Study on the adsorption property for Cu$^{2+}$ of Chitosan/Ploy (SSS-HEMA-AA) hydrogel

Jiangang Zhou$^{1,*}$, Yong Zhang$^2$

1 Faculty of Resources and Environmental Science, Hubei University, Wuhan, China  
2 School of materials science and engineering, Hubei University, Wuhan, China

*Corresponding author email: zhoujg@hubu.edu.cn

Abstract. Chitosan hydrogel, as a new type of macromolecule adsorbent material, has dual advantages of gel and various functional groups. It is easy to introduce functional groups which can chelate with heavy metal ions or electrostatic adsorption. It has large specific surface area and fast adsorption rate for heavy metal ions. It has quickly become a research hotspot in separation field. Based on this, the hydrogels of different components were prepared by integrating different proportions of copolymer monomers into chitosan hydrogels. The hydrogels of the same components were separately taken from aqueous solutions with different concentrations of Cu$^{2+}$ for adsorption experiments. The heavy metal Cu$^{2+}$ could be adsorbed and captured by a large number of functional groups such as sulfonic group, hydroxyl group, carboxyl group and amino group in the chemical structure. The effect of the same component on the hydrogel properties was also investigated. The molecular structure and internal morphology of the hydrogel and the effect of the amount of sodium styrene sulfonate (SSS) on the adsorption capacity of Cu$^{2+}$ and the amount of glutaraldehyde on the water swelling rate were also investigated. The results show that the chitosan-P (SSS-HEMA-AA) hydrogel has a three-dimensional cross-linked network structure and has a high adsorption and removal efficiency for Cu$^{2+}$. Its adsorption capacity for Cu$^{2+}$ increases with the increase of the amount of sodium styrene sulfonate (SSS) in the preparation process, and the water absorption and swelling rate decreases with the increase of the amount of glutaraldehyde.

Keywords: Chitosan; hydrogel; copper ion.

1. Introduction
With the rapid development of industry, heavy metal pollution of water is more and more serious. As heavy metal pollution is different from other toxic compounds, it is generally rich and difficult to degrade, so it cannot reduce or eliminate the toxicity of pollutants through the purification ability of nature itself. Most heavy metal elements have serious pollution effects on the environment, such as chromium, lead, nickel, cadmium, copper, arsenic and other toxic heavy metal pollutants [1]. Because heavy metal is very toxic to human body, it is easy to remain in human body and produce harmful effects on other organisms. Therefore, it is particularly important to find an effective way to deal with heavy metal ions.
At present, a large number of literature data show that there are several methods to deal with heavy metals in water, such as adsorption, chemical precipitation, membrane separation technology, oxidation-reduction, electrochemical method, extraction, molecularly imprinted method, ion exchange method, biological method, etc. [2-9], among which adsorption is the most commonly used method [10]. Adsorption method is to use adsorption materials to carry out physical or chemical adsorption of heavy metal ions in water. Generally, adsorption materials have special functional groups or the structure with dense micro Nano pores and high specific surface area. Chitosan and its derivative hydrogels are excellent adsorbents for heavy metal ions, [11-12]. They have a large number of polar groups which can chelate with metal ions, and electrostatic adsorption. Therefore, heavy metal ions are adsorbed around them, which is highly concerned about [13].

In recent years, because of the special structure of chitosan, the amino groups in molecular chains can be combined with transition metal ions. Therefore, the research on adsorption of heavy metal ions is very active. [14-17], a lot of researches have been done on chitosan and its derivative hydrogels as heavy metal ion sorbent. [17-21] The main reasons for the adsorption of hydrogels and heavy metals are chelation, electrostatic adsorption and ion exchange [22-23]. First, the polymer network structure of hydrogels can provide a place for the adsorption of metal ions. The porous structure of hydrogels can provide a channel for the free movement of heavy metal ions, and can rapidly diffuse the [24] inside the gel network. Secondly, the hydrogel is composed of three-dimensional network structure of polymer. The polymer chain composed of network structure can introduce specific functional groups according to needs, and have electrostatic adsorption or ion exchange with metal ions. Compared with other polymer materials, the specific surface area of hydrogel is large. The molecules of unit mass can be contacted with more metal ions, and the adsorption rate and adsorption capacity are larger.

Therefore, according to the above mechanism, this study is to prepare different components of hydrogels by adjusting the different ratios of copolymers of synthetic chitosan hydrogels. The hydrogel of the same component is adsorbed in aqueous solutions of different concentrations of Cu$^{2+}$, and it can adsorb and capture heavy metals by using a large number of functional groups such as sulfonic group, hydroxyl group, carboxyl group and amino group in the chemical structure. Cu$^{2+}$, to study the effect of different components on the performance of hydrogels, and provide a possible method for large-scale sewage treatment.

2. Materials and methods

2.1. Instruments

2.1.1. The main experimental instruments are electronic balance, magnetic stirrer, 1ml medical syringe, 20ml glass bottle, vacuum drying oven, oven Fourier infrared spectroscopy (FT-IR, Perkin Elmer company of the United States), thermogravimetry analyzer (tga-1, METTLER TOLEDO group of Switzerland), scanning electron microscope (SEM, Japan Electronics Co., Ltd.), ultraviolet spectrometer (UV Vis, Shanghai mapda company), etc.

2.2. Experimental design

2.2.1. The preparation of chitosan /P (SSS-HEMA-AA) hydrogel was accurate. A number of 5mL 50 g/L chitosan solutions were selected in the glass bottle of 20mL, and the hydroxyethyl methacrylate (HEMA), acrylic acid (AA), sodium styrene sulfonate (SSS) solution, glutaraldehyde solution and potassium persulfate solution were added to the glass bottles respectively, among which HEMA, AA, and carbon containing carbon double bond were used as comonomers and glutaraldehyde. As a crosslinking agent, potassium persulfate is used as the initiator. When heated, free radicals are produced to initiate the free radical copolymerization of monomers. Because aldehydes are very active, in order to avoid reaction or slow reaction before even mixing, we make them fully mixed at low temperature. After being fully mixed, they were put into the oven at 70 degrees Celsius. After a certain reaction time,
different components of hydrogels were generated. Different hydrogels were synthesized by adjusting their ratios to study the effects of different components on the properties of hydrogels.

2.2.2. Copper ion adsorption test. Hydrogel of the same component was adsorbed in aqueous solution of different concentrations of Cu$^{2+}$. The hydrogel was sucked. The residual solution was washed in deionized water. The thermogravimetric analysis and Cu$^{2+}$ adsorption was tested by thermogravimetric analyzer after drying. The same method was used to test the thermogravimetric curves and Cu$^{2+}$ adsorption capacity of chitosan /P (SSS-HEMA-AA) hydrogels with different components at the same Cu$^{2+}$ concentration. The thermogravimetric curves and Cu$^{2+}$ adsorption capacity of chitosan hydrogel with or without AA were measured respectively, and the influencing factors on the amount of copper ion adsorption were studied. The adsorption capacity of chitosan hydrogel in CuSO$_4$ solution was determined.

2.2.3. Copper ion adsorption rate test. Configuration 7 Cu$^{2+}$ of 0.25 g/L of copper sulphate solution 10mL in glass bottles, 6 samples of 0.2 g SSS (0.08 g) P (SSS-HEMA-AA) hydrogel were accurately added into the above prepared copper sulphate solution, marking, respectively, at 10, 20, 30, 40, 60, 90min after visible UV spectrophotometer to test the adsorption in glass bottle. The concentration of copper ion in solution was calculated according to the decrease of Cu$^{2+}$ concentration with time, and the adsorption rate of Cu$^{2+}$ on hydrogel was calculated.

2.2.4. Internal structure test of hydrogel. The internal structure of the hydrogel was measured by scanning electron microscope (SEM). The soaked hydrogel was frozen in the refrigerator to form ice. Then it was freeze-dried for a long time in the freeze dryer. The dried sample was broken and the microstructure of the section was measured under the scanning electron microscope.

3. Results and discussion

3.1. Internal morphology of hydrogels

Two kinds of hydrogels containing different glutaraldehyde content were soaked in deionized water for a long time, so that they were completely swellable and frozen in the fridge. After freezing, they were frozen and dried in a freeze dryer. The scanning electron microscope (SEM) of the section was measured after drying completely. As shown in Fig.1, the porous network structure can be clearly seen through the SEM picture, in which, the pore diameter of Fig.1 (a) is mostly distributed in 4-6 μm, and that of Fig.1 (b) is mostly distributed in 8-10 μM. Because samples a and B are consistent in other variables, the content of glutaraldehyde used is different, 0.3ml and 0.2ml respectively. In Figure 1 (a), the amount of glutaraldehyde is large, and the three-dimensional network skeleton of the hydrogel is more compact, so the pores formed are smaller. The results show that with the increase of the amount of glutaraldehyde, the three-dimensional network structure is more compact.

![Fig.1](image_url) The SEM images of hydrogels with different glutaraldehyde content (a 0.3mL; b 0.2mL)
3.2. Thermogravimetry (TGA)

Hydrogel samples with different SSS content were added to the Cu$^{2+}$ solution of 2g/L. After sufficient adsorption time, the samples were removed. The residual liquid was cleaned with deionized water. Then the 24h was dried in the oven, so that the water in the gel was completely lost, and the dried hydrogel samples were obtained after the adsorption of Cu$^{2+}$. In the oxygen atmosphere, the dried hydrogel samples were heated to 800 degrees centigrade, and the thermogravimetric curves were tested as shown in Figure 2.

The test results are shown in Figure 2 below: a, b, c and d in Fig.2 are the thermogravimetric curves of hydrogels adsorbed Cu$^{2+}$ after SSS content of 0.01, 0.05, 0.1 and 0.2g respectively. It can be seen from Figure 2 that when the temperature reaches 500 ℃, the sample quality will not change any more. At this time, the material after combustion should be CuO. With the increase of SSS content, the more CuO remains, indicating that the adsorption amount of Cu$^{2+}$ is directly proportional to the SSS content. This is because the SSS monomer has the structure of sodium sulfonate, which is ionized into sulfonate anion in the solution, while Cu$^{2+}$ in the solution is positively charged, and the negatively charged sulfonate ion group has electrostatic attraction with Cu$^{2+}$ in the solution, so that a large number of copper ions are enriched around the sulfonate. Therefore, the more the content of SSS monomer with sulfonic group, the stronger the adsorption performance of hydrogel formed on Cu$^{2+}$.

![TGA curves of hydrogel adsorption Cu$^{2+}$ with different SSS content](image)

Fig.2 TGA curves of hydrogel adsorption Cu$^{2+}$ with different SSS content (a 0.01g; b 0.05g; c0.1g; d 0.2g)

The adsorption capacity of two kinds of hydrogels of different components to copper ions is shown in Figure 3 below: a and b curves are P (SSS-HEMA-AA) hydrogel and chitosan/P (SSS-HEMA-AA) hydrogel adsorbed in copper sulfate solution with mass concentration of 250mg/L in a long time. It can be seen from Fig. 3 that the residual rate of the curve in a is higher and longer in the mild region at 420 degrees Celsius, indicating that the adsorption capacity of a (P) (SSS-HEMA-AA) hydrogel on copper ion is stronger than that of b /P (SSS-HEMA-AA) hydrogel under the same conditions. Because B has a chitosan in the corresponding hydrogel, the molecular network skeleton is closer and the cation ammonium group has heavy metal repels, which results in a decrease in the proportion of sulfonated radical groups in the same hydrogel.
3.3. Comparison of adsorption capacity of copper ion

The adsorption capacity of hydrogel and pure chitosan hydrogel with different glutaraldehyde content on Cu$^{2+}$ ion was measured by visible ultraviolet spectrophotometry. Before the test, the absorption intensity of copper ion at the wavelength of 800 nm was determined to be the best by spectral scanning of CuSO$_4$ solution. The final test results are shown in Fig. 4: the a curve in Figure 4 is the absorbance curve of the CuSO$_4$ solution with a concentration of 0.25g/L; the b curve is the absorbance curve of 0.2g pure chitosan hydrogel adsorbing 0.25g/L CuSO$_4$ solution; c, d, e and f curves are the absorbance curves of 0.1, 0.2, 0.4, and glutaraldehyde content of the hydrogels after adsorption. The greater the absorbance of the solution after the adsorption of Cu$^{2+}$ ions by the hydrogel, the higher the concentration of Cu$^{2+}$ ions in the solution, the less the Cu$^{2+}$ ions adsorbed by the hydrogel. The result is that the adsorption ability of the hydrogel to Cu$^{2+}$ ions is weaker. It can be seen from Fig. 4 that the absorbance values of the five curves of b, c, d, e and F are smaller than those of the original concentration 250mg/L CuSO$_4$ solution, indicating that the five hydrogels have certain effect on the adsorption of Cu$^{2+}$ ions. The absorbance value of B is larger than that of c, d, e and F, indicating that the adsorption capacity of pure chitosan hydrogel to Cu$^{2+}$ ion in solution is less than that of chitosan/P (SSS-HEMA-AA) type hydrogel. The absorbance values of the four curves of c, d, e and f decreased successively, indicating that the adsorption capacity of chitosan/P(SSS-HEMA-AA) hydrogel to Cu$^{2+}$ ions in sequence increased with the increase of the amount of crosslinking agent glutaraldehyde. The reason for analysis is that the reaction of -CHO in glutaraldehyde with -NH$_3^+$ in the main chain of chitosan can reduce -NH$_3^+$ in the hydrogel skeleton, while the decrease of -NH$_3^+$ can reduce the repellent effect of hydrogels on Cu$^{2+}$. Therefore, as the amount of crosslinking agent glutaraldehyde increased, the adsorption capacity of chitosan /P (SSS-HEMA-AA) hydrogel to Cu$^{2+}$ increased.

![Fig.3 TGA curves of different hydrogel adsorption Cu$^{2+}$](image)

![Fig.4 Absorbance of hydrogel adsorption Cu$^{2+}$ with different components (a primary concentration; b pure CS; c 0.1mL; d 0.2mL; e 0.4mL; f 0.8mL glutaraldehyde)](image)
3.4. Adsorption rate of copper ion

The absorbance test results are shown in Figure 5 below. The curve in Fig. 5 is the absorbance curve of the copper ion solution with an initial concentration of 250mg/L. The curves of B, C, D, e, F and G are 0.2g (SSS) content of 0.08g 0.2g (hydrogel), and the absorbance curve of the copper ion solution of the copper ion solution with a concentration of 0.

![Absorbance of hydrogel adsorption Cu²⁺ with different time](image)

Fig.5 Absorbance of hydrogel adsorption Cu²⁺ with different time (a 0min; b 10min; c 20min; d 30min; e 40min; f 60min; g 90min)

It can be seen from Fig.5 that P (SSS-HEMA-AA) hydrogel has obvious adsorption effect on copper ions. After adsorption of 10min, the absorbance of copper ions in the solution can be clearly measured. With the increase of adsorption time, the concentration of copper ion in the solution decreases gradually. It is clear that the adsorption of copper ions by P (SSS-HEMA-AA) hydrogel is not completed in one step, but gradually adsorbed. This is due to two reasons, one is that in the process of adsorption, copper ions begin to adsorb on the surface of the hydrogel, and then slowly penetrate into the hydrogel. The reason two is that the sulfonic acid in hydrogel molecules begins in deionized water and forms in the form of ion pairs with sodium ions. When copper sulphate solution is applied, the copper ions in the solution will exchange ions with the sodium ions in the hydrogels and thus accumulate around the hydrogel. Therefore, the interaction of permeation and ion exchange makes the adsorption process of copper ion complete gradually rather than step by step.

4.  Conclusion

The molecular structure and internal morphology of chitosan hydrogels were investigated by infrared spectroscopy (FT-IR) and scanning electron microscope (SEM) respectively. The influence of SSS dosage on the adsorption capacity of Cu²⁺ was investigated by thermogravimetric analyzer (TGA).

(1) SEM test showed that the microstructure of the synthesized hydrogel was three dimensional network porous structure, and with the increase of the amount of crosslinking agent glutaraldehyde, the three dimensional network porous structure of the hydrogel was more compact, and the smaller the pore size, the smaller the free mobility of the basic skeleton of the hydrogel.

(2) Chitosan/P(SSS-HEMA-AA) hydrogel three-dimensional network molecular chain structure contains a large number of -NH₂, -SO₃²⁻, -COOH, -OH and other functional groups, which has the function of chelating adsorption, electrostatic adsorption and ion exchange adsorption with heavy metal ions, and has obvious adsorption effect on Cu²⁺.

(3) The results of TGA and visible UV spectrophotometer showed that the amount of Cu²⁺ absorbed by the synthesized hydrogel was directly proportional to the content of SSS, and was directly proportional to the amount of crosslinking agent glutaraldehyde.

(4) In CuSO₄ aqueous ammonia solution, the amount of Cu²⁺ adsorbed by AA containing hydrogel increased significantly. Because the -COOH group reacts as -COO⁻ anion in ammonia solution, on the one hand, it maintains the relatively large expansion rate of hydrogel. On the other hand, the negative electricity of hydrogels is larger, and the adsorption capacity of Cu²⁺ increases in two ways.
The adsorption rate test showed that the adsorption process of Cu\(^{2+}\) by hydrogel was gradually accomplished through the combined action of osmosis and ion exchange.

References
[1] Yan H, Dai J, Yang Z, et al. Enhanced and selective adsorption of copper (II) ions on surface carboxymethylated chitosan hydrogel beads[J]. Chemical Engineering Journal, 2011, 174(2):586-594.
[2] Gupta V K, Suhas. Application of low-cost adsorbents for dye removal--a review[J]. Journal of Environmental Management, 2009, 90(8):2313-2342.
[3] Aksu Z. Application of biosorption for the removal of organic pollutants: a review[J]. Process Biochemistry, 2005, 40(3-4):997-1026.
[4] Gupta V K, Tyagi I, Agarwal S, et al. Experimental study of surfaces of hydrogel polymers HEMA, HEMA–EEMA–MA, and PVA as adsorbent for removal of azo dyes from liquid phase[J]. Journal of Molecular Liquids, 2015, 206:129-136.
[5] Ma Qian, Zhang Xiaolong. Research progress of new technologies for heavy metal wastewater treatment at home and abroad [J]. Journal of environmental engineering, 2007, 1 (7): 10-14
[6] Wu Yanjun, Zhang Linnan, Li Zhenshan. The latest progress of harmless treatment technology of heavy metal wastewater [J]. Industrial water treatment, 2009, 29 (3): 1-3
[7] Jesús E P A, Sabino M A. Effect of the presence of lignin or peat in IPN hydrogels on the sorption of heavy metals[J]. Polymer Bulletin, 2010, 65(5):495-508.
[8] Ngah W S W, Endud C S, Mayanar R. Removal of copper (II) ions from aqueous solution onto chitosan and cross-linked chitosan beads[J]. Reactive & Functional Polymers, 2002, 50(2):181-190.
[9] Saliba R, Gauthier H, Gauthier R, et al. Adsorption of copper(II) and chromium(III) ions onto amidoximated cellulose[J]. Journal of Applied Polymer Science, 2015, 135(16):1624-1631.
[10] Ge junsen, Liang qu. hazardous situation of heavy metals in water and treatment methods [J]. Guangzhou chemical industry, 2007, 35 (5): 69-70
[11] Yao Ruihua, Meng Fanping, Zhang Longjun, et al. Research and application progress of heavy metal ion adsorption by modified chitosan [J]. Materials guide, 2008, 22 (4): 65-70
[12] Liu Yafei, Li Yijiu, et al. Study on the adsorption properties of chitosan and its derivatives for heavy metals [J]. Industrial water treatment, 2004, 24 (5): 10-12
[13] Wu N, Li Z. Synthesis and characterization of poly(HEA/MALA) hydrogel and its application in removal of heavy metal ions from water[J]. Chemical Engineering Journal, 2013, 215–216(3):894-902.
[14] C. Gerente, V. K. C. Lee, P. Le Cloirec, et al. Application of Chitosan for the Removal of Metals From Wastewaters by Adsorption—Mechanisms and Models Review[J]. Critical Reviews in Environmental Science and Technology, 2007, 37(1):41-127.
[15] Miretzky P, Cirelli A F. Hg(II) removal from water by chitosan and chitosan derivatives: A review[J]. Journal of Hazardous Materials, 2009, 167(1-3):10.
[16] Ngah W S W, Teong L C, Hanafiah M A K M. Adsorption of dyes and heavy metal ions by chitosan composites: A review[J]. Carbohydrate Polymers, 2011, 83(4):1446-1456.
[17] He Y Q, Zhang N N, Wang X D. Adsorption of graphene oxide/chitosan porous materials for metal ions[J]. Chinese Chemical Letters, 2011, 22(7):859-862.
[18] Crini G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment[J]. Progress in Polymer Science, 2005, 30(1):38-70.
[19] Crini G, Badot P M. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature[J]. Progress in Polymer Science, 2008, 33(4):399-447.
[20] Wu F C, Tseng R L. Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan.[J]. Water Research, 2001, 35(3):613.