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Application and research of hydrogels in wastewater treatment

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Abstract. With the rapid development of the economy and technology, heavy metal industrial wastewater has caused a great impact on the environment and has gradually become a global concern. As a new type of environmentally friendly adsorption material, the gel has a good adsorption capacity because of its special network structure, so it can be used in wastewater treatment, water purification, and other fields. In this paper, the structure, classification, and application direction of gels are discussed in detail.

Keywords: Hydrogel, Microstructure, Scanning Electron Microscope (SEM), Adsorption of Dyes; Adsorption of Metal Ions.

1. Introduction

With the development of industrial technology, more and more industrial wastewater is discharged into rivers and oceans, causing water pollution. Among them, heavy metal pollution has become the most non-negligible problem, which poses a great threat to human health and survival. To deal with this problem, many scholars from all over the world have carried out research work and made great progress. At present, ion exchange, chemical precipitation, membrane separation, and adsorption are commonly used in wastewater treatment. Although there are many methods to deal with heavy metal pollution, they all have problems such as high cost, low reuse rate, complex process, and single treatment of metal ions, so they cannot achieve ideal results. In comparison, the adsorption method has the advantages of a wide application range, simple operation, and recyclability, so it has received great attention around the world. In addition, due to the continuous emergence of new varieties of dyes, the amount of textile printing and dyeing wastewater is also increasing, so the pollution caused by dye wastewater has attracted the world's high attention. Because of the secondary pollution caused by other technologies, adsorption is also used in the treatment of dye wastewater. As a new type of environmentally friendly adsorption material, the gel has unique advantages and plays an important role in wastewater treatment.

A gel is a mixture, which is a semi-solid substance composed of a solid gel factor and a solvent and when colloidal particles or polymers in a sol or solution are connected under certain conditions, a spatial network structure will be formed. Hydrogel will be a specific example to illustrate the property and structure of gel in the following. Hydrogels are cross-linked by covalent bonds, a hydrogen bond, or van der Waals forces to form a three-dimensional network structure so that it can swell and retain a

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large amount of water. Due to its three-dimensional network structure, the hydrogel can respond to extremely small changes in the external environment through swelling and contraction. (temperature, pH, etc.) In addition, hydrogels also have the advantages of large adsorption capacity, abundant raw materials, high removal rate, rapid adsorption, and environmental friendliness, which are more suitable for the enrichment and separation of a low-concentration heavy metal ion. Therefore, the removal of heavy metal ions by hydrogel materials has become an important development direction of the treatment technology of low-concentration heavy metal pollution in the future.

2. Classification of gels

More types of hydrogels are innovated with in-depth research on hydrogels in recent years. According to different standards, hydrogels can be divided into the following categories.

(1) From the perspective of gel factors, hydrogels can be divided into two categories: single-component hydrogel and composite hydrogel. Single-component hydrogels are formed by chemical or physical reactions of only one component. Composite hydrogels are composed of two components at least, and each component has its specific function. As a result, the characteristic of a composite hydrogel depends on the physical and chemical properties of the components. Meanwhile, because of the large number of components, the properties of the hydrogel can be regulated by changing the proportion of each component. The most commonly used polymer in the composite hydrogel is hydroxyl-containing polymers such as PVA and its copolymers. Polyvinyl alcohol (PVA) is a type of organic compound with the chemical formula $[C_2H_4O]n$ .It is an odorless white powdered solid that is soluble in water. Due to the high adhesion between its elements, PVA has strong film forming ability. The formed film is colorless and transparent, with good mechanical strength. In addition, PVA will not be affected by weak acids, bases or organic solvents and has high oil resistance.At the same time, due to the high activity of the hydroxyl group in the molecule, PVA can carry out typical chemical reactions with lower alcohols, such as esterification, etherification, acetal, etc., and can react with many inorganic or organic compounds. Therefore, PVA is regarded as a linear polymer with secondary hydroxyl group, which can be used as an adhesive.The hydrogels prepared by PVA not only have the properties of water absorption, water retention, slow release and sensitive response to external stimuli, but also have the advantages of low toxicity, low toxicity, good physical and mechanical properties and excellent biocompatibility [1].

(2) According to the response of hydrogels to the changes in the external environment, hydrogels can be divided into traditional hydrogels and intelligent hydrogels. Traditional hydrogel is a kind of hydrogel that keeps the morphology of raw materials while its properties do not change when the external conditions and environment change. Intelligent hydrogels are sensitive to changes or stimuli in the external environment such as temperature, pH, pressure, and light, and respond to different changes the first time [2]. The swelling and shrinking process of intelligent hydrogel is mainly the process of absorbing and releasing water molecules by polymer polymerization network. Serizawa et al. added silica particles into the prepolymerization solution. After the polymerization, the silica particles were removed by hydrofluoric acid at room temperature to obtain porous PNIPAM hydrogel. Compared with the traditional PNIPAM hydrogel, the porous PNIPAM hydrogel has 80 times higher temperature-sensitive response efficiency [3-4]. Xue et al. changed the water content of the hydrogel before freezing and then controlled and adjusted the size of the inner hole of the hydrogel after freezing treatment. When the water content in equilibrium is more than 10 times the amount of polymer, it only takes 30 ~ 40 s for the frozen hydrogel to shrink in half of the volume, which is more than 100 times faster than the ordinary traditional hydroge [[5].

3. Characterzatioin methods

3.1. Microscopic morphology characterization

To better analyze and observe the microstructure, composition, and phenomenon of a specific material, we have many methods such as Transmission electron microscopes (TEM) and Scanning Electron microscopes (SEM) in the process of research. Scanning electron microscope (SEM) can be

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used in the field of material science. It uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. Wang Shuang first added 200 mL of anhydrous ethanol into a bottle with a condensing tube and heated it to reflux, then added 40 mL of 0.5% SA solution while stirring. After two hours, it is cooled to room temperature and separated from the solution to obtain NNSA. The prepared NNSA was placed into 80 mL $CaCl_2$ solution under magnetic agitation. After waiting one hour for the cross-linking reaction (the cross-linking of Ca^{2+} enhances the stability of this particular structure), NNCA hydrogels are obtained. Then she used the scanning electron microscope to observe the micromorphology of the hydrogels. It could be seen clearly that NNSA has a three-dimensional mesh nanostructure morphology (Figure 1). Similarly, NNCA also has a 3D mesh nanostructure morphology, as shown in Figure 2[6].

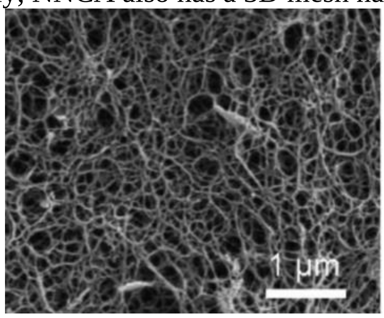

Figure 1. SEM image of NNSA hydrogel.

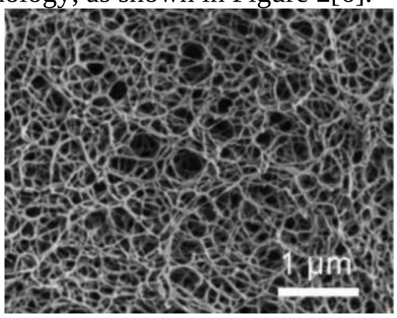

Figure 2. SEM image of NNCA hydrogel.

Jie Xile from Xi’an Technological University compared and observed the prepared polyacrylic acid hydrogels (PAA hydrogels, PAA-CS hydrogels) by using the scanning electron microscope. It can be seen that the surface of the hydrogel has a three-dimensional pore network structure, and there are many holes capable of absorbing metal ions. It is shown that the surface area of PAA-CS hydrogels is much larger than that of PAA hydrogels, which can provide more adsorption sites for heavy metal ions and facilitate the adsorption process (Figure 3, Figure 4) [7].

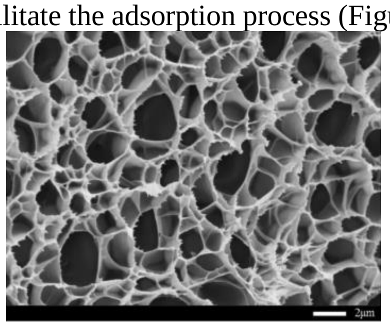

Figure 3. SEM image of PAA hydrogel.

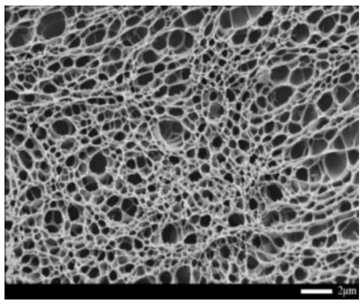

Figure 4. SEM image of PAA-CS hydrogel.

Another normal characterization method is transmission electron microscopes. Transmission electron microscopes (TEM) are microscopes that use a particle beam of electrons to visualize specimens and generate a highly-magnified image. TEMs can magnify objects up to 2 million times. TEM has a higher resolution than SEM. TEM samples are even more demanding and need to be thin because the electron beam has very little penetration. Wang Shuang prepared bi-functional Fe_3O_4/Ag-NNCA hydrogels with magnetic separation and antibacterial functions (by adding Fe_3O_4 NPs and Ag NPs to make it have magnetic separation and antibacterial functions) and performed characterization tests on them. Figure 5 and figure 6 below showed that some smaller nanoparticles were evenly distributed on the gel network structure. Based on SEM and TEM images, it can be inferred that the formation of three-dimensional network nanostructures provides a carrier for nanoparticles to prevent their aggregation, while the presence of nanoparticles prevents the aggregation of nanohydrogels [6].

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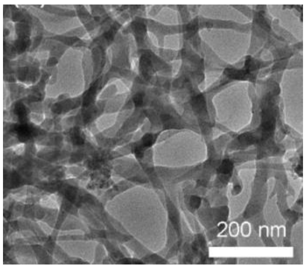

Figure 5. Low power TEM image of Fe_3O_4/Ag-NNCA hydrogel.

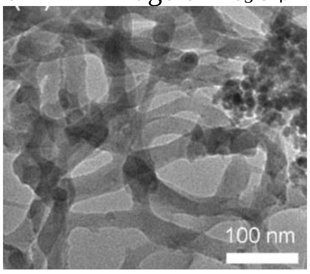

Figure 6. High magnification TEM image of Fe_3O_4/Ag-NNCA hydrogel.

3.2. Characterization of assembly method

X-ray diffraction (XRD) is a type of analytical technique used in material science to identify the crystal structure of the material. It is to use the X-ray diffraction phenomenon in the crystal to obtain the diffraction X-ray signal characteristics, and then obtain the diffraction pattern after processing. The spectrogram information can be used not only to determine the phase of the conventional microscope but also to see whether there are defects (dislocations) and lattice defects inside the crystal. Similarly, Wang Shuang also conducted an XRD test on the prepared Fe_3O_4/Ag-NNCA hydrogel.

The XRD pattern in figure 7 shows that the diffraction peaks observed at 2θ of 30.2°, 35.5°, 43.1°, 53.6°, 56.8°, and 62.4° correspond to (220), (311), (400), (422), (511) and (440) crystal planes of Fe_3O_4 respectively. Also corresponding to the (111), (220), and (311) crystal planes of Ag NPs at 38.2°, 64.4°, and 77.5°, it can be concluded that Fe_3O_4 and Ag NPs have been successfully introduced into NNCA hydrogels [6].

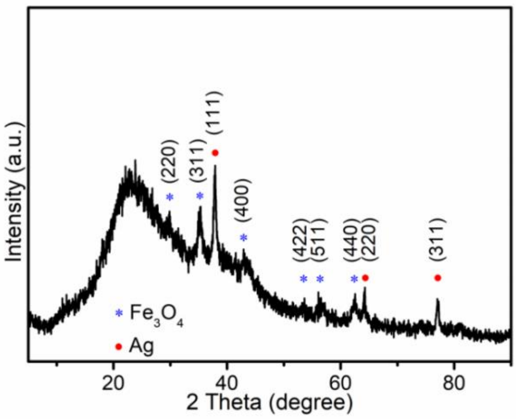

Figure 7. XRD pattern of Fe_3O_4/Ag-NNCA.

Jiang Jiacheng also conducted XRD characterization tests on the prepared sodium alginate (SA) /polyvinyl alcohol (PVA) / cyclodextrin (CD) gel. As shown in the figure 8 below, the wide peak at 20.36 ° in the XRD pattern of SA proves the amorphous structure of SA. The XRD pattern of CD shows multiple diffraction peaks, indicating that CD has an amorphous structure. The spectrum of SA/PVA/CD is similar to that of PVA and SA, indicating that SA/PVA/CD also has an amorphous structure. It can also be seen from the figure that when 2θ of SA/PVA/CD is 13.92 °, 20.36 °, 19.44 °, 40.86 °, 12.42 °, 17.92 °, the specific diffraction peaks of SA, PVA and CD appear respectively [8].

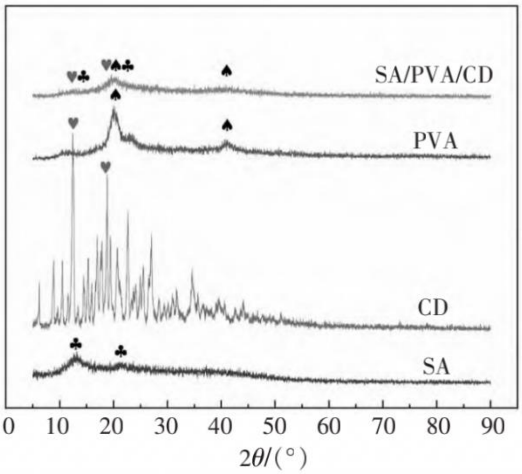

Figure 8. XRD spectra of SA/PVA/CD gel beads and raw materials.

4. Application in water pollution

4.1. Adsorption of dyes by hydrogels

Ruihua Mu et al. analyzed the surface morphology of the prepared P(AM-AANa) hydrogel by scanning electron microscopy after vacuum drying at 50℃. Then the hydrogels adsorbed with different dyes (ST, $C_{20}H_{10}N_4C_1$, methylene blue (MB), malachite green (MG), and crystal violet (CV)) were placed in a vacuum and dried at 50℃. The morphology of the hydrogels was observed by scanning electron microscopy. Figure 9 shows that before adsorption, the P(AM-AANa) hydrogel is filled with pores and has an uneven surface. After adsorbing the dye solution, the folds on the surface of P(AM-AANa) hydrogel became shallower and fuller (Figure 10).

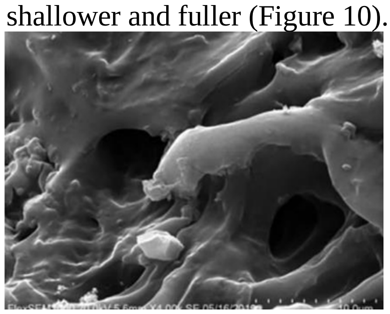

Figure 9. SEM diagram of P (AM -AANa) hydrogel.

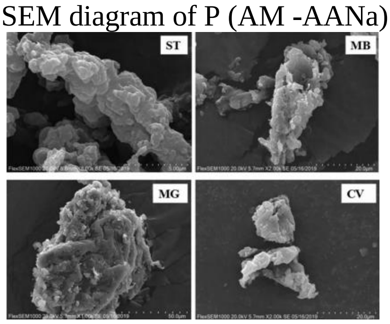

Figure 10. SEM diagram of P(AM-AANa) hydrogel after dye adsorption.

This experiment investigated the adsorption properties of P(AM-AANa) hydrogel for ionic dyes MG, CV, ST, and MB. The results showed that when the initial dye concentration of P(AM-AANa) was 10mg/L and the powder mass of hydrogel was 2 mg, the adsorption rates of ST, MB, MG, and CV on

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hydrogel were 2.6%,16.2%,7.9%, and 12.0%, respectively. Therefore, MB has the best adsorption effect, followed by CV, and the adsorption effect on ST and MG is not obvious [9].

Luting Zhao et al. prepared hemicelluellulose-based magnetic hydrogels by free radical polymerization and in situ co-precipitation and studied their adsorption properties of methylene blue dyes. As shown in figure 11, the adsorption capacity of methylene blue by magnetic hydrogel increased rapidly during the first 60 minutes. With the increase of time, the adsorption volume gradually slowed down until it reached equilibrium after 170 minutes. The main reason for this phenomenon is that there are a huge amount of adsorption sites on the surface of magnetic hydrogel that can bind to methylene blue in the beginning. When the adsorption site on the surface is saturated with the dye, the methylene blue dye can only bind to the internal adsorption site, so the adsorption becomes slow. It can be seen from Figure 12 that the removal rate of methylene blue increases with the increase in the amount of magnetic hydrogel. When the amount of magnetic hydrogel was 0.015g, the removal rate reached 97%. Therefore, it can be concluded that when the amount of magnetic gel is 0.015g and the adsorption time is 180 minutes, the adsorption effect is the best [10].

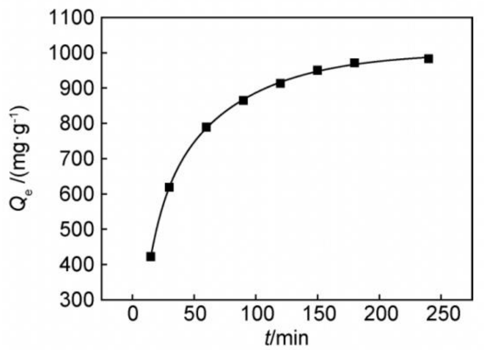

Figure 11. Effect of time on methylene blue adsorption capacity.

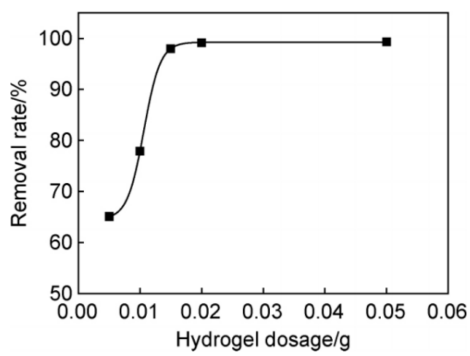

Figure 12. Effect of magnetic hydrogel dosage on methylene blue removal rate.

4.2. Adsorption of metal ions by hydrogels

Wang Shuang prepared NNCA hydrogels that have high adsorption properties by cross-linking reaction with sodium alginate as raw material. The experiment investigated the adsorption effect of the NNCA hydrogel in Cd^{2+} and Cu^{2+} solutions at different temperatures and concentrations. The collected data show that the structure of sodium alginate contains mannuronic acid (M) and guluronic acid (G). The former is mainly responsible for the ion exchange and adsorption function, while the latter mainly reflects the characteristics of the gel. In the presence of Ca^{2+}, the Na^{+} on the G unit has ion exchange with Ca^{2+}, and the G unit accumulates, resulting in the formation of hydrogels with a three-dimensional network structure.

The results showed that when the initial concentration increased from 1mg/L to 15mg/L, the adsorption capacity of the hydrogel for Cd2+ increased gradually, then slowed down slightly, and finally became stable (about 70%). Similarly, the removal rate of NNCA hydrogels for Cu^{2+} rose steadily, then tend to be stable in the end, with about 82%(Fig 13). To conclude, with the increase of

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concentration of Cu^{2+} and Cr^{2+} solution, the adsorption capacity of the NNCA hydrogel also increased. It can be seen that the concentration of metal ion solutions has a great impact on the adsorption property of NNCA hydrogels (Figure 14) [6].

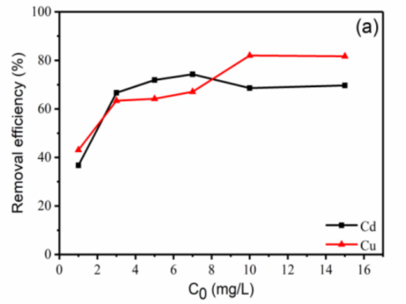

Figure 13. The removal rate varies with the initial concentration of Cu^{2+} and Cd^{2+}.

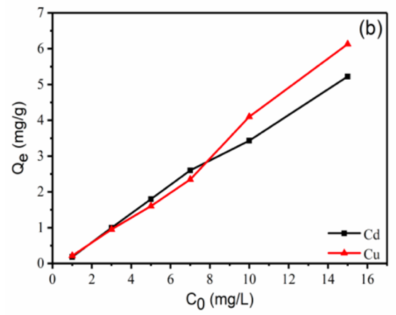

Figure 14. The adsorption of NNCA hydrogel with the concentration of Cu^{2+} and Cr^{2+}.

Similarly, Wang Shuang also explored the influence of temperature and contact time on the adsorption properties of NNCA hydrogels. As shown in Figure 15, with the increase of time, the removal rate of Cu increased from 82.73% to 86.69%, and the removal rate of Cd increased from 66.08% to 69.42%. It can be seen from figure d that the removal rate of Cd^{2+} and Cu^{2+} ions by NNCA hydrogel gradually increases with the increase in temperature. Therefore, high temperature is conducive to the adsorption of heavy metal ions (Figure 16) [6].

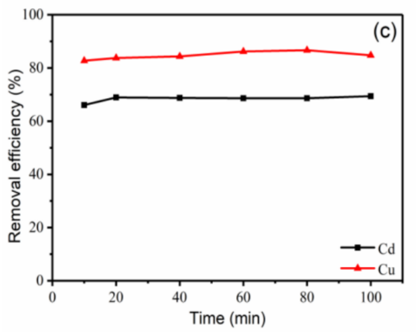

Figure 15. The removal rate of Cu and Cd over time.

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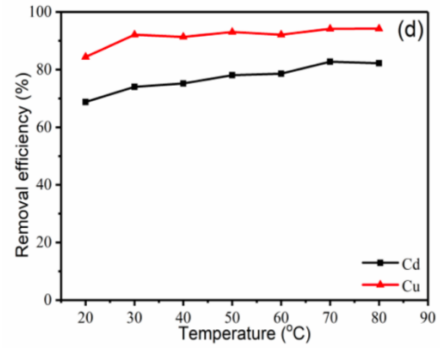

Figure 16. The removal rate of Cu and Cd with temperature.

Yu Zhongpeng dissolved 0.5g sodium alginate and tannic acid in ultra-pure water according to proportion and added the pre-treated rice hemicellulose. The STR gel pellets were obtained by stirring, rinsing, and drying after the mixture was dropped into $CaCl_2$ solution. Then he investigated the effects of different Fe^{3+} concentrations on STR gel spheres. As shown in the figure 17, the adsorption capacity of STR gel spheres increased with the increase in iron ion concentration. When it reached 200mg/L, the adsorption capacity of the gel sphere did not increase significantly. The main reason is that when the concentration of iron ion solution is low, there are more adsorption sites, so there are enough adsorption sites for STR gel spheres when the concentration of iron solution is increased. However, when the solution concentration reached 200mg/L, the adsorption sites of STR gel spheres gradually reached saturation, so the adsorption capacity of the gel spheres did not change significantly [11].

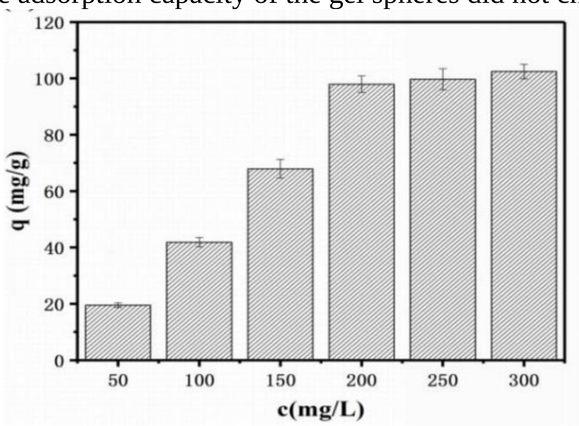

Figure 17. Change of adsorption capacity of gel spheres with Fe^{3+} concentration.

5. Conclusion and prospect

Hydrogels have been widely used in water pollution treatment because of their good chemical and physical properties. Although its preparation and application are still in the basic research stage, remarkable achievements have been made in the treatment of dye wastewater and heavy metal ion wastewater [12]. In the future, the research focus of hydrogels can be carried out in the following aspects:

(1) Preparing personalized hydrogels, such as strengthening the selective adsorption capacity, developing specific functional hydrogels with high sensitivity to heavy metal ions and so on. (2) Develop new crosslinking agents to improve the adsorption capacity of hydrogels and so on. (3) Improve the cross-linking technology and preparation process to reduce the preparation cost of hydrogel. Due to the deterioration of the environment and the constant depletion of resources, I believe that hydrogel materials with its advantages of low cost and no pollution will certainly achieve great success and harvest in the future environmental protection and sustainable development [13].

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