Preparation of *L*-arginine modified magnetic adsorbent by one-step method for removal of Zn(II) and Cd(II) from aqueous solution

Shuangzhen Guo^a; Pengpeng Jiao^a; Zhigang Dan^{b*}; Ning Duan^{a,b}; Guanyi Chen^a; Jian Zhang^c

Abstract

A new type of magnetic adsorbent was prepared using a simple one-step synthesis for the removal of Zn(II) and Cd(II) from aqueous solution. Structure characterization demonstrated that the surface of the magnetic nanoparticles (MNPs) had been modified by *L*-arginine. Factors that affect the adsorption of Zn(II) and Cd(II) onto the MNPs modified with *L*-arginine (MNPs-L), such as pH, ionic strength, initial concentration, contact time, temperature, and compete adsorption, were investigated. The adsorption kinetic data followed the

pseudo-second-order model (PSOE) and the intra particle diffusion model (IPD). Isotherm data demonstrate that the Langmuir absorption model was the best-suited model for this research, and the calculated maximum adsorption capacities of Zn(II) and Cd(II) were 150.4 mg/g and 120.2 mg/g, respectively. Thermodynamic parameters indicated a spontaneous and endothermic adsorption process. In addition, regeneration studies suggested that MNPs-L were stable. Thus, MNPs-L could be a promising material for removing Zn(II) and Cd(II) from wastewater.

Keywords: *L*-arginine; magnetic nanomaterials; Zn(II) and Cd(II); adsorption

Introduction

Heavy metal pollution in industrial wastewater is a major problem and a common concern in society. According to the World Health Organization (WHO) ^[1], zinc and cadmium are two of the most toxic heavy metals. When consumed in large amounts, zinc and cadmium are difficult for the body to process, which may lead to the accumulation of these metals in various organs and cause serious illness. According to WHO guidelines, the concentrations of Zn(II) and Cd(II) that are allowed in drinking water are limited to 3 mg/L and 0.003 mg/L ^[2], respectively. The harmful health effects that may occur because of

consuming larger amounts of cadmium include diarrhea, stomach problems, kidney damage and, occasionally, death ^[3]. The accumulation of cadmium in the body may adversely affect different organs, including the pancreas, lungs, liver, and intestines ^[4]. Excessive amounts of zinc in the human body may lead to serious health problems, such as cramps, stomach nausea, anemia, vomiting, and skin irritation ^[5]. It is critical and urgent for society to begin to address Zn(II) and Cd(II) pollution.

Numerous technologies and methods for the removal of Zn(II) and Cd(II) from aqueous solution have been developed, such as reverse osmosis, chemical precipitation, ion-exchange and membrane separation ^[6-9]. However, it is not economical to use the above techniques to treat a large amount of heavy metal wastewater. Instead, adsorption was demonstrated to be an economical method to treat heavy metal wastewater because of its lower cost, higher efficiency, and ease of the operation of removing the heavy metal ions. Many adsorbents have been used for the removal of heavy metal ions from aqueous solution, including red mud ^[10], carbon nanotubes ^[11], graphene ^[12], and hydroxyapatite ^[13]. These adsorbents have also achieved good adsorption results. However, the ultimate goal of this project was to develop a synthetic adsorbent with high adsorption efficiency, low cost, large adsorption capacity, and simple preparation.

Separation of the adsorbent from the solution is difficult after

adsorption is completed. Filtration, sedimentation, and centrifugation were often used for separating the adsorbent from the solution ^[14]. Magnetic separation had an exceptional advantage, allowing the adsorbent to be easily separated from the aqueous solution when in the presence of an external magnetic field. In recent years, Fe₃O₄ nanoparticles were used as an adsorbent by several researchers ^[15-16], since Fe₃O₄ nanoparticles could easily be prepared and cover a high specific surface area. However, Fe₃O₄ magnetic particles have several drawbacks, such as low stability in strong acidic environments and low selectivity, as it contains hydroxyl, a functional group on the surface of particles. To overcome this issue, the surface of the Fe₃O₄ nanoparticles was modified, which stabilizes abundant functional groups. Traditional modified materials include silica ^[17, 18] and polymer ^[19, 20]. When analyzing the synthesis of the modified magnetic Fe₃O₄ nanoparticles mentioned above, it is important to note that the actual synthesis process often requires two or more steps, resulting in a low efficiency, time-consuming process.

In this paper, MNPs were modified by *L*-arginine using a one-pot hydrothermal synthesis method. Due to the abundant amino groups and carboxyl groups that are modified on the particle surface, as well as the strong magnetic responsivity, the prepared nanoparticles have high adsorption capacity and can be rapidly separated from aqueous solution.

2. Experimental Section

2.1 Materials

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, *L*-arginine, sodium thiosulfate, $\text{Zn}(\text{NO}_3)_2$, and $\text{Cd}(\text{NO}_3)_2$ were purchased from Guoyao Chemical Reagents Corporation in Shanghai, China. All reagents were of analytical grade. Only deionized water was used throughout this study.

2.2 Synthesis of MNPs-L using a one-step method

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1.39 g) was dissolved in 14 mL of water, then $\text{Na}_2\text{S}_2\text{O}_3$ (1.24 g) was added to the mixed solution under vigorous stirring for 10 minutes at room temperature. *L*-arginine (0.5 g) was added to the mixed solution followed by NaOH (10 mL, 1.0 mol/L), which was added drop by drop into the mixed solution, again under vigorous stirring. Next, the solution was transferred to the autoclave and heated at 413 K for 12 hours. The product was gathered by magnetic separation; later, it was washed five times using deionized water and dried at 333 K for 24 hours. MNPs were prepared in the same step without addition of *L*-arginine. The MNPs-L nanocomposite is shown schematically in Fig. 1.

2.3. Characterization

Scanning electron microscope (SEM) images were obtained using a Sigma VP scanning electron microscope (Carl Zeiss, Germany). X-ray powder diffraction (XRD) results were obtained on Rigaku instrumentation (Japan) with Cu Ka radiation ($\lambda = 0.1542 \text{ nm}$) in the

range of 25 to 70 degrees at 30 kV. The Fourier transform infrared (FT-IR) spectra of MNPs and MNPs-L was obtained using an FT-IR spectrometer (Thermo Nicolet 380, USA). The hysteresis loops were tested with a vibrating sample magnetometer (LDJ 9600, USA), and the particle sizes of MNPs and MNPs-L were measured using a laser particle analyzer (Agilent Technologies, USA). The thermo gravimetric analysis (TGA) was obtained using a thermo gravimetric analyzer (Mettler Toledo 851, Swit). The concentration of Zn(II) and Cd(II) was determined by AAS (Analytik Jena 350, Germany).

2.4. Adsorption experiments

The adsorption of Zn(II) and Cd(II) by MNPs-L was complete at 298 K. The aqueous solution of Zn(II) and Cd(II) was confected by dissolving a calculated dosage of $\text{Zn}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ in deionized water. The pH of aqueous solution was adjusted by using 0.1 mol/L of NaOH and 0.1 mol/L of HNO_3 . Generally, 25 mg of MNPs-L was added to 50 mL of the Zn(II) and Cd(II) aqueous solution. The aqueous solution was shocked for a period of time. Afterward, the MNPs-L were removed from the solution with the introduction of an external magnetic field. The amount of heavy metal ions adsorbed (q) is given as follows:

$$q = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where the amount of metal ions adsorbed per unit mass is represented by q (mg/g). The initial concentration of the metal ions as well as the

concentration of the metal ions at the time of equilibrium is represented by C_0 and C_e (mg/L), respectively. The mass of MNPs-L is represented by m (g). V (L) represents the volume of aqueous solution.

3. Results and Discussion

3.1 Characteristics of the prepared MNPs-L and MNPs

The morphology of MNPs and MNPs-L was analyzed by using SEM images and particle diameter results, which are displayed in Fig. 2. SEM imaging shows that MNPs-L and MNPs exhibited different morphologies. The morphology of the MNPs is polyhedral, while the morphology of the MNPs-L is rod-like. The morphology of the MNPs is consistent with the typical morphology of Fe_3O_4 . The size of MNPs-L is in the range of 180 to 230 nm, while the size of the MNPs is in the range of 80 to 120 nm, which is nearly consistent with the results of the laser particle analysis, which exhibits average diameter particle sizes of 202.5 ± 11.5 nm and 92.6 ± 13.7 nm (Fig. 2).

FT-IR spectra results of MNPs and MNPs-L are shown in Fig. 3; the peaks of all samples occurred at 568 cm^{-1} , which is representative of the Fe-O vibration. For the MNPs-L sample, the peaks at 2930 and 1384 cm^{-1} are characteristic of C-H peaks. Peaks at $2358\text{--}2232\text{ cm}^{-1}$ could be ascribed to the bending vibration of $\text{C}\equiv\text{N}$. This finding may be observed because $\text{C}=\text{N}$ was isomerized at a high temperature and pressure. The absorption peak of $\text{C}=\text{O}$ is red shifted to 1640 cm^{-1} due to the influence of

the amino group as the electron donating group and the intra molecular hydrogen bond, which overlaps with the absorption peak of C=N. The peaks at 1210–1010 cm^{-1} , double peaks at 3317-3124 cm^{-1} , and peaks at 1640 cm^{-1} are ascribed to the C-N stretch vibration, N-H stretching, and C=N stretch vibration, respectively, which indicate the existence of -NH₂ and C=NH. This finding signifies that MNPs have been modified by *L*-arginine.

The XRD results of MNPs and MNPs-L are shown in Fig. 4. The XRD patterns show the feature peaks of magnetic Fe₃O₄ at 30.1° (220), 35.5° (311), 43.1° (400), 53.4° (422), 57.0° (511), and 62.6° (440), which are consistent with the data in the JCPDS file (PDF No. 85-1436). The peak position of Fe₃O₄ and MNPs-L are the same, which indicates that the *L*-arginine modification does not influence the crystallization of Fe₃O₄.

The thermo gravimetric curves (Fig. 5) reflect the thermal stability of MNPs and MNPs-L. Actually, the MNPs show two decomposing stages of 3.57% from 50°C to 125°C and of 3.86% from 570°C to 750°C, corresponding to adsorbed water and hydroxyl decomposition of the MNPs surface, respectively. MNPs-L shows weight loss in four stages. The first stage is a decomposing stage with a loss of 2.28% from 50°C to 135°C; this weight loss is attributed to the loss of absorbed water in MNPs-L. There is a second stage with a loss of 5.79% from 193°C to

277°C, which relates to the decomposing of amino acids, which were modified on the surface of the MNPs-L. The third decomposing stage with a loss of 0.89% from 390°C to 430°C is related to carboxyl decomposition. The last stage of weight loss is related to hydroxyl decomposition, which is similar to the MNPs decomposition at the range of 500 to 900°C. TG results show that *L*-arginine, which was modified on surface of the MNPs, was calculated to be approximately 6.44% for the total mass of MNPs-L.

Fig. 6 shows the magnetization of MNPs and MNPs-L. The magnetization saturation values of the MNPs and MNPs-L were 57.59 and 26.98 emu/g, respectively. As *L*-arginine has no magnetic properties, it shields the magnetization of the MNPs. Consequently, it follows that the more the *L*-arginine is modified on surface of the MNPs, the lower the magnetization saturation values of the MNPs will be, which also follows Liren Fan's theory ^[21]. Although magnetization strength decreased after *L*-arginine chelating, it could also be inferred that the separation of the MNPs-L in the solution could be controlled by external magnetic fields with magnetization strength ^[22]. According to Z.Y. Ma ^[23] theory, 16.3 emu/g is enough for magnetic separation by the use of a traditional permanent magnet. Thus, the magnetization of MNPs-L is sufficient to be separated from the permanent magnetic field.

3.2 Adsorption experiments

3.2.1 Effect of pH

Many researchers have observed that pH is an important factor in the adsorption process ^[24], and Fig. 7 shows the change of adsorption capacity with different values of pH. It is already known that Zn(II) and Cd(II) form a hydroxyl complex with precipitation at $\text{pH} > 6$. In Fig. 7, the adsorption capacity reaches the maximum values of 125 mg/g and 102 mg/g for Zn (II) and Cd (II), respectively, at a pH of approximately 6.0. When the pH value is low, the adsorption capacity is small because of competitive adsorption. The H^+ radius is smaller than the radius of Zn(II) and Cd(II), and H^+ more easily covers the surface of MNPs-L. Due to steric hindrance and charge repulsion, metal ions could not enter the surface of MNPs-L, which leads to lower adsorption capacity at lower pH values. With increasing of pH values, steric hindrance and charge repulsion force becomes weak, which created more active sites on the surface that were available to Zn(II) and Cd(II). The results of Samia's ^[25] and Smaail Radi's ^[26] work also shows that the adsorption capacity of Zn (II) and Cd (II) increases as pH increases from 1 to 6.

3.2.2 Effect of ionic strength

Fig. 8 shows the effect of ionic strength on the adsorption progress. Using data related to ionic strength, we could determine the outer-space surface complexation and the inner-space surface composite. Furthermore, the decrease of adsorption capacities is also related to the outer-sphere

surface complexation, but the inner-sphere surface composite does not change or increase with increases of ionic strength ^[26]. In Fig. 8, we observe that the adsorption capacities of Zn(II) and Cd(II) first increase and later decrease, which subsequently results in an increase in ionic strength. When ionic strength is equal to 0.01 mol/L KNO₃, adsorption capacities reach maximum values. Fig. 8 also demonstrated that outer-sphere surface complexation exists in the adsorption process. This finding can be explained because of the nature of electrostatic interactions attraction between the functional groups and the metal ions at low ionic strength. With the increase of ionic strength from 0.1 to 1.0 mol/L KNO₃, the electrostatic interaction changed from attractive to repulsive in nature, which meant that increasing numbers of positive ions were adsorbed on the surface of MNPs-L as ionic strength increased. Thus, less metal ions were adsorbed due to the electrostatic repulsion. However, negative ions on the surface of MNPs-L increased. The existence of negative ions in the boundary layer ultimately resulted in a decrease of electrostatic interactions between metal ions and functional groups. Furthermore, the ionic strength influenced the activity coefficients of Cd(II) and Zn(II) ions, which limit metal ions transferring to the MNPs-L surface. It has been reported ^[27] that the addition of cations would affect the interaction constants of metal ions due to the accumulation of charges on the surface of MNPs-L. The adsorption capacities of Zn (II) and Cd (II), the

modified carbon nanotubes ^[25], and the MNPs-L all reached maximum values of 0.1 mol/L KNO₃, but the MNPs-L are more likely to be affected by the ionic strength.

3.2.3 Effect of contact time and kinetic modeling

To achieve the suitable contact time, the following experiments were performed. Fig. 9 shows the amount of the adsorbed Zn(II) and Cd(II) from MNPs-L and the amount of contact time. When the contact time increases, the amount of the metal ions adsorbed increases. During the first stage (0–10 min), the rate of removing metal ions was fast because all of the active sites of the MNPs-L were vacant, and the concentration gradient of the metal ions was high. This finding also indicates that the speed of adsorption was a rapid process, with equilibrium being reached in less than 10 min. Ten minutes later, the speed of adsorption became slow, due to a decrease in the concentration gradient. According to the results, suitable contact time was finally obtained after 20 min.

To understand the adsorption process of metal ions and MNPs-L, three kinetic models were used to simulate the experimental data. The equations of pseudo-first-order kinetics (2) and pseudo-second-order kinetics (3) are shown as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{K_2(q_e)^2} + \frac{t}{q_e} \quad (3)$$

where the rate constant of pseudo-first-order kinetics and pseudo-second-order kinetics are represented by K_1 and K_2 (min^{-1}), respectively. The amounts of Cd (II) and Zn (II) are adsorbed at the time of equilibrium and at any time t is represented by q_e and q_t (mg/g). Using these equations, the data of the fitted models are shown in Table 1. The R^2 value of the pseudo-second-order model is higher than the R^2 value of the pseudo-first-order model, which means that the pseudo-second-order model is better suited than the pseudo-first-order model. Hence, the pseudo-second-order model is more appropriate to describe the adsorption behavior of Zn (II) and Cd (II) by MNPs-L.

In general, the process of adsorption commonly proceeds through three stages: (1) metal ions were moved from the bulk solution to the boundary layer; (2) metal ions were diffused through the boundary layer to the surface of adsorbent; (3) metal ions were adsorbed at an active site. To investigate the metal ions diffusion rule, the intraparticle diffusion model Eq (4) can be used.

$$q_t = K_i t^{0.5} + C \quad (4)$$

where C is a constant that relates to the thickness of the boundary layer, and K_i is the rate constant. Fig. 10 shows q_t versus $t^{0.5}$ plots for the adsorption of Zn (II) and Cd (II). It is shown that q_t versus $t^{0.5}$ plots have three distinct regions. The first linear part represents external mass transfer. The second linear section represents intra particle diffusion. The

third linear portion stands for the adsorption–desorption equilibrium. For Zn(II) and Cd(II), K_{id1} was much larger than K_{id2} (Table 1), which indicated that the main rate-limiting step in the adsorption process is intra particle diffusion. Comparatively, the intra particle diffusion of Cd(II) is likely controlled by the adsorption kinetics more than that of Zn(II) ($K_{id2}(\text{Zn}) > K_{id2}(\text{Cd})$). It might also be related that the ionic radius of Cd(II) is larger than Zn(II).

3.2.4 Effect of initial concentration and isotherm modeling

The concentration of metal ions is a very important factor that influences the driving force that penetrates mass transfer resistance between solid and aqueous phases. It is essential to obtain the suitable concentration of metal ions for MNPs-L. The influence of the initial concentration of Zn(II) and Cd(II) on adsorption in the solution is displayed in Fig. 11. As shown in Fig. 11, adsorption capacity increased along with increases in the initial Zn(II) and Cd(II) concentrations during the first stage, which was in the range of experimental concentration. Adsorption capacity maintained the maximum level with increases of metal concentration. This is because more Zn(II) and Cd(II) surrounded the functional group of MNPs-L under a higher concentration, thus the adsorption process was more efficient ^[28]. With the increasing concentration of metal ions, the surface of the MNPs-L functional group was gradually saturated (150 mg/L and 120 mg/L for Zn(II) and Cd(II)),

respectively), and the adsorption rate slowed. The adsorbent capacity of Zn(II) (125 mg/g) was greater than that of Cd(II) (102 mg/g) at the same concentration (>150 mg/L). This finding is observed because the MNPs were modified by *L*-arginine. According to the Irving-Williams series ^[29], Cd(II) has a similar affinity for amino acids as that of Mn(II) $< \text{Fe(II)} \approx \text{Cd(II)} < \text{Zn(II)} < \text{Ni(II)} \ll \text{Cu(II)}$. Zn(II) is more approachable than Cd(II) to *L*-arginine; thus, MNPs-L can absorb more Zn(II) than Cd(II) at the same concentration. These results are consistent with the work of I. Sóvágó, K. ^[30].

To obtain the adsorption isotherms and analyze the adsorption model, we conducted the adsorption experiments with various initial Zn(II) and Cd(II) concentrations. Adsorption isotherms were obtained by studying the relationship between the equilibrium concentration and the equilibrium capacity.

The Freundlich isotherm and the Langmuir isotherm model are the most commonly used models for analyzing the adsorption equilibrium data. The Langmuir isotherms equation (5) and Freundlich isotherms equation (6) are shown as follows:

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

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

where the adsorption capacity and concentration of metal ions at

equilibrium are represented by q_e (mg/g) and C_e (mg/L), respectively. The maximum adsorption capacity of adsorbents is represented by q_m (mg/g). K_L and K_F represent the Langmuir isotherms model and Freundlich isotherms model constants, respectively. n is the adsorption strength of the Freundlich isotherms model.

The degree of appropriate of MNPs-L drawn toward Zn (II) and Cd (II) is predicted from the values of separation factor constant (R_L), which is shown as follows:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

where the initial concentration of metal ions is represented by C_0 (mg/L). The Langmuir isotherm constant is represented by K_L . The value of R_L revealed that the adsorption of metal ions onto the MNPs-L is favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$), and linear ($R_L = 1$) and unfavorable ($R_L > 1$) [31]. In this study, the values of R_L were between 0 and 0.6 for Zn (II) and Cd (II) (Table 2), signifying favorable adsorption of the metal ions by MNPs-L. In the Freundlich isotherms model, values of n in range of 2 to 10, 1 to 2, and 0 represents good, poor, and difficult adsorption characteristics, respectively [32]. As shown in Table 2, the values of n were 2.9672 and 3.0347 for Zn (II) and Cd (II), respectively, which means that Zn (II) and Cd (II) were adsorbed on the surface of MNPs-L. This is interpreted as good adsorption.

The data produced using the Freundlich model and Langmuir model

are exhibited in Table 2. Table 2 shows that the R^2 values of the Langmuir model are higher than in Freundlich model, which suggests that the monolayer and physical adsorption of Zn (II) and Cd (II) are on energetically identical sites within the MNPs-L.

3.2.5 Thermodynamics of the adsorption process

Temperature is an important factor that affects adsorption progress. Temperature can influence the rate of diffusion and the viscosity of the solution; thus, it is necessary to investigate the relationship between temperature and adsorption. Fig. 12 shows the influence of temperature on adsorption capacity. In Fig. 12, it is proved that the equilibrium adsorption capacity was clearly affected with increases of temperature. When the temperature increased from 25 to 40°C, the metal ions uptake capacity increased from 125 to 134 mg/g and from 102 to 109 mg/g for Zn(II) and Cd(II), respectively. With increases of temperature, which decreases the viscosity of the aqueous solution, the diffusion rate of the metal ions increases across the external boundary layer and the surface of MNPs.

To determine the possibility of spontaneous adsorption, it is essential to study thermodynamics conducted by the Gibbs free energy change (ΔG^0). The thermodynamic parameters of adsorption progress, such as entropy change (ΔS^0), free energy change (ΔG^0), and enthalpy change (ΔH^0) were derived by the following Eqs.(8), (9), and (10)

$$K_d = \frac{q_e}{C_e} \quad (8)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

$$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 \quad (10)$$

where C_e (mg/L) and q_e (mg/g), respectively, represent the concentration and adsorption capacity at equilibrium. The temperature in adsorption progress is represented by T (K) and the gas constant is represented by R (8.314 J/mol•K). A straight line was obtained by $\ln K_d$ fitted with $1/T$ (seen in Fig. 13). Table 3 shows that the change of thermodynamic parameters for the adsorption process. The negative values of ΔG^0 suggested the adsorption process is spontaneous. The positive values of ΔH^0 and ΔS^0 proved that the process is endothermic in nature, with increasing uncertainty during the solid/liquid interface, which demonstrated that rising temperature was a positive factor on the adsorption kinetics. The spontaneity of the adsorption process is the result of increased entropy.

3.2.6 Effect of mixtures of heavy metals

Competitive adsorption among metal ions is an important factor in wastewater treatment, as metal ions naturally exist together. Fig. 14 revealed that the changes of adsorption capacity in the Zn(II) and Cd(II) mixture occurred with an increase in the concentration of metal ions. As is shown in Fig. 14, the adsorption capacity first increased and then reached stable value, with increases in the concentration of the mixed Zn

(II) and Cd (II) solution. However, maximum adsorption capacity is just 87 and 39 mg/g for Zn (II) and Cd (II), respectively. Compared to pure Zn (II) or Cd (II) solutions, the adsorption capacities are decreased 30.4% and 61.76% for Zn (II) and Cd (II), respectively. Cd (II) adsorption reduction is much larger than Zn (II). When analyzing the competitive adsorption of Zn (II) and Cd (II), NiO^[33] shows that Zn (II) is superior to Cd (II) adsorption, but tourmaline^[34] demonstrates that Cd (II) is superior to Zn (II) adsorption. Unfortunately, there is no consensus between researchers about the competitive adsorption of metal ions in solutions, which can be influenced by different affinities and various factors.

Zn and Cd are (II) B elements, and they are all d^{10} arrangements of extra nuclear electrons. Since the ionic radius of Cd is larger than Zn, the deformation and inter diffusion of Cd ions is stronger than Zn ions (electronegativity of Cd and Zn are 1.69 and 1.65, respectively), resulting in a stronger the covalent bond of Cd, and stronger chelating groups. However, Cd (II) has a bigger ionic radii (0.97 Å) than Zn (II) (0.74 Å); hence, the smaller the radius of the metal ions, the easier it is for metal ions to diffuse through the boundary layer and to be adsorbed onto the surface of the MNPs-L. The intra particle diffusion model also proved that Cd (II) was harder to transfer than Zn (II) ($K_{id2}(Zn) > K_{id2}(Cd)$). Furthermore, the lower adsorption capacity of Cd (II) may be related to

the lower tendency of Cd(II) to form hydrolysate, and Cd (II) cannot compete effectively with Zn (II) for variably charged surfaces. Consequently, its adsorption progress is more restricted to permanent charge sites.

3.3 Comparison with other adsorbents

The maximum adsorption capacity (q_{max}) of different types of adsorbents ^[35-40] for Zn (II) and Cd (II) are shown in Table 4. So far, researchers have used many adsorbents for removing Zn (II) and Cd (II). The maximum adsorption capacity of Zn (II) and Cd (II) on the MNPs-L were 150.2 and 120.2 mg/g, respectively. These adsorption capacities are higher than capacities of other adsorbents. MNPs-L exhibited promising potential in Zn (II) and Cd (II) adsorption, since they exhibit high adsorption capacity and can be easily separated by introducing an external magnetic field.

3.4 Regeneration and reuse of MNPs-L

Regeneration of the adsorbent for reuse is important in the industrial practice of removing heavy metals from wastewater. Zn (II) and Cd (II) can be regenerated by using 5–6 mL 6 mol/L HCl per gram. The regenerated MNPs-L adsorbent could still keep approximately 86% of its capacity in the fifth consecutive adsorption-regeneration cycle (Fig. 16), indicating that this material has potential industrial application.

4. Conclusions

In this study, a functional magnetic material (MNPs-L) was prepared using a simple one-pot method and applied as a valid adsorbent to improve Zn(II) and Cd(II) adsorption. The structure characterization suggested that the carboxyl and amino groups were successfully modified on the surface of the MNPs. Kinetic study indicated that the most suitable kinetic model to apply is the pseudo-second-order model. The rate-limiting step is intra particle diffusion, and the time to equilibrium during adsorption is 20 min. Competition adsorption indicated that Zn (II) has more competitive force than Cd(II) on the MNPs-L. Ionic strength results proved the existence of outer-sphere surface complexation in the adsorption process. In addition, the isotherm data demonstrate that the Langmuir model is the best fitting model, and the calculated maximum adsorption capacity of Zn(II) and Cd(II) are 150.4 mg/g and 120.2 mg/g at 298 K and pH 6.0. Thermodynamics data suggested that endothermic tendencies and spontaneity in the adsorption process. The adsorption-desorption studies suggest that MNPs-L is a promising adsorbent for Zn(II) and Cd(II) removal.

Acknowledgments

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Table 1
Dynamic parameters for the adsorption of Zn (II) and Cd (II) onto MNPs-L.

Met al ion	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion model					
							The first stage			The second stage		
	K_1	q_e	R^2	K_2	q_e	R^2	K_{id1}	C_1	R_1^2	K_{id2}	C_2	R_2^2
Zn	0.2732	141.7	0.9834	0.0062	141.2	0.9931	37.214	-2.823	0.9932	12.362	71.560	0.9861
Cd	0.3126	102.2	0.9763	0.0161	103.4	0.9962	32.686	-2.322	0.9863	10.617	57.692	0.9814

Table 2
Isotherm modeling parameters for the adsorption of Zn (II) and Cd (II) onto MNPs-L.

Metal ion	Langmuir isotherm model				Freundlich isotherm model		
	$q(\text{mg/g})$	K_L	R_L	R^2	$K_F(\text{mg/g})$	n	R^2
Zn	150.4	0.0268	0.199-0.550	0.9957	22.1983	2.9672	0.9494
Cd	120.2	0.0308	0.178-0.520	0.9949	19.4567	3.0347	0.8178

Table 3
Thermodynamic parameters for the adsorption of onto MNPs-L

Metal ion	$\Delta H^0(\text{kJ/mol})$	$\Delta S^0(\text{J/k}\cdot\text{mol})$	$T(\text{K})$	$\Delta G^0(\text{kJ/mol})$
Zn	2.99	16.97	298	-2.07
			303	-2.15
			308	-2.24
			313	-2.32
			298	-2.10
Cd	3.10	17.46	303	-2.19
			308	-2.28
			313	-2.36

Table 4

Comparison of Zn (II) and Cd (II) adsorption by MNPs-L with other adsorbents

Adsorbent material	Adsorption capacity(mg/g)		reference
	Zn	Cd	
Nano-TiO ₂	7.9	15.3	[35]
Amino silica spheres	193	190.5	[36]
Nano-hydroxyapatite	-	64.1	[37]
Magnetic poly(vinylbenzyl chloride-co-styrene-co-divinyl benzene),	67.3	-	[38]
Silica particle modified by 25 Conjugated β -Ketoenol Furan		55.6	[39]
Magnetic ChNTs	-	23.8	[26]
Activated carbon	-	33.6	[40]
This study	150.4	120.2	

Fig.1

Fig. 1. Physical structure of MNPs-L nanocomposite

Fig.2

Fig. 2. SEM and particle diameter of MNPs(a) and MNPs-L(b)

Fig.3

Fig. 3. The IR spectra of MNPs and MNPs-L

Fig.4

Fig. 4. XRD patterns of MNPs and MNPs-L

Fig.5

Fig. 5. Thermogravimetric curve of MNPs and MNPs-L

Fig.6

Fig. 6. Magnetization curve of the MNPs and MNPs-L measured at room temperature

Fig.7

Fig. 7. Effect of initial pH value on the adsorption capacity (Experimental conditions: metal ion concentration is 150 mg/L, contact time is 20 min, 25 mg MNPs-L in 50 mL solution and an ionic strength of 0.1 M KNO_3 , at 298 K)

Fig.8

Fig. 8. Effect of ionic strength on the adsorption capacity (Experimental conditions: metal ion concentration is 150 mg/L, pH=6, 25 mg MNPs-L in 50 mL solution and contact time 20 min, 298 K)

Fig.9

Fig. 9. Effect of contact time on the adsorption capacity (Experimental conditions: metal ion concentration is 150 mg/L, pH=6, 25 mg MNPs-L in 50 mL solution and an ionic strength of 0.1 M KNO₃, 298 K)

Fig.10

Fig. 10. Intraparticle diffusion model for the adsorption of Zn (II) and Cd (II)

Fig.11

Fig. 11. Effect of metal ion concentration on adsorption by MNPs-L from aqueous solution. (Experimental conditions: pH = 6, contact time is 20 min, 25 mg MNPs-L in 50 mL solution and an ionic strength of 0.1 M KNO₃, at 298 K)

Fig.12

Fig. 12. Effect of temperature on the adsorption capacity (Experimental conditions: metal ion concentration is 150 mg/L, pH=6, contact time is 20 min, 25 mg MNPs-L in 50 mL solution and an ionic strength of 0.1 M KNO_3)

Fig.13

Fig. 13. Thermodynamics plot for adsorption of Zn (II) and Cd (II) by MNPs-L

Fig.14

Fig. 14. Effect of metal completion on the adsorption capacity (Experimental conditions: contact time 20 min, pH = 6, 25 mg MNPs-L in 50 mL solution and an ionic strength of 0.1 M KNO_3 , 298 K)

Fig. 15

Fig. 15. Repetitive adsorption and desorption of Zn (II) and Cd (II) by MNPs-L