Synthesis and adsorption properties of acrylic acid/styrene binary copolymer resin

Jian Tang, Yifei Wang, Jiannan Huang, and Shifan Wang*

School of Chemistry and Chemical Engineering, Xuzhou University of Technology, Xuzhou, 221018, China.

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

Abstract. In order to improve the adsorption of heavy metals in polyacrylic hydrogels, the experiment uses acrylic acid and styrene as raw materials, potassium per sulfate as initiator, and ethylene glycol as crosslinker to synthesize polyacrylic acid/styrene hydrogel. The effects of monomer ratio, acrylic acid neutralization degree, crosslinker dosage and temperature on product properties were studied by orthogonal test. In addition, the copolymer was characterized by Fourier transform infrared spectroscopy. The adsorption of heavy metal performance test found that when the ratio of acrylic acid and styrene is 1:0.2, the degree of neutralization is 65%, the crosslinker accounts for 1.0% of the monomer mass fraction, and the temperature is 65 °C, the polyacrylic acid/styrene copolymer hydrogel is optimal. The adsorption of Pb²⁺ in the optimal group was 328.25 mg/g.

1. Introduction

Polyacrylic hydrogel is a new type of polymer functional material with 3D network structure formed by moderate cross-linking. Polyacrylic hydrogels are a typical ion exchange resin, and the principle of ion exchange is: a specific functional group on the ion exchange resin produces an ion effect on a specific heavy metal ion, and a specific functional group on the ion exchange resin is used to displace heavy metal ions in the heavy metal wastewater, and even a heavy metal resource can be recovered [1]. However, in the ion exchange process, secondary pollution is easy to occur. Because the reaction usually produces some acid-base products and is highly polluted, it is not recommended for industrial use. The ion exchange resin can be regenerated after exchange adsorption saturation. The raw method is to elute the functional groups on the resin by means of high concentration ions in the regenerate [2, 3], so that the ion exchange resin can be recycled and reused.

The polyacrylic hydrogel molecule contains a large number of groups such as a hydroxyl group, a carboxyl group, a sulfonic acid group and an amide group which have strong chelation with heavy metal ions [4]. Therefore, polyacrylic hydrogel not only has good water absorption and liquid absorption properties, but also can absorb heavy metal ions [5], used for recovery and separation of heavy metal ions, and high molecular weight heavy metal ion adsorbent due to its superior adsorption. Heavy metal ion performance has a good development prospect [6]. The adsorbent has simple operation, high efficiency of absorbing heavy metal ion wastewater and low secondary pollution, so the polymer heavy metal ion adsorbent is in full compliance with the requirements of environmental protection improvement projects [7, 8]. However, at present, due to its current high production cost, high recycling
cost, and different heavy metal ions can effectively adsorb the specific functional groups of the adsorbent. The research and production of high molecular heavy metal ion adsorption materials still needs great improvement \[9, 10\].

In this paper, acrylic acid (AA) and styrene (S) were used as raw materials, potassium persulfate was used as initiator, and ethylene glycol was used as crosslinker to prepare polyacrylic acid/styrene hydrogel. The polyacrylic acid/styrene resin was modified by orthogonal test with different ratios of acrylic acid and styrene, and different temperature, neutralization degree and mass fraction. The structure of the prepared polyacrylic acid/styrene resin was determined by characterization by infrared spectroscopy. The adsorption effect of the prepared polyacrylic acid/styrene resin on heavy metal ions was observed by atomic absorption spectrometry. The adsorption amount of the adsorbed heavy metal ions of the polyacrylic acid/styrene resin was measured, and the synthesis conditions for the adsorption effect of the hydrogel on the heavy metal ions were found.

2. Experiment

2.1. Materials and characterization
Acrylic acid (AA); Styrene (S); Potassium persulfate (K₂S₂O₈); Ethylene glycol (EG); Lead nitrate (Pb(NO₃)₂) were procured from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and were used without any further purification.

The FTIR analysis was performed on a SAR sample using a NEXUS470 Fourier transform infrared spectrometer produced by American Thermoelectric Corporation. The concentrations of Pb(II) ions in the filtrates were determined by an inductively coupled plasma atomic emission spectrometer (ICP, VISTAPRO, Varian, USA).

2.2. Preparation
Add 34.4ml of acrylic acid to the beaker equipped with magnetic stirrer and stir. Stir well, add sodium hydroxide and styrene and continue stirring for 30 minutes. When the transparent liquid is obtained, 0.2% by mass of the initiator potassium persulfate and the cross-linking agent ethylene glycol are added and stirring is continued for 10 min. The polymer in the beaker was poured into a dry and clean reaction dish, and placed in an electric heating constant temperature blast oven for 4 hours. After the preliminary completion of the polymerization, the binary AA/S copolymer superabsorbent resin which has been solidified is turned over, and the temperature of the electric blast oven is set to 90 °C for 8 hours until the polymer is completely dried to obtain binary copolymerization. Highly water-absorbent resin finished.

2.3. Adsorption studies
Heavy metal ion concentration in the solution, that is, accurately weigh 0.1g of dry hydrogel in a 100ml Erlenmeyer flask, add 50ml of 1g / L lead ion solution and stir with magnetic particles for 2h, static sedimentation. 1 ml of the supernatant was taken with a pipette, and then pipetted with 9 ml of deionized water and diluted in a clean weighing bottle, sampled, and the amount of adsorption of the hydrogel was measured and calculated by an atomic absorption spectrophotometer.

The calculation formula is as follows:

\[ Q_e = \frac{V (C_0 - C_e)}{M} \]  \hspace{1cm} (1)

Qe: Hydrogel adsorption capacity (mg/g); V: Volume of heavy metal ions (L); C₀: Initial concentration of heavy metals in solution (mg/L); Cₑ: Final concentration of heavy metals in solution (mg/L); M: Weigh the quality of the hydrogel before adsorption (g).
3. Results and discussion

Table 1. Four factors designs.

| Level | (A) Monomer ratio (AA/S) | (B) Neutrality (%) | (C) Crosslinker (%) | (D) Temperature (°C) |
|-------|--------------------------|--------------------|--------------------|---------------------|
| 1     | 1:0.05                  | 60                 | 0.6                | 55                  |
| 2     | 1:0.1                   | 65                 | 0.8                | 60                  |
| 3     | 1:0.2                   | 70                 | 1.0                | 65                  |
| 4     | 1:0.5                   | 75                 | 1.2                | 70                  |

Table 2. Result analysis.

| Test number and level | A | B | C | D | Empty column | Adsorption capacity |
|-----------------------|---|---|---|---|--------------|---------------------|
| 1                     | 1 | 1 | 1 | 1 | 1            | 285.40              |
| 2                     | 1 | 2 | 2 | 2 | 2            | 318.18              |
| 3                     | 1 | 3 | 3 | 3 | 3            | 313.82              |
| 4                     | 1 | 4 | 4 | 4 | 4            | 260.44              |
| 5                     | 2 | 1 | 2 | 3 | 4            | 310.59              |
| 6                     | 2 | 2 | 1 | 4 | 3            | 316.34              |
| 7                     | 2 | 3 | 4 | 1 | 2            | 298.66              |
| 8                     | 2 | 4 | 3 | 2 | 1            | 302.43              |
| 9                     | 3 | 1 | 3 | 4 | 2            | 305.10              |
| 10                    | 3 | 2 | 4 | 3 | 1            | 325.44              |
| 11                    | 3 | 3 | 1 | 2 | 4            | 313.45              |
| 12                    | 3 | 4 | 2 | 1 | 3            | 299.03              |
| 13                    | 4 | 1 | 4 | 2 | 3            | 294.16              |
| 14                    | 4 | 2 | 3 | 1 | 4            | 326.02              |
| 15                    | 4 | 3 | 2 | 4 | 1            | 308.71              |
| 16                    | 4 | 4 | 1 | 3 | 2            | 302.54              |
| k1                    | 294.46                  | 298.81             | 304.43             | 302.28             | 305.49             |
| k2                    | 307.00                  | 321.49             | 309.13             | 307.05             | 306.12             |
| k3                    | 310.75                  | 308.66             | 311.84             | 313.10             | 305.83             |
| k4                    | 307.86                  | 291.11             | 294.67             | 297.65             | 302.62             |
| Ranger                | 16.29                   | 30.38              | 17.17              | 15.45              | 3.50               |

In the vicinity of 1451 cm\(^{-1}\) is a scissor bending vibration peak of -CH\(_2\). The skeleton vibration of the benzene ring appeared near 1451 cm\(^{-1}\) to 1551 cm\(^{-1}\). The strongest peak of the C-O bond (strong polarity) appeared at 1050 cm\(^{-1}\). This shows that an AA/S binary copolymer hydrogel was produced. In order to determine the best experimental conditions, this experiment designed orthogonal test of four factors including monomer ratio (AA/S), neutralization degree, crosslinker, and temperature. The results are shown in table 1 and table 2.

The effects of monomer ratio (AA/S), neutrality, crosslinker, and temperature on the adsorption of polyacrylic acid/styrene were investigated by orthogonal experiment. The primary and secondary order of each factor is determined by the range analysis result. Since R\(_B\)>R\(_C\)>R\(_A\)>R\(_D\), This indicates that the degree of copolymerization neutralization is the main influencing factor, the amount of cross-linking agent and the monomer ratio are second, and the temperature factor is the weakest.

As shown in figure 1, the adsorption effect of acrylic acid/styrene is 1:0.2, and the adsorption effect does not increase with the increase of the amount of acrylic acid and styrene. When the monomer ratio is lower than 1:0.2, the adsorption effect of the polyacrylic acid/styrene resin increases as the ratio increases; This is because the number of monomers generated in a certain range increases, and the crosslinker is better, and the adsorption effect on heavy metal ions is more obvious.
Figure 1. Effect of monomer ratio on adsorption capacity.

Figure 2 shows the effect of the degree of neutralization of acrylic acid on the adsorption capacity. The degree of neutralization of acrylic acid is 65%, the adsorption effect is most obvious, and the adsorption effect does not increase as the degree of neutralization increases. When the degree of neutralization is less than 65%, the adsorption effect of the polyacrylic acid/styrene resin increases as the degree of neutralization increases:

Figure 2. Effect of neutralization degree on adsorption capacity.

The adsorption effect is most obvious and the effect of adsorption does not increase as the degree of neutralization increases when the degree of neutralization of acrylic acid is 65%. Because when the acidity of acrylic acid is too high, the self-crosslinking reaction of acrylic acid itself occurs, and when the concentration of acrylic acid is high, the self-crosslinking speed increases, thereby forming a highly cross-linked polymer, resulting in a decrease in the efficiency of adsorption of heavy metal ions by the product. When the degree of neutralization exceeds 65%, the polymerization efficiency is lowered due to excessive neutralization of acrylic acid by NaOH.

In Figure 3, the adsorption effect is most pronounced when the crosslinker mass fraction is 1.0%. This may be the theory of Flory gel. When the amount of cross-linking agent is low, the degree of crosslinking of polyacrylic acid/styrene is low, and the polymerization reaction produces insufficient three-dimensional crosslinking network. During the adsorption experiment, the microspheres may contain a highly soluble polyacrylic acid/styrene resin dissolved in a solvent. The dissolved polyacrylic acid/styrene resin causes the adsorption efficiency to become low. However, as the mass fraction of the crosslinker continues to rise, the 3D cross-linking network is more perfect, and thus the ability of the microsphere to adsorb heavy metal ions is also continuously enhanced. When the degree of crosslinker exceeds a certain value, the degree of crosslinker of the polyacrylic acid/styrene polymerization reaction is too large, and a dense 3D crosslinking network of the polymer is formed, so that the molecular chain extension of the resin after the adsorption of the microspheres is limited.
Figure 3. Effect of crosslinker dosage on adsorption capacity.

The microspheres have a small molecular space and a low swelling property. The solvent, that is, the heavy metal ions, is difficult to sufficiently contact the resin, and the adsorption capacity is lowered, and the magnification of the heavy metal and water adsorbed by the microspheres is reduced.

Figure 4. Effect of temperature on adsorption capacity.

It can be seen from Figure 4 that the AA/S superabsorbent resin synthesized at a temperature of 65 °C has the best adsorption effect. The adsorption effect increases with the increase of temperature when the temperature is lower than 65 °C; the polymerization temperature increases, the active center increases, the chance of collision is increased, the chain breaks easily, the length of the main chain decreases, and the molecular weight becomes smaller. The adsorption ratio decreases as the temperature rises when the temperature exceeds 65 °C. This may be due to the fact that when the reaction temperature is too high, the decomposition rate of the initiator is too fast, the gel effect is obvious, and the explosion occurs.

Figure 5. FTIR spectra of AA/S.
Through the visual analysis of the test results, the best scheme of the orthogonal experiment is obtained. The optimal solution is: monomer ratio 1:0.2, neutralization degree 65%, cross-linking agent accounting for 1% of monomer mass fraction, temperature 65 °C. According to the experimental optimization scheme, the optimal experimental synthesis and adsorption experiments were designed. According to the experimental optimization scheme, the optimal experimental synthesis and adsorption experiments were designed.

As shown in figure 5, the vibration peak of -OH appeared at a wavelength of 3398 cm\(^{-1}\). The -CH stretching peak on the benzene ring appeared near the sample wavelength of 3030 cm\(^{-1}\). An asymmetric stretching peak of -CH\(_2\)- appeared in the vicinity of 2934 cm\(^{-1}\). C=O in the carboxyl group appeared near 1650 cm\(^{-1}\).

4. Conclusion
The orthogonal experimental design was used to study the main influencing factors to optimize the experimental scheme. The analysis showed that the order of the influencing factors was neutralization > crosslinker > monomer ratio > temperature. The performance test of adsorbing heavy metal ions showed that when the ratio of acrylic acid to styrene was 1:0.2, the degree of neutralization was 65%, the crosslinker accounted for 1.0% of the monomer mass fraction, and the temperature was 65 °C, the obtained polymerization Acrylic/styrene copolymer hydrogels have the best effect on the adsorption of heavy metal ions. The optimum amount of Pb\(^{2+}\) adsorbed by the atomic spectrophotometer was 328.25 mg/g

References
[1] Zhou, Guiyin, et al. Rapid and efficient treatment of wastewater with high-concentration heavy metals using a new type of hydrogel-based adsorption process. Bioresource technology, 219 (2016): 451-457.
[2] Karnitz Jr, Osvaldo, et al. Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. Bioresource technology, 98.6 (2007): 1291-1297.
[3] Kaşgöz, Hasine, Saadet Ö zgümüş, and Murat Orbay. Modified polyacrylamide hydrogels and their application in removal of heavy metal ions. Polymer, 44.6 (2003): 1785-1793.
[4] Kunkel, Robert, and Stanley E. Manahan. Atomic absorption analysis of strong heavy metal chelating agents in water and waste water. Analytical Chemistry, 45.8 (1973): 1465-1468.
[5] Francis, Sanju, Manmohan Kumar, and Lalit Varshney. Radiation synthesis of superabsorbent poly (acrylic acid)–carrageenan hydrogels. Radiation Physics and Chemistry, 69.6 (2004): 481-486.
[6] Ceglowski, Michal, et al. A new low-cost polymeric adsorbents with polyamine chelating groups for efficient removal of heavy metal ions from water solutions. Reactive and Functional Polymers, 131 (2018): 64-74.
[7] Yener, Julide, et al. Dynamic analysis of sorption of methylene blue dye on granular and powdered activated carbon. Chemical Engineering Journal, 144.3 (2008): 400-406.
[8] Tsibranska, Iren, and Elena Hristova. Use of activated carbons from apricot stones for heavy metals removal. Comptes Rendus De L Academie Bulgare Des Sciences, 64.6 (2011): 831-838.
[9] Volesky, Bohumil, and Z. R. Holan. Biosorption of heavy metals. Biotechnology progress, 11.3 (1995): 235-250.
[10] Demirbas, Ayhan. Heavy metal adsorption onto agro-based waste materials: a review. Journal of hazardous materials, 157.2-3 (2008): 220-229.