Preparation and properties of ternary copolymer hydrogel materials

Cheng Kang, Haoran Zhang, Yuan Yuan, GuoPing Zhou, Bing Yao, Shifan Wang *

School of Material and Chemical Engineering, Xuzhou Institute of Technology, Xuzhou 221018, China

*Corresponding author e-mail: shifanwang@xzit.edu.cn

Abstract. In order to improve the adsorption of heavy metal ions on acrylic hydrogels, P(AA-co-AM-co-S) hydrogels were synthesized from acrylic, acrylamide and styrene as raw materials. During the synthesis, potassium persulfate was used as the initiator, N, N'-methylenebisacrylamide was used as the crosslinking agent, and the degree of neutralization was 80%. The structure of the prepared hydrogel was determined by infrared spectroscopy. The adsorption properties of hydrogels on Ni\(^{2+}\) at different times and pH were determined. The results show that the adsorption capacity of Ni\(^{2+}\) ions on the hydrogel reaches the equilibrium adsorption capacity in about 2 hours and reaches 159 mg/g. The second-order kinetic model fits well. The optimal pH for the adsorption of Ni\(^{2+}\) ions by the hydrogel is 3.5 ~ 4.5 and the adsorption capacity is 160 mg/g. This study has important theoretical and practical significance for the development of high-efficiency, environmentally friendly, low-cost heavy metal ion hydrogels.

Keywords: acrylic acid; hydrogel; heavy metal ion; adsorption property.

1. Introduction
Due to the economic development of our country in recent years, the situation of man-made destruction of the natural environment has become increasingly serious. A large amount of heavy metal waste is discharged into the environment, causing heavy metal pollution that harms animal and plant growth and reproduction, human health, and threatens the living environment[1]. Heavy metals generally refer to metals with a density greater than 4.5 g/cm\(^3\). There are currently about 45 heavy metals, such as copper (Cu), lead (Pb), zinc (Zn), iron (Fe), cobalt (Co), nickel (Ni), manganese (Mn), cadmium (Cd), and mercury (Hg), gold (Au), silver (Ag), etc. Heavy metal pollution refers to environmental pollution caused by certain types of heavy metals or their compounds in the environment due to human factors exceeding a certain range, which will cause harm to the ecological environment and human health[2-4].

Hydrogel is a functional polymer material with low crosslinking degree, multiple hydrophilic groups or partial crystals and a three-dimensional network structure. Although hydrogels can swell in water and retain a certain amount of water, they are insoluble in water. The structural characteristics of the hydrogel make the hydrogel have a better adsorption capacity for heavy metals[5-6]. With the development of industry, heavy metal pollution seriously threatens the growth and reproduction of animals and plants, as well as human health and the living environment. Therefore, an important subject
in the field of environmental protection is to establish a method for treating heavy metal ion wastewater with high efficiency, environmental protection and low cost[7-9].

In this work, P(AA-co-AM-co-S) hydrogel was synthesized using acrylic acid, acrylamide and styrene as raw materials. During the synthesis, potassium persulfate was used as the initiator, N, N'-methylenebisacrylamide was used as the crosslinking agent, and the degree of neutralization was 80%. To further understand the hydrogel, FTIR spectra were used to determine its structure. The effects of different time and pH on the adsorption properties of P(AA-co-AM-co-S) ternary copolymer hydrogels were studied.

2. Experimental

2.1. Materials and characterization
Acrylic acid; Acrylamide; sodium hydroxide; Styrene; N,N'-methylenebisacrylamide; Potassium persulfate; Nickel sulfate hexahydrate; Copper nitrate trihydrate; Concentrated hydrochloric acid (Sinopec Group Chemical Reagent Co., Ltd.), the above reagents are of analytical grade and the experimental water is deionized water.

Analytical Balance (FA1104); Heat-collecting Constant Temperature Magnetic Stirrer (DF-101S); Electric Heating Constant Temperature Blast Drying Box (101-OBS); Multifunctional Shredder (800Y); Fourier Transform Infrared Spectrometer (ALPHA); Atomic Absorption Spectrometer (WYS2000); PH Meter (PHS-2F)

2.2. Preparation of P(AA-co-AM-co-S)
20.6 g of acrylic acid was slowly poured into a 250 mL three-necked flask, and then 24 ml of a sodium hydroxide solution was slowly added. After the flask was cooled to room temperature, 7.11 g of acrylamide and 5.7 ml of styrene were added in this order. Then 0.51 g of potassium persulfate and 0.17 g of N, N'-methylenebisacrylamide were added and stirred until clear. After that, the reactant was thoroughly dried and pulverized to obtain a ternary copolymer hydrogel finished product.

2.3. Adsorption studies
Place accurately weighed 0.1 g of dry hydrogel powder together with 50 mL of Ni²⁺ solution into a 100 mL Erlenmeyer flask. The mixture was shaken isothermally at 25 ℃ and 200 r/min. The solution was allowed to stand for two minutes before the prescribed experimental time, and then the supernatant was taken and diluted to the specified volume. By measuring the concentration of the heavy metal ion solution with an atomic absorption spectrometer, the amount of adsorption of the hydrogel was calculated. Finally, according to the test results of different adsorption times, pseudo-first-order and second-order kinetic equations and particle diffusion equations are drawn up.

Configure six servings 50mL Ni²⁺ solutions with a concentration of 1g/L. Control the pH of the solution between 1.5 and 6.5. Add 0.10 grams of hydrogel to each solution and label it. Then, the solution was stirred at room temperature for two hours. The amount of hydrogel adsorption was calculated by measuring the concentration of the supernatant after the stirring was completed. The adsorption capacity Qe (mg/g) of P(AA-co-AM-co-S) toward metal ions at equilibrium was calculated as following Eq. (1):

\[
Qe = \frac{(C_0 - C_e)NV}{M}
\]

(1)

And the adsorption efficiency (E) was calculated using the Eq. (2):

\[
E = \frac{(C_0 - C)}{C_0} \times 100\%
\]

(2)

Where C₀ and Ce are the initial and equilibrium concentrations (mg/L) of metal ions in solution, respectively. V (L) is the volume of solution and M (g) is the mass of P(AA-co-AM-co-S). C (mg/L) is the concentration of heavy metal ions in the solution after adsorption and N is the dilution factor.
3. Results and discussion

3.1. FTIR spectra analysis

Figure 1 is an infrared spectrum of a P(AA-co-AM-co-S) hydrogel. The peak at 3438 cm\(^{-1}\) is due to the stretching vibration of -OH and -NH\(_2\) in the gel, while the peaks at 2959 cm\(^{-1}\) and 2832 cm\(^{-1}\) are due to the stretching vibration of -CH\(_2\)- and the symmetrical stretching absorption of -CH. The skeletal vibration of the benzene ring caused the appearance of the peak at 1592 cm\(^{-1}\). However, -C=O- symmetrical vibration stretching and -C=O- in-plane bending vibration absorption in -COONa caused the peaks of 1365cm\(^{-1}\) to 1175cm\(^{-1}\). The out-of-plane bending vibration of -CH in the benzene ring caused the peak of 779 cm\(^{-1}\). The above analysis illustrates the generation of P (AA-co-AM-co-S) hydrogel[10].

![Infrared spectrum of P (AA-co-AM-co-S) ternary copolymer hydrogel](image)

**Fig. 1** Infrared spectrum of P (AA-co-AM-co-S) ternary copolymer hydrogel

3.2. Research on Adsorption Behavior

3.2.1. Adsorption Kinetics. The pseudo-first-order, second-order kinetic equations and particle diffusion equations were performed for the hydrogel adsorption time (Fig 2). The driving force for ion adsorption is mainly the difference between the adsorption amount Qe at equilibrium and the adsorption amount Qt at time t. The pseudo-first-order kinetic equation of Ni\(^{2+}\) is \(y=-0.0062x-0.00335\) and the correlation coefficient \(R^2=0.83497\). The pseudo-second-order kinetic equation is \(y=0.35038x+2.37458\) and the correlation coefficient \(R^2=0.99915\). The particle diffusion equation is \(y=0.047x+2.03363\) and the correlation coefficient \(R^2=0.89952\). As displayed in Fig. 2b and Table 1, the pseudo-second-order kinetic model is suitable for describing the adsorption process of Ni\(^{2+}\) ions by the hydrogel (\(R^2>0.995\)). The adsorption rate is controlled by chemisorption. As displayed in Fig. 2c, the linear correlation of the entire adsorption process is not high. Moreover, \(R^2\) between 0.89 and 0.94 can only explain the existence of particle diffusion during the adsorption of Ni\(^{2+}\) solution by hydrogel. As displayed in Fig. 3, within 120min, the adsorption amount of Ni\(^{2+}\) reaches 159mg/g. But after that, until 360min, the adsorption amount of Ni\(^{2+}\) on the hydrogel was only 6mg/g. It can be seen that the adsorption rate of ions in 120 min is relatively large. Over time, the increase in the amount of adsorption tends to be gentle.

![Adsorption kinetic models](image)

**Fig. 2** (a) Pseudo-first-model; (b) pseudo-second-order model; (c) particle diffusion model.
3.2.2. Effect of pH on Ni\textsuperscript{2+} ions adsorption by P(AA-co-AM-co-S). The initial pH of the Ni\textsuperscript{2+} ion solution was measured by a pH meter to be 3.52. During the adsorption process, the precipitation and hydrolysis of the heavy metal ion solution have a great relationship with the pH value of the solution. In the case that the heavy metal ion solution does not precipitate, the adsorption amount of Ni\textsuperscript{2+} ions by the hydrogel under different pH conditions is measured. Then, the adsorption amount and adsorption rate of Ni\textsuperscript{2+} ions by the hydrogel were calculated. The experimental results as displayed in Fig. 4.

As displayed in Fig. 4, the adsorption performance of the hydrogel under different pH conditions was studied under the conditions of a temperature of 25 °C, an initial ion concentration of 1000 mg/L and a certain amount of hydrogel. By analyzing the influence of the pH value of the Ni\textsuperscript{2+} ion solution on the adsorption effect of the hydrogel, it can be known that the optimal pH value of the hydrogel to absorb the Ni\textsuperscript{2+} ion is between 3.5 and 4.

4. In conclusion
P(AA-co-AM-co-S) hydrogel was synthesized using acrylic acid, acrylamide and styrene as raw materials. During the synthesis, potassium persulfate was used as the initiator, N, N'-methylenebisacrylamide was used as the crosslinking agent, and the degree of neutralization was 80%. The structure of the prepared hydrogel was determined by infrared spectroscopy. The adsorption performance of Ni\textsuperscript{2+} on hydrogels was measured at different time and pH. It is best to maintain the pH of the solution in which the hydrogel adsorbs Ni\textsuperscript{2+} ions to be 3.5 to 4.0. At this time, the adsorption
amount of Ni$^{2+}$ ions by the hydrogel was 160 mg/g. The adsorption of Ni$^{2+}$ ions by the hydrogel tended to be gentle at about 120 min, and the adsorption amount reached 159 mg/g.

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