Polyvinyl Alcohol / Fulvic Acid Composite Adsorbent Gel Prepared by Microreactor

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Abstract. Polyvinyl alcohol/fulvic acid (PVA/FA) composite hydrogel was synthesized in a microreactor using fulvic acid and polyvinyl alcohol as raw materials. The adsorption properties of the composite hydrogels for Pb2+ in water were investigated. The results show that the PVA/FA composite hydrogel is a three-dimensional porous network structure with uniform pore distribution and long-time water stability. When the mass fraction of fulvic acid was 1.5% and the freeze-thaw times were 3 times, the rate of saturated adsorption of PVA/FA composite hydrogels could be reaching to 72.3%.

1. Introduction

With the rapid development of industry, water pollution has become a bottleneck factor restricting the further development of national and regional economy. Heavy metal ion pollution is the main factor causing water pollution [1-3]. Among many heavy metal ion treatment methods, adsorption has attracted wide attention because of its high adsorption efficiency and selectivity. Its principle is to use adsorbents with porous structure or special functional groups to adsorb heavy metal ions.

Fulvic acid (FA) is a kind of common adsorbent. It can interact with heavy metal ions to form stable chelates to achieve adsorption effect [4]. Some researchers combined FA with minerals and nanomaterials to improve adsorption effect. Wei Yunxia et al. prepared chitosan cross-linked insoluble humic acid adsorbent. It was found that the adsorbing capacity on Pb2+ at 25°C of this adsorbent reached to 5.9 mg/g. To seek a suitable material to combine with FA is a key problem. Polyvinyl alcohol (PVA) hydrogels have attracted much attention because of their low toxicity, excellent mechanical properties and good biocompatibility. Especially, the PVA gel prepared by freezing thawing (FT) has porous structure and has certain mechanical and chemical stability. The porous network structure of PVA gel can also increase the specific surface area of adsorbent [5-6]. At present, there is no report on the preparation and properties of FA and PVA composite gel, and there is no report about its adsorption of heavy metal ions.

In this paper, FA and PVA were used as raw materials. Micro-Reactor (MR) with good heat/mass transfer performance and high mixing efficiency was used as chemical reaction vessel by freeze-thaw method, in order to obtain polyvinyl alcohol/fulvic acid (PVA/FA) composites with uniform morphology and good thermal stability. Furthermore, the adsorption capacity of prepared PVA/FA composites for Pb2+ in water was studied.
2. Experimental

2.1. Hydrogel Preparation
Preparation of PVA/FA mixtures: Y-type micro-reactor with 1 mm channel size was used to pre-mix a certain mass fraction of PVA aqueous solution with a certain mass fraction of FA aqueous solution under 5 MPa pressure and then enter the micro-mixer to fully mix (the whole mixing process is about 1 minute); in addition, as a comparative experiment, the conventional mechanical stirring method was used to mix the above-mentioned reactants for 30 minutes.

Preparation of PVA/FA composite gel: after injecting 20 mL of the above mixture into the self-made PTFE mold, the mold was then frozen in the refrigerator freezer (-18°C) for 2 h. The frozen samples were thawed at room temperature for 2 hours and recorded as freezing-thawing once. By repeating the above operations, PVA/FA composite gel with multiple freezing and thawing times can be obtained.

2.2. SEM Characterization
Cubic specimens for SEM investigations (6 mm×4 mm×2 mm) were cut from hydrogel samples and investigated with SEM (Hitachi S-4800, Japan).

2.3. Swelling Test
A weighed amount ($W_a$, g) of the hydrogel samples were immersed in deionized water at 25°C for different periods and then weighted ($W_b$, g) after wiping off surface water with a filter paper.

The swelling ratio ($Q$) of the sample was calculated according to the following equation (1):

$$ Q = \frac{W_b - W_a}{W_a} $$

2.4. Adsorption experiment
A certain mass of composite gel was added to the Pb$^{2+}$ solution with a concentration of 10 mg/L. The supernatant was taken at regular intervals, and the concentration of Pb$^{2+}$ was measured by atomic absorption spectrophotometer. All the above experiments were conducted at least three times. The adsorption rate of adsorbent for Pb$^{2+}$ was calculated according to the following equation:

$$ \omega = \frac{C_0 - C_t}{C_0} \times 100\% $$

$C_0$ is the initial concentration of Pb$^{2+}$ before adsorption, in mmol/L; $C_t$ is the concentration of Pb$^{2+}$ at different time, in mmol/L.

3. Result and Discussion
The mass fraction of PVA aqueous solution used in this paper is 8%, and the freezing-thawing times are 3 times. For simple expression, the PVA/FA composite gel prepared by the combination of microreactor mixing (MR) and freezing thawing (FT) is MR-FT-x, where x represents the mass percentage of FA.

3.1. Microstructure of PVA/FA composite gel
Fig. 1 is a scanning electron microscope (SEM) diagram of MR-FT-1.5-PVA/FA composite gel. It can be seen from Fig. 1a that there is a relatively uniform pore structure inside the MR-FT-1.5 composite gel, and the pore size can reach micron level. It can be seen from Fig. 1b that the microstructure of PVA/FA composite gel prepared by this method is three-dimensional. According to the adsorption theory, porous structure materials usually have enough large specific surface area to absorb more heavy metal ions. Based on the above analysis, the three-dimensional porous network structure of PVA/FA composite gel synthesized by MR-FT method is very beneficial to heavy metal ions adsorption.
3.2. **Swelling test of PVA/FA composite gel**

In order to study the swelling properties of PVA/FA composite gels, the same quality PVA gel were taken from MR-FT-0.5, MR-FT-1.5 and MR-FT-2.5 composite gels and placed in 25°C water bath for 48 h to observe their swelling. The swelling rate can be expressed by the slope of the lines in Fig. 2. It could be seen obviously from Fig. 2 that the swelling rate of all gels in water is fast at beginning, then slow down, and tends to be balanced after 25 h. This is because the physical crosslinking between FA and PVA molecules has formed a three-dimensional network. With the increase of FA content, the swelling ratios of the gels first increase and then decrease. This is due to the increase of FA content, which makes more FA molecules cross-linked with PVA molecules, resulting in swelling. When FA content is about 1.5%, the swelling ratio of the composite gel presents a maximal value. It indicates that the content of FA has been saturated for PVA solution with mass fraction of 8%.

3.3. **Adsorption analysis of PVA/FA composite gel**

Different series of composite gels were taken respectively. Recording to the experimental data of atomic absorption spectrometry, the adsorption kinetics curve of PVA/FA composite gel was obtained (Fig. 3). It can be seen from Fig. 3 that the adsorption of MR-FT and MT-FT composite gels accords with Langmuir adsorption, and the gel adsorption rate increased obviously in the first 30 minutes. Subsequently, the gel adsorption rate increased slowly until the equilibrium approached. The MR-FT and MT-FT composite gels reached the adsorption capacity at 60 min and 90 min respectively. The
saturated adsorption rate of MR-FT composite gel reaches 72.3% when FA content is 1.5%. The saturated adsorption rate of MT-FT composite gel under the same conditions is only 68.3%.

**Figure 3.** Adsorption kinetics of Pb$^{2+}$ on MR-FT and MT-FT composite gels

**4. Conclusion**

In this study, PVA/FA composite gel was prepared by microreactor and applied to the adsorption of Pb$^{2+}$ in water. The experimental results show that the PVA/FA composite gel prepared by microreactor can maintain gel state at room temperature for a long time. It is expected to be further applied to traditional organic synthesis reaction to improve its reaction efficiency and yield.

**References**

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