



Cr(III) ionic imprinted polyvinyl alcohol/sodium alginate (PVA/SA) porous composite membranes for selective adsorption of Cr(III) ions

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ABSTRACT

In the present study, we prepared Cr(III) ionic imprinted membrane adsorbents (Cr(III)-PVA/SA) by blending sodium alginate (SA) with polyvinyl alcohol (PVA). In these new membrane adsorbents, polyethylene glycol was used as porogen, and glutaraldehyde was the cross-linking agent. Our new developed membrane adsorbents can be used without centrifugation and filtration. To investigate the adsorption kinetics of Cr(III) ions from aqueous solution onto this newly developed Cr(III)-PVA/SA, we performed a batch of experiments under different conditions by changing the concentration of Cr(III) ions in the Cr(III)-PVA/SA, pH value of the solution, adsorbent dose, initial Cr(III) ions concentration, adsorption temperature and contact time. Our Cr(III)-PVA/SA exhibited the maximum Cr(III) ions uptake capacity of 59.9 mg/g under the following conditions: 0.078 wt% of Cr(III) ions in the Cr(III)-PVA/SA, solution pH value of 6.0, adsorbent dose of 0.5 g/L, the initial Cr(III) ions concentration of 50 mg/L, at 25 °C. To study the mechanism of adsorption process, we examined the intra-particle diffusion model, Lagergren pseudo-first-order kinetic model and pseudo-second-order kinetic model, and found pseudo-second-order kinetic model exhibited the best correlation with our experimental data. Furthermore, our adsorption equilibrium data could be better described by the Langmuir equation. Competitive adsorption studies of the binary system of Cr(III)/Cu(II), Cr(III)/Cd(II) and the ternary system of Cr(III)/Cu(II)/Cd(II) were also investigated using Cr(III)-PVA/SA, the results indicated that selectively adsorbed amount of Cr(III) ion on Cr(III)-PVA/SA is significantly higher than that of Cu(II) and Cd(II) ions. We also used five times consecutive adsorption-desorption experiments to show that the Cr(III)-PVA/SA has high adsorption and desorption efficiencies.

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1. Introduction

With the rapid increase in global industrial activities, heavy metal pollution has become more serious. The discharge of toxic and polluting heavy metal ions into the environment by the mining operations, metallurgical, electroplating, battery manufacturing, nuclear and other industries is posing serious risk to the environment [1,2]. Treatment for high volumes of wastewater containing low concentrations of heavy metals pollutants is becoming increasingly important as the discharge regulations become more stringent. One of the major toxic metal ions endangering human life is chromium. Cr(III) ions compounds are widely used in modern industries, such as leather making, metal finishing and petroleum refining, which inevitably results in a large quantity of Cr(III) ions contaminated industrial effluents. Waters containing a high concentration of Cr(III) ions are extremely harmful to human beings

because they are non-biodegradable in living tissues and would induce toxic and carcinogenic health effects on humans [3–5]. Therefore, the technology for effective removal of Cr(III) from water and wastewater is urgently needed.

Over the past decades, a number of technologies have been developed to remove heavy metal ions from aqueous solutions, such as adsorption, co-precipitation, ion exchange, chemical reduction and membrane separation [6–17]. Removal of Cr(III) ions from wastewater by adsorption has been investigated by many researchers. The main advantages of the adsorption are recovery of the heavy metal, high selectivity, less sludge volume produced, simplicity of design and the meeting of strict discharge specification. Also, it has been a strong alternative to other processes because of its ability to reduce dissolved chromate concentration to none detectable levels in the water treatment plants.

One of the recently developed techniques for the preparation of highly effective adsorbent is the ion-selective imprinting technique, where the specific recognition capability is provided to the host molecules by addition and subsequent extraction of template molecules/ions [18–20]. Molecular imprinting is a

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promising technique for preparing polymeric materials with artificial receptor-like binding sites for various substances, and the molecular imprinted materials for its recognition function has been utilized in many fields, such as solid-phase extractions, membrane separations and sensors [21–24]. Recently, the heavy metal ions imprinting adsorbent, for its excellent selective separation performance for trace heavy metals, has become more concerned.

In recent years, increased attention has been focused on the use of naturally available low cost biomaterials for removing heavy metal ions from wastewater [25,26]. Compared to other traditional treatment processes, heavy metal adsorption using biomaterials can reduce total capital cost greatly. Use of biomaterials also even makes the adsorption process more environmental friendly and more technically feasible. SA is naturally occurring polysaccharides obtained mainly from marine brownalgae belonging to the Phaeophyceae, composed of two monomeric units, *h-d*-mannuronic acid and *a-l*-guluronic acid [27]. SA, for its good membrane forming properties and high activity with carbonyl and hydrogen groups on its chain, has been attracted considerable attention currently.

The objective of this present work is to explore the potential utilizing of Cr(III) ionic imprinted Cr(III)-PVA/SA for adsorption removal of Cr(III) ions contaminated from wastewater. To investigate the effects of operating factors on the adsorption capacity of the Cr(III)-PVA/SA for Cr(III) ions, We carried out a batch of adsorption experiments under different conditions by varying the concentration of Cr(III) ions in the Cr(III)-PVA/SA, pH value of the solution, adsorbent dose, initial Cr(III) ions concentration of the solution, adsorption temperature, and contact time. By testing various adsorption and kinetics models to fit our experiment data, we also studied the adsorption kinetics and isotherms of Cr(III) ions adsorption for the Cr(III)-PVA/SA. The competitive adsorption of Cr(III)-PVA/SA for Cr(III) ions from binary heavy metal mixed system and ternary heavy metal mixed system were examined, and the desorption and reusability of the Cr(III)-PVA/SA for adsorption Cr(III) ions were also investigated.

2. Experimental

2.1. Materials and analytical method

All the chemicals and reagents used were of analytical grade and obtained from Sinopharm Chemical Reagent Co. Ltd. A stock solution of 100 mg/L of Cr(III) ions was prepared by dissolving 1.5420 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 2000 mL distilled water. This solution was diluted as required. A series of standard Cr(III) ions solution were prepared by appropriate dilution of the stock Cr(III) ions solution. Solutions of 0.1 M NaOH or HCl were used for pH adjustment. The concentration of Cr(III) ions in the samples was determined from the linear calibration curve.

2.2. Preparation of Cr(III) ionic imprinted Cr(III)-PVA/SA composite membranes

1 g of PVA, 1 g of SA and 0.06 g of polyethylene glycol(PEG) were dissolved in deionized water and stirred at 90 °C for 90 min, then the hot solution were filtered. This was followed by the addition of various amount of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Cr^{3+} account for 0.026, 0.52, 0.067, 0.078, 0.091 and 0.104 wt% based on the total amount of PVA, SA and PEG) solution drop by drop with continuous stirring. Then, 5 wt% GA (2.0 mL) and 1.0 M HCl (2.0 mL) were added into the above solution and stirred vigorously for 60 min. The resulting solution was cast on a glass plate, and then dried in an oven at 70 °C for 120 min. The dried membranes were subsequently peeled off and immersed into deionized water for one day to remove the porogen PEG. Finally, the obtained membranes were immersed into 0.1 M HCl for 60 min to

remove the imprinted Cr(III) ions, then immersed into deionized water again for one day. The resulted membranes were dried in an oven at 100 °C for 120 min, then, stored in a desiccator for further experiment.

2.3. Membrane characterization

FT-IR spectra of the Cr(III)-PVA/SA before and after Cr(III) ions adsorption were scanned in the range from 4000 to 400 cm^{-1} with an accumulation of 16 scans on a Nicolet-740. The surface morphology of the Cr(III)-PVA/SA before and after adsorption were also characterized by using SEM (LEO 1530, Oxford Instruments), equipped with the energy dispersive X-ray spectroscopy, which was operated at EHT = 20 kV.

2.4. Adsorption procedure

The stock Cr(III) ions solution with concentration of 100 mg/L was prepared by using $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as a source of Cr(III) ions. Experimental solutions of the desired concentrations were obtained by successive dilution. The pH of the solution was maintained at desired value by adding 0.1 M HCl or NaOH solution before adsorption experiment. Adsorption experiments were carried out in a 500 mL volumetric flask using 250 mL Cr(III) ions solution with required amount of adsorbent. The flasks were placed on an orbital shaker running at 120 rpm at 25 ± 1 °C until equilibrium was reached. 5 mL of the sample was drawn at regular intervals for residual concentration testing. The chromium equilibrium concentration was spectrophotometrically measured using standard procedure at $\lambda = 420$ nm [28]. All the experiments were performed in triplicate and the average of three was taken for subsequent calculations. The difference between duplicate experimental values was in the range of $\pm 1.5\%$.

The adsorption capacity of the Cr(III)-PVA/SA was evaluated by using the following expression:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where q_t is the amount of Cr(III) ions adsorbed on unit mass of the adsorbent PVA/SA (mg/g), C_0 and C_t are the concentration of the Cr(III) ions in the initial solution and in aqueous phase after adsorption for a t min (mg/L); V is the volume of the aqueous phase (L); and m is the amount of adsorbent Cr(III)-PVA/SA used (g), respectively.

2.5. Selectivity adsorption experiments

0.125 g of Cr(III) ionic imprinted Cr(III)-PVA/SA was added to a 250 mL of Cr(III)/Cd(II), Cr(III)/Cu(II) binary mixed solutions and Cr(III)/Cd(II)/Cu(II) ternary mixed solution (initial concentration of single species 50 mg/L), respectively; then, the pH value of the solution was adjusted to 6.0 by adding certain amount of 0.1 M HCl; finally, the flasks were placed on an orbital shaker running at 120 rpm at 25 ± 1 °C until equilibrium was reached. The concentration of Cr(III), Cd(II) and Cu(II) in the solutions were spectrophotometrically measured.

2.6. Desorption of heavy metal ions and membrane reusability

Desorption of heavy metal ions was achieved using 0.1 M HCl as a desorbing agent. The metal loaded Cr(III)-PVA/SA membrane samples were placed in the 250 mL desorption medium at 25 °C, with a shaking speed of 120 rpm for 120 min. The membrane samples were washed with a deionized water several times and subjected again to adsorption/desorption process for five cycles.

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