The Second SREE Conference on Chemical Engineering

The Adsorption of CHS-1 Resin for Cr (Ⅵ) of Low Concentration from Electroplating Wastewater

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Abstract

The adsorption property of CHS-1 resin for Cr (Ⅵ) was investigated by chemical analysis. Experiment results show that CHS-1 resin has the best adsorption ability for Cr (Ⅵ) at pH=2-3. The exchange adsorption rate of the resin for Cr (Ⅵ) at low concentration is controlled by liquid film diffusion and chemical reaction. The behavior obeys the Freundlich isotherm and Langmuir equation. Its saturated sorption capacity is 347.22 mg/g at 298K. The thermodynamic adsorption parameters, enthalpy change $\triangle H$ and free energy change $\triangle G_{298}$ of the adsorption are 1.39 kJ/mol and -5.3 kJ/mol. Cr (Ⅵ) adsorbed on CHS-1 resin can be eluted by 5% NaOH -5% NaCl quantitatively without apparent decrease in sorption capacity.

Keyword: Cr(Ⅵ);ion exchange;adsorption;dynamics;thermodynamics;desorption

1. Introduction

The problem of removing pollutant from water and wastewater has grown with rapid industrialization. Several industries like paint and pigment manufacturing, corrosion control, leather tanning, chrome plating, textile, etc. discharge effluent containing hexavalent chromium, Cr (Ⅵ), to surface water. Cr (Ⅵ) is of severe toxicity, and can be gathered in water, living creatures and farm crops. It can also be absorbed by the human body through the food chain and accumulated inside the body. So Cr (Ⅵ)-contained waste

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water is nowadays recognized as one of the most serious harmful effects and has been listed by the National Environmental Protection Bureau of China.

There are many different ways of treatment for Cr (Ⅵ). Currently, there are mainly two major types of method. One is reduction [1-3], which creates great quantity of dirty mire in the process and easily causes secondary pollution. The other is direct processing for Cr (Ⅵ), and the ion exchange method is one of them. Compared with the others, the main advantages of ion exchange are recovery of metal value, selectivity, less sludge volume produced and the meeting of strict discharge specification. Recently, the research on dealing with wastewater containing Cr (Ⅵ) by resin has been very active [4-6]. In this work, the adsorption behavior and mechanism of CHS-1 resin adsorbing Cr (Ⅵ) in electroplating waste water of low concentration were studied, and the basic adsorption parameters were determined.

2. Experimental

2.1 Materials and instruments

PHS-3c pH meter, SHA-C temperature constant shaking machine and 722 spectrophotometer were used.

CHS-1 resin was provided by Shanghai Jingkai resin chemical company, China. Wastewater of Cr (Ⅵ) was from an electroplating factory. 0.1% diphenyl carbohydrazide solution was used as a developer.

2.2 Adsorption and analytical method

A desired amount of CHS-1 resin after pretreatment was weighed and added into a conical flask, and then a required amount of solution of Cr (Ⅵ) was added, then the flask was shaken at constant temperature until the concentration of Cr (Ⅵ) maintained invariable. The amount of Cr (Ⅵ) was measured by the spectrophotometric determination of diphenyl carbohydrazide. According to the concentration change of Cr (Ⅵ) solution adsorbed, the adsorption amount Q and the adsorption distribution coefficient D were calculated respectively as follows:

$$Q = (c_0 - c_e) v / m \tag{1}$$

$$D = Q / c_e \tag{2}$$

Q is the adsorption amount of resin to Cr (Ⅵ) in the equilibrium state, mg/g; c_0 is the initial concentration of Cr (Ⅵ) in solution, mg/L; c_e is the equilibrium concentration of Cr (Ⅵ) in solution, mg/L; m is the resin mass, g; and V is total volume of solution, L.

3. Results and discussion

3.1 Effect of pH on adsorption

Several parts of appropriate resins were weighed accurately and put into conical flask respectively. Under the experimental conditions of T=298K and c_0=45mg/L, HCl and NaOH were added to adjusted the pH, and shaken to equilibrium intermittently. The effect of pH on adsorption amount is shown in Fig.1.
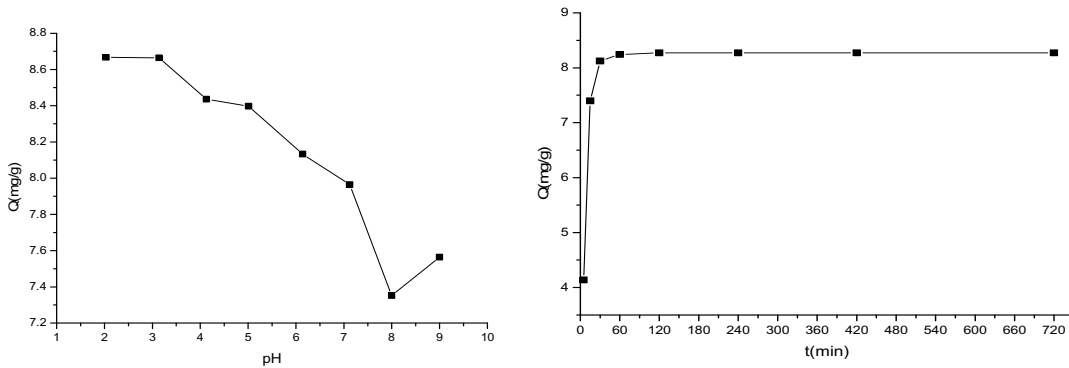
Fig.1 Effect of pH on adsorption amount of Cr (Ⅵ)   Fig.2 Adsorption kinetic curve of Cr (Ⅵ)

3.2 Adsorption dynamics

3.2.1 Control of adsorption rate progress and determination of adsorption rate constant

Several parts of appropriate resins were weighed accurately and the experimental condition is the same as 3.1, a little solution was taken out at intervals to determine the concentration until it reached equilibrium. According to formula (1), the adsorption capacity of the resin can be figured out. After the remains were kept constant, a series of data were obtained (Fig.2). When the adsorption amount was half of that at equilibrium, the required time $t_{1/2}$ was about 0.2 h. The required time of the adsorption equilibrium was 2 h. BOYD et [4], who studied ion exchange adsorption process in sorbet, deemed that exchange adsorption rate was controlled by a slow process of liquid film diffusion, particle diffusion and chemical reaction.

Particle diffusion equation:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(\frac{D\pi^2 n^2 t}{r_0^2}) \tag{4}$$

Liquid film diffusion equation:

$$\lg(1 - F) = (R / 2.303)t \tag{5}$$

Chemical reaction equation:

$$\lg(1 - F) = (S / 2.303)t \tag{6}$$

Where $F = Q_t/Q_\infty$, Q_t and Q_∞ are the resin adsorption amounts of every gram resin at adsorption time t and at equilibrium, respectively; $R = 3D_l/r_0 \triangle r_0 k$, D_l is the film diffusion constant, r_0, the particle radius, $\triangle r_0$, the film thickness, and k, the distribution constant; $B = \pi^2 Di/r_0^2$, and D_i is the internal diffusion coefficient; S is the mass action constant.

If the graph of Bt vs t shows a linear relationship, the exchange rate will be controlled by particle diffusion. If the graph of –lg (1-F) vs t is linear, the exchange rate will be controlled by liquid film diffusion or the chemical reaction [8,9]. Fig. 3 shows that the plot of Bt vs t is almost liner. While the relationship between –lg (1-F) and t is linear (Fig. 4), According to Fig. 4, the apparent adsorption rate constant k_{298} is 1.246×10^{-4} s^{-1}, and the correlation coefficient r is 0.9969 at 298K.
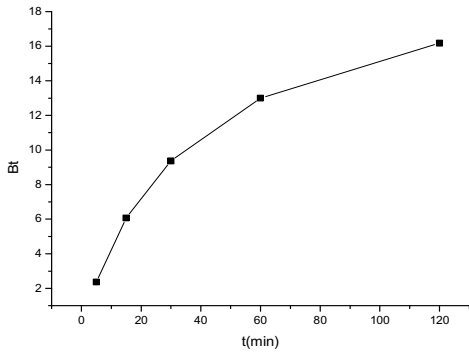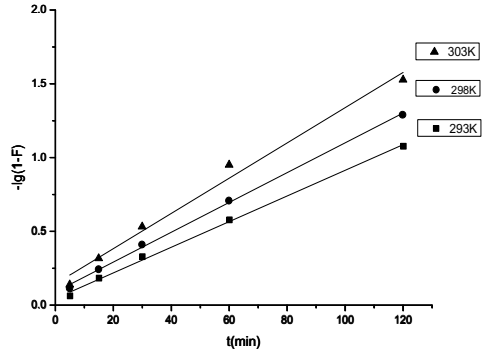
Fig.3 Plot of Bt vs time

Fig.4 Determination of adsorption rate constant

3.2.2 Isotherm adsorption curve

The isotherm are studied by varying 50mL the initial Cr (Ⅵ) concentration in the range of 250 mg/L~550mg/Lwith 85 mg resin at 298K. The results are shown in Fig. 5 and Fig. 6. The adsorption isotherm is correlated to the well-known Freundlich equation (6)[9-12] and Langmuir isotherm(7)[13]:

$$Q_e = aC_e^{1/b} \; namely \; \lg Q_e = 1/b \lg C_e + \lg a \tag{7}$$

$$C_e/Q = C_e/Q_0 + 1/(Q_0 b) \tag{8}$$

Where a and b are constants. We have the following result of model analysis

Table 1 Freundlich and Langmuir isotherm parameters on the resin

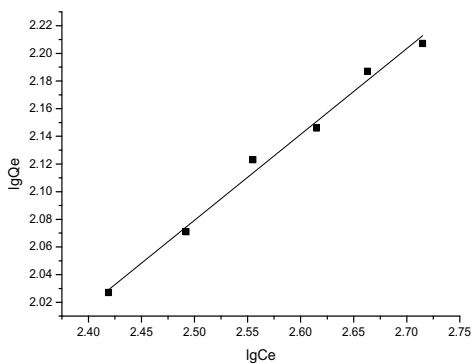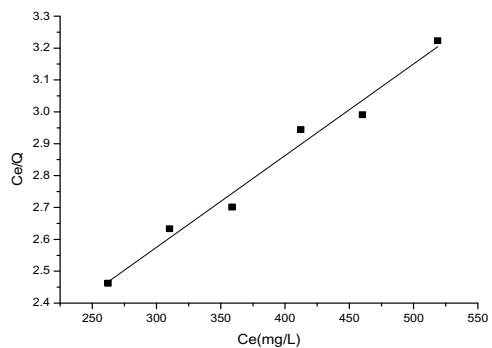| Freundlich			Langmuir		
b	a	R^2	Q_0	b	R^2
1.612	3.376	0.9892	347.22	0.00168	0.9766

Fig.5 Relationship between lg Qe and lg c_e

Fig. 6 Relationship between Ce/Q and C_e

3.3 Effect of temperature on Cr (Ⅵ) adsorption percentage and determination of thermodynamic parameter

Several parts of appropriate resin were weighed accurately. According to the experimental conditions as 3.1, the distribution coefficient of the resin for Cr (Ⅵ) was determined at temperature of 293K, 298K and 303K. According to Formula (2), the corresponding distribution coefficient was figured out. From the result shown in Fig. 4, it can be seen that increasing the adsorption temperature leads to better adsorption. This means that the adsorption process is endothermic. Therefore, the adsorption reaction is a chemical process. According to $lgD = -\Delta H / (2.303RT) + \Delta S/R$ [17-18], the straight line was obtained by plotting lgD vs $1/T$ (Fig. 7). From the slope of the line, ΔH of 1.39 kJ/mol is obtained. ΔS can be gained from the intercept of the line, which is 22.45 J/ (mol · K). At T=298K, $\Delta G_{298}=\Delta H-T\Delta S=-5.30$ kJ/mol. the thermodynamic results of $\Delta H>0$, $\Delta G<0$ in the adsorption indicate that the process is endothermic in a certain temperature range
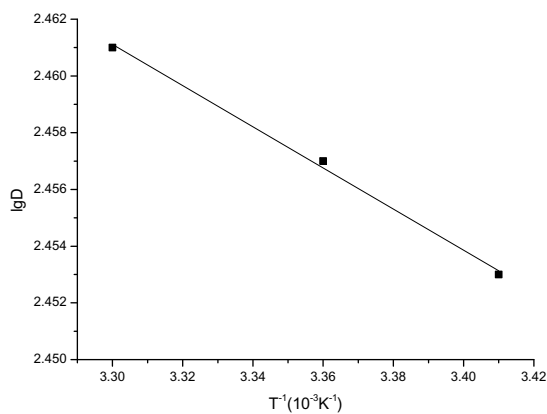

Fig. 7 Effect of temperature on distribution coefficient

3.4 Desorption and recovery of resin

Four parts of appropriate resin was weighed accurately and put into experiment at T=298K and c_0=45mg/L. After the equilibrium reached, using 2% NaOH, 5% NaOH, 8% NaOH and 5% NaOH-5% NaCl regenerate them. Calculate the percentage of desorption, experimental result shows in table 1.

Table 2. Desorption of CHS-1 resin for Cr (Ⅵ)

eluant	Percentage of elution / %
2% NaOH	55.72
5% NaOH	74.40
8% NaOH	82.37
5%NaOH-5%NaCl	98.02

4. Conclusions

(1) Result of the adsorption experiment show that Cr (Ⅵ) can be optimally adsorbed at pH=2-3. Cr (Ⅵ) can be eluted by the 5%NaOH-5%NaCl solution, and the percentage of elution is up to 98.02% initially.

(2) The exchange adsorption rate of resin for Cr (Ⅵ) is controlled by liquid film diffusion and chemical reaction. The behavior obeys the Freundlich isotherm and Langmuir equation.

(3) The results of $\Delta H > 0$, $\Delta G < 0$ in the adsorption shows that the process is a spontaneous endothermic in a certain temperature range.

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