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Layer-by-Layer Assembly of Polyelectrolytes on Urchin-like MnO_2 for Extraction of Zn^{2+} , Cu^{2+} and Pb^{2+} from Alkaline Solutions

Dong Chen ^{1,2} and Zhongren Nan ^{1,*}
¹ Gansu Key Laboratory for Environmental Pollution Prediction and Control, College of Earth and Environmental Sciences, Lanzhou University, Lanzhou 730000, China; chend16@lzu.edu.cn

² School of Agriculture and Forestry Economics and Management, Lanzhou University of Finance and Economics, Lanzhou 730020, China

* Correspondence: nanzhongren@lzu.edu.cn; Tel.: +86-0931-891-2328

Abstract: Three-dimensional (3D) urchin-like MnO_2 @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 Zn^{2+} from alkaline media. The adsorption performance of Zn^{2+} on MnO_2 , MnO_2 @PSS/PDDA/PSS, and MnO_2 @(PSS/PDDA)₃/PSS was investigated in batch experiments. The adsorption of Zn^{2+} on MnO_2 @PSS/PDDA/PSS has been studied under various conditions, such as initial Zn^{2+} concentration, adsorbent dosage, the solution's pH, and reaction time. The Zn^{2+} adsorption process is well represented by the pseudo-second-order kinetic model, and the equilibrium data fit the Freundlich isotherm well. MnO_2 @PSS/PDDA/PSS also showed high efficiency for Pb^{2+} and Cu^{2+} 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 Pb^{2+} , Cu^{2+} , and Zn^{2+} , from slightly alkaline wastewater.

Keywords: urchin-like MnO_2 ; LBL assembly; heavy metal ions; adsorption; polyelectrolytes

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1. Introduction

The dissolved phase of heavy metals, such as Pb^{2+} , Cu^{2+} , and Zn^{2+} , 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 (Pb^{2+}), mainly from petrol, paint, plumbing, pipes, car batteries, pigments, has a tolerable daily intake (TDI) value set at levels of $<3.5 \mu\text{g/kg}$ body weight. An overdose of Pb^{2+} over a long period might cause irreversible damage to the central nervous system [4,5]. Copper (Cu^{2+}) and zinc (Zn^{2+}) 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 Zn^{2+} from acidic [20,21] to neutral wastewater; however, little information is available for Zn^{2+} adsorption in slightly alkaline water [22,23]. Manganese oxide (MnO_2) 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 MnO_2 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 MnO_2 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 MnO_2 , 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 MnO_2 to form 3D adsorbent $\text{MnO}_2@(\text{PSS}/\text{PDDA}/\text{PSS})$. The adsorption properties of Zn^{2+} on $\text{MnO}_2@(\text{PSS}/\text{PDDA}/\text{PSS})$ were studied in batch experiments. Different experimental conditions affecting the uptake of Zn^{2+} 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

$\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 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 $\text{M}\Omega \text{ cm}$ 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 $\text{MnO}_2@(\text{PSS}/\text{PDDA}/\text{PSS})$ 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 Pb^{2+} , Cu^{2+} , and Zn^{2+} solution was monitored with a UV-vis spectrometer (Shanghai Jinghua 756MC, Shanghai, China).

2.3. Preparation of Urchin-like MnO_2

Urchin-like MnO_2 were prepared based on the following protocol. Typically, 10.7817 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 14.6048 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were dissolved in 70.0 mL of deionized water and heated at 120 $^\circ\text{C}$ 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 $^\circ\text{C}$ for 12 h.

2.4. Layer-by-Layer Assembly of Polyelectrolytes on MnO_2

For the LBL deposition, the PSS and PDDA were coated in an adsorption-centrifugation cycle. In a typical procedure, 0.05 g of MnO_2 was added into 5.0 mL of the polyelectrolyte solution (5 mM). The particles were incubated at 25 $^\circ\text{C}$ 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 $\text{MnO}_2@(\text{PSS}/\text{PDDA})_3/\text{PSS}$. The coating procedure was repeated 3 times, and finally, $\text{MnO}_2@(\text{PSS}/\text{PDDA})_3/\text{PSS}$ was obtained.

2.5. Adsorption Experimental Procedure

In a single system, the effect factors, including pH value, the initial concentration of Zn^{2+} , the dosage of adsorbent, and reaction time on adsorption were studied in a 50 mL conical flask with 20 mL of Zn^{2+} ($\text{Cu}^{2+}/\text{Pb}^{2+}$) solution. The mixture was stirred at a speed of 250 rpm/min for 24 h to reach adsorption equilibrium. The concentration of Zn^{2+} ($\text{Cu}^{2+}/\text{Pb}^{2+}$) 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]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{h} \quad (2)$$

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 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are rate constants for pseudo-first-order and second-order kinetics, respectively. The equation $h = k_2 q_e^2$ 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]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \quad (3)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (4)$$

where q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/L), $q_{\max}$ 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 , $\text{MnO}_2/\text{PSS}/\text{PDDA}/\text{PSS}$ and $\text{MnO}_2/(\text{PSS}/\text{PDDA})_3/\text{PSS}$

Figure 1 shows the TEM images of $\text{MnO}_2@(\text{PSS}/\text{PDDA})_3/\text{PSS}$ and $\text{MnO}_2@(\text{PSS}/\text{PDDA})_3/\text{PSS}$. 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 $\text{MnO}_2@(\text{PSS}/\text{PDDA})_3/\text{PSS}$ (A) and $\text{MnO}_2@(\text{PSS}/\text{PDDA})_3/\text{PSS}$ (B).

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 ($\text{MnO}_2@\text{PSS}/\text{PDPA}/\text{PSS}$ and $\text{MnO}_2@(\text{PSS}/\text{PDPA})_3/\text{PSS}$, 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 $\text{MnO}_2@\text{PSS}/\text{PDPA}/\text{PSS}$ (50 ± 11 nm, Figure 2E).

Figure 2. SEM images of MnO_2 (A,D), $\text{MnO}_2@\text{PSS}/\text{PDPA}/\text{PSS}$ (B,E) and $\text{MnO}_2@(\text{PSS}/\text{PDPA})_3/\text{PSS}$ (C,F).

The FT-IR spectra of MnO_2 and $\text{MnO}_2@\text{PSS}/\text{PDPA}/\text{PSS}$ 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 $-\text{S}=\text{O}=\text{S}-$ and $-\text{SO}_3$ symmetric vibrations of PSS, indicating the coating of PSS/PDPA 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. FT-IR spectra of MnO_2 and $\text{MnO}_2@\text{PSS}/\text{PDPA}/\text{PSS}$.

As shown in Figure 4A, the presence of Mn, N, and S elements in the sample of $\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$ 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 Mn 2p, 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 $\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$: wide scan (A), Mn 2p spectra (B), N 1s spectra (C), S 2p spectra (D).

3.2. Adsorption of Zn^{2+} on MnO_2 , $\text{MnO}_2/\text{PSS}/\text{PDDA}/\text{PSS}$, and $\text{MnO}_2/(\text{PSS}/\text{PDDA})_3/\text{PSS}$

The adsorption performance on MnO_2 , $\text{MnO}_2/\text{PSS}/\text{PDDA}/\text{PSS}$, and $\text{MnO}_2/(\text{PSS}/\text{PDDA})_3/\text{PSS}$ 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 , $\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$ and $\text{MnO}_2/(\text{PSS}/\text{PDDA})_3/\text{PSS}$ (121, 108 and 54 m^2/g , respectively), it could be concluded that the decreased adsorption capacity of $\text{MnO}_2/(\text{PSS}/\text{PDDA})_3/\text{PSS}$ 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 $\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$ and $\text{MnO}_2/(\text{PSS}/\text{PDDA})_3/\text{PSS}$ 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 $\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$ would combine approximately 2.701 mmol of Zn^{2+} , which is close to the experimental adsorption capacity (177.74 mg/g). Thus, $\text{MnO}_2/\text{PSS}/\text{PDDA}/\text{PSS}$ was chosen for the following experiments.

Figure 5. Zn^{2+} adsorption on MnO_2 , $MnO_2/PSS/PDDA/PSS$, and $MnO_2/((PSS/PDDA)_3)/PSS$ with an initial concentration of 100 mg/L at 25 °C (A), and their corresponding adsorption capacity and removal efficiency (B).

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.

Figure 6. Effect of pH on Zn^{2+} adsorption with an initial concentration of 100 mg/L at 25 °C (A). Adsorption capacity and removal of Zn^{2+} on $MnO_2@PSS/PDDA/PSS$ at different pH values (B).

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.

Figure 7. The effect of initial concentration on Zn^{2+} adsorption under a pH of 13.0 at 25 °C (A). Adsorption capacity and removal of Zn^{2+} on $MnO_2@PSS/PDDA/PSS$, with different initial Zn^{2+} concentrations at 25 °C (B).

3.5. Effect of Adsorbent Dosage

Figure 8 shows the effect of adsorbent dosage on Zn^{2+} removal by $MnO_2/PSS/PDDA/PSS$. 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.

Figure 8. The effect of adsorbent dosage on Zn^{2+} adsorption with an initial concentration of 100 mg/L at 25 °C (A). The adsorption capacity and removal of Zn^{2+} on $MnO_2@PSS/PDDA/PSS$ with different adsorbent dosages at 25 °C (B).

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 $\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$, with an initial concentration of 100 mg/L, under a pH of 13.0 at 25 °C.

Initial	q_{exp}	Pseudo-First-Order			Pseudo-Second-Order		
conc. mg/L	mg/g	$k_1 \times 10^{-2}$ min^{-1}	q_e mg/g	R^2	$K_2 \times 10^{-3}$ $\text{g}/(\text{g} \cdot \text{min})$	q_e mg/g	R^2
100	177.74 ± 0.21	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 $\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$ 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 $\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$.

Temperature	Langmuir			Freundlich		
K	q_{max} (mg/g)	b (L/mg)	R^2	K_f (L/mg)	$1/n$	R^2
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

$\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$ 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 $\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$ as an adsorbent material. It may be concluded that the adsorption affinity of metals onto $\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$ occurs in the following order: $\text{Zn}^{2+} \approx \text{Pb}^{2+} > \text{Cu}^{2+}$. 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 $\text{MnO}_2@\text{PSS}/\text{PDDA}/\text{PSS}$ 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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