Experimental study on removal of Cu^{2+} in water by nano-modified hydroxyapatite

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Abstract. Nano-hydroxyapatite prepared by homogeneous precipitation using calcium nitrate and diammonium phosphate as raw materials has a good effect on removing heavy metal ions in water, and its reaction mechanism belongs to an adsorption action. The adsorption capacity of heavy metal ions on nano-hydroxyapatite modified by modifier was greatly improved. At present, the laboratory has been able to successfully synthesize nano hydroxyapatite and modify its surface with modifier.In this paper, the surface modification of nano hydroxyapatite using different modifiers was briefly introduced, and the effect of modified nano hydroxyapatite on removing Cu^{2+} in water was studied. Based on the results of the data, we find out the modifier with the highest removal rate of Cu^{2+}, which is used to guide the applications of the future in industry.

1. Introduction

Hydroxyapatite, hereinafter referred to as HAP.It is the main inorganic component of human and animal bones and teeth. It has attracted wide attention of materials workers and medical workers all over the world due to its good biological activity and biocompatibility.Nanotechnology is a new research field in this century, because of the nano particles with surface effect, small size effect, quantum effect and unique performance, the HAP nanoparticles due to its unique surface porous structure, large specific surface area, strong adsorption ability, such as performance, so in catalysis, separation and ion exchange and so on have a wide range of applications.

HAP crystal is a hexagonal crystal system, belonging to P63/m spatial group, surface is a hexagon, a and b axis Angle is 120°, crystal lattice constant is a=b=9.432, c=6.881. The unit cell contains $10Ca^{2+}$,$6PO_4$ and 2OH. Figure 1 shows the structure and composition of HAP crystal structure and XRD[1].

With the development of social productivity, water quality pollution is one of the common environmental problems that human beings are facing.The main heavy metal ions in the waste water include Cu^{2+}, Fe^{2+}, Zn^{2+}, etc,which are widely distributed in non-ferrous metal mining, smelting industry, electroplating industry and other industries[2]. The harm to human body is persistent, highly toxic and convertible.Therefore, the treatment of wastewater containing heavy metals has been the focus and difficulty of research.Natural apatite has good chemical adsorption characteristics, is harmless to human body, has high safety in the food industry, has good adsorption effect on most heavy metal ions, and will not produce secondary pollution [3]. Therefore, it provides one of the most promising functional materials for the treatment of heavy metal wastewater.

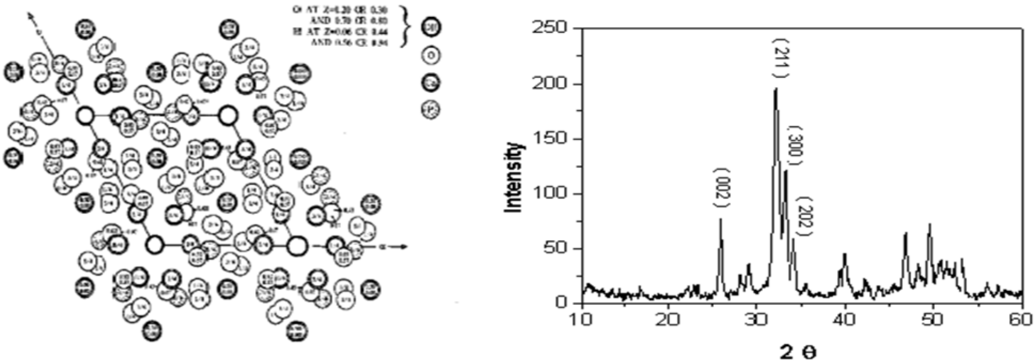

Figure 1. Crystal structure diagram of HAP & XRD patterns of the HAP.

The modification principle of nano hydroxyapatite is that the molecules of surfactant have two functional groups of solubility or different polarity, which are hydrophilic group (non-polar group) and hydrophilic group (polar group) respectively. Through the adsorption of the groups on the surface of the particles, the surfactant makes the nanoparticles present a stable monodisperse state in the disperse medium, and changes the surface state of the nanoparticles[4]. The main research content of this experiment is to select appropriate surfactant to modify the surface of hydroxyapatite and use its product to effectively remove copper ions in water.The experimental study on removal rate of Cu^{2+} in water has guiding significance for practical application of Cu^{2+} wastewater treatment.

2. Materials and methods

2.1. The main synthesis methods of nano hydroxyapatite

The nano-modified hydroxyapatite was prepared by homogeneous precipitation[5]. The process usually involves mixing substances of different chemical components in the solution state, adding appropriate precipitant to prepare the precursor precipitate of ultrafine particles, and then drying and calcining the precipitate to make the corresponding ultrafine particles.In this experiment, $Ca(NO_3)_2{\bullet}4H_2O$ and $(NH_4)_2HPO_4$ were used as reactants to prepare nano-hydroxyapatite. When fully reacted, the modifier was added to the solution and quickly stirred to facilitate a more uniform reaction. The equation is as follows:

$$Ca(NO_3)_2 \bullet 4H_2O + (NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 \quad (1)$$

2.2. The modification of nano HAP by surfactant

The molecules of surfactants have two functional groups with different solubility or polarity. They are hydrophilic group (non-polar group) and hydrophilic group (polar group) respectively. Through the adsorption of the groups on the surface of the particles, the surfactant makes the nanoparticles present a stable monodisperse state in the disperse medium, and changes the surface state of the nanoparticles. The surface polarity of nanoHAP particles is very high. When grafted with surfactant, the polar groups of nano HAP particles tend to form a firm bond on the surface.For example, carboxylic acid ions in carboxylic acid can be adsorbed on the vacancy formed by OH^-, and the hydrocarbon chain extends to the water phase. The length of hydrocarbon chain can determine the size of semi-micelle formed on the surface of HAP.An amino surfactant whose ammonia ions can be absorbed by hydrogen bonds with phosphate ions on the surface of HAP, or a semi-micelle can be formed by the co-adsorption of hydrocarbon chains and ammonia ions. However, for a surfactant with a larger end group, an ammonia-containing bond cannot form a good semi-micelle on the surface of HAP particles due to the large end group.Therefore, four representative modifiers were selected for comparison in this experiment.They aresodium dodecyl benzene sulfonate(SDBS), triethanolamine, ethanolamine and oleic acid[6].

3. Results and discussion

The nano-hydroxyapatite synthesized with different modifiers has different effects on the removal of copper ions in water. We demonstrated this with a lot of experimental data. After mixing and settling, the absorbance of the reaction solution was determined by atomic absorption spectrometer. The concentration of Cu^{2+} in the solution was obtained, and the removal rate of copper ions was calculated.The specific test results can be reflected by the following chart. Table 1 is the comparative data of the removal rate of copper ions using different modifiers of HAP and unmodified HAP. Figure 2-6 are the corresponding curve.

Table 1. Removal rates of Cu^{2+} by HAP with different modifiers.

The dosage of HAP(g/L)	SDBS (%)	Triethanolamine (%)	Ethanolamine (%)	Oleic acid (%)	Unmodified (%)
1	80.9	35.9	62.8	75.6	55.3
2	88.5	48.2	68.7	86.1	67.2
4	95.1	73.1	75.4	83.4	73.6
6	98.4	85.5	81.1	91.7	77.8
8	99.7	93.5	83.8	92.4	85.4
10	100	95.8	86.5	97.6	89.7
12	——	96.4	89.4	99.8	92.3
14	——	97.5	90.1	100	96.9

Table 1 shows the statistics of the removal rate of copper ions by HAP after modification and unmodified. Under the condition that the initial concentration of copper ions is consistent, the removal rate of Cu^{2+} is observed by gradually increasing the amount of HAP. The removal rate of HAP modified with triethanolamine was lower than that without modification, which means it's not suitable for a modification to the nano-HAP. The removal rate of SDBS modifier can be increased by more than 20%, indicating that the modifier still has good effect.One of the interesting problems is that excessive amounts of oleic acid inhibit the adsorption of the nano-modified hydroxyapatite against copper ions in water. In view of this situation, we should study the amount of the best modifier in the future.

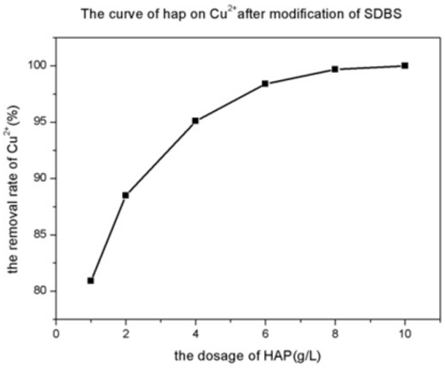

Figure 2. The curve of HAP on Cu^{2+} after modification of SDBS.

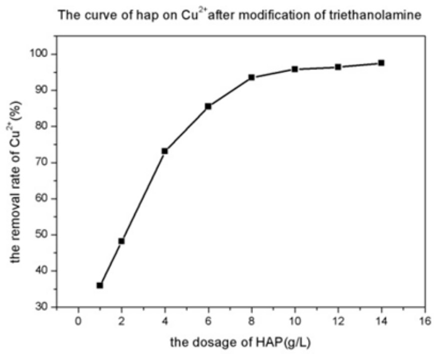

Figure 3. The curve of HAP on Cu^{2+} after modification of triethanolamine.

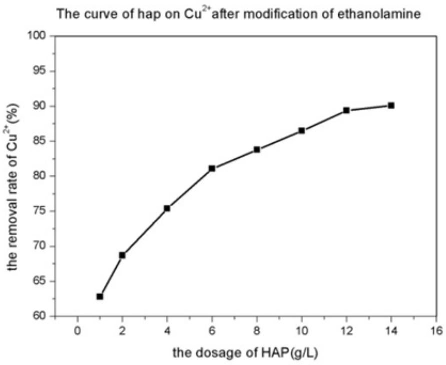

Figure 4. The curve of HAP on Cu^{2+} after modification of ethanolamine.

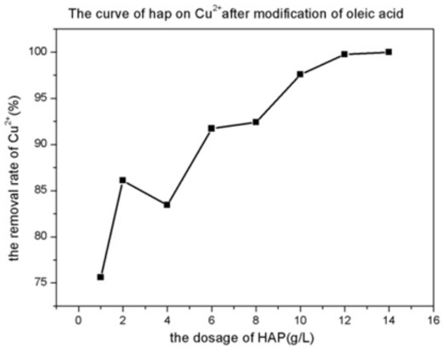

Figure 5. The curve of HAP on Cu^{2+} after modification of oleic acid.

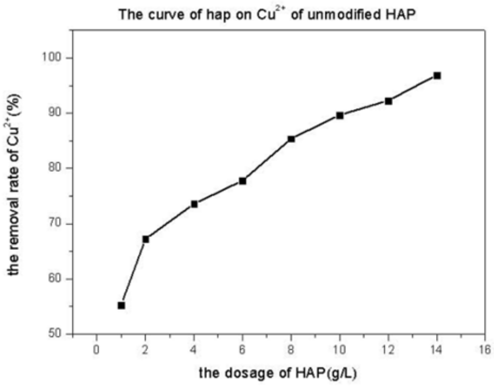

Figure 6. The curve of HAP on Cu^{2+} of unmodified HAP.

The following conclusions can be reflected more intuitively through thetable and figures.

(1) The nano-modified HAP has good adsorption effect on Cu^{2+} in water.
(2) The removal rate of Cu^{2+}has a good positive correlation with the dosage of HAP.
(3) Through the comparison of these four modifiers, SDBS is considered as a better modifier, with the highest removal rate reaching 100%.
(4) The effect was second only to SDBS when oleic acid was used as the modifier, but the removal effect was unstable from the perspective of removal rate curve, which was not conducive to practical application.The removal efficiency of the other two modifiers was even less satisfactory. It is not suitable for practical application.

4. Conclusions

It is proved that the nano-hydroxyapatite added with modifier is effective in removing copper ions in water. Through the comparison of several modifiers, SDBS is considered as the effective modifier. The highest removal rate can reach 100%, which is second only to SDBS in the use of oleic acid as the modifier. However, there are fluctuations in the removal rate curve and the correlation is poor, which is not conducive to application.

In summary,the research of nano-modified hydroxyapatite in removing heavy metal ions in water has a good prospect. China has abundant phosphate mineral resources, ranking second in the world. As the preparation and modification process of hydroxyapatite is simple and easy to operate, and the generated material is non-toxic and harmless, which will not cause secondary pollution to water[7]. The technological process is not complicated and is suitable for large area promotion. The research results of this subject can be applied in actual industrial production and have certain guiding significance. It is believed that it will play a significant role in sewage treatment, especially in sewage treatment with heavy metal ions.

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