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Cr(VI) Adsorption on Acid Modified Diatomite

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Abstract. Cr(VI) adsorption onto diatomite has been investigated. Cr(VI) adsorption effects on original diatomite and acid modified diatomite were compared. The adsorption kinetics of Cr(VI) on acid modified diatomite were described by pseudo-first-order and pseudo-second-order models. The experimental data fit to pseudo-second-order kinetics better. Langmuir and Freundlich isotherms were used as the model adsorption equilibrium data. The thermodynamic parameters were evaluated including $\triangle G$ (Gibb's Free energy change), $\triangle H$ (enthalpy change), and $\triangle S$ (entropy change).

1. Introduction

The heavy metals caused by high-volume discharge of industry wastewater are one of the major component among toxic compounds in the effluents. Heavy metals are toxic and carcinogenic in the living bodies[1]. Chromium is well-known heavy metal contaminant in wastewater as well as ground water. There are two predominant forms of chromium: trivalent and hexavalent. Chromium has been widely used in many industry such as electroplating, metal cleaning, textiles and leather etc., so the water pollution caused by Cr(VI) has aroused wide public concern[2]. The toxicity of Cr(VI) to animals is greater than that of Cr(III), due to generally low solubility of hexavalent chromium compounds. Therefore, Cr(VI) wastewater should be treated before being discharged into the environment. Various methods have been used to remove Cr(VI), such as chemical precipitation, membrane filtration, ion exchange, photocatalytic reduction, biological operations, catalytic oxidation and adsorption[3-6]. However, each one of these processes has a few limitations. Among all methods, adsorption is considered as a potential process based upon its simplicity and high efficiency. Diatomite is a kind of siliceous sedimentary rock, which consists mainly of ancient diatom remains[7]. China has abundant diatomite reserves, amounting to 320 million tons. Diatomite has some unique properties, such as porosity, low density, large specific surface area, relative incompressibility and chemical stability. Diatomite has been used to adsorb heavy metals and dye wastewater [7-8]. The adsorption behaviours of Cr(VI) on acid modified diatomite have been studied, and then the adsorption kinetics, isotherms and thermodynamics were further studied.

2. Experiment

2.1. Adsorbent and adsorbate

Diatomite was obtained from Tianjin Fuchen chemical reagents factory, China. Diatomite samples (10.0g) were stirring continuously with 100mL H_2SO_4 (2mol/L) at 100 ºC water bath for 6h, and sulfur acid was added to activate diatomite fully. After cooling, the supernatant was

discarded. The precipitation was washed to neutral with double distilled water and dried for later use. Cr (VI) stock solution was prepared by dissolving a certain mass of potassium dichromate (K₂Cr₂O₇) in double distilled water in volumetric flask. The desired Cr(VI) concentrations used in the experiment was prepared to dilute the stock solution with a certain dilute hydrochloric acid.

2.2. Experiments of adsorption
Adsorption experiments were carried out by mixing diatomite with 50 mL solution of known Cr(VI) concentration in each 250mL conical flask placed in rotary shaker at 170rpm/min at 25 °C (excluding temperature experiments) for 180min. The Cr(VI) adsorbance in residual was measured by spectrophotometer and analysed by standard curve. Equation (1) was used to calculate the percentage of Cr(VI) adsorption, and equations (2) was used to calculate q_e (the amount of Cr(VI) per unit weight of diatomite, mg/g).

$$\text{Adsorption efficiency E (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100\% \qquad (1)$$

$$\text{Adsorption capacity } q_e = \frac{(C_0 - C_e) \times V}{M} \qquad (2)$$

Where C_0 (mg/L) are the initial concentration of Cr(VI) and C_e (mg/L) are the final concentration of Cr(VI) in solution; m is the weight (grams) of modified diatomite; V is the Cr(VI) solution volume in liters.

3. Results and Discussion

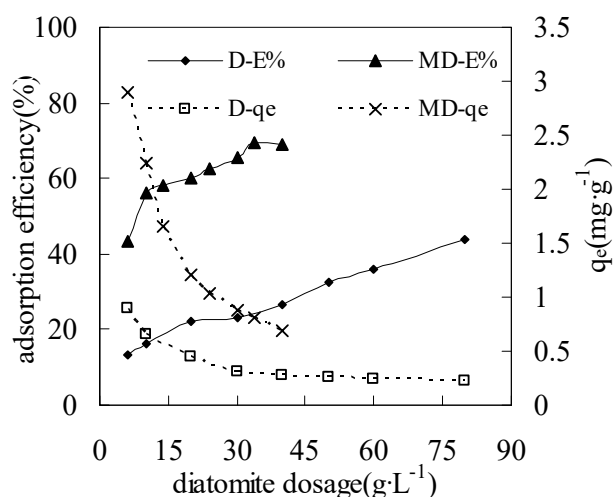*3.1. Effect of diatomite dosage on Cr(VI) adsorption*

Figure 1. Comparison of original diatomite (D) and modified diatomite (MD) dosage on Cr(VI) adsorption

The effect of original diatomite and modified diatomite dosage on Cr(VI) adsorption was as shown in figure 1. E% of Cr(VI) raised with an increase in the diatomite dosage . However, q_e decreased with diatomite dosage increasing. At the same diatomite dosage, the adsorption and q_e of Cr(VI) on acid modified diatomite was absolutely higher than those on original diatomite. E% of Cr(VI) on original diatomite and modified diatomite was 16.4% and 56.0% at adsorbent dosage of 10g/L, respectively. E% of Cr(VI) on original diatomite and modified diatomite was 23.2% and 65.6% at adsorbent dosage of 30g/L, respectively. The result showed that Cr(VI) adsorption on acid modified diatomite was much better.
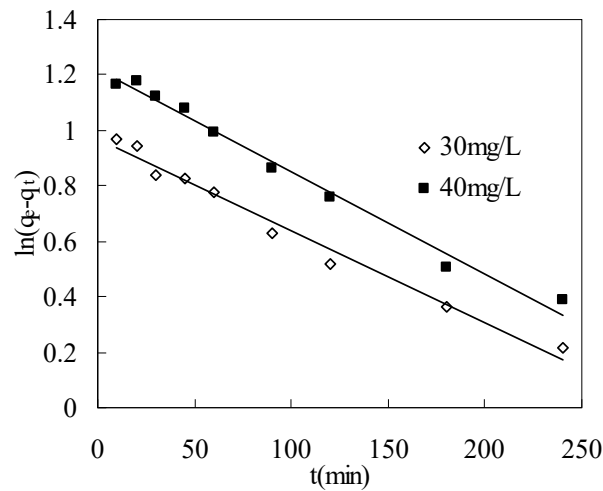
3.2. Adsorption kinetics

Figure 2. Pseudo-first-order kinetics diagram of Cr(VI) adsorption on modified diatomite
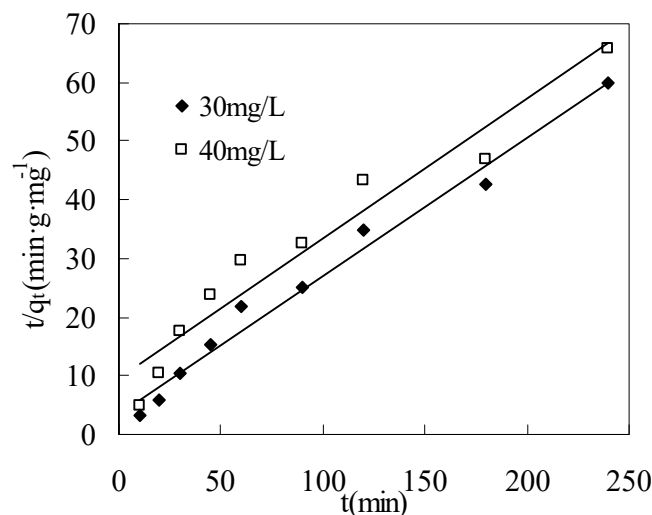

Figure 3. Pseudo-second-order kinetics diagram of Cr(VI) adsorption on modified diatomite
Pseudo-first-order kinetics model is based on Lagergren first-order rate equation of solid adsorption [9].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

where q_t are the adsorption capacity per unit mass at any time t, and k_1 is the pseudo-first-order adsorption rate constant.

The pseudo-second-order kinetics model was used to describe the sorption of metal ions[10]. Equation (4) was its representation formula.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

where k_2 is the adsorption rate constant of the pseudo-second-order.

The comparison results for Cr(VI) (initial concentration of 30 and 40mg/L) adsorption the acid modified diatomite (10g/L) were shown in Figure 2 and 3. The pseudo-second-order model fit better than the pseudo-first-order model, and the experimental kinetic data were closer to the actual values, which meant the chemisorption process.

3.3. Adsorption isotherm

Langmuir and Freundlich isotherm models (5) were applied to comprehend the adsorption behaviour of 40 mg/L Cr(VI) on 10g/L acid modified diatomite at 298K~313K. Fitting curves are shown in Fig. 4 and Fig. 5. The linear form of Langmuir and Freundlich model was equation (5) and (6), respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \tag{5}$$

$$\ln q_e = \ln k + \frac{1}{n}\ln C_e \tag{6}$$

Where q_m is the amount of adsorbate per unit mass of the adsorbent at complete monolayer converage, mg/g; and b is a constant related to the affinity of binding sites, L/mg. The slopes and intercepts (Figure 4) could be applied to calculate q_m and b value, respectively, for the linear plots of C_e/q_e versus C_e. In the equation (6), k and 1/n are the Freundlich constants.
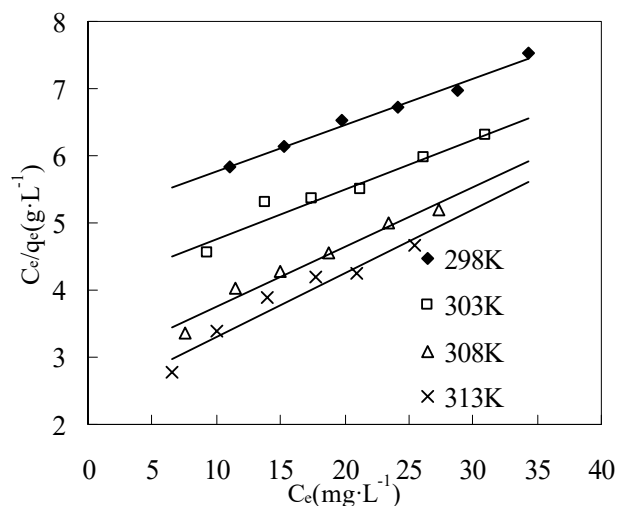

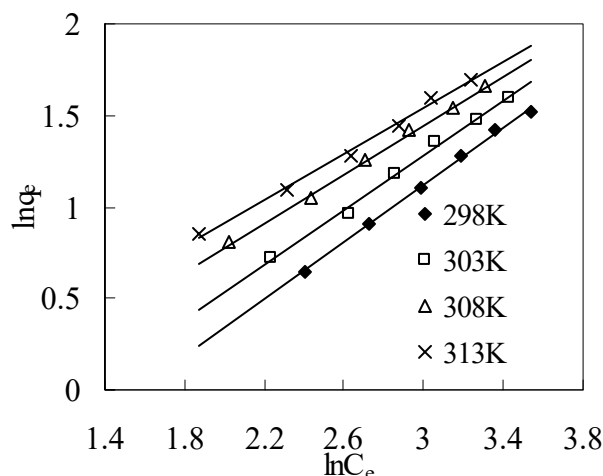Figure 4. Langmuir isotherm for Cr(VI) adsorption on modified diatomite

Figure 5. Freundlich isotherm for Cr(VI) adsorption on modified diatomite

The results show that the adsorption of Cr(VI) on acid modified diatomite is well described by Langmuir adsorption isotherm models, as well as the Freundlich adsorption isotherm models. The Freundlich adsorption isotherm model fit well the experimental data in the temperature range studied (correlation coefficient ≥0.99). The calculated q_m was 14.4mg/g, 13.5 mg/g, 11.3mg/g and 10.6mg/g, respectively, during 298K~313K for Cr(VI) adsorption on modified diatomite. The values of 1/n and k

were determined from the linear plot of $\ln q_e$ versus $\ln C_e$. The values of the empirical parameter $1/n$ during 298K~313K were less than unity, so the Cr(VI) adsorption on acid modified diatomite was favorably.

3.4. Adsorption thermodynamic
Thermodynamic parameters, e.g., ΔG, ΔH, and ΔS were calculated from the following equation (7) and (8) with initial Cr(VI) concentration of 40~90mg/L at temperatures of 298K, 303K, 308K and 313K, respectively.

$$\Delta G = -RT \ln \frac{q_e}{C_e}$$

(7)

$$\Delta G = \Delta H - T\Delta S$$
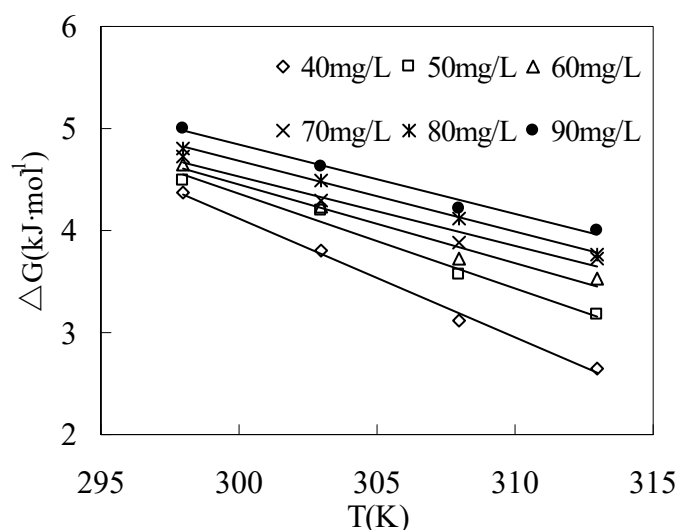
(8)

Where T is absolute temperature, R is a gas constant.

Figure 6. The plot of $\triangle$G against T for the adsorption of Cr(VI) on modified diatomite

The results were shown in Figure 6. Gibbs free energy change of adsorption was estimated during 2~5 kJ/mol for the adsorption of Cr(VI) on modified diatomite by equation (7). $\triangle$G was positive at all the temperatures, which displayed the non-spontaneous reaction. $\triangle$H and $\triangle$S can be got by the slope and intercept of the diagram of $\triangle$G vs. T. The values of $\triangle$H (24 ~ 40kJ/mol) were positive, indicating that the adsorption reaction was endothermic. The positive values of $\triangle$S [67~117 J/(mol·K)] reflected an increase in the randomness at the solid-solution interface during the adsorption process.

4. Conclusion
The adsorption of Cr(VI) on diatomite has been studied. The result shows that the Cr(VI) adsorption effect on acid modified diatomite was better than on original diatomite. The kinetics of Cr(VI) adsorption fit pseudo-second-order with better correlation coefficient. The adsorption isotherm for the adsorption of Cr(VI) follows both the Langmuir and Freundlich isotherm models. The maximum adsorption capacity obtained from Langmuir isotherm model was 14.4mg/g at 298K. Thermodynamic parameters, $\triangle$H, $\triangle$S and positive $\triangle$G indicate the endothermic, increased randomness and non-spontaneous nature of adsorption.

Acknowlegement

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