 3. Results and discussion

#### 3.1. Characterization of adsorbents

The X-ray fluorescence analysis results (presented in Table 1) showed that the contents of MnO\(_2\) and Al\(_2\)O\(_3\) in p-MnO\(_2\) were 71.4 and 26.0 (wt.%), respectively, indicative the successful pillaring of layered MnO\(_2\) by Al\(_2\)O\(_3\).

The XRD patterns of samples are compiled in Fig. 1. Diffraction peaks of \( \delta \)-MnO\(_2\) (Fig. 1a) were observed with \( 2\theta \) at 12.18°, 24.52°, and 36.54°, indicative of a \( \delta \)-crystalllographic form [16]. The diffraction peaks of TMAOH-MnO\(_2\) were identified at 9.10°, 18.42°, and 36.50° (Fig. 1b). In comparison with \( \delta \)-MnO\(_2\), (001) diffraction peak of TMAOH-MnO\(_2\) shifted to a low \( 2\theta \) value, indicative of a larger interlayer space than that of \( \delta \)-MnO\(_2\) due to the successful pillaring by organic species [22]. Heating TMAOH-MnO\(_2\) at 300 °C in air for 3 h led to nearly complete disappearance of diffraction peaks (Fig. 1c), reflecting that TMAOH-MnO\(_2\) was unstable and easily collapsed. Upon exchanging of TMAOH-MnO\(_2\) with Al\(_{13}\) Keggin ion, the diffraction peaks remained nearly identical (Fig. 1d). After heating at 300 °C for 3 h, the diffraction peaks of p-MnO\(_2\) shifted to low \( 2\theta \) values at 10.42° and 37.54° (Fig. 1e), reflecting that the organic pillars were replaced by inorganic Al\(_2\)O\(_3\) pillars due to the decomposition of organic amines. The interlayer space of p-MnO\(_2\) was calculated to be 0.85 nm according to the Bragg equation \( 2d \sin \theta = n \lambda \) [23]. It was previously reported that the diameter of the spherical Al\(_{13}\) polyoxocation and the crystallographic thick-

**Fig. 4.** Full-scan XPS spectra of (a) \( \delta \)-MnO\(_2\), (b) \( \delta \)-MnO\(_2\) after Pb(II) adsorption, (c) p-MnO\(_2\) and (d) p-MnO\(_2\) after Pb(II) adsorption.

**Fig. 5.** O1s XPS spectra of (a) \( \delta \)-MnO\(_2\), (b) \( \delta \)-MnO\(_2\) after Pb(II) adsorption, (c) p-MnO\(_2\) and (d) p-MnO\(_2\) after Pb(II) adsorption.

**Fig. 6.** Mn 2p XPS spectra of (a) \( \delta \)-MnO\(_2\), (b) \( \delta \)-MnO\(_2\) after Pb(II) adsorption, (c) p-MnO\(_2\) and (d) p-MnO\(_2\) after Pb(II) adsorption.
ness of MnO₂ nanosheet were 0.86 and 0.52 nm, respectively [16]. Hence, the repeating distance of p-MnO₂ bilayer was expected to be 1.38 nm (0.86 + 0.52 nm), much larger than the value (0.85 nm) calculated from XRD data. The low repeating distance of p-MnO₂ was likely because the nanosheets with extremely small thickness were very flexible and could easily bend to cover or wrap these intercalation compounds. The pillared layered structure of p-MnO₂ was also confirmed by TEM observation and the TEM images of the samples are shown in Fig. 2. The ordered layered structures of δ-MnO₂ and p-MnO₂ were clearly visible. Additionally, the basal spacing of p-MnO₂ was calculated to be 0.88 nm, which was in good agreement with XRD results.

The N₂ adsorption-desorption isotherms of the δ-MnO₂ and p-MnO₂ are shown in Fig. 3a, and the resulting parameters are summarized in Table 1. For δ-MnO₂, the isotherm showed a very small hysteresis loop, indicative of a nonporous structure. The Brunauer-Emmett-Teller (BET) surface area of δ-MnO₂ was calculated to be 14 m² g⁻¹, and the pore size distribution (Fig. 3b) was decentralized with the average pore diameter of 42.3 nm. The t-plot analysis further confirmed that the surface area of δ-MnO₂ predominantly contributed from the external surface without the formation of micropores. On the contrary, p-MnO₂ had a very high BET surface area of 166 m² g⁻¹ and a narrow pore size distribution with average pore diameter centered at 4.3 nm. Consistently, the pore volumes of the δ-MnO₂ and p-MnO₂ were 0.02 and 0.11 cm³ g⁻¹, respectively. The N₂ adsorption-desorption results clearly revealed the formation of porous structures after Al₂O₃ pillaring.

The XPS survey spectra of δ-MnO₂ and p-MnO₂ are shown in Fig. 4. The presence of Al 2p peak in Fig. 4c clearly confirmed successful Al₂O₃ pillaring in the interlayers of p-MnO₂. Additionally, detailed scans in O1s and Mn sp regions of δ-MnO₂ and p-MnO₂ are conducted and shown in Figs. 5 and 6, respectively. The O1s spectrum of δ-MnO₂ was highly asymmetrical and was divided into two peaks (Fig. 5) positioned at 529.9–530.1 eV and 531.4–532.1 eV, assigned to oxygen containing species of Mn–O–M (M = Mn, Al) and −OH, respectively [24]. As for p-MnO₂, similar oxygen containing species to those of δ-MnO₂ were observed, but the content of surface −OH sharply increased, which could be attributed to the abundant hydroxyl groups from either Al₂O₃ or internal surface of manganese oxides [25]. The Mn 2p spectrum (Fig. 6) consisted of a spin–orbit doublet from Mn 2p₁/₂ and Mn 2p₃/₂, assigned to a mixed-valent manganese system of Mn⁴⁺ and Mn³⁺ [26]. After Al₂O₃ pillaring, the area ratio of Mn 2p₁/₂ to Mn 2p₃/₂ was almost unchanged, reflecting the high stability of MnO₂ sheet.

### Table 1

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Content (wt.%)¹</th>
<th>S_{BET} (m² g⁻¹)</th>
<th>Vₚ (cm³ g⁻¹)</th>
<th>V_{micro} (cm³ g⁻¹)</th>
<th>dₚ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>91.3</td>
<td>13.7</td>
<td>0.02</td>
<td>0.00</td>
<td>42.3</td>
</tr>
<tr>
<td>p-MnO₂</td>
<td>71.4</td>
<td>26.0</td>
<td>0.11</td>
<td>0.02</td>
<td>4.3</td>
</tr>
</tbody>
</table>

¹ Determined by X-ray fluorescence analysis.
² Total pore volume, determined at P/P₀ = 0.97.
³ Micropore volume, determined by t-plot method.
⁴ Most probable pore diameter, determined by BJH pore size distribution.

The kinetics of Pb(II) adsorption onto the sorbents are shown in Fig. 7a. The Pb(II) adsorption on δ-MnO₂ increased rapidly in initial 10 min and reached equilibrium within 30 min, whereas Pb(II) adsorption on p-MnO₂ achieved equilibrium within 180 min, reflecting a much higher rate of Pb(II) adsorption on δ-MnO₂ than that on p-MnO₂. In order to clearly interpret adsorption mechanism, pseudo first-order and pseudo second-order equations were used to further evaluate Pb(II) adsorption kinetics. The pseudo first-order kinetics and pseudo second-order kinetics can be described as (3) and (4), respectively [27,28]:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \(q_e\) and \(q_t\) (mg g⁻¹) are the adsorption capacities of Pb(II) on the adsorbents at the equilibrium and at time \(t\) (min), \(k_1\) (min⁻¹) and \(k_2\) (g mg⁻¹ min⁻¹) are the rate constants of the pseudo first-order equation and pseudo second-order equation, respectively.

Fig. 7b and c displays the linear fitting plots of Pb(II) adsorption on the adsorbents to the pseudo first-order and pseudo second-order kinetics, respectively. The fitting kinetic parameters are summarized in Table 2. It was observed that the pseudo second-order kinetics fitted the experimental data well with correlation coefficients of 0.99. Additionally, the high consistency of calculated \(q_e^\prime\) values with the experimental data further confirmed that Pb(II) adsorption on the sorbents followed pseudo second-order kinetics, indicative of chemical adsorption processes in nature [27]. The adsorption rate constants were calculated to be 0.0085 and 0.0013 g mg⁻¹ min⁻¹ for Pb(II) adsorption on δ-MnO₂ and p-MnO₂, respectively, reflecting a decreased adsorption rate upon Al₂O₃ pillaring. The much lower Pb(II) adsorption rate on p-MnO₂ than on δ-MnO₂ is likely due to Pb(II) diffusion in additional micro- and mesopores of p-MnO₂ formed by Al₂O₃ pillaring.

To clearly clarify Pb(II) adsorption kinetics on the sorbents, Weber-Morris model is used to further fit the experimental data, which is expressed as follows [29]:

\[
q_t = k_{ad} t^{1/2} + C_i
\]

where \(k_{ad}\) (mg g⁻¹ min⁻¹/²) is the intraparticle diffusion rate constant, \(C_i\) is the intercept. Fig. 7d presents the plots of \(q_t\) versus \(t^{1/2}\) for adsorption of Pb(II) on δ-MnO₂ and p-MnO₂ and the fitting parameters are listed in Table 3. The \(q_t - t^{1/2}\) plots of p-MnO₂ consisted of three linear portions. The first linear portion was attributed to Pb(II) adsorption on the external surface, the second one was assigned to the Pb(II) diffusion into the pores of p-MnO₂, and the third one was characteristic of adsorption equilibrium [10]. For the first linear portion, \(C_i\) was found to be 0.80, suggesting the existence of external mass transfer resistance in Pb(II) adsorption process [30]. Notably, the majority of Pb(II) adsorption on p-MnO₂ was observed in second linear portion, characteristic of Pb(II) diffusion into sorbent pores, which was in good agreement with the high specific surface area and the presence of pores of p-MnO₂. In contrast, the \(q_t - t^{1/2}\) plots of nonporous δ-MnO₂ consisted of two linear portions, in which the first linear portion could be assigned to Pb(II) diffusion to sorbent external surface and the second one to the final equilibrium stage, accounting for the fast adsorption kinetics on δ-MnO₂.
3. Adsorption kinetics

The adsorption isotherms of Pb(II) on p-MnO₂, Al₂O₃ and δ-MnO₂ are depicted in Fig. 8. For p-MnO₂, Pb(II) adsorption amount was 87.8 mg g⁻¹ at an equilibrium concentration of 16.3 mg L⁻¹, while Pb(II) adsorption amount of δ-MnO₂ was 30.0 mg g⁻¹ at 19.9 mg L⁻¹, reflecting a much higher adsorption capacity of p-MnO₂ than that of δ-MnO₂. Considering that p-MnO₂ contained 26.0 wt.% of Al₂O₃ and Al₂O₃ was possibly active for Pb(II) adsorption, Al₂O₃ was also prepared and Pb(II) adsorption isotherm on Al₂O₃ is presented in Fig. 8. The equilibrium adsorption amount of Al₂O₃ was 13.7 mg g⁻¹ at Pb(II) concentration of 18.1 mg L⁻¹, much lower than those of δ-MnO₂ and p-MnO₂. The Pb(II) adsorption data were further fitted to Sips, Toth, Langmuir and Freundlich isotherm models to elucidate the adsorption mechanism. The Temkin, Langmuir and Freundlich isotherm models are expressed as Eqs. (6)–(9).

\[
q_e = \frac{q_m K_s C_e}{1 + K_s C_e} 
\]

(6)

\[
q_e = \frac{q_m C_e}{(b_l + C_e^{n_l})^{1/n_l}} 
\]

(7)

\[
C_e = \frac{C_e}{q_m} + \frac{1}{q_m b} 
\]

(8)

\[
\log q_e = \log K_f + \frac{1}{n} \log(C_e) 
\]

(9)
where $C_e$ (mg L$^{-1}$) is the equilibrium concentration of Pb(II), $q_e$ (mg g$^{-1}$) is the equilibrium adsorption amount of Pb(II), $q_m$ (mg g$^{-1}$) is the maximum adsorption capacity, $K_f$ (L mg$^{-1}$) is the Sips isotherm constant, $s$ is the Sips isotherm exponent, $b_i$ (L mg$^{-1}$) is the Toth model constant, $n_i$ is the Toth model exponent, and $n$ is the linearity index reflecting the intensity of adsorption.

For $\delta$-MnO$_2$ and p-MnO$_2$ sorbents, Pb(II) adsorption could be well described by the Sips adsorption model and Toth adsorption model, respectively, with $R^2$ greater than 0.99, suggesting a heterogeneous distribution of adsorption sites on the adsorbents. The maximum adsorption capacities calculated by Sips and Toth model were 18.0 and 45.8 mg g$^{-1}$ for $\delta$-MnO$_2$, and 48.6 and 349.4 mg g$^{-1}$ for p-MnO$_2$, respectively, further confirming the higher adsorption capacity of p-MnO$_2$ than that of $\delta$-MnO$_2$, which was likely owing to the increased BET surface area and enlarged basal spacing after Al$_2$O$_3$ pillaring.

The fitting parameters of Langmuir and Freundlich isotherm models for Pb(II) adsorption onto Al$_2$O$_3$ and $\delta$-MnO$_2$ are listed in Table 4. The adsorption data fitted better to the Freundlich model than to the Langmuir model, indicating that the surface active sites of the sorbents for Pb(II) adsorption were heterogeneous in nature [31]. The Freundlich coefficient $K_f$ values of $\delta$-MnO$_2$ and Al$_2$O$_3$ were 13.33 and 4.85 mg$^{-1}$ L$^{-1/2}$ g$^{-1}$, respectively, confirming a higher adsorption capacity and affinity of Pb(II) on $\delta$-MnO$_2$ than Al$_2$O$_3$. In addition, the $n$ values of $\delta$-MnO$_2$ and Al$_2$O$_3$ were 3.99 and 2.96, respectively, characteristic of favorable process for Pb(II) chemisorption onto the adsorbents. Notably, p-MnO$_2$ consisted of $\delta$-MnO$_2$ and Al$_2$O$_3$ with different adsorption sites on which contributed respectively to Pb(II) adsorption, as reflected by Pb(II) adsorption on Al$_2$O$_3$ and Al$_2$O$_3$. Hence, it is not possible to simulate Pb(II) adsorption on p-MnO$_2$ singly with the Langmuir or Freundlich isotherm model. It is appropriate to fit the adsorption isotherm on p-MnO$_2$ using a linear regression of Pb(II) adsorption on $\delta$-MnO$_2$ and Al$_2$O$_3$, which can be described as follows:

$$q_e = K_d q_{e0} + K_h q_{eA}$$

where $q_{e0}$ (mg g$^{-1}$) is the equilibrium adsorbed amount on p-MnO$_2$, $K_d$ and $K_h$ are the amount of Pb(II) adsorbed on the $\delta$-MnO$_2$ surface and Al$_2$O$_3$ surface at equilibrium according to the Langmuir model, respectively, and $q_{eA}$ is the Al$_2$O$_3$ content (wt.%), respectively, and $K_d$ and $K_h$ are linear regression coefficients.

The adsorption isotherm of Pb(II) to p-MnO$_2$ and the fitting curve are shown in Fig. 8. The chi-square value obtained for Pb(II) adsorption to p-MnO$_2$ was 4.16, indicating that Pb(II) adsorption could be well described by the dual-adsorption model. Additionally, the $K_h$ and $K_d$ values were calculated to be 4.49 and 0.08, confirming Pb(II) adsorption on Al$_2$O$_3$ pillar and $\delta$-MnO$_2$ surfaces. If p-MnO$_2$ was completely reconstructed by Al$_2$O$_3$ pillar and Mn$_2$O$_3$ nanosheets and if Pb(II) adsorption to occurred on independent Al$_2$O$_3$ and Mn$_2$O$_3$ nanosheets, the theoretical linear regression coefficients $K_h$ and $K_d$ would both be 1. It is noteworthy that the fitting value of $K_d$ was much lower than the theoretical value, which was likely due to blocking of interlayer adsorption sites on Al$_2$O$_3$ pillars surfaces. In contrast, the fitting $K_h$ value was much higher than the theoretical value, which suggested that more adsorption sites with stronger adsorption affinity for Pb(II) were exposed when Al$_2$O$_3$ expanded the layer spacing larger [32]. However, the increased adsorption quantity of Pb(II) did not match the increase of N$_2$ adsorption amount, which $q_{e0}$ was about 12.2 times higher than that of $\delta$-MnO$_2$. This difference was likely because the N$_2$ molecule and lead hydrated ions varied in size and the adsorption reaction was driven by different driving forces.

![Fig. 9. Pb 4f XPS spectra of (a) $\delta$-MnO$_2$, (b) $\delta$-MnO$_2$ after Pb(II) adsorption, (c) p-MnO$_2$, and (d) p-MnO$_2$ after Pb(II) adsorption.](image)

![Fig. 10. Effect of pH on Pb(II) adsorption to $\delta$-MnO$_2$ and p-MnO$_2$. Initial Pb(II) concentrations: 25 mg L$^{-1}$ for $\delta$-MnO$_2$, 80 mg L$^{-1}$ for p-MnO$_2$.](image)

After Pb(II) adsorption, as seen in Fig. 9, p-MnO p-MnO$_2$ showed two peaks with Pb 4f$_{7/2}$ and Pb 4f$_{5/2}$ derived from spin-orbit splitting. The binding energy of Pb 4f$_{7/2}$ core level was observed at 137.0 eV, corresponding to orthorhombic PbO compound (137.4 eV) [33]. This reflected no hydroxides or carbonates precipitation of Pb during adsorption. As for O1s spectra, after Pb(II) adsorption no new peak was observed in $\delta$-MnO$_2$ and p-MnO$_2$, but the content of surface –OH decreased in both $\delta$-MnO$_2$ and p-MnO$_2$, which was possibly due to complexation interactions between –OH and Pb(II).

3.4. Effect of pH

Fig. 10 displays the influence of pH on Pb(II) adsorption over p-MnO$_2$ and $\delta$-MnO$_2$. For both $\delta$-MnO$_2$ and p-MnO$_2$, increasing pH from 2.0 to 7.0 led to a monotonic increase of Pb(II) adsorption, which was attributed to the alleviated adsorption completion from H$^+$ with the increase of pH. Notably, at pH below 2, negligible Pb(II) adsorption was observed on $\delta$-MnO$_2$ due to the strong adsorption completion from H$^+$. In contrast, marked Pb(II) adsorption amount remained (approximate 30.0 mg g$^{-1}$) on p-MnO$_2$ at pH below 2, reflecting the strong complexation interactions between Pb(II) and hydroxyl groups on p-MnO$_2$.

3.5. Effect of co-existing cations and dissolved humic acid

The co-existing ions are important factors influencing Pb(II) adsorption because those ions are commonly monitored in natural waters and industrial wastewater. The effects of Na(I) and Ca(II) on the uptake of Pb(II) onto p-MnO$_2$ are showed in Fig. 11a. At low ionic strength, increasing the concentrations of co-existing ions enhanced Pb(II) adsorption, while further increasing ionic strength only resulted in slightly increased Pb(II) adsorption amount, indica-
Fitting parameters of Pb(II) adsorption isotherms on the sorbents using the Langmuir and Freundlich isotherm models.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( b ) L mg(^{-1} )</td>
<td>( q_m ) mg g(^{-1} )</td>
</tr>
<tr>
<td>( \delta )-MnO(_2)</td>
<td>0.84</td>
<td>29.2</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.09</td>
<td>22.4</td>
</tr>
</tbody>
</table>

Fig. 11. Effect of (a) co-existing ions on Pb(II) adsorption on \( \delta \)-MnO\(_2\) and (b) adsorption isotherms of Pb(II) on p-MnO\(_2\) in absence of humic acid and in presence of dissolved humic acid (10.2 mg L\(^{-1}\)).

3.6. The use of p-MnO\(_2\) for adsorptive removal of Cu(II) and Cd(II)

To explore the probability of using p-MnO\(_2\) to remove other cations in addition to Pb(II), Cu(II) and Cd(II) adsorption on the sorbents was studied and the results are shown in Fig. 12. For p-MnO\(_2\), the Cu(II) and Cd(II) adsorption amounts were 72.9 and 47.8 mg g\(^{-1}\) at the equilibrium concentrations of 48.7 mg Cu L\(^{-1}\) and 48.1 mg Cd L\(^{-1}\), respectively, whereas the Cu(II) and Cd(II) adsorption amounts of \( \delta \)-MnO\(_2\) were 25.7 and 21.2 mg g\(^{-1}\) at the respective equilibrium concentrations of 49.5 mg Cu L\(^{-1}\) and 44.3 mg Cd L\(^{-1}\), further confirming the enhanced adsorption capacities of p-MnO\(_2\) for heavy metal ions by exfoliation and pillaring. Note that Pb(II) adsorption amount of p-MnO\(_2\) was 87.8 mg g\(^{-1}\) at equilibrium concentration of 16.3 mg Pb L\(^{-1}\), the equilibrium adsorption amounts of p-MnO\(_2\) for three heavy metal ions within the tested concentration range can be ordered as follows: Pb(II) > Cu(II) > Cd(II). Al\(_2\)O\(_3\) pillared layered MnO\(_2\) exhibited a fairly high adsorption efficiency for Cu(II) and considerable adsorption capacity for Cd(II) from aqueous solutions, which is worthy of further investigation.

4. Conclusions

In this study, Al\(_2\)O\(_3\) pillared layered MnO\(_2\) (p-MnO\(_2\)) was synthesized through delamination and pillaring of \( \delta \)-MnO\(_2\) with Al\(_2\)O\(_3\), and Pb(II) adsorption onto the adsorbent was investigated. The characterization results indicates that Al\(_2\)O\(_3\) pillared layered MnO\(_2\) has a large BET surface area, abundant pores and large basal spacing. Accordingly, p-MnO\(_2\) displayed substantially enhanced Pb(II) adsorption as compared with \( \delta \)-MnO\(_2\). Pb(II) adsorption isotherms on \( \delta \)-MnO\(_2\) and Al\(_2\)O\(_3\) can be well fitted by the Freundlich model, while the Pb(II) adsorption on p-MnO\(_2\) can be evaluated using a dual-adsorption model consisting of Pb(II) adsorption on both \( \delta \)-
MnO₂ and Al₂O₃. The Pb(II) adsorption kinetics follows the pseudo second-order kinetics, and the decreased adsorption rate of p-MnO₂ is attributed to the intraparticle diffusion. Increasing pH substantially enhances Pb(II) adsorption due to gradually alleviated adsorption competition from H⁺. Additionally, p-MnO₂ exhibits high selective Pb(II) adsorption at the presence of co-existing cations, and the presence of dissolved humic acid has a negligible influence on Pb(II) adsorption on p-MnO₂. p-MnO₂ also displays good adsorption capacities for aqueous Cu(II) and Cd(II) in a preliminary test. The present results highlight the great potential of p-MnO₂ as a highly effective adsorbent for adsorptive removal of heavy metal ions in water.

Acknowledgments

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References