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Ferric chloride modified zeolite in wastewater on Cr (VI) adsorption characteristics

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Abstract.Zeolite was modified by ferric chloride（Fe-Z）removal Cr (VI) ion from wastewater. The results showed that the effect of Cr(VI) adsorption on modified zeolite depended significantly on pH. It is favorable for the adsorption of Cr(VI) in acid condition. The Langmuir isotherm model has high fitting accuracy with experimental data, demonstrated that is monolayer adsorption and chemical adsorption.The pseudo-second-order equation provided the best correlation to the data. The model can describe the adsorption reaction process well.

1. Introduction

Chromium as a typical heavy metal element, mainly demanded usage in the industrial fields of metal processing, electroplating, leather tanning, metallurgy ,paints and paper.[1]However,A large amount of chromium wastewater was discharged. Long term exposure in Cr (VI) has caused toxic effect on the organisms, such as nausea, arcinogenic and mutagenic.[2] The treatment technologies including reduction, ion exchange, electrolysis ,biological, electro-chemical precipitation, and adsorption .

Among various treatments, adsorption has proven to be one of the most effective and reliable physicochemical treatment methodologies. Natural zeolite is a microporous silicate mineral. It has many properties, like adsorption, ion exchange ability, catalytic and thermal stability and acid resistance.[3, 4]However, natural zeolite has no affinity for oxygen-containing anions or nonpolar organic compounds.[5, 6] Modification of zeolite by ferric chloride can transform its surface properties to enhance adsorption efficiency. The objective of the present work is to investigate the feasibility of the prepared Fe-Z in removing Cr (VI) from wastewater. In order to provide the basic data for the application of zeolite on the adsorption and modified.

2. Materials and methods

Material. Zeolite raw materials provided by the Guilin Xinzhu natural biological material Co. Ltd.A stock solution of 100mg/L was prepared by dissolving 0.2829g dried in 110℃for 2h of potassium dichromate in 1000mL volumetric flask and completed to 1000mL with distilled water. Then use the stock solution to have the standard curve and prepare the working solution with different concentrations ranged between 20 and 250mg/L. The initial pH of the solution is adjusted to require value with 0.1M HCl or 0.1M NaOH.

To quantify the Cr(VI) concentration in solution, a linear standard curve relating the UV-Vis peak intensity at 540nm.The residual Cr(VI) concentration after treatment can be calculated from the standard curve. To evaluate the efficiency of different adsorbents, removal percentage (RP,%) is introduced as a criterion which can be calculated using eqn (1).

$$\mathrm{RP} = \frac{C_0 - C_r}{C_0} \times 100\% \tag{1}$$

where C_0 and C_r are, respectively, the initial concentration of the Cr(VI) solution and the remaining Cr(VI) concentration after treatment.

Preparation of modified zeolite. 1.2mol/L ferric chloride solution mixed with the zeolite according to the ratio of 1:10 kg/L to 100mL beaker (pH 6), stirring at 25℃for 2h .After standing for 42h in constant temperature water bath, the zeolite was filtration, drying out 60℃, grinding through a 100 mesh sieve, namely modified zeolite (Fe-Z).

3. Results and discussion.

Effects of pH. The variations in the amount adsorbed of Cr (VI) from solution at various solution pHs are shown in Fig.1. The surface properties of the adsorbent and the stability of different morphologies of Cr (VI) in aqueous solution are affected by pH. The main forms of pH=2.0~6.0 are CrO_4^{2-} and $HCrO^{4-}$, while the free energy of $HCrO^{4-}$ is lower than CrO_4^{2-}[7], which is more favorable for adsorption.From the figure, it is evident that the maximum amount adsorbed of dye is observed at pH 3.Can be seen from Fig.1 under the condition of acid, Fe-Z adsorption of Cr (VI) effect is better than in alkaline conditions.

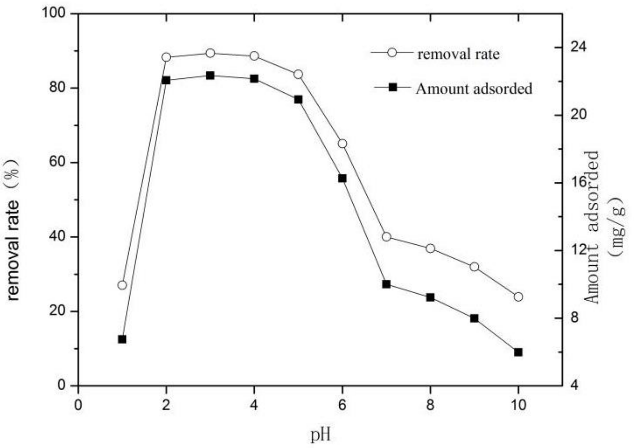

Fig.1 Effect of pH on adsorption of Cr(VI) by Fe-Z

Adsorption kinetics. To provide valuable insights into the reaction pathways and the mechanism of the reactions, it is necessary to study of adsorption equilibrium and kinetics. The kinetics of Fe-Z adsorption by set up the pseudo-first-order equation , the pseudo-second-order model and Elovich model to analyze.

The pseudo first order kinetic model (pesudo-first-order model) is one of the most widely used dynamic model. The equation as follows:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{2}$$

Where q_e and q_t are the amount of Cr (VI) adsorbed at equilibrium (mg/g) and at the time t (mg/g), respectively, the K_1 is the equilibrium rate constant of pseudo-first-order adsorption (g/mg min).

Pseudo-second-order model. The pseudo-second-order equation as follows:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \tag{3}$$

Where q_e and q_t are the amount of Cr (VI) adsorbed at equilibrium (mg/g) and at the time t (mg/g), respectively, the K_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg min).

As shown in Table 1, the correlation coefficient R^2 of the experimental data in fitting the pseudo-first-order kinetic model is much less than 0.99, and the adsorption process does not fitted to the pseudo first order kinetic model.

The correlation coefficient of the experimental results of R^2 pseudo-second order kinetic model in Table 1 are close to 1,indicating that the adsorption process fit pseudo-second order kinetic model well.And shown that the adsorption process is mainly rely on chemical adsorption.

Tab 1 Relevant parameters of Kinetic equation on the adsorption of Cr(VI) by Fe-Z

Adsorption temperature	pseudo-first order kinetic model			pseudo-second order kinetic model		
	q_e	K_1	R^2	q_e	K_2	R^2
25℃	0.5860	0.006	0.7482	16.606	0.0673	0.9995
35℃	0.5534	0.005	0.7439	16.606	0.0652	0.9997
45℃	0.5746	0.005	0.7489	16.645	0.0649	0.9998

Adsorption isotherm. In order to optimize the design of an adsorption system for adsorption Cr(VI) by Fe-Z, to establish the most appropriate balance curve correlation is very important. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. Experimental conditions: Fe-Z dosage is 0.1g, pH is 3, adsorption time is 12h, and initial concentration of Cr (VI) is 20, 50, 100, 150, 200, 250mg/L, respectively, at T=25, 35, 45, respectively.The data were fitted with the Langmuir equation and the Freundlich equation.

The Langmuir equation is based on a kinetic approach and assumes a uniform surface, a single layer adsorbed material at constant temperature. The Langmuir equation as follows:.

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (4)$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed (mg/g), K_L and q_m (Langmuir constants) are the affinity of adsorbent towards adsorbate and monolayer adsorption capacity, respectively.

A plot of C_e/q_e against C_e (Fig. 2) gave a fitted curve, and generates Langmuir constants from the plot of sorption data (Table 2). Can be seen from Table 2 and Figure 2, the temperatures are 25°C, 35°Cand 45°Cconditions, the correlation coefficients are 0.99702, 0.9919, and 0.98801, respectively, the correlation coefficient is close to 1.The adsorption of Cr (VI) on the Fe-Z surface is monolayer adsorption, a chemical adsorption.

Freundlich isotherm. The Freundlich isotherm model is derived by assuming the non-uniform surface of the adsorption theory of the relationship between adsorption capacity and adsorption heat. The nonlinear form of the Freundlich model can be expressed as follows:

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed (mg/g), K_F and n (Langmuir constants) are the adsorption capacity of the adsorbate and gives the information on favorability of the adsorption process, respectively.

A plot of $\ln q_e$ against $\ln C_e$ (Fig. 3) gave a fitted curve, and generates Freundlich constants from the plot of sorption data (Table 2). Can be seen from Table 2 and Figure 3, the temperatures are 25 °C, 35 °C and 45 °C conditions, The R^2 obtained by Freundlich isothermal model is less than 0.97, and the correlation of reaction fitting is not significant. The 1/n calculated by isothermal equation is less than 1, which shows that the adsorption process is easy to reaction.

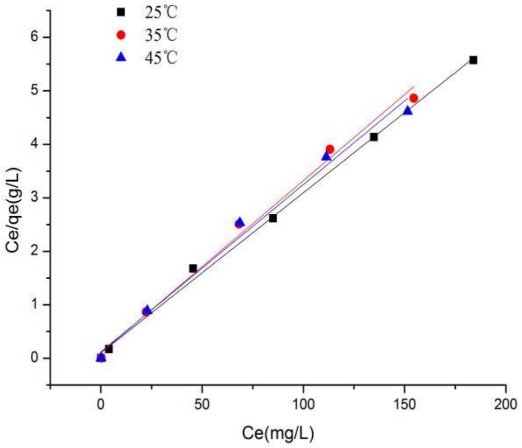

Fig.2 Langmuir plots for adsorption of Cr(VI) by Fe-Z

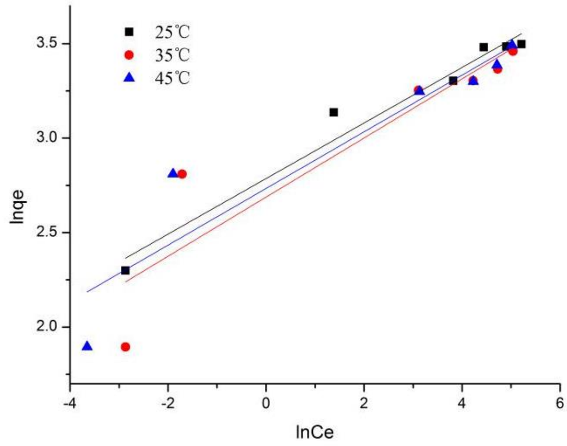

Fig.3 Freundlich plots for adsorption of Cr(VI) by Fe-Z

Tab.2 Relevant parameters of isothermal equation on the adsorption of Cr(VI) by Fe-Z

Adsorption temperature	Langmuir			Freundlich		
	q_m	K_L	R^2	1/n	K_F	R^2
25°C	33.38898	0.297595	0.99702	0.14699	16.21554	0.96151
35°C	31.0752	0.310498	0.9919	0.15645	14.69813	0.79869
45°C	31.95909	0.260468	0.98801	0.14994	15.38649	0.84373

4. Conclusions

This study shows that ferric chloride modified zeolite is an effective adsorbent for the removal of Cr (VI) from the aqueous solution. It is evident that the maximum amount adsorbed of Cr (VI) is observed at pH 3. Kinetic studies of Cr (VI) on Fe-Z were performed based on pseudo-second-order model. The adsorption experimental results were analyzed by using the Langmuir and Freundlich isotherms models.

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