ATLANTIS PRESS
Advances in Engineering Research, volume 94
2nd International Conference on Sustainable Development (ICSD 2016)

Removal of Cr^{3+} in Aqueous Solutions by Zeolite A/Activated Carbon Composite Synthesized from Elutrilithe

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***Abstract*—In this work, the zeolite A/activated carbon (A/AC) composite was synthesized from elutrilithe and pitch, and the removal of Cr^{3+} from aqueous solutions has been evaluated. The effects of batch experiment conditions, such as solution pH, contact time and initial concentration, on Cr^{3+} adsorption performances were investigated. The results demonstrated A/AC exhibited effective adsorption ability for the removal of Cr^{3+} in comparison with elutrilithe. The adsorption isotherm data could be better fitted by Langmuir-Freundlich model. The fitted data shows that the adsorption surface is heterogeneous. Removal of Cr^{3+} contributes to the ion exchange of zeolite and electrostatic adsorption of activated carbon.**

Keywords-Chromium removal; Adsorption; Zeolite A/ activated carbon; Isotherms

I. INTRODUCTION

Heavy metals release in industrial wastewater is very harmful to plants, animals and human beings because that these elements are difficult to be biodegraded in the environment and may accumulate in living organisms [1]. In recent years, the removal of toxic heavy metal ions from industrial and sewage has been extensively studied. Trivalent chromium ion, as one of the most frequently present heavy metals, is arising from many chemical industrial processes [2] and commonly related to cytotoxicity and carcinogenicity. Hence, it is necessary to reduce chromium concentration from wastewaters before being released to the environment.

Among the many methods available to remove heavy metal ions from wastewater, the adsorption method is one of the most effective techniques for removing the heavy metal from wastewater. Many adsorbents for chromium removal have being made, such as activated carbon [3, 4], resins [5] and zeolites [6, 7]. Although activated carbon is widely used adsorbent because of its large specific surface area, adequate surface functional groups and high adsorption ability [8], it is expensive and difficult to regenerate after the adsorption process. From an economic point of view, this has encouraged research into using low-cost adsorbent materials to purify contaminated water. Natural zeolites, which have the lower cost and good ion exchange ability, are employed as the promising adsorbents [9]. In order to take full advantage of the merits of these two materials, our group successfully synthesized zeolites/activated carbon composite by using the dumped elutrilithe [10] and these prepared materials were applied in the wastewater treatments such as phenol adsorption by zeolite X/activated carbon composite [11] and Ni^{2+} removal by zeolite A/activated carbon composite [12].

The present work focused on utilizing zeolite A/ activated carbon composite prepared from elutrilithe and pitch to remove Cr^{3+} ions from aqueous solutions. Batch experiments were carried out to investigate the effect of various operation conditions such as the pH, initial concentration and adsorption time on the adsorption process. Adsorption isotherm was analyzed and fitted with different models.

II. EXPERIMENTAL

The zeolite A/activated carbon composite (A/AC) was prepared by using elutrilithe as raw material according to the method described in our previous work [10]. The mixture of elutrilithe and 25 wt.% of pitch was used as starting material and extruded into a cylinder (3.0 mm × 6.0 mm). The extrudate was carbonized by N_2 and then activated using CO_2 at 850 °C for 12 h. The resulting activated sample was hydrothermally treated in a Teflon lined autoclave containing NaOH solution at 60 °C for 6 h, followed by 90 °C for 12 h under stirring. The obtained composite was zeolite NaA/activated carbon composite, which could be converted to zeolite CaNaA/activated carbon composite by an ion-exchange process containing $CaCl_2$ solution.

0.4 g of prepared zeolite A/activated carbon composite was added into a vessel, containing 150 mL of Cr^{3+} solution at 10~90 mg/L concentration. The mixture solution was stirred for certain time and then centrifuged to obtain the upper solution. The Cr^{3+} solution was analyzed by potassium permanganate oxidation-diphenylcarbohydrazide spectro photometric method. The amount of Cr^{3+} adsorbed on the prepared material was defined as adsorption amount.

The equilibrium adsorption amount of Cr^{3+}, q_e (mg/g), was evaluated using the following expressure:

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

The equilibrium adsorption data was fitted by Langmuir, Freundlich and L-F isotherm equations.

The Langmuir isotherm assumes that the adsorption takes place at specific homogeneous sites on the surface of the adsorbent and form a monomolecular adsorbed layer, which can be expressed as the following formula [13]:

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$

Where q_m (mg/g) and b are the Langmuir constants related to the maximum adsorption capacity of the adsorbent and energy of adsorption, respectively.

The Freundlich isotherm is often used to describe the adsorption of inorganic and organic components in solution [14]. It provides an empirical isotherm, which assumes that non-ideal sorption takes place on a heterogeneous surface with different adsorption energy and characters. It is represented as:

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

Where K_F (mg/g)(L/mg) and 1/n are Freundlich constants, related to adsorption capacity and adsorption intensity, respectively.

L-F isotherm proposed by Sips [15] is a combined form of Langmuir and Freundlich expressions. It can be used for predicting the heterogeneous adsorption systems witha finitelimitof the rising adsorbate concentration when the pressure is sufficiently high. It is expressed as:

$$q_e = q_m \frac{(bC_e)^{(1/n)}}{1 + (bC_e)^{(1/n)}}$$

Where q_m is the saturation adsorption capacity, parameter b represents the interaction between adsorbate and adsorbent, and n could be regarded as the parameter characterizing the system heterogeneity.

III. Results and Discussion

A. Characteristics of Adsorbents

The XRD patterns of the samples are demonstrated in Fig. 1. From Fig. 1, it can be seen the composite A/AC shows the typical X-ray diffractogram of a well-crystallized zeolite 4A, which indicates the zeolite A/activated carbon composite is successfully obtained. It is obviously that the relatively intensities of XRD peaks of the composite A/AC become weaker than those of pure zeolite 4A, because of the existence of activated carbon in the composites.

The pore structure parameters of the samples are listed in Table I. As is known, N_2 adsorption–desorption isotherms of zeolite 4A demonstrated type I isotherm, due to the sole micropores of zeolite 4A, but the isotherms of AC and A/AC present both type I and IV isotherm (not listed), corresponding to hierarchical porosity ranged from micro-pore, meso-pore to macro-pore. The surface areas are 247 m^2/g and 662 m^2/g for AC and A/AC, respectively. In comparison with the activated sample AC, N_2 adsorption capacity and the pore volume of A/AC increased obviously, attributing to aluminosilicate in the activated sample was extracted from the mixture to form zeolite 4A by the hydrothermal crystallization.

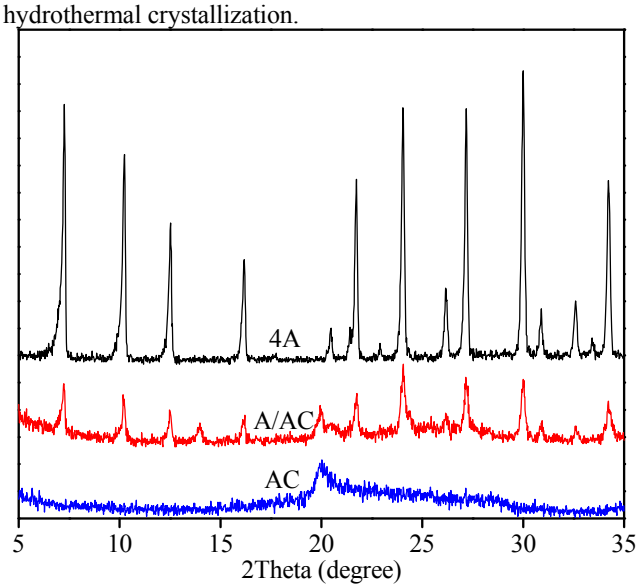

Figure 1. XRD patterns of the samples.

The SEM images of these samples are given in Fig. 2. Fig. 2A shows a typical LTA single-crystal morphology and the crystals are in cubic shapes with truncated edges [16]. A/AC synthesized can be clearly seen in Fig. 2B, Fig. 2C displays that AC has a porous structure. The SEM images confirm the existence of zeolite 4A crystals in A/AC, and crystal aggregates have been covered by activated carbon. Moreover, the surface of activated carbon in A/AC is looser and more porous compared to AC.

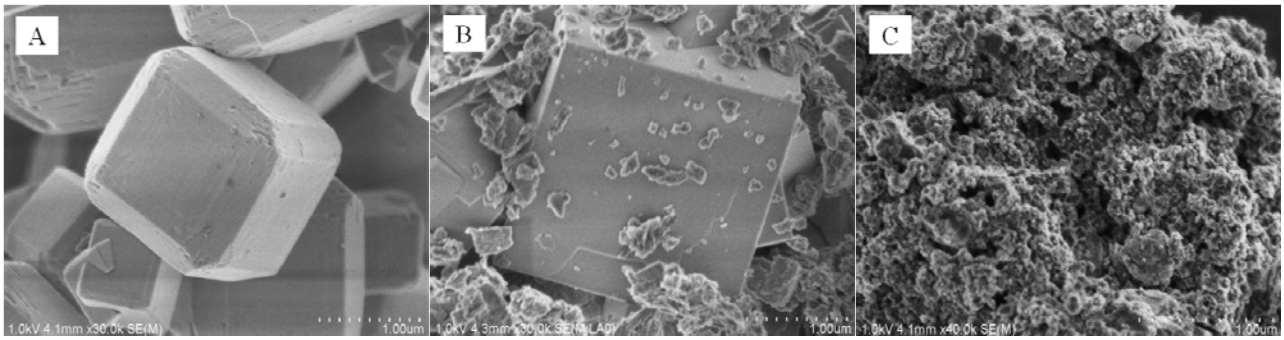

Figure 2. SEM images of the samples A: zeolite 4A; B: A/AC; C:AC.

B. *Effect of the Solution pH*

In aqueous solution, the pH plays an important role on Cr^{3+} adsorption, since the solution pH determines the surface charge of the adsorbents. The adsorption capacities of Cr^{3+} in the pH range of 2~5.5 were performed and illustrated in Fig. 3A and the concentration of Cr^{3+} in the initial solution was 21.5 mg/L. It can be observed that the adsorption capacity of Cr^{3+} is poor in low pH solution and the adsorption amount obviously enhanced with increasing pH value of the solution. When the solution was 4.2, the prepared material obtained the maximal adsorption amount of Cr^{3+}. This was assignable for the competitive adsorption of H^+ and Cr^{3+} on the A/AC surface and the large amount of H^+ limited the exchange capacity for Cr^{3+}. At higher pH, the adsorption process was restrained by enhanced hydrolysis degree of Cr^{3+}. So the prepared material could obtain the best adsorption amount of Cr^{3+} when the pH of the solution was about 4.2.

C. *Effect of Adsorption Time*

The adsorption efficiency is a very important criterion to the adsorbed substance. A solution with 21.1 mg/L was used as the original simulated solution and the effect of adsorption time on the adsorption amount was presented in the Fig. 3B. It is evident that the adsorption amount gradually increased as the extension of stir time. The adsorption equilibrium of A/AC was obtained with a max adsorption amount of 4.9 mg/g, when the A/AC was added into the solution for 2 h, which hardly changed as longer adsorption time. It also proved that the prepared A/AC composite had stable adsorption to Cr^{3+}.

D. *Effect of Initial Concentration of Cr^3*

The effect of initial concentration of Cr^{3+} on the adsorption amount of A/AC material and the quantity of Cr^{3+} removed per gram of A/AC material were presented in Fig. 3C. In the 150 mL solutions with 0.4 g of A/AC, as the concentration of Cr^{3+} in the water increased from 10 to 80 mg/L, the amount of Cr^{3+} removed per gram increased drastically, while the removal percentage by A/AC decreased. It was proposed that the theoretical max adsorption amount of Cr^{3+} was much larger than the actual adsorption amount, so the A/AC material had enough capacity to capture the Cr^{3+} in the higher initial concentration solutions. However, the removal percentage was limited by the adsorption equilibrium in the A/AC material at higher Cr^{3+} concentration.

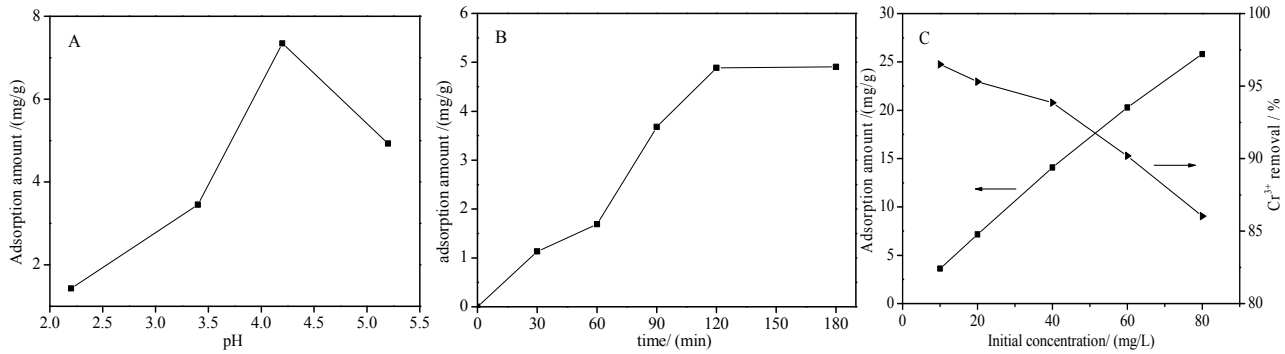

Figure 3. Effect of initial pH, adsorption time and initial concentration on Cr^{3+} adsorption.

E. Adsorption Isotherm

Fig. 4 showed the equilibrium isotherm data for Cr^{3+} uptake onto the A/AC material, when the adsorption of Cr^{3+} reached the adsorption equilibrium. Three isotherm models: Langmuir, Freundlich and Langmuir-Freundlich (L-F) were applied to fit the experimental data. The isotherm parameters and the values of the correlation coefficient (R^2) were given in Table II. According to the results, the values of R^2 were higher for L-F equation and Langmuir equation than that of Freundlich equation, indicating that L-F equation and Freundlich equation gave the better fitting in the adsorption of Cr^{3+} on A/AC. The L-F constant *n* (1.159) was closer to 1 indicating that the surface of A/AC is heterogeneous. It was mainly due to the adsorption material was a composite which was composed of zeolite and activated carbon. Thus, the surface of A/AC contained different functional groups.

IV. CONCLUSION

The results obtained in this study clearly demonstrated the composite A/AC, prepared from waste elutrilithe, was a low-cost and effective adsorbent for Cr^{3+} removal from aqueous solutions. The influence of process parameters, such as effect of pH, contact time and initial concentration, were investigated. Moreover, in comparison with Langmuir and Freundlich equations adsorption isotherm, the equilibrium adsorption data were better described by Langmuir-Freundlich equations, indicating the surface of A/AC contains different functional groups. This study highlights that the zeolite A /activated carbon may be used successfully as an alternative adsorbent for removal of Cr^{3+} from wastewater.

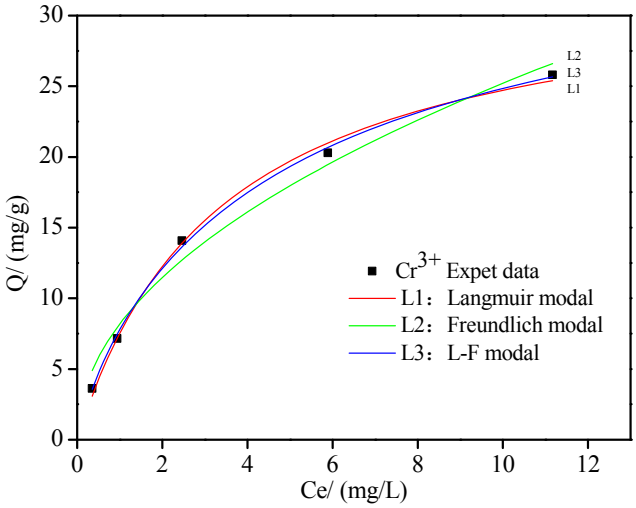

Figure 4. Adsorption isotherms of Cr^{3+} on A/AC.

TABLE I. PORE STRUCTURE PARAMETERS OF THE SAMPLES.

Samples	S_{BET} (m^2/g)	S_{ext} (m^2/g)	S_{mic} (m^2/g)	V_{mic} (cm^3/g)	V_t (cm^3/g)
A/AC	662	91	571	0.24	0.36
AC	247	34	213	0.13	0.19

TABLE II. ISOTHERM ADSORPTION EQUATIONS OF CHROMIUM ONTO A/AC COMPOSITE MATERIAL

Langmuir	R^2	Q_{max}	b_1	-
	0.9971	33.15	0.293	-
Freundlich	R^2	k	-	n_1
	0.9836	8.174	-	2.041
L-F	R^2	Q_{max}	b_2	n_2
	0.9987	38.21	0.255	1.159

ACKNOWLEDGMENT

This work is supported by the National Science Foundation of China (NSFC, No. 51204120, 51579168, 51409184), Scientific and technological project of Shanxi Province (No. 20140311016-6), Natural Science Foundation of Shanxi (No.2014021014-1).

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