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Original article

Optimization of polyacrylonitrile–cysteine resin synthesis and its selective removal of Cu(II) in aqueous solutions

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ABSTRACT

Polyacrylonitrile beads (PAN) cysteine (CS) was synthesized from polyacrylonitrile beads (PAN) and cysteine (CS). The content of the functional group and the percentage conversion of the functional group of PAN-CS prepared under the optimum condition using response surface methodology (RSM) for the first attempt were 3.22 mmol/g and 35.78%. The structure was characterized by FT-IR and elemental analysis. The adsorption properties of the resin for Cu(II) were investigated by batch and column experiments. Batch adsorption results suggested that PAN-CS had higher adsorption capability for Cu(II) than other metal ions and maximum saturated adsorption capacity was 184.7 mg/g. The resin and its metal complexes were studied by FT-IR. Furthermore, the resin can be eluted easily using 1 mol/L HCl. PAN-CS can provide a potential application for selective removal of copper from waste solution.

1. Introduction

Copper is a nonferrous metal largely applied in industry for the production of various conduction parts of cables, electrical units, and jewelry. It serves as a component of different alloys, and is also used as catalytic agents. Meanwhile, copper is known as a trace element necessary for life; however, the excessive intake of heavy metals causes significant harm to human health. Since heavy metal pollution has made a great impact to environment in recent years, development of novel methods to remove and reuse copper from waste disposal is vital to the environment for alleviating issues of copper pollution [1–8]. Recently, adsorption has been considered one of the most popular and effective methods for the removal of pollutants at different industrial facilities and from different natural environments. Because adsorption is an interfacial phenomenon, it has certain qualities, such as fast kinetics, flexibility in design, and mild regeneration condition [9].

Polyacrylonitrile (PAN) is an ideal polymeric matrix with a series of merits such as mechanical stability, solvent resistance, and abrasion resistance [10]. Active nitrile groups (C≡N) in PAN can easily be converted into a number of new functional groups via special reactions. Deng et al. [11–13] used aminated polyacrylonitrile fibers to remove copper, lead, and chromium ions from aqueous solutions; however, the adsorption capacity was not high, and selectivity was not mentioned. Our initial report showed that the cysteine functionalized polyacrylonitrile resin can be used for selective adsorption of Cu(II) from solutions with a good adsorption capacity.

Response surface methodology (RSM) is a collection of statistical and mathematical techniques which has been successfully used for developing, improving, and optimizing processes [14].

In this work, we designed a novel chelating resin (PAN-CS) by grafting cysteine on the surface of PAN beads, which has promising potential for the application of the separation and preconcentration of Cu(II) from multicomponent solutions. The synthesis conditions such as reaction temperature, molar ratio of reagents, and reaction time have been optimized with the use of RSM. The synthetic resin was characterized by FT-IR and elemental analysis (EA). The resin was designed to fit in with environmental protection goals.

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2. Experimental

2.1. Materials

Mesoporous-type cross-linked polyacrylonitrile beads (PAN), cross-linked with 7% divinylbenzene (DVB), nitrogen content 22.18%, functional groups content 15.83 CN mmol/g, specific surface area 27.8 m^2/g, pore size 25.1 nm, were purchased from Chen Guang Chemical Industrial Institute of China. Cysteine was purchased from Aladdin Industrial Corporation, China. Aqueous solutions of ions at various concentrations were prepared from $NiSO_4{\cdot}6H_2O$, $HgCl_2$, $CuCl_2{\cdot}2H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, and $Pb(NO_3)_2$, and were used as sources for Ni(II), Hg(II), Cu(II), Zn(II), Cd(II), and Pb(II), respectively. All other reagents and solvents were of analytical reagent grade and were used without further purification.

2.2. Apparatus

IR spectra for the samples were obtained from a Nicolet 380 Fourier transform infrared (FT-IR) spectrometer. The concentrations of metal ions were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). C, N, and S elements were analyzed by a Vario EL III Elemental Analyzer. The specific surface area and the mean pore size of the resins were determined on an Autosorb-1 automatic surface area and pore size analyzer. A Mettler Toledo delta 320 pH meter was used for pH measurements.

2.3. Preparation of PAN-CS

The preparation procedure is simple and described as follows: PAN beads and N,N-dimethylformamide (DMF) were added into a three-neck round-bottom flask, swelling overnight. Then, CS and a small amount of metallic sodium used as catalyst were added to the flask. The mixture reacted with 100 rpm stirring speed under a nitrogen atmosphere. The solid product was carefully washed thoroughly with DMF and deionized and then washed with acetone and ether. After that, the obtained resin was dried in vacuum at 50 °C. The conversion of the functional group of the synthetic resin can be calculated from the nitrogen content by the following equations:

$$F_c = \frac{N_c}{14 \times n_c} \times 1000$$

$$X = \frac{F_n \times 1000}{1000 \times F_0 - \Delta m \times F_n \times F_0} \times 100\%$$

where F_0 (mmol of Cl/g) and F_c are the contents of the functional group of polystyrene and the synthesized resin, respectively, X is the functional group conversion (%), m is the incremental synthesis reaction resin (g/mol), n_c is the number of nitrogen atoms of ligand molecules, and N_c is the nitrogen content of the synthesized resin (%).

2.4. Resin adsorption and desorption experiments

Batch experiments were carried out to investigate the Cu(II) adsorption property on the prepared PAN-CS resin by placing 15.0 mg resin in a series of flasks containing 30 mL of the studied metal ions at the desired initial concentration and pH. Then, the contents of the flasks were shaken in a flask-shaker at specific temperatures for a given time with a speed of 100 rpm. The residual concentration of the studied metal ions in the solution was determined by ICP-OES. The adsorption capacity (Q, mg/g) and distribution coefficient (D, mL/g) were calculated with the following expression:

$$Q = \frac{C_0 - C_e}{W} V$$

$$D = \frac{C_0 - C_e}{W C_e} V$$

where C_0 is the initial concentration of Cu(II) (mg/mL), C_e is the residual concentration of Cu(II) in solution (mg/mL), V is the solution volume (mL), and W is the resin dry weight(g). Desorption experiments were carried out following the completion of the adsorption experiments. After adsorption experiments, the resins were separated from the aqueous solution by filtration, washed with deionized water, and shaken with different eluent solutions of various concentrations at 298 K for 24 h. After that time the concentration of Cu(II) was similarly analyzed as described above. After each adsorption–desorption cycle, the resin beads were washed and reconditioned for adsorption in the succeeding cycle. The desorption ratio (E) was calculated as follows:

$$E(\%) = \frac{C_d V_d}{(C_0 - C_e) V} \times 100\%$$

where C_d is the concentration of the solutes in the desorption solutions, V_d is the volume of the desorption solution, and C_0, C_e and V are the same as defined above.

3. Results and discussion

3.1. Analysis of variance (ANOVA) and development of regression model equation

Experimental data obtained using the Design Expert 8.0.4 software for multiple regression equation, and gained objective function quadratic regression equation on the conversion rate of the functional group of PAN-CS:

$$Y = 43.28 + 1.43A - 1.44B + 2.27C - 1.45A2 - 0.49B2 - 2.29C2 - 1.38AB + 0.18AC - 0.54BC$$

The results for analysis of variance for quadratic regression are given in Table 1. From the analysis results in Table 1, the overall model is highly significant ("Pr > F" value <0.0001), no significant lack of fit items ("Pr > F" value = 0.7348 > 0.05), which is desirable. The model can be used to predict the conversion rate of the functional group of PAN-CS for different conditions. The determination coefficient R^2 = 0.9840, and the coefficient of variation (C.V%) 1.27% is within an acceptable range, which indicates that the experiment as described is operable. The adjusted R-square $R^2_{adj} = 0.9635$, demonstrates 96.35% of the variability of the data can be explained by the model. Adeq Precision is to detect a noise signal ratio and it is operable once the ratio is over 4. The experimental Adeq Precision is 19.072, which is moderate, indicating that this model can accurately predict the experimental results. It is seen from the F value of each single factor that the molar ratio has the most significant impact on the conversion rate. Compared with the single factor experimental results, which found that the molar ratio within a certain range has the greatest impact on the conversion rate; the effects of time and temperature were not significant ("Pr > F" value > 0.05).

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