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Porous Spherical Cellulose Carrier Modified with Polyethyleneimine and Its Adsorption for Cr(III) and Fe(III) from Aqueous Solutions☆

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ABSTRACT

An efficient porous spherical polyethyleneimine-cellulose (PEI-cell) absorbent was synthesized and characterized. The main influencing factors and adsorption mechanism for two typical metal ions, Cr^{3+} and Fe^{3+}, were investigated. The adsorption performance primarily depends on the initial concentration of metal ions, pH value and temperature, and the chelation action between N atoms of PEI-cell and metal ions plays an important role. Under dynamic adsorption conditions, the saturation adsorption of polyethyleneimine-cellulose is 83.98 $mg \cdot g^{-1}$ for Cr(III) and 377.19 $mg \cdot g^{-1}$ for Fe(III), higher than reported data and that of unmodified cellulose. The adsorption can be well described with second-order kinetic equation and Freundlich adsorption model, and ΔH, ΔG and ΔS of the adsorption are all negative. With 5% HCl as eluent, the elution ratio of Cr(III) and Fe(III) achieved 99.88% and 97.74% at 313 K, respectively. After the porous PEI-cell was reused 6 times, it still presented satisfactory adsorption performance. Above results show the advantages such as easily-acquired raw material, high efficiency, stable recycling performance and biodegradability.

1. Introduction

Many industries, such as pharmacy, battery, rubbers, leather tanning, dye, paper, coating, car, aeronautic and steel generate large quantities of wastewater containing chromium and iron [1,2]. The two metal ions are readily infused in underground water and contaminate drinking water because they are highly water-soluble and diffusible. Effective removal of heavy metals in wastewater is of great importance. Various methods have been developed and employed, such as adsorption, neutralization, ion exchange, precipitation and biological purification [3–7]. Among these methods, adsorption is one of the most popular and effective techniques, which offers great flexibility in design, operation, and regeneration in many situations. Some adsorbents reported for Cr(III) and Fe(III) include lignin [8], biochar and sugarcane pulp residue [9], bread mold fungus [10], activated carbon [11], sugarcane bagasse modified with sodium hydroxide and citric acid [12], zeolite synthesized from fly ash [13], thiourea cross-linked chitosan [14], unmodified raphia palm fruit endocarp [15], hazelnut hull [16], chitosan–tripolyphosphate beads [17], imprinted polymer [18], polyacrylamide grafted activated carbon [19], and so on.

As abundant renewable and biodegradable adsorbent materials, cellulose and modified cellulose are widely used in wastewater treatment, chemical industry, and medication adsorption [20,21]. Cellulose can interact with adsorbates through hydrogen bond, complexation and other interactions. Different porous cellulose adsorbents with high performance can be prepared by grafting functional polymers on the surface, which are effective to remove heavy metals [22]. The solid adsorption materials can well combine the functionality of polymers and excellent properties of porous cellulose, such as low cost, high specific area, environmentally friendly, strong mechanical property, and good chemical and thermal stability.

Polyethyleneimine (PEI) is a water-soluble polyamine and its aqueous solution is alkaline with a lot of amino groups on its macromolecular chains. Commercial PEI is a branched macromolecule and the ratio of primary, secondary and ternary amine groups is approximately 1:2:1 [23], which is well known for its metal chelation potentiality. In this study, PEI is grafted onto the surface of porous cellulose particles to obtain a solid adsorbent PEI-cell, which is used to remove Cr(III) and Fe(III) ions from their aqueous solutions. Compared with some adsorbents reported [24–26], the raw material is relatively more available and cheap, and the two-step synthesis process is simple. The PEI-cell adsorbent has an intense adsorption capability for Cr(III) and Fe(III) due to the strong chelation between nitrogen atoms and metal ions. This is a

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promising method to graft functional polymer on porous cellulose to prepare efficient adsorbents for the removal of heavy metal ions from industrial wastewater.

2. Experimental

2.1. Materials

Medical degrease cotton (100% cotton fiber) was provided by Hualu Hygienic Material Co. Ltd., Shandong, China. PEI (99% purity) was provided by Hangjia Biological Medicine Co. Ltd., Sichuan, China. 1,5-Diphenyl carbazide and phenanthroline (purity > 98%) was purchased from Chengdu Kelong Reagent Co. Ltd., Sichuan, China. Other reagents were all of analytical grade.

2.2. Two-step synthesis of porous polyethyleneimine-cellulose particle

(1) The cotton was infused with 5 mol·L^{-1} NaOH aqueous solution for 2 h and aged at 25 °C for 2 days. 1.5 mol·L^{-1} NaOH was added to get liquid glue after sulfonation with CS_2. The brilliant yellow solution and nano-$CaCO_3$ were stirred efficiently with the shaker. Then the mixture was transferred to a large round bottom flask containing transformer oil and stirred persistently at 90 °C for 2.5 h. After the mixture was cooled to room temperature, the porous cellulose particles were rinsed with ultrapure water several times and external nano-$CaCO_3$ was removed with HCl. The porous cellulose particles were sieved with size range from 100 to 200 mesh. Finally, the resultant was infused in 20% ethanol at 4 °C.

(2) 5 g of wet porous cellulose reacted with 5 ml epichlorohydrin and 10 ml of 2 mol·L^{-1} NaOH in a three-neck round bottom flask at 40 °C for 2.5 h, followed by adding 3.0 ml PEI, and the mixture was stirred at 90 °C for 9 h under nitrogen gas. The product was washed with distilled water and dried at 40 °C for 6 h in vacuum.

2.3. Characterization of cellulose particles and porous PEI-cell

The morphology of cellulose particle was first observed by a JEM-100CX-II scanning electron microscope (SEM) (JEOL, Japan). Fourier transform infrared spectra, obtained with a NEXUS 670 spectrometer (Thermo Nicolet, USA) using potassium bromide pellets, were applied to characterize the porous PEI-cell. The amount of amino groups on the PEI-cell was determined by the titration method with hydrochloric acid according to the following procedure: 0.2 g of dry PEI-cell was mixed with 15 ml of 0.3 mol·L^{-1} HCl solution and the mixture was placed on the shaking table for 8 h. 5 ml of sample in supernatant was diluted with 50 ml of redistilled water and 3 drops of phenolphthalein were added into the sample as the indicator. The mixture was demarcated with 0.15 mol·L^{-1} NaOH solution until the color changed from colorless to pink. The content of amino groups (Y) is calculated by

$$Y = \frac{C_1V_1 - C_2V_2}{G} \times 16 \times 100\% \quad (1)$$

where C_1 and C_2 (mol·L^{-1}) are the concentrations of HCl and NaOH solutions, respectively, V_1 and V_2 (L) are the volume of HCl and NaOH solutions, respectively, and G (g) is the mass of sample.

2.4. Adsorption kinetics for Cr(III) and Fe(III)

100 ml of $Cr(NO_3)_3$ and $FeCl_3$ solutions with initial concentrations of 100 and 1250 mg·L^{-1} was placed in two conical flasks, and 0.2 g of porous PEI-cell particles was added into the solution separately. The two conical flasks were placed in a shaker at 30 °C. 0.5 ml of supernatant liquid was taken out from the flask at intervals. The concentrations of Cr(III) and Fe(III) were determined at 540 nm and 510 nm, respectively, by a TU1720 UV–visible spectrophotometer (Puxitongyong Instrumental Co. Ltd., China) after the analytes were mixed with 1,5-diphenyl carbazide and phenanthroline. The standard curves of Cr(III) and Fe(III) are determined with stand solutions with gradient concentrations as $y = 0.00672 + 0.63298x$ ($R_c = 0.9992$) and $y = 0.01381 + 0.19314x$ ($R_c = 0.9995$), respectively. The adsorption amount is calculated by

$$Q = \frac{(C_o - C) \times V_k}{m} \quad (2)$$

where Q (mg·g^{-1}) is the adsorption amount, C_o (mg·L^{-1}) is the initial concentration of $Cr(NO_3)_3$ or $FeCl_3$ solution, C (mg·L^{-1}) is the final concentration, V_k (L) is the volume of metal salt solution, and m (g) is the mass of porous PEI-cell.

2.5. Isothermal adsorption experiment

50 ml of $Cr(NO_3)_3$ solution in a concentration range of 5–100 mg·L^{-1} and $FeCl_3$ solution in a concentration range of 250–1500 mg·L^{-1} were transferred into different conical flasks, and 0.2 g of PEI-cell particles was added. Then the conical flasks were placed on the shaker at 30, 40 and 50 °C separately to reach adsorption equilibrium. The concentrations of Cr(III) and Fe(III) were determined before adsorption (C_o, mg·L^{-1}) and at adsorption equilibrium (C_e, mg·L^{-1}) to calculate the adsorption amount per mass adsorbent (Q_e, mg·g^{-1})

$$Q_e = \frac{(C_o - C_e) \times V_i}{m} \quad (3)$$

where V_i represents the solution volume (L) and m represents the absorbent mass (g).

2.6. Investigation of major factors affecting adsorption capacity

The amount of absorbent, temperature and pH value are important factors in adsorption processes. pH values of solutions were adjusted with HCl or NaOH and measured by a pHS-25 digital pH meter (Leica Instrumental Co. Ltd., China) to determine their effect on the adsorption capacity of porous PEI-cell. The adsorption experiments were implemented with different amounts of PEI-cell particles for a given amount of metal. The influence of temperature (20, 30, 40, 50, 60 °C) was also explored for the adsorption capacity of porous PEI-cell particles.

2.7. Continuous adsorption and desorption experiments

2.02 g of PEI-cell was filled in a glass column with an inner diameter of 1 cm by a wet packing mode. The concentrations of Cr(III) and Fe(III) were 100 and 1250 mg·L^{-1}, respectively, and the flow rate was controlled at 9.42 bed volume per hour (BV·h^{-1}). Metal concentrations in the effluent were monitored with spectrophotometry at regular time intervals. The saturated adsorption amount can be calculated with obtained concentrations and above equations.

The elution experiments were performed with 5% HCl as an eluting reagent, and the flow rate of elution was controlled at 16.35 BV·h^{-1}.