

Synthesis of Polyethylenamine Cellulose and Its Absorbing Ability to Chromium (VI)

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Keywords: Polyethylenamine Cellulose, Adsorbent, Cr(VI), Adsorption Dynamics

Abstract. The study was conducted regarding the adsorption effect of Cr(VI) on polyethylenamine cellulose, the affecting factors on the adsorption of Cr(VI), such as pH value, adsorption time, polyethylenamine cellulose dose and initial concentration of Cr(VI) were investigated. The results showed that adsorption efficiencies of Cr(VI) is more than 90%, the suitable conditions for the adsorption are as following: pH 2, adsorption time 10h, polyethylenamine cellulose 10 g/L, initial concentration of Cr(VI) 10 mg/L. The adsorption isotherms could be well fitted by both Langmuir and Freundlich equation. The law of dynamics for the adsorption can be simulated by pseudo-first order and pseudo-second order kinetics models.

Introduction

Electroplating, tanning, mining, and dye industries have produced large amounts of mercury, lead, cadmium, arsenic and chromium in waste water, which are detrimental to human health and ecological environment. Currently, there are several techniques to treat heavy metals in wastewater [1], heavy metal ions can be removed by oxidation-reduction [2], chemical precipitation [3], ion exchange [4], and membrane separation [5] methods. Especially adsorption and ion exchange methods, which are the common methods to treat heavy metal, have the advantages of high efficiency, easy to operate and lower energy consumption. Activated carbon and ion exchange resins are common adsorbents and ion exchange agent, but they are expensive and have regeneration difficulties. In recent years, researchers have been working to find low-cost adsorption material, and then the cellulose has its own unique advantages. Cellulose adsorption material is taken from the agricultural and sideline products, and is cheap, so the material has bright prospects.

In this paper, polyethylenamine cellulose is employed as the adsorbent to remove Cr(VI) in solution, the factors, which are interrelated with Cr(VI) removing, the pH value, the adsorption time, the amount of polyethylenamine cellulose and the initial concentration of Cr(VI), were investigated, then the suitable conditions for the adsorption was optimized.

Materials and Experimental Method

Reagents and Instruments. All reagents and solvents were of analytical grade. The measurements were carried out with a 722 spectrophotometer (Shanghai, China) using 1.00-cm quartz cells. The pH measurements were performed with a pH-meter (pHS-3C pH meter) equipped with a glass electrode with the Ag/AgCl reference electrode.

Experimental Methods. 3 g straw cellulose was immersed in a solution of 30 g sodium hydroxide in 70 mL deionized water. The mixture was then stirred at room temperature for 1h and the cellulose was filtered. Then, the cellulose was reacted with 8% sodium hydroxide solution and 15mL epichlorohydrin at 45° for 15h, which was filtered, washed firstly with deionized water, then with acetone, and dried at 70°C. Thus, the epoxidized cellulose was obtained. After this, 100mL deionized water, 1g sodium carbonate, epoxidized cellulose and diethylenetriamine in a mass ratio

(1:1) were added into flask. The mixture was reacted at 50°C for 8h. Next, the product was filtered, washed to neutral, dried in an oven at 70°C and used as an adsorbent. Its structure was characterized by scanning electronic (SEM) and Fourier transform infrared spectrum (FTIR) [6].

The absorption experiments of Cr(VI) ions on polyethylenamine cellulose were performed from aqueous solution of bichromate of potash at room temperature for different pH value and periods of time. Also, the effects of polyethylenamine cellulose dosage and the initial concentrations of Cr(VI) ions in solution were studied. All the experiments were carried out in batch process. Polyethylenamine cellulose was shaken in 50 mL Cr(VI) ions solution in 100 mL beaker. The residual concentration of Cr(VI) is calculated with standard working curve, which is determined by diphenylcarbohydrazide spectrophotometric method [7]. The removal rate and the adsorption capacity of Cr(VI) by polyethylenamine cellulose were calculated by the following equation:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

where, η (%) is removal rate of Cr(VI), C_0 (mg/L) and C_e (mg/L) are original and equilibrium concentration of Cr(VI) in solution, respectively, q_e (mg/g) is adsorption capacity for adsorbent, V (L) is the volume of processing solution, and m (g) is the adsorbent mass.

Results and Discussions

The Effect of Solution pH. When solution pH value is 2, η is 91.1%; when solution pH < 2, η declines, as the acid concentration increases, the $H_2Cr_2O_7$ concentration also increases, which affects exchange interaction between $-NH_3^+$ and $HCr_2O_7^-$ or $Cr_2O_7^{2-}$; when solution pH value is 13, η is only 18.1%, the figure shows, when solution pH value between 2 and 3, η is more than 85%. Therefore, in these experiments the initial solution pH value will be adjusted to 2.

The Effect of Adsorption Time. The removal rate approximately took place in the first 9h and reached equilibrium after about 10h, and then reached 91.1%. Next the adsorption rate gradually slow down, removal rate remained stable. In subsequent experiments, the adsorption time was maintained 10h.

The Effect of Polyethylenamine Cellulose Dosage. When increasing the polyethylenamine cellulose dosage, the removal rate of Cr(VI) is improved. When the amount of polyethylenamine cellulose is 10 g/L, the removal rate is 91.1%. Continue to increase the dosage, the curve approached to a flat, the increasing degree of removal rate of Cr(VI) improved in decreasing trend, which is fitted regularity of absorption. The amount of polyethylenamine cellulose dosage is selected as 10 g/L in the succedent experiments.

The Effect of Initial Concentration of Cr(VI) in Solution. With the initial concentration of Cr(VI) increasing, the removal rate is decreasing. When the initial concentration of Cr(VI) is less than 10 mg/L, the removal rate is up to 90%; when the initial concentration is 50 mg/L, the removal rate was 64.39%. So the polyethylenamine cellulose is suitable for treating low concentration of Cr(VI) wastewater.

Adsorption Isotherm Investigation. Knowledge of adsorption isotherm is required for better understanding features of the adsorbent/adsorbate system like their affinity or sorption capacity. The polyethylenamine cellulose dosage is fixed to 10 g/L, and the initial concentrations of Cr(VI) are changed under the conditions of pH 2, the solution is stirred 10 h to make adsorption equilibrium, the residual concentrations of Cr(VI) in solution were determined, according which the adsorption capacities of Cr(VI) by polyethylenamine cellulose were calculated, the adsorption isotherm of Cr(VI) on polyethylenamine cellulose is depicted in Fig. 1. The adsorption isotherm proceedings are characterized by Langmuir and Freundlich equations [8], the results are shown in Fig. 2 and Fig. 3.

Langmuir adsorption isotherm equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_1 \cdot q_m} \quad (3)$$

Freundlich adsorption isotherm equation:

$$\lg q_e = \lg k_f + \frac{1}{n} \lg C_e \quad (4)$$

In the Eq. (3) and (4), q_e (mg/g) is adsorption equilibrium capacity, q_m (mg/g) is saturated adsorption capacity, k_1 is adsorption equilibrium constant, C_e (mg/L) is the adsorption equilibrium concentration, k_f is Freundlich adsorption coefficient, n is the constant.

The parameters are shown in Table 1, the correlation coefficient of matched curve shows, the Langmuir and the Freundlich isotherm equations are well fitted results. The maximum adsorption capacity of Cr(VI) on polyethylenamine cellulose is 3.64 mg/g from the Langmuir equation. The Freundlich adsorption constant k_f is often used to indicate the relative quantity of absorbability, $1/n$ is used to represent the adsorption degree of difficulty.

Table 1. Langmuir and Freundlich adsorption isotherm constants.

Langmuir isotherm		Freundlich isotherm			
q_m (mg/g)	k_1	R^2	$\frac{1}{n}$	k_f	R^2
3.64	0.2016	0.8246	0.39	0.88	0.9431

*Symbols are defined in the text

The Adsorption Kinetics Model. The rate of adsorption is highly important in the design and evaluation of adsorbents in removing Cr(VI) from the solution. There are a variety of adsorption kinetic models, pseudo-first and pseudo-second order models are employed to correlate the kinetic data. The pseudo-first-order kinetic adsorption model was suggested for the sorption of solid/liquid systems [9]. The pseudo-second order model is based on the assumption that the rate limiting step may be chemisorption which involves valence forces by sharing or electron exchange between the adsorbent and the adsorbate [10].

The integral of pseudo-first and pseudo-second order kinetic model can be expressed as given below [11, 12]:

$$\ln(q_e - q_t) = \ln q_e - kt \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_1 q_e^2} + \frac{t}{q_e} \quad (6)$$

where, q_e and q_t (mg/g) are the adsorption loading of Cr(VI) at equilibrium and at time t (min), respectively, k [g/(mg·min)] and k_1 [g/(mg·min)] are pseudo-first and pseudo-second rate constants of adsorption, respectively.

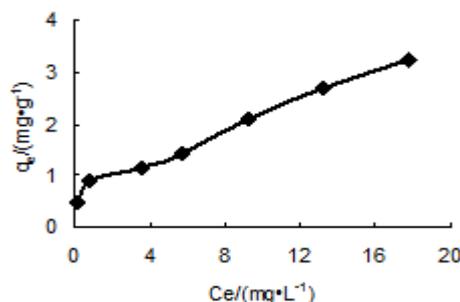


Fig. 1 Adsorption isotherm of Cr(VI) on polyethylenamine cellulose.

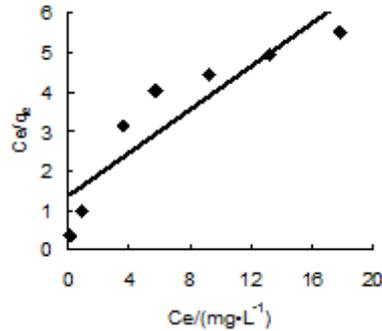


Fig. 2 The Langmuir adsorption isotherm of Cr(VI) on polyethylenamine cellulose.

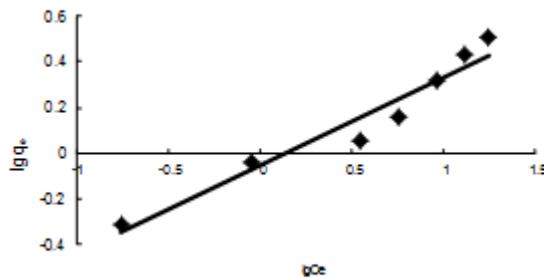


Fig. 3 The Freundlich adsorption isotherm of Cr(VI) on polyethylenamine cellulose.

A plot of $\ln(q_e - q_t)$ versus t is provide in Fig. 4, from which k and q_e were calculated as $0.003 \text{ g}/(\text{mg}\cdot\text{min})$ and $0.9105 \text{ mg}/\text{g}$, respectively. Plotting t/q_t against t (Fig. 5), a straight line is obtained and the rate constant k_2 as well as q_e can be calculated as $0.0186 \text{ g}/(\text{mg}\cdot\text{min})$ and $0.8768 \text{ mg}/\text{g}$, respectively. The linear coefficients (r) were 0.833 and 0.9303 for pseudo-first and pseudo-second order kinetic mode, respectively.

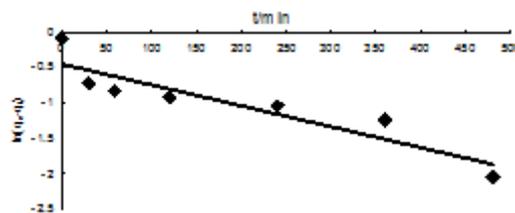


Fig. 4 Pseudo-first order plot of Cr(VI) adsorption onto polyethylenamine cellulose.

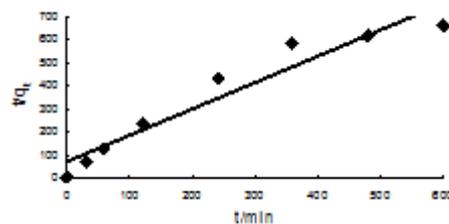


Fig. 5 Pseudo-second order plot of Cr(VI) adsorption onto poly-ethylenamine cellulose.

Conclusions

The results showed that the adsorption efficiencies of Cr(VI) on polyethylenamine cellulose is more than 90%. The factors such as pH value, adsorption time, amount of polyethylenamine cellulose and initial concentration of Cr(VI) all affect the Cr(VI) removing rate. The suitable conditions for Cr(VI) adsorption are as following: pH 2, adsorption time 10h, polyethylenamine cellulose dosage $10 \text{ g}/\text{L}$, initial concentration of Cr(VI) $10 \text{ mg}/\text{L}$.

The adsorption isotherm of Cr(VI) on polyethylenamine cellulose matches the Langmuir and the Freundlich adsorption isotherm, the correlation coefficients were 0.8246 and 0.9431, respectively, the correlation coefficient of the Freundlich adsorption is greater than one of the Langmuir, therefore, the Freundlich isotherm model is more suitable for describing the adsorption process of Cr(VI) on polyethylenamine cellulose than ones of the Freundlich.

The adsorption kinetics of Cr(VI) on polyethylenamine cellulose are fitted to the pseudo first and second order kinetic equation, and the correlation coefficients were 0.833 and 0.9303, respectively. So, the adsorption kinetic of Cr(VI) on polyethylenamine cellulose is more fitted to the second order kinetic equation than that of the first ones.

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