

Preparation of Fe₃O₄/poly(L-glutamic acid) microspheres and their adsorption of Cu(II) ions

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ABSTRACT: Fe₃O₄/poly(L-glutamic acid) (P-L-Glu) magnetic microspheres were synthesized in an L-glutamic acid solution by coprecipitation and a dehydration condensation reaction and were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, and ζ -potential measurement. P-L-Glu was coated on the surface of Fe₃O₄ microspheres. The average particle diameter of Fe₃O₄/P-L-Glu was 388 nm and dispersed homogeneously in water. The adsorption of Cu(II) ions on Fe₃O₄/P-L-Glu was further studied. The effect of different pH values and reaction times on the adsorption of Fe₃O₄/P-L-Glu was discussed. The adsorption equilibrium was reached in 40 min, and the maximum adsorption for Cu(II) ions was more than 500 mg/g; this value occurred at pH 8 in water. The adsorption dynamic process fit the Freundlich isotherms well, and the adsorption kinetics followed the adsorption mechanism of the pseudo-second-order equation, which was the main complexation reaction. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43730.

KEYWORDS: adsorption; functionalization of polymers; kinetics

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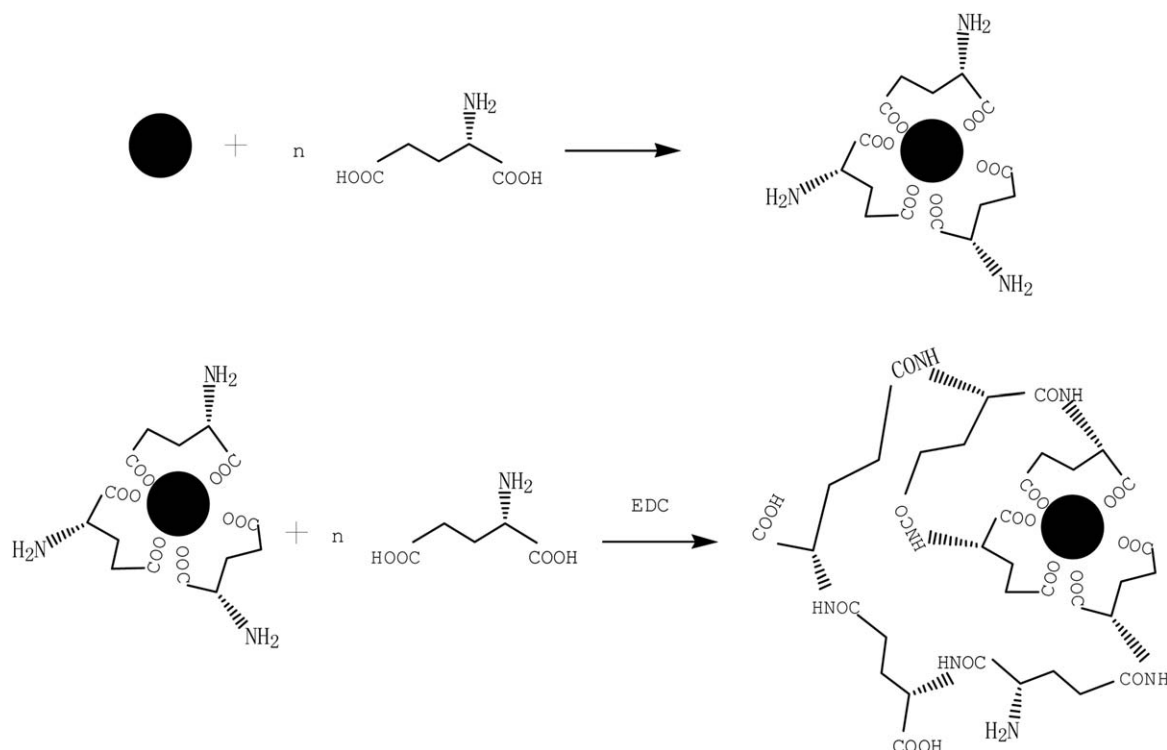
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INTRODUCTION

Sorbents have been used widely in contaminated water treatment to remove heavy metals. This method is easier to implement and can prevent secondary pollution because the sorbents can be collected and reused.¹ In particular, magnetic bead sorbents have attracted much attention because of their magnetic characteristics and large surface area. Magnetic beads can be collected in a magnetic field and dispersed again once the magnetic field is removed, which make solid–liquid separation faster and more convenient.² In recent years, research has mainly focused on the functional surface coat preparation or surface modification for obtaining efficient and selective magnetic beads, in which the surface functional groups are commonly amino, carboxyl, hydroxyl, and so on. For example, magnetic beads coated by Ethylene Diamine Tetraacetic Acid modified polystyrene (PS–EDTA),³ chitosan,⁴ carboxymethyl cellulose–poly(ethylene imine),⁵ polycysteine,⁶ or poly(γ -glutamic acid)⁷ have been reported. However, compared with the traditional adsorption materials,⁶ the adsorption capacity of the beads on heavy-metal ions shown previously has not been significantly improved. According to the literature, the adsorption of these beads on heavy-metal ions is of the Langmuir monolayer type, and the absorption content cannot increase significantly. So, it is of interest to develop a new type of surface-coating magnetic beads with a better adsorption capacity.

Adsorption materials require amino or carboxyl groups on their surface; these can chelate heavy-metal ions. Research on natural L-glutamic acid (L-Glu) modified magnetic nanomaterials exists. Obviously, the structure is made of amounts of amino acids by a condensation reaction. Poly(L-glutamic acid) (P-L-Glu) peptide dendron was synthesized, and dopamine was immobilized on it as the ligand on the surface of Fe₃O₄ magnetic nanoparticles via ligand exchange.⁸ Yin *et al.*⁹ observed the distribution of Fe₂O₃ nanoparticles in mice; this was coated with glutamic acid and traced by ⁵⁹Fe. In these studies, L-Glu was combined with Fe₃O₄ via surface adsorption. However, they did not consider whether glutamic acid polymerized and did not pay attention to its surface properties. The Chinese fermentation capacity of glutamic acid approached nearly 1.6 million tons.¹⁰ This could provide a large number of materials for the production of new adsorbent materials and could have wide industrial prospects.

In this study, P-L-Glu was synthesized on the surface of nano-Fe₃O₄ by a dehydration condensation reaction with a 1-(3-dimethylaminopropyl)-3-ethyl carbon diimine hydrochloride (EDC) catalyst. The performance of particles and the mechanism as an adsorbent for Cu(II) in the aqueous solution were extensively investigated. The results show that the Fe₃O₄/P-L-Glu had a good adsorption capacity for Cu(II) ions.



Scheme 1.

EXPERIMENTAL

Materials

Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), poly(ethylene glycol) 400, hydrochloric acid (HCl), sodium hydroxide (NaOH), and sodium citrate were purchased from Tianjin Damao Chemical Reagent Factory (China). L-Glu, sodium diethyldithiocarbamate, and EDC (97%) were purchased from Chengdu Xiya Reagent Co., Ltd. (China). All of the reagents were analytical grade. Deionized water was self-made and was used throughout the study.

Synthesis of the $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ Microspheres

The $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ magnetic microspheres were prepared under basic conditions with L-Glu as a stabilizer. The complexation reaction happened between L-Glu and Fe^{2+} or Fe^{3+} .² $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.96 g), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (13.6 g), sodium citrate (0.6 g), and L-Glu (3 g) were dissolved in 200 mL of deionized water, and we removed oxygen by ultrasound for 30 min. The obtained solution was put into a round-bottomed flask and stirred for 15 min under nitrogen at room temperature. A volume of 177 mL of NaOH solution (2 mol/L) was added dropwise into the flask under continuous stirring. Then, the mixture was heated to 75 °C for 30 min. The obtained black products were separated, collected with a permanent magnet, and washed repeatedly with deionized water until it was neutral. We removed 10 mL from the product of the previous step, and L-Glu (2 g), poly(ethylene glycol) 400 (5 mL), and 90 mL of deionized water were added. Then, 0.05 g of EDC dissolved in 10 mL of deionized water and was added dropwise into the flask. The mixture was heated to 35 °C and stirred with ultrasound for 1 h. $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ magnetic microspheres were obtained after separation and washing

and immersed in HCl solution (pH 4) for 24 h. The possible synthetic route is shown in Scheme 1.

Characterization

Fourier transform infrared (FTIR) analysis was taken as KBr pellets with an FTIR spectrometer (Bruker Tensor 27, Berlin, Germany). FTIR spectra were recorded from 4000 to 400 cm^{-1} . The samples and KBr for measurements were dried in a vacuum oven for 10 h. The morphological characteristics of the samples were determined with a JSM-6380 scanning electron microscope (JEOL, Ltd., Japan). The ζ potentials and particle size distributions of the samples were measured by a ζ -potential analyzer (Malvern Mastersizer 2000, Malvern, United Kingdom).

Adsorption Experiments

First, to measure the pH effect on the adsorption, 20 mL of a 5 mg/L Cu(II) solution and 0.001 g of $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ were put into several glass bottles. With 0.1 mol/L NaOH and 0.1 mol/L HCl, the pH values of the solutions were adjusted to 2, 3, 4, 5, 6, 7, 8, 9, and 10, respectively. The $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ microspheres were dispersed by ultrasound for 5 min, separated, and collected with a magnet after storage at room temperature for 3 h. A volume of 5 mL of 0.2% sodium diethyldithiocarbamate was added to 2.5 mL of the remaining solution, and 5 mL of butanol was added after 3 min. The absorbance of the solutions was measured with a UV spectrophotometer (UV759S, Shanghai, China) at a 440-nm wavelength in 1 h.

Second, to measure the adsorption kinetics, 20 mL of a 5 mg/L Cu(II) solution and 0.001 g of $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ were put into several glass bottles, and the pH values of the solutions were adjusted to 8 (± 0.05). The microspheres were separated with a magnet at certain time intervals, and solution was left behind.

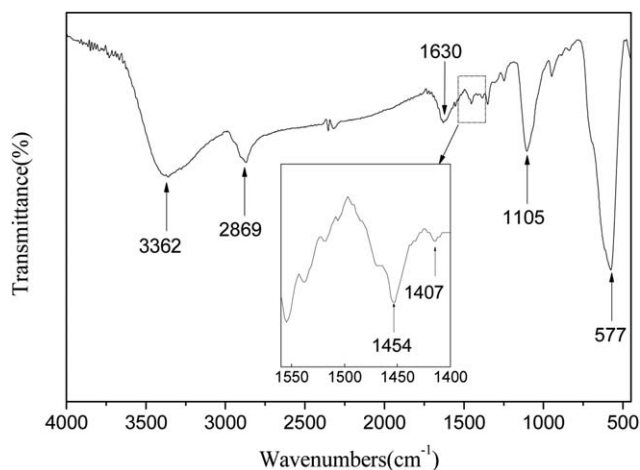


Figure 1. FTIR spectrum of $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$.

Then, the concentrations of copper ions in the solutions were measured by a UV spectrophotometer (UV759S, Shanghai, China) at 440 nm.

Third, to measure the adsorption isotherm, 20 mL of Cu(II) solutions with different concentrations and 0.001 g of $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ were put into several glass bottles, and the pH values of the solutions were adjusted to 8 (± 0.05). The $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ microspheres were separated with a magnet after 2 h. Similarly, the concentrations of Cu(II) were measured by UV spectroscopy at 440 nm.

RESULTS AND DISCUSSION

FTIR Spectroscopy Analysis

The surface functional groups of $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ were analyzed by FTIR spectrometry, as shown in Figure 1. The IR spectra gave peaks specific to P-L-Glu, with a strong amide absorption at a wave number of 1630 cm^{-1} .¹¹ The peaks at 1407 and 1105 cm^{-1} were representative of the C=O group and C-N stretching vibrations, respectively, whereas the stretching observed at 3362 cm^{-1} was representative of the hydroxyl group.¹¹ The peaks at 2869 and 1454 cm^{-1} associated with carboxyl groups and C-H bending vibrations of L-Glu, respec-

tively. It was also shown that the characteristic absorption band of the Fe-O bond was at 577 cm^{-1} .¹² Obviously, the P-L-Glu modified Fe_3O_4 magnetic microspheres were successfully synthesized by the coordination reaction.

Morphological and Particle Size Analysis

The scanning electron microscopy image of $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ is shown in Figure 2(a). It indicates that the morphology of each microsphere was a single spherical nanoparticle, and the particle size distribution was uniform. The morphology and size of the microspheres were observed well. This information was also verified by a particle size analyzer. The particle size distribution of $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ in deionized water is shown in Figure 2(b). The average particle diameter was 388 nm, and the dispersion coefficient was 5.4%. In summary, the microspheres were prepared in a high dispersive degree and in a narrow size range.

ζ -Potential Analysis

The ζ potential at different pH values ranging from 2 to 10 of a 0.1 g/L $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ suspension is shown in Figure 3; it was dispersed in a 0.001 mol/L NaCl aqueous solution. We observed that the $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ microspheres show positive ζ potentials in acidic solution; this demonstrated the presence of surface positive charges. However, in neutral and alkaline solutions, a negative value of surface potential indicated a preferred exposure of $-\text{COO}^-$ in relation to H^+ , whereas the opposite would happen when the potential is positive.¹³ According to Figure 3, when the ζ potential reached the zero point, the value of the pH was close to 6, which was the isoelectric point. In neutral and alkaline solutions, the high negative charge of the microsphere caused electrostatic repulsion between the microspheres and high stability; this was reflected by good dispersion. In conclusion, agglomeration hardly occurred between the microspheres.

Effect of pH on the Adsorption

The acidity of the aqueous solution exerted a profound influence on the adsorption process because it could affect the functional groups on the surface of the adsorbents. The effect of pH on Cu(II) adsorption was investigated at pH 4–10. As shown in Figure 4, with increasing pH value, the adsorption capacity of the $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ microspheres for Cu(II) increased and then decreased. A possible reason was the competitive adsorption

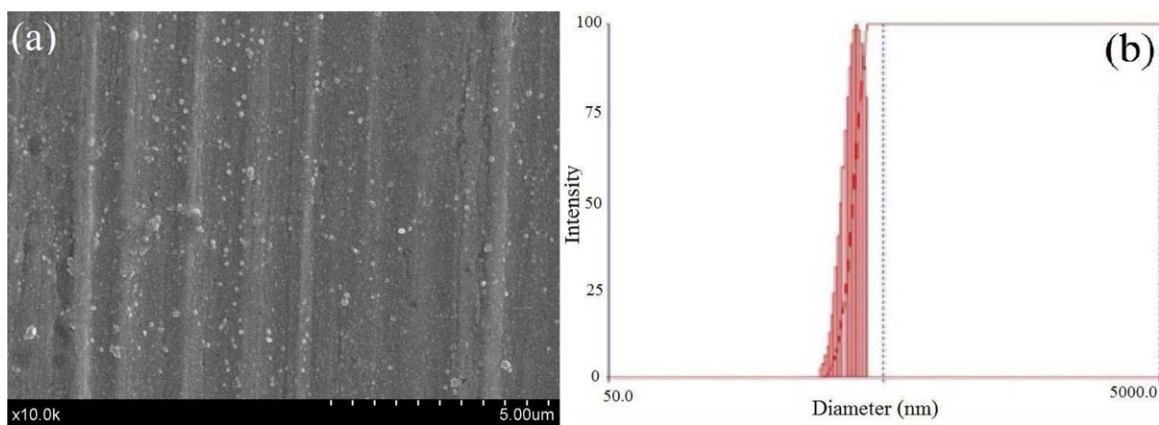


Figure 2. (a) Scanning electron microscopy images of $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ and (b) particle size and distribution of $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

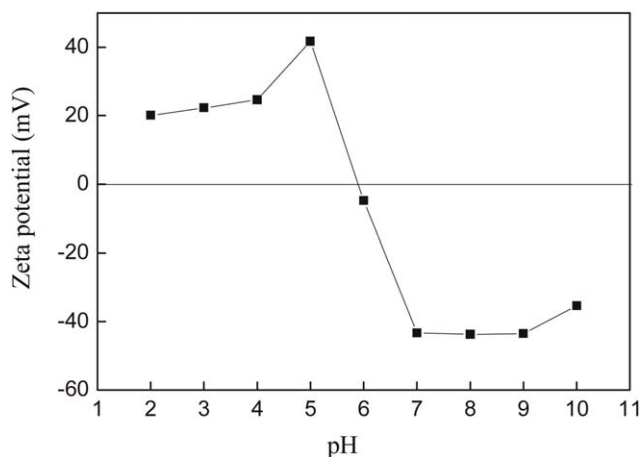


Figure 3. ζ potential of $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ at different pH values.

between H^+ and Cu(II) on the surface of the $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ microspheres. At low pH values, the protonation of the $-\text{COO}^-$ reduced the binding ability between the active sites and metal ions.¹⁴ The adsorption capacity to Cu(II) was weaker when the pH value was lower than 6, whereas the concentration of H^+ decreased, and there were significant increases in the removal rate of Cu(II) with increasing pH values of the test solution from 4 to 6. Then, the adsorption amount of Cu(II) reached a maximum at pH 8. At pH values greater than 8, the adsorption amount of Cu(II) decreased because hydroxide precipitates were separated out with increasing OH^- and Cu(II) .

Adsorption Kinetics Study

The adsorption kinetic curve of the $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ microspheres for Cu(II) is shown in Figure 5. We observed that the adsorption amount of Cu(II) increased rapidly with time in the initial stage, and the equilibrium time was found to be 40 min.

Several kinetic models were applied to determine the adsorption mechanism.¹⁵ The pseudo-first-order kinetic model was more suitable at a low concentration of solute.¹⁶ The linear form of the pseudo-first-order equation is expressed as follows:

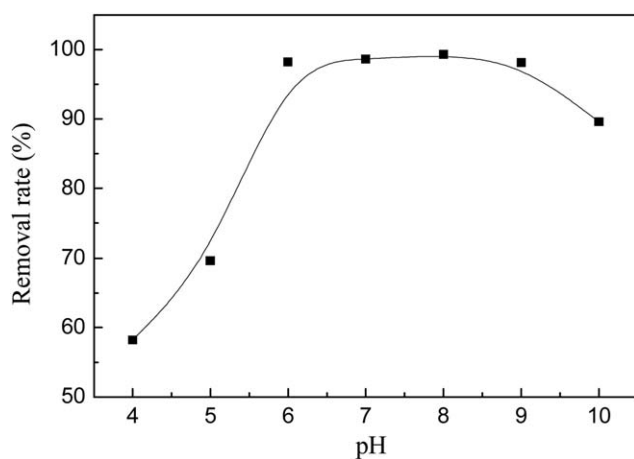


Figure 4. Effect of the pH value on the Cu(II) adsorption capacity.

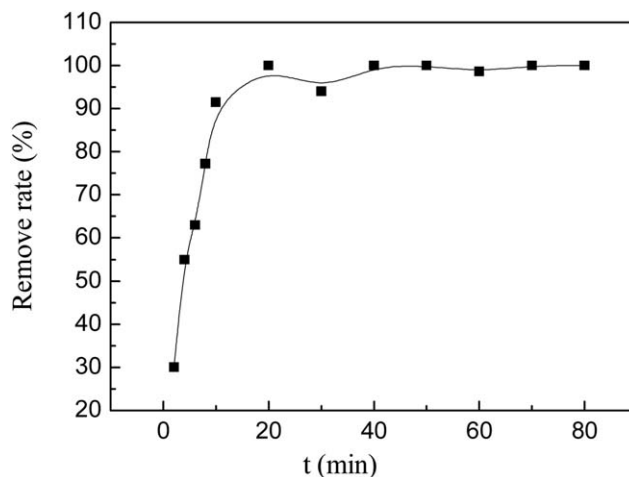


Figure 5. Kinetic curve for the adsorption of Cu(II) by $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$.

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} t \quad (1)$$

where t is the reaction time (min); q_e and q_t are the adsorption amounts of Cu(II) on the $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ microspheres at equilibrium and at time t (mg/g), respectively; and k_1 is the rate constant of the pseudo-first-order equation (min^{-1}).

The pseudo-second-order equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where k_2 is the pseudo-second-order rate constant at equilibrium ($\text{g mg}^{-1} \text{min}^{-1}$).

The plot of the pseudo-first-order kinetic model is shown in Figure 6(a). In the first 10 min, the correlation coefficient (R^2) was 0.96941. Although the plot of the pseudo-second-order model is shown in Figure 6(b), R^2 was 0.99807 ($R^2 > 0.99$). R^2 for the pseudo-second-order kinetic model is closest to 1; this was much higher than the R^2 value derived from the pseudo-first-order kinetic model. Moreover, the kinetic adsorption data were fitted to eq. (1), the obtained results were that k_1 was 0.03353 min^{-1} , and q_e was 541.58 mg/g . When fitted to eq. (2), k_2 was $0.00319 \text{ g mg}^{-1} \text{ min}^{-1}$, and q_e was 104.60 mg/g . The value derived from the pseudo-second-order kinetic model was adjusted to the experimental value, in which q_e was 99.72 mg/g . From the previous discussion, the adsorption of $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ microspheres for Cu(II) followed the pseudo-second-order kinetic model and belonged to chemical adsorption.^{6,16}

Adsorption Isotherm

The Langmuir model assumes that a monomolecular layer is formed when adsorption takes place without any interaction between the adsorbed molecules. The Langmuir model can be represented as follows¹⁵⁻¹⁷:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (3)$$

where C_e is the equilibrium ion concentration in solution (mg/L), q_e is the amount of Cu(II) adsorbed on $\text{Fe}_3\text{O}_4/\text{P-L-Glu}$ microspheres at equilibrium (mg/g), b is the Langmuir constant (L/mg), and q_m is the maximum adsorption capacity (mg/g). q_m

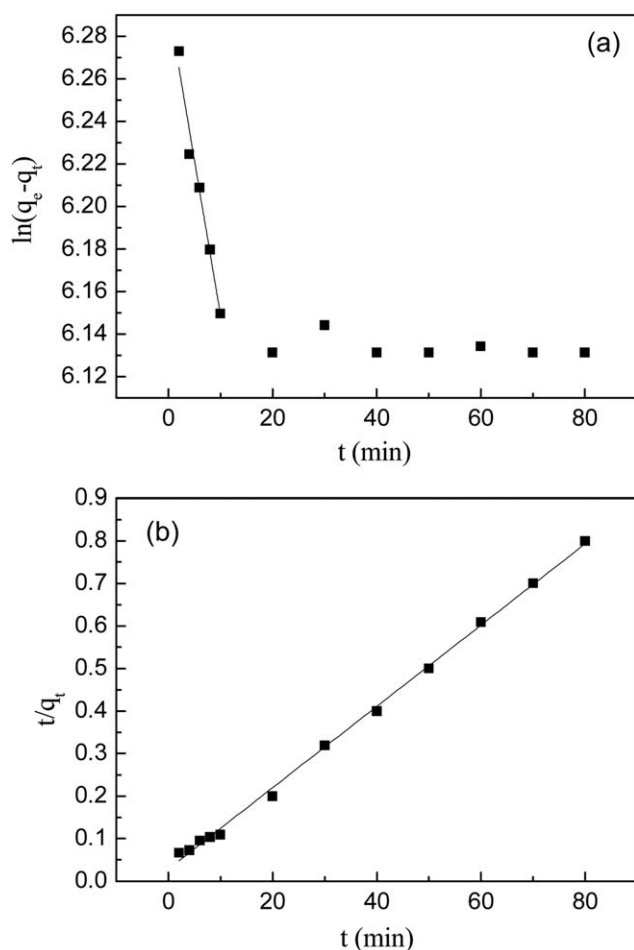


Figure 6. (a) Pseudo-first-order and (b) pseudo-second-order kinetic models for Cu(II) adsorption on Fe₃O₄/P-L-Glu.

represents the particle-limiting adsorption capacity when the surface is fully covered with Cu(II) and assists in the comparison of the adsorption performances.

The Freundlich model involves equilibrium on a heterogeneous surface, where the sorption energy is not homogeneous for all sorption sites. The expression is an exponential equation that is not restricted to the formation of the monolayer. This empirical equation takes the form¹⁷

$$qe = k_F C_e^{1/n} \quad (4)$$

where k_F and n are the Freundlich constants.

The adsorption isotherm of Cu(II) is shown in Figure 7(a). The adsorption capacity of Fe₃O₄/P-L-Glu to Cu(II) was greater than 500 mg/g when the concentration of Cu(II) was 30 mg/L and the concentration of Fe₃O₄/P-L-Glu was 50 mg/L; this was far higher than those of other traditional absorbent materials, such as chitosan (174.75 mg/g) and NaA zeolite (156.74 mg/g).⁶ The Langmuir and Freundlich isotherm models were applied to simulate the experimental data.

The curves are shown in Figure 7(b,c). The R^2 values were 0.67920 and 0.99763 ($R^2 > 0.99$). R^2 for the Freundlich isotherm

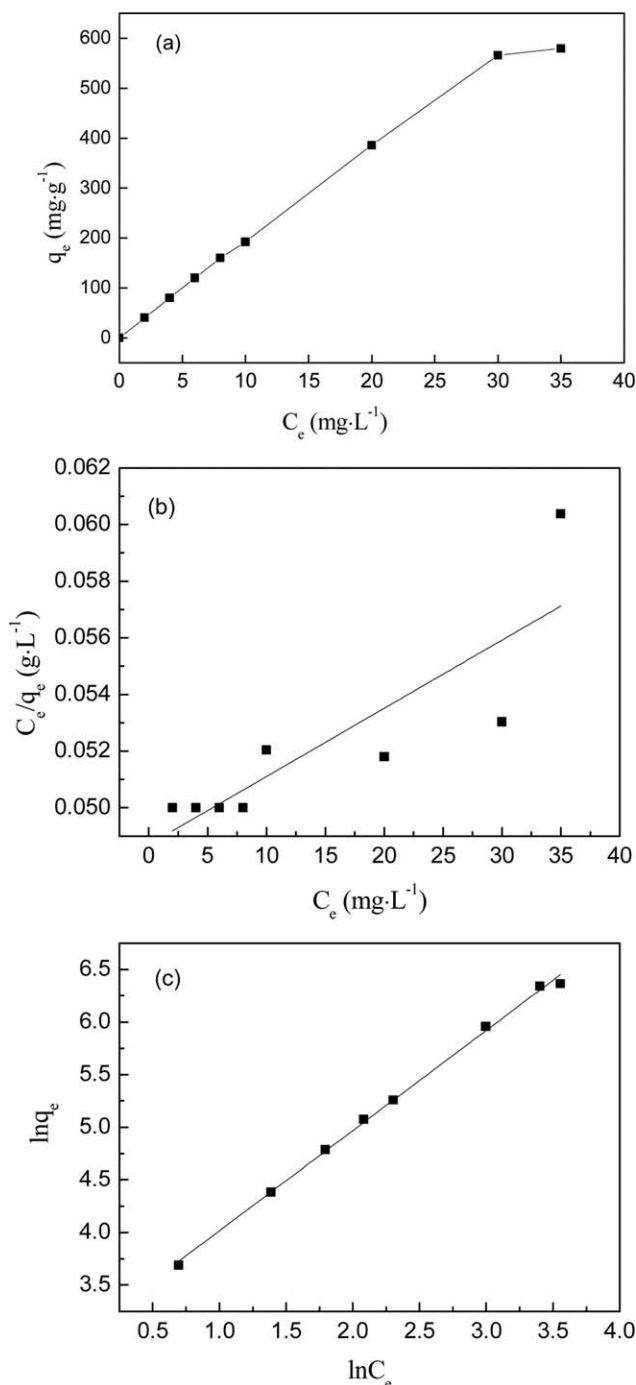


Figure 7. (a) Relationship between q_e and C_e and (b) Langmuir and (c) Freundlich isotherms for the adsorption of Fe₃O₄/P-L-Glu to Cu(II) at different initial Cu(II) concentrations.

model was closest to 1; this was much higher than the R^2 value derived from the Langmuir isotherm model.

CONCLUSIONS

In the first step of this study, Fe₃O₄/P-L-Glu magnetic microspheres were synthesized in the L-Glu solution by coprecipitation and a dehydration condensation reaction. In the second step, the

Fe₃O₄/P-L-Glu magnetic microspheres were characterized with FTIR spectroscopy, scanning electron microscopy, and ζ-potential measurement. The results show that P-L-Glu modified Fe₃O₄ magnetic microspheres were synthesized successfully, and the average particle size of Fe₃O₄/P-L-Glu was 388 nm; this was dispersed homogeneously in water. Then, the adsorption of the prepared Fe₃O₄/P-L-Glu magnetic microspheres for the Cu(II) from aqueous samples was investigated. The effects of different pH values and reaction times on adsorption of Fe₃O₄/P-L-Glu was researched. The adsorption kinetics followed the mechanism of the pseudo-second-order equation, and the adsorption dynamic process fit the Freundlich isotherms well. The adsorption capacity of Fe₃O₄/P-L-Glu for Cu(II) was greater than 500 mg/g when the concentration of Cu(II) was 30 mg/L and the concentration of Fe₃O₄/P-L-Glu was 50 mg/L; these values were far higher than those of other traditional absorbent materials.⁶

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