Layer-by-Layer Assembly of Polyelectrolytes on Urchin-like MnO₂ for Extraction of Zn²⁺, Cu²⁺ and Pb²⁺ from Alkaline Solutions

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Abstract: Three-dimensional (3D) urchin-like MnO₂@poly (sodium 4-styrene sulfonate) (PSS)/poly (diallyl dimethylammonium chloride) (PDDA)/PSS particles were prepared via the layer-by-layer (LBL) assembly of polyelectrolytes for the extraction of Zn²⁺ from alkaline media. The adsorption performance of Zn²⁺ on MnO₂, MnO₂@PSS/PDDA/PSS, and MnO₂@PSS/PDDA/PSS was investigated in batch experiments. The adsorption of Zn²⁺ on MnO₂/PSS/PDDA/PSS has been studied under various conditions, such as initial Zn²⁺ concentration, adsorbent dosage, the solution’s pH, and reaction time. The Zn²⁺ adsorption process is well represented by the pseudo-second-order kinetic model, and the equilibrium data fit the Freundlich isotherm well. MnO₂@PSS/PDDA/PSS also showed high efficiency for Pb²⁺ and Cu²⁺ removal from slightly alkaline water. Thus, our research provides a deep insight into the preparation of 3D manganese oxides with polyelectrolyte films for the extraction of heavy metal ions, such as Pb²⁺, Cu²⁺, and Zn²⁺, from slightly alkaline wastewater.

Keywords: urchin-like MnO₂; LBL assembly; heavy metal ions; adsorption; polyelectrolytes

1. Introduction

The dissolved phase of heavy metals, such as Pb²⁺, Cu²⁺, and Zn²⁺, in wastewater has become a matter of increasing concern due to their great transferability and bioavailability, as well as their severe cytotoxicity [1–3]. Lead (Pb²⁺), mainly from petrol, paint, plumbing, pipes, car batteries, pigments, has a tolerable daily intake (TDI) value set at levels of <3.5 µg/kg body weight. An overdose of Pb²⁺ over a long period might cause irreversible damage to the central nervous system [4,5]. Copper (Cu²⁺) and zinc (Zn²⁺) are necessary for organism development in small quantities, but excessive exposure to them can lead to toxicity, disrupting the normal functions of cells and organs [6–8]. Thus, exploring efficient and cost-effective methods for heavy metal treatment is in demand, especially in developing countries.

Various materials, such as adsorbents [9,10], ion exchange resins [11,12], chemical precipitation agents [13,14], electrochemical anodes [15] and membranes [16,17] have been used to remove heavy metal ions [18]. Among them, adsorbents are widely used due to their highly cost-effective properties and easy operation [19]. Many studies have been published related to the removal of Zn²⁺ from acidic [20,21] to neutral wastewater; however, little information is available for Zn²⁺ adsorption in slightly alkaline water [22,23]. Manganese oxide (MnO₂) has been extensively reported as an efficient scavenger of many heavy metals, due to their unique physical and chemical properties, with the controllable tuning of structure [24–26], while it is still important to improve their stability and chemical activity. It has been reported that MnO₂ with a 3D urchin-like structure, with modest corrugating patterns, are considered to exhibit noticeable chemically stable and active properties,
significantly differentiating them from particles with smooth surfaces [27–29]. Furthermore, the derivatizing process of urchin-like MnO₂ surfaces with macromolecular components also noticeably enhances their affinity for heavy metals. Layer-by-layer assembly (LBL) is one way to permit the molecular engineering of surfaces through the continuous depositing process of polyelectrolytes and numerous functional compounds [30,31].

In the present work, the urchin-like MnO₂, with outer diameters of 2 to 5 µm, was prepared in a hydrothermal process. Then, the polyelectrolytes, PSS and PDDA, were deposited sequentially via LBL assembly to form a strong, dense coating on urchin-like MnO₂ to form 3D adsorbent MnO₂@(PSS/PDDA/PSS). The adsorption properties of Zn²⁺ on MnO₂@(PSS/PDDA/PSS) were studied in batch experiments. Different experimental conditions affecting the uptake of Zn²⁺ were investigated, and the experimental data were fitted with various models to further understand the adsorption mechanisms.

2. Materials and Methodology

2.1. Reagents and Materials

MnSO₄·H₂O and (NH₄)₂S₂O₈ were purchased from the Keda Reagent Factory (Shenyang, China). Nafion solution (5%) was obtained from the Yilong Energy Technology Co. Ltd. (Suzhou, China). Poly (sodium 4-styrene sulfonate) (PSS, Mw 70,000 g/mol) and poly (diallyl dimethylammonium chloride) (PDDA, Mw 200,000–350,000 g/mol) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Ultrapure water with a resistivity of 18.2 MΩ cm was obtained directly from a Milli-Q Plus water purification system (Millipore Corporation, Burlington, MA, USA). All other reagents used in the experiments were analytical grade and obtained from Guangfu Fine Chemical Research Institute (Tianjin, China).

2.2. Characterization and Instruments

The surface morphology of MnO₂@PSS/PDDA/PSS was observed using a transmission electron microscope (TEM, FEI Tecnai G2 20, San Diego, CA, USA) and a scanning electron microscope (SEM) (Merlin Compact, Tokyo, Japan). The FTIR spectra were measured using a Thermo Nicolet NEXUS FTIR spectrometer at room temperature to analyze the surface functional groups of samples. The oxidation state of elements in the samples was analyzed by XPS (ESCALAB 250Xi, Waltham, MA, USA). The concentration of the Pb²⁺, Cu²⁺, and Zn²⁺ solution was monitored with a UV-vis spectrometer (Shanghai Jinghua 756MC, Shanghai, China).

2.3. Preparation of Urchin-like MnO₂

Urchin-like MnO₂ were prepared based on the following protocol. Typically, 10.7817 g of MnSO₄·H₂O and 14.6048 g of (NH₄)₂S₂O₈ were dissolved in 70.0 mL of deionized water and heated at 120 °C for 2 h. The dark precipitate was then centrifuged at 6000 rpm for 15 min, washed three times with DI water, and then dried at 70 °C for 12 h.

2.4. Layer-by-Layer Assembly of Polyelectrolytes on MnO₂

For the LBL deposition, the PSS and PDDA were coated in an adsorption-centrifugation cycle. In a typical procedure, 0.05 g of MnO₂ was added into 5.0 mL of the polyelectrolyte solution (5 mM). The particles were incubated at 25 °C for 30 min, placed in a centrifuge at 4500 rpm for 15 min, and then washed for three cycles. The final products were denoted as MnO₂@PSS/PDDA@PSS. The coating procedure was repeated 3 times, and finally, MnO₂@PSS/PDDA)₃/PSS was obtained.

2.5. Adsorption Experimental Procedure

In a single system, the effect factors, including pH value, the initial concentration of Zn²⁺, the dosage of adsorbent, and reaction time on adsorption were studied in a 50 mL conical flask with 20 mL of Zn²⁺ (Cu²⁺/Pb²⁺) solution. The mixture was stirred at a speed of 250 rpm/min for 24 h to reach adsorption equilibrium. The concentration of Zn²⁺ (Cu²⁺/Pb²⁺) in the solution was measured at a predetermined time. In the competition
experiment with the presence of co-existing ions, adsorption performance was investigated in the solution of Zn\(^{2+}\), Cu\(^{2+}\) and Pb\(^{2+}\) (the concentration of each metal ion was 50 mg/L). Each adsorption was replicated three times. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples to determine the margin of error.

2.6. Modeling of Adsorption Kinetics

The adsorption kinetics were evaluated using pseudo-first-order (1) and pseudo-second-order (2) equations in this study [32,33]:

\[
\ln\left(\frac{q_e}{q_t}\right) = ln\frac{q_e}{q_{\text{max}}} - k_1t
\]

\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{h}
\]

where \(q_e\) and \(q_t\) are the amount of adsorbed Zn\(^{2+}\) at equilibrium and time \(t\) (mg/g), \(k_1\) (min\(^{-1}\)) and \(k_2\) (g·mg\(^{-1}\)·min\(^{-1}\)) are rate constants for pseudo-first-order and second-order kinetics, respectively. The equation \(h = k_2q_e^2\) gives the initial adsorption rate when \(t\) approaches 0.

2.7. Modeling of Adsorption Isotherm

The Langmuir and Freundlich models are used in this case study. The non-linear form of the Langmuir and Freundlich equations are presented as [34,35]:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{K_Lq_{\text{max}}}
\]

\[
lnq_e = \frac{1}{n}lnC_e + lnK_F
\]

where \(q_e\) is the equilibrium adsorption capacity (mg/g), \(C_e\) is the equilibrium concentration (mg/L), \(q_{\text{max}}\) is the maximum adsorption capacity (mg/g), which is the amount of adsorbate adsorbed per unit weight (mg/g of adsorbent), and \(K_L\) is the Langmuir constant related to the adsorption energy. \(K_F\) and \(n\) are the Freundlich constants.

3. Results and Discussion

3.1. Characterization of MnO\(_2\), MnO\(_2\)/PSS/PDDA/PSS and MnO\(_2\)/(PSS/PDDA)\(_3\)/PSS

Figure 1 shows the TEM images of MnO\(_2\)/@PSS/PDDA/PSS and MnO\(_2\)/@PSS/PDDA\(_3\)/PSS. It can be seen that the thickness of the covering layer on the branches of urchin-like MnO\(_2\) increases significantly from about 1 ± 0.3 nm (Figure 1A) to 5 ± 0.7 nm (Figure 1B) as the number of coating layers increases, which might be due to the deposition of different amounts of polyelectrolytes. It was also found that the shape of the urchin-like MnO\(_2\) hardly changed after coating with one and three layers of polyelectrolytes.

![Figure 1. TEM images of the MnO\(_2\)/@PSS/PDDA/PSS (A) and MnO\(_2\)/@(PSS/PDDA)\(_3\)/PSS (B).](image-url)
Figure 2A shows the successful preparation of urchin-like MnO$_2$. Figure 2B,C shows the conformal coating, with one layer and three layers of polyelectrolytes (MnO$_2$@PSS/PDDA/PSS and MnO$_2$@(PSS/PDDA)$_3$/PSS, respectively. With the three-layer coating, the thickness of the branches increases to 300 ± 58 nm (Figure 2F), which is much larger than that of pristine MnO$_2$ (20 ± 4 nm, Figure 2D) and MnO$_2$@PSS/PDDA/PSS (50 ± 11 nm, Figure 2E).

![Figure 2](image_url)

Figure 2. SEM images of MnO$_2$ (A,D), MnO$_2$@PSS/PDDA/PSS (B,E) and MnO$_2$@(PSS/PDDA)$_3$/PSS (C,F).

The FT-IR spectra of MnO$_2$ and MnO$_2$@PSS/PDDA/PSS are shown in Figure 3. The peaks at 515, 518.3 cm$^{-1}$ can be attributed to Mn-O vibration. The band at nearly 1390 cm$^{-1}$ can be assigned to the Mn=O stretching vibration, which decreased dramatically after the LBL deposition of polyelectrolytes. It might be due to the possible reaction between Mn=O and coated polyelectrolytes or the attraction between MnO$_2$ and oppositely charged polymers, which is not currently fully understood [36]. The peaks at 1178, 1129, 1034.6 cm$^{-1}$ are related to the –S=O=S– and –SO$_3$ symmetric vibrations of PSS, indicating the coating of PSS/PDDA film on the surface of urchin-like MnO$_2$ [37,38]. The analysis of IR is consistent with the previous reports [30,36].

![Figure 3](image_url)

Figure 3. FT-IR spectra of MnO$_2$ and MnO$_2$@PSS/PDDA/PSS.
As shown in Figure 4A, the presence of Mn, N, and S elements in the sample of MnO$_2$@PSS/PDDA/PSS is due to the deposition of PSS/PDDA on the surface of manganese oxides. Moreover, the polymer coating might decrease the intensity of the Mn peak. Figure 4B shows the spectrum of Mn2p, in which the peaks of 652.4 eV and 641.6 eV are in agreement with an earlier report on MnO$_2$ [39]. The peak in Figure 4C appearing at 397.4 eV is assigned to N1s, which would come from the N-enriched polymer (PDDA). Figure 4D shows the spectrum of the S2p$_{1/2}$ peak (166.6 eV). These results indicate the coating of polymer layers on MnO$_2$.

Figure 4. XPS spectra of MnO$_2$@PSS/PDDA/PSS: wide scan (A), Mn 2p spectra (B), N 1s spectra (C), S 2p spectra (D).

3.2. Adsorption of Zn$^{2+}$ on MnO$_2$, MnO$_2$/PSS/PDDA/PSS, and MnO$_2$/([PSS/PDDA]$_3$/PSS

The adsorption performance on MnO$_2$, MnO$_2$/PSS/PDDA/PSS, and MnO$_2$/([PSS/PDDA]$_3$/PSS were tested at pH 13.0. The results are shown in Figure 5. For the control experiment from Zn$^{2+}$-bearing alkaline solutions (pH of 13.0), there is no precipitate observed over 24 h in the absence of prepared materials, indicating that the removal of Zn$^{2+}$ from these alkaline solutions is solely due to the presence of the prepared materials as adsorbents. As shown in Figure 5, after coating with one layer of PSS/PDDA/PSS on urchin-like MnO$_2$, the highest adsorption capacity was achieved (177.74 mg/g), and as the number of coating layers continuously increased to three, the adsorption capacity of Zn$^{2+}$ decreased. Based on the measured surface area of MnO$_2$, MnO$_2$@PSS/PDDA/PSS and MnO$_2$@([PSS/PDDA]$_3$/PSS (121, 108 and 54 m$^2$/g, respectively), it could be concluded that the decreased adsorption capacity of MnO$_2$@([PSS/PDDA]$_3$/PSS might be caused by the ultra-dense coating of polyelectrolytes on urchin-like MnO$_2$, which would significantly reduce the surface area of MnO$_2$ and also block the active sites of MnO$_2$. The number of coated polymers in MnO$_2$@PSS/PDDA/PSS and MnO$_2$@([PSS/PDDA]$_3$/PSS samples was calculated to be 2.173 g and 5.515 g/g of MnO$_2$, respectively, based on their FTIR spectra. As each Zn$^{2+}$ would bind two unit-charge sites of PSS, theoretically, the amount of polymer coating on 0.05 g of MnO$_2$@PSS/PDDA/PSS would combine approximately 2.701 mmol of Zn$^{2+}$, which is close to the experimental adsorption capacity (177.74 mg/g). Thus, MnO$_2$/PSS/PDDA/PSS was chosen for the following experiments.
3.3. Effect of Solution pH

The effect of pH on Zn$^{2+}$ adsorption was investigated in the pH range from 5.0 to 13.0. As shown in Figure 6, the removal efficiency of Zn$^{2+}$ continued to increase as the pH increased. At pH 13.0, the highest adsorption capacity of Zn$^{2+}$ on MnO$_2$/PSS/PDDA/PSS was obtained. This is mainly because of the electrostatic attraction between Zn$^{2+}$ and negatively charged PSS film. When the solution was acidic, there would be more H$^+$ in the solution, which would compete with Zn$^{2+}$ to occupy the active sites.

3.4. Effect of Initial Concentration

The effect of the initial Zn$^{2+}$ concentration was investigated at a pH of 13.0. The concentrations were studied at 20, 50, 100, 200, and 300 mg/L. The results of the initial concentration experiment are shown in Figure 7. It was found that the adsorption capacity was highest at an initial concentration of 100 mg/L. The removal rate increased as the initial Zn concentration increased from 20 mg/L to 100 mg/L, and then began to decrease sharply. This might be due to the fact that the adsorption site was occupied quickly; metal ion adsorption involves higher energy sites at low metal-ion concentrations. With an increase in the initial Zn$^{2+}$ concentration (20 to 100 mg/L), the large concentration difference between the solution and the materials drives greater binding of Zn$^{2+}$ and increases the removal rate [40]. Therefore, an optimal zinc concentration of 100 mg/L was selected for further experiments.
3.4. Effect of Initial Concentration
The effect of the initial Zn$^{2+}$ concentration on Zn$^{2+}$ adsorption was studied at 20 to 100 mg/L. The removal rate increased as the initial Zn$^{2+}$ concentration increased from 20 mg/L to 100 mg/L and then began to decrease. This is mainly because with the increase in the amount of adsorbent, more unoccupied adsorptive sites were left and their mass could still be used for the calculation of adsorption capacity [41,42]. Therefore, the amount of adsorbent used in the experiments was selected to be 0.5 g/L.

3.5. Effect of Adsorbent Dosage
Figure 8 shows the effect of adsorbent dosage on Zn$^{2+}$ adsorption with MnO$_2$@PSS/PDDA/PSS. The highest removal efficiency of Zn$^{2+}$ was reached when the dose of MnO$_2$@PSS/PDDA/PSS was 0.5 g/L. When the adsorbent dosage is lower than 0.5 g/L, less surface area is available for adsorption due to there being fewer active sites present, leading to a decreased adsorption efficiency. With an increase in the adsorbent dose, the adsorption capacity, $q_e$, decreased. This is mainly because with the increase in the amount of adsorbent, more unoccupied adsorptive sites were left and their mass could still be used for the calculation of adsorption capacity [41,42]. Therefore, the amount of adsorbent used in the experiments was selected to be 0.5 g/L.

3.6. Adsorption Kinetics
The pseudo-first-order and pseudo-second-order kinetic models were applied to describe the experimental data. The relevant kinetic parameters for Zn$^{2+}$ adsorption are displayed in Table 1. The results show that the correlation coefficient of the pseudo-second-order kinetic equation was 0.9989, higher than that of the first-order kinetic curve, indicating that the experimental data closely conformed to the second-order model.
Table 1. Parameters of the kinetics model for the adsorption of Zn\(^{2+}\) with MnO\(_2\)@PSS/PDDA/PSS, with an initial concentration of 100 mg/L, under a pH of 13.0 at 25 °C.

| Initial conc. (mg/L) | q\(_{\text{exp}}\) (mg/g) | Pseudo-First-Order | Pseudo-Second-Order |
|----------------------|--------------------------|--------------------|---------------------|
| 100                  | 177.74 ± 0.21            | k\(_1\) \times 10^{-2}\) min\(^{-1}\) | q\(_e\) (mg/g) | R\(^2\) | K\(_2\) \times 10^{-3}\) g/(g min) | q\(_e\) (mg/g) | R\(^2\) |
|                      |                          | 0.173 ± 0.02       | 177.56 ± 0.44       | 0.9321   | 7.26 ± 0.01       | 94.97 ± 0.37   | 0.9989   |

3.7. Adsorption Isotherm Models

The fitted results of the Langmuir and Freundlich isotherm models in this study are presented in Table 2. The results showed that the Langmuir model with R\(^2\) higher than 0.99 was a better fit than the Freundlich model, indicating that Zn\(^{2+}\) adsorption onto MnO\(_2\)@PSS/PDDA/PSS can be considered to be a monolayer adsorption process, mainly achieved via electrostatic attraction.

Table 2. Parameters of the isotherm model for the adsorption of Zn\(^{2+}\) onto MnO\(_2\)@PSS/PDDA/PSS.

| Temperature | Langmuir | Freundlich |
|-------------|----------|------------|
|             | K        | q\(_{\text{max}}\) (mg/g) | b (L/mg) | R\(^2\) | K\(_f\) (L/mg) | 1/n | R\(^2\) |
| 25°C        | 298      | 246.91 ± 0.22 | 0.296 ± 0.025 | 0.9990   | 3.4261 ± 0.097 | 0.8339 ± 0.082 | 0.9469   |

3.8. Adsorption of Other Heavy Metals in Alkaline Solution

MnO\(_2\)@PSS/PDDA/PSS was used as an adsorbent to test the removal of Pb\(^{2+}\) and Cu\(^{2+}\) from alkaline water. The results are shown in Figure 9A. It can be seen that the maximum adsorption capacities of Pb\(^{2+}\) and Cu\(^{2+}\) were 177.63 mg/g and 150.93 mg/g, respectively, indicating the efficient removal of Zn\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\) from alkaline water when using MnO\(_2\)@PSS/PDDA/PSS as an adsorbent material. It may be concluded that the adsorption affinity of metals onto MnO\(_2\)@PSS/PDDA/PSS occurs in the following order: Zn\(^{2+}\) ≈ Pb\(^{2+}\) > Cu\(^{2+}\). Moreover, the competition experiments were conducted with the presence of Pb\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) in the solution. The results show that the adsorption performance of Zn\(^{2+}\) slightly decreased in the presence of Pb\(^{2+}\) and Cu\(^{2+}\) (Figure 9B), which is likely due to the substitution of Zn\(^{2+}\) already adsorbed on the adsorption sites with Pb\(^{2+}\).

To simulate a real-life application, we collected tap water in the lab and Yellow River water in the city of Lanzhou, then prepared each solution of Zn\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\) with an initial concentration of 100 mg/L. The adsorption of Zn\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\) from tap water and Yellow River water was investigated. As shown in Table 3, the adsorption capacity of Zn\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\) in the tap water and Yellow River water was comparable to that in DI water, indicating the possible real application of this process in wastewater treatment.

Figure 9. The adsorption of Pb\(^{2+}\) and Cu\(^{2+}\) on MnO\(_2\)@PSS/PDDA/PSS in a single system (A) and ternary system (B).
Table 3. The adsorption capacity of Zn\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\) in tap water and Yellow River water.

| Metal Ions | Adsorption Capacity (mg/g) |
|------------|---------------------------|
|            | Tap Water | Yellow River Water |
| Zn\(^{2+}\) | 178.32 ± 0.89 | 171.66 ± 1.28 |
| Pb\(^{2+}\) | 174.85 ± 0.61 | 169.15 ± 1.72 |
| Cu\(^{2+}\) | 146.17 ± 0.50 | 138.22 ± 2.80 |

4. Conclusions

In this work, 3D urchin-like MnO\(_2@\)PSS/PDDA/PSS particles were prepared via the layer-by-layer (LBL) assembly of polyelectrolytes on MnO\(_2\) for the extraction of Zn\(^{2+}\) from alkaline media. The characteristics of the pH effect, adsorbent dosage, the initial Zn\(^{2+}\) concentrations, and contact time for MnO\(_2@\)PSS/PDDA/PSS were tested. The results showed that MnO\(_2@\)PSS/PDDA/PSS was very effective in removing Zn\(^{2+}\) from an aqueous solution at pH 13. Adsorption kinetics and equilibrium studies were applied to investigate the adsorption behavior of MnO\(_2@\)PSS/PDDA/PSS. The results showed that the experimental data fitted well with the second-order equation, and the adsorption isotherm was closely related to the Langmuir model. It was found that both the urchin-like structure of MnO\(_2\) and the surface coating of negatively charged PSS contributed to the efficient adsorption process. The competitive adsorption investigation suggests that Zn\(^{2+}\) adsorption could be interfered with by other cations present in wastewater. MnO\(_2@\)PSS/PDDA/PSS can be considered as a promising alternative for the adsorption of Zn\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\) from alkaline wastewater. We anticipate that more studies will take place on the efficient adsorption of Zn\(^{2+}\) using non-synthetic wastewater for real-life applications in future work.

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