

A green, eco-friendly and self-supporting geopolymer membrane for Cr (VI) removal from aqueous solution

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Abstract: In this study, a self-supporting geopolymer membrane was prepared for the treatment of Cr(VI) containing wastewater. The membrane has the advantages of low raw material cost, free of sintering, simple preparation process, good removal effect. The phase structure of the membrane was amorphous gel structure with a specific surface area of 34.48 m²/g. The influence of pH and initial concentration on the removal effect of Cr(VI) were investigated. The Cr(VI) removal amount reached to 45.56 mg/g and the removal rate reached to 82.69% under favorable conditions. Further mechanism study showed that the removal of Cr(VI) by the membrane mainly depends on the Donnan effect caused by electrostatic repulsion, which is fundamentally different from the removal for positively charged heavy metal ion such as Pb²⁺, Ni²⁺ and Cu²⁺. This study not only provides a membrane material for chromium-containing wastewater, but also broadens the scope of geopolymer materials in the field of water treatment, and provides theoretical support for its treatment of anionic pollutants (Cr(VI) presents as HCrO₄⁻ and Cr₂O₇²⁻).

1. Introduction

Among many heavy metal ions, chromium is considered to be one of the most toxic heavy metals, and its main sources are electroplating, tanning, dye, mining, textile industry and metallurgical industry. Chromium normally presents as Cr(III) or Cr(VI). Cr(VI) have a greater risk than Cr(III), Cr(VI) in the form of CrO₄²⁻ or HCrO₄⁻, penetrates through the cell membrane diffusion cell can be carcinogenic teratogenic, pose a serious threat to the ecological environment and human health[1]. It is very important to explore a more appropriate treatment method for heavy metal wastewater.

Geopolymer, a concept first put forward by Joseph Davidovits[2], which is composed of silicon oxygen tetrahedron and aluminum oxygen tetrahedron with amorphous and crystalline characteristics of the three-dimensional network of gels. Geopolymer has the advantages of simple preparation process, non-sintering, low cost, low-carbon and environmentally-friendly, and can realize large-scale solid waste resources recycling, etc. Since its invention, the material has been widely used in many fields, including construction materials, automobile, aviation, electrician, casting, metallurgy, road, plastic, refractories and so on [3].

Because of its molecular size-like structure and porous properties, geopolymers are used as adsorbents in water treatment[4] [5]. But from the point of the present study, the main use of geopolymer materials depends on space exclusion effect of suspended solids and the adsorption of metal ions in water treatment, and the main objects are metal ions that exist as positive ions in aqueous solutions such as Ni²⁺, Pb²⁺ or macromolecular organic matter. The main reason is that the geopolymer materials in aqueous solution presents negatively charged due to the dissolution of large amounts of Na⁺, resulting the adsorption for positively charged ions[6]. Quite a few of pollutants exist as anions in aqueous solution, but there are few studies on small-scale anionic pollutants. Therefore, it is very necessary to study the removal ability and mechanism of geopolymers to anions.

In this study, a self-supporting geopolymer membrane were synthesized applied in Cr(VI) removal in aqueous solution. The structure characterization and the technological conditions of geopolymer membrane have been studied. The influences of processing conditions on Cr(VI) removal ability are studied, and the mechanism of removing are analyzed. This study provides not only a kind of green environmental protection material and heavy metal processing, but also more theoretical support of the application of geopolymer materials in negative ion pollutants.

2. Materials and Methods

2.1 Materials and Characterizations

In this experiment, metakaolin and sodium silicate were used as the main raw materials. Metakaolin was purchased from Jinyuan Kaolin Co., LTD.in Datong city, Shanxi province. Sodium silicate was purchased from Litian Chemical Co., LTD in Guangdong province. ($\text{Na}_2\text{O}=8.38\text{wt}\%$, $\text{SiO}_2=26.41\text{wt}\%$). Sodium hydroxide, potassium dichromate, hydrochloric acid, nitric acid, sodium chloride, sodium nitrate, sodium sulfate were all analytically-pure.

The S-3400 scanning electron microscope of Hitachi was used to observe the morphology of the samples. The crystal phase of the sample was measured by MiniFlex 600 X-ray diffractometer ($2\theta =5^\circ \sim 70^\circ$). The pore structure characters of samples were analyzed by the American Micromeritic Gemini 2390 specific surface area and pore structure analyzer. The specific surface area of the sample was calculated by BET equation, and the pore diameter distribution was calculated by BJH method. Zeta potential was analyzed by Malvern NANO ZS90A particle size analyzer. The Cr(VI) content in the solution was analyzed with Mettler Toledo 722N spectrophotometer, with the analysis wavelength of 540 nm.

2.2 Experimental process

(1) Preparation process

According to previous research work, sodium silicate ($n_{\text{SiO}_2}/n_{\text{Na}_2\text{O}}=1.3$) metakaolin and deionized water were mixed according to the optimal molar ratio of $\text{SiO}_2 / \text{Na}_2\text{O} = 3.78$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.77$, $\text{SiO}_2 / \text{Al}_2\text{O}_3 = 2.93$, $\text{H}_2\text{O}/\text{Na}_2\text{O} = 21$, using dispersion machine at speed of 2000 r min^{-1} under mechanical stirring for 10 min. A quick geopolymer slurry was obtained, then it was grouted to plastic circular mould with diameter of 50 mm and sealed. After curing at 60°C for 24 h, the geopolymer self-supporting membrane can be obtained. Geopolymer membrane was washed in water, until the pH of washing water was close to neutral. After dry the membrane, grind and thin it to 6.5 mm.

(2) Cr(VI) removal performance

The experimental temperature was 25°C . 1000 mL Cr(VI) solution was transferred from each group of membrane and the membrane was pumped by circulating water multi-purpose vacuum pump under the pressure difference of 0.1MPa. Ultraviolet spectrophotometer was used to detect the concentration of Cr(VI) in the solution before and after filtration. The removal rate R and removal quantity Q_t of self-supporting geopolymer membrane with different thickness can be calculated, and the calculation formulas are Eq.(1) and Eq.(2) respectively.

$$R = \frac{c_0 - c_i}{c_0} \times 100\% \quad (1)$$

$$Q_t = \frac{V \cdot (c_0 - c_i)}{m} \quad (2)$$

Where,

c_0 -- initial Cr(VI) concentration in solution before filtration, mg L^{-1}

c_i - residual Cr(VI) concentration in solution after filtration, mg L^{-1}

V - Total volume of the membrane solution, L

m - Dry weight of the inorganic membrane (baked to a constant weight in an oven at 60°C), g

3. Results and discussion

3.1 Characterization of materials

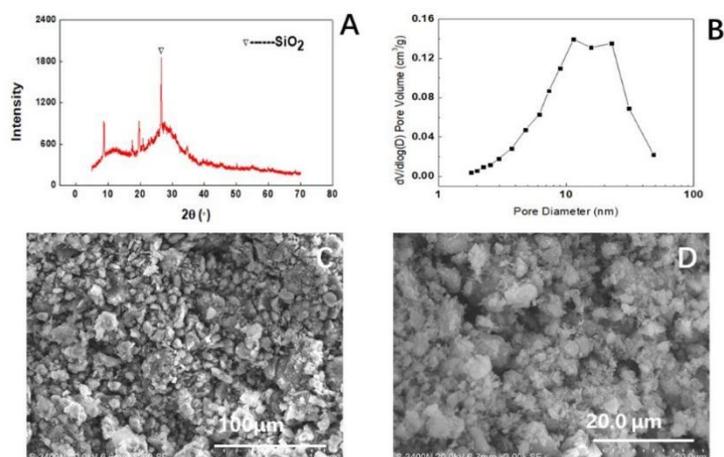


Figure 1 (A) XRD patterns of self-supporting geopolymer membrane; (B) Pore diameter distribution of self-supporting geopolymer membrane; SEM images of self-supporting geopolymer membrane (C) :500 times, (D):2000 times

As shown in Figure 1(A), the XRD characterization results of the geopolymer self-supported membrane show that the dispersion peak is formed between 2θ of $15^\circ\sim 40^\circ$, indicating that the self-supported geopolymer membrane is mainly amorphous structure.

The microscopic morphology of geopolymer materials was presented through SEM images in Fig.1C and D. The field of view was mainly amorphous and irregular gel particles with sizes ranging from several microns to tens of microns, without obvious regular and crystal particles, which was consistent with XRD results in section 3.1.1.

The specific surface area of self-supporting geopolymer membrane is $34.48\text{ m}^2/\text{g}$, and the average pore structure of the material was 10.55 nm. The pore size distribution is shown in Figure 1(B). The overall pore size ranges from 8-22 nm, among which the pore size ranges from 9 nm to 11 nm are more widely distributed, indicating that the pore structure of the material is dominated by mesoporous. Combined with specific surface area and pore diameter distribution, the pore structure of the material meets the requirements of membrane material for membrane water treatment[5].

3.2 Membrane performance

As shown in Figure 2(A), with the increase of the initial pH value of the solution, the Cr(VI) removal performance of self-supporting geopolymer membranes enhanced: removal amount increased from 27.51 mg/g to 31.37 mg/g and removal rate increased from 79% to 89%, which indicates that pH has a great influence on the performance of the membrane. As shown in Figure 2(B), with the increase of initial Cr(VI) concentration, the removal rate showed a slight upward trend, from 75.15% to 82.69%, but the removal amount showed an obvious upward trend, from 18.75 mg/g to 45.56 mg/g.

In order to further study the influence mechanism of solution pH on Cr(VI) removal, zeta potential of geopolymer membrane in aqueous solution with different pH values was analyzed in this study, and the results were shown in Figure 2(C). Within the pH range of 2-7, the zeta potential was negative ($-15.78\text{ mV} \sim -25.66\text{ mV}$), indicating that the membrane was negatively charged under this condition. In the range of pH =2-7 in this experiment, Cr(VI) exists mainly in the form of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, both of which are negative. As shown in Figure 2(D), when the negatively charged HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ movement spread to the surface of geopolymer membranes, due to the membrane itself also negatively charged, the membrane can produce repulsion to HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, thus HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ gets hard to through the membrane. The Cr(VI) concentration in the membrane surface nearby is

much higher than that in the solution, and the Cr(VI) in the solution is difficult to diffuse to the surface of the geopolymer membrane, then more difficult to pass through the geopolymer membrane, thus achieve the removal of Cr(VI), this is the role of the Donnan effect [7, 8].

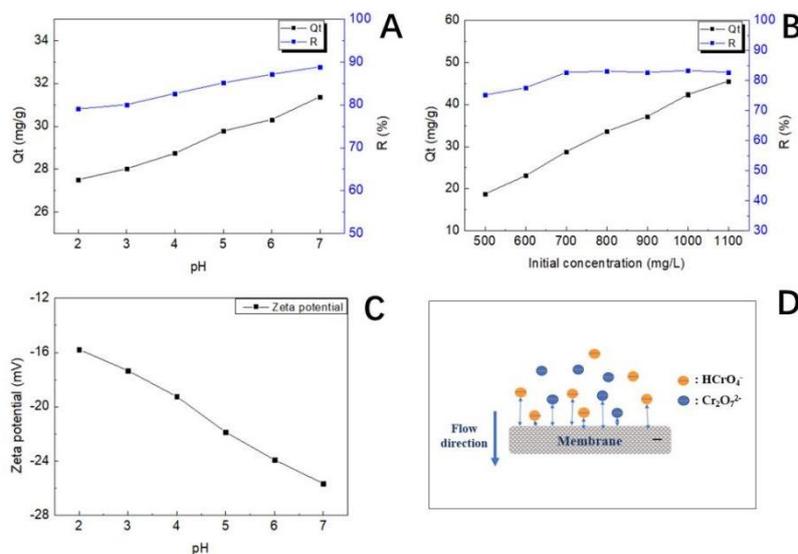


Figure 2 (A) The removal effect of Cr(VI) under different pH (800 mg·L⁻¹ Cr(VI) solution, pH =2, 3, 4, 5, 6 and 7); (B) The removal effect of Cr(VI) under different initial concentration of Cr(VI) (500, 600, 700, 800, 900, 1000 and 1100 mg L⁻¹ Cr(VI) solution, pH = 7.); (C) Zeta potential of the membrane in different pH solutions of Cr(VI); (D)Removal mechanism diagram of Cr(VI) by geopolymer membrane

This is contrary to the results of studies on the removal of Pb²⁺, Ni⁺, Cu²⁺ and other heavy metal ions by geopolymers[5, 9, 10]. In the above relevant literatures, the interaction with the negatively charged geopolymer is based on electrostatic adsorption. It can be seen that the removal mechanism of Cr(VI) in geopolymer materials is fundamentally different from that of Pb²⁺, Ni²⁺ and Cu²⁺.

4. Conclusion

In this study, metakaolin was used as the main raw material to prepare a self-supporting geopolymer membrane for the treatment of Cr(VI) containing wastewater. It was found that increasing pH and initial solution concentration is beneficial to improve removal rate within the range of experimental conditions. Through the mechanism study, it is found that the removal of Cr(VI) by the geopolymer membrane mainly depends on the Donnan effect caused by electrostatic repulsion, which is fundamentally different from the removal mechanism for positively charged heavy metal ion such as Pb²⁺, Ni²⁺ and Cu²⁺. This provides a theoretical reference for the study of geopolymer in the removal of negative ion pollutants. In conclusion, the geopolymer membrane has the advantages of low raw material cost, simple preparation process, good removal effect, and has a certain potential in the field of treatment of chromium-containing wastewater.

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