A preparation method for the treatment of Cr(VI) composite adsorbent Ca-AC

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Abstract. The effects of weight ratio of Eucalyptus and $CaCl_2$, carbonization temperature and carbonization time on the composite adsorbent (Ca-AC) were studied. The best conditions for composite adsorbent (Ca-AC) were obtained: the weight ratio of $CaCl_2$ to the eucalyptus sawdust was 2:1; the carbonization temperature was 650 ℃; the carbonization time was 80 min. The Ca-AC yield reached 28.88%; the Cr(VI) adsorption value was 131.03 $mg \cdot g^{-1}$. The morphology and structure of the adsorbents were characterized. The results showed that the specific surface area of Ca-AC can reach 713 $m^2 \cdot g^{-1}$. The carboxyl, hydroxyl, lactones groups and amino could be determined on the activated carbon surface.

1 Introduction

Chromium is one of the harmful heavy metals to the human body. The presence of high levels of chromium in the environment may cause long-term health risks to humans and ecosystems[1,2]. Adsorption method is generally known to be one of the most effective and popular techniques for chromium removal and recovery from wastewater[3,4]. Metal ions are selectively adsorbed onto the adsorbent surface from wastewater with the quantity of the removed pollutant depending on the adsorption capacity of the adsorbent.

To solve the problems of swelling, agglomeration and performance reduction of $CaCl_2$ during the process of ammonia adsorption and effectively remove the toxic heavy metals from wastewater, the eucalyptus and $CaCl_2$ are used as raw materials, and the method of carbonization for creating pores is used for the preparation of composite adsorbent[5]. Studies concerning the effects of the weight ratio, carbonization temperature and carbonization time are presented and discussed. The orthogonal test data were analyzed to determine the best preparation conditions of composite adsorbent.

2 Experimental

2.1 Preparation of the adsorbent

The Guangxi Guilin Farm, China, provided the raw material, eucalyptus sawdust, with particles of 0.25~0.42 mm selected by sieving. The following chemicals were purchased and used without further purification: $CaCl_2$, I_2, KI, $Na_2S_2O_3 \cdot 5H_2O$, soluble starch, methylene blue, $K_2Cr_2O_7$, acetone, reagent grade, H_2SO_4, H_3PO_4, HCl, and NaOH.

The eucalyptus sawdust (10.00 g) with particle size between 0.25 mm and 0.42 mm was mixed with varying amounts of $CaCl_2$ (20.00, 30.00, 40.00, 50.00 g) in a ceramic crucible with a lid. The blending material liquid was dipped in a thermostat oscillator at 80 for 5 h (vibration velocity is 120 $r \cdot min^{-1}$) and then heated in a thermostatic drying oven until the water completely dried. The samples produced from the dipping process was heated and carbonized in a muffle furnace pre-heated to a specified temperature (500, 600, 700, 800 ℃) and maintained at this temperature for the specified time (40, 60, 80, 100 min). After cooling, the resulting mixture was soaking in the hydrochloric acid(10%) for a period of time(12 h) and then washed with distilled water to pH=7.0. The activated carbon was separated using a filtering method, dried at 110 ℃ for 24 h and stored in tightly closed bottles until further analysis.

The total surface area was determined by specific surface and porosity analyzer (USA, NOVAe1200). Fourier transform infrared spectrometer (USA, Thermo Nexus 470FT-IR) was used to characterize the surface functional groups of sample.

2.2 Analytical methods

The Ca-AC yield using the following equation:

$$Yield\ (\%) = (A/B) \times 100\% \quad (1)$$

Where A is the weight of the composite absorbent and B is the weight of dried eucalyptus.

The Cr(VI) adsorption value was determined by 1.5diphenylcarbohydrazide spectrophotometric method (GB7467-87 standard)

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2.3 Orthogonal test

An L9(3^4) orthogonal array with four operational parameters was used to evaluate corresponding optimal values. These parameters, their range and levels are summarized in Table 1.

Table 1. The factors and levels in orthogonal experiment.

Levels	Symbol A	Symbol B	Symbol C
	weight ratio	carbonization temperature (°C)	carbonization time (min)
1	2:1	500	40
2	3:1	600	60
3	4:1	700	80

3 Results and discussion

3.1 Effect of weight ratio and carbonization temperature on adsorption performance

At the carbonization time of 60 min, the effect of weight ratio and carbonization temperature on adsorption performance is shown in Figs. 1-2.

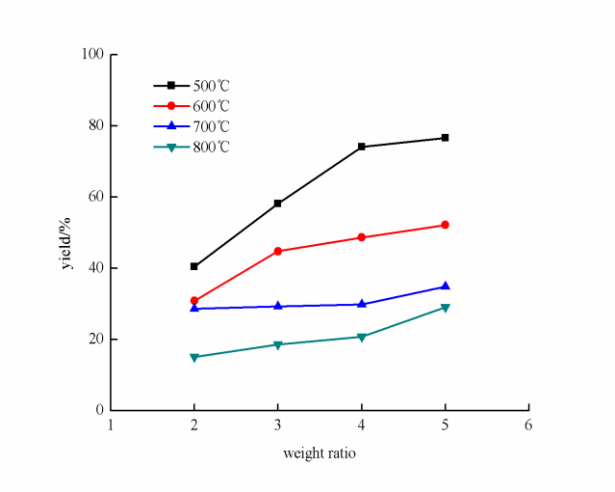

Figure 1. Effect of weight ratio and carbonization temperature on yield

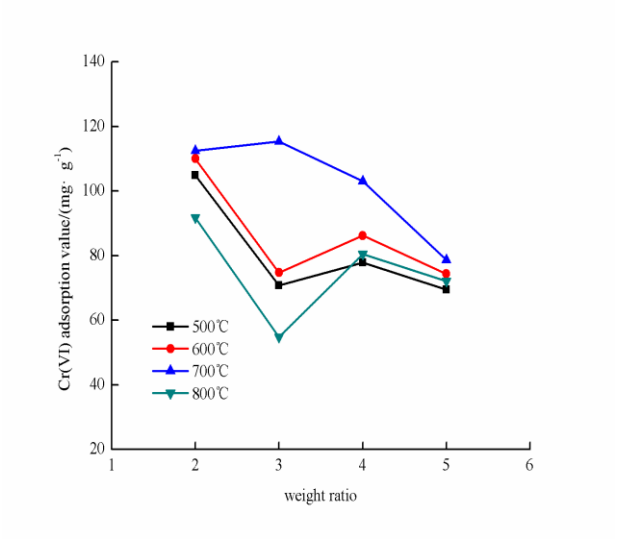

Figure 2. Effect of weight ratio and carbonization temperature on Cr(VI) adsorption value

From Figure 1, it is noted that the higher the carbonization temperature was, the less the yield was, and the yield could be increased by enhancing the weight ratio. At high temperature, the water and other volatile substances in the sample had been removed during the process of carbonization, and the higher the carbonization temperature was, the more the ignition lost was. And the $CaCl_2$ will not reduce in this process. However, the content of $CaCl_2$ could be increased by enhancing the weight ratio, and the higher the weight ratio was, the more the yield was.

The Figure 2 showed that the highest adsorption was found at 600~700 °C and the weight ratio of 2:1~3:1. The melting point of $CaCl_2$ is 772 °C, $CaCl_2$ is liable to be sintered at higher carbonization temperature, which leads to the crystallinity increased. It can improve the content of $CaCl_2$ by using hybrid method, but $CaCl_2$ is uneven distribution in the porous media, it easy to cause inflation and agglomerate, which block pore. But micropores and mesopores are major factors in their adsorption . Therefore, the weight ratio should not be too high, the best weight ratio is 2:1 and carbonization temperature is 650 °C.

3.2 Effect of carbonization time on adsorption performance

At the carbonization temperature of 650 °C, the weight ratio of $CaCl_2$ to the timber surplus of eucalyptus was 2:1, the effect of carbonization time on adsorption performance is shown in Figs. 3-4.

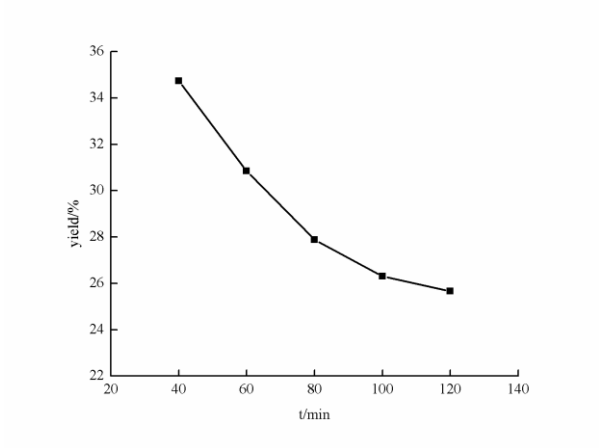

Figure 3. Effect of weight ratio and carbonization temperature on yield

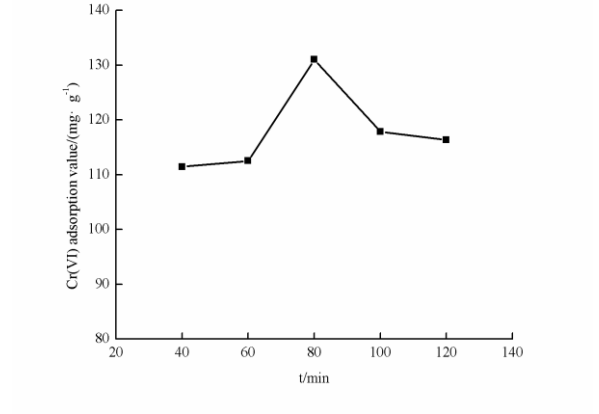

Figure 4. Effect of weight ratio and carbonization temperature on Cr(VI) adsorption value

From Figure 3, it can be seen that under the same weight ratio and carbonization temperature, the yield decreases with extending time until a stable. This is because of that, the no rules of carbon in carbon skeleton pores were selectively consumption which leads to quickly weightlessness in the initial stage. In the stable stage, the carbon of carbon skeleton was consumed, the reaction rate was slow and the weightlessness was small in a short period of time, so that the change of yield back into balance.

The Figure 4 showed that the adsorption value was rising at 40~80 min, because the formation of micropores continuously increased over time. In addition, a large number of micropores also begin to be destroyed into holes, when the carbonization time is more than 80 min, the adsorption began to decline. This is because the long carbonized time can lead to serious carbon weightlessness. If carbon skeleton have been burned, the pore which had formed will collapse. So the best carbonized time is 80 min.

3.3 Results of orthogonal experiment

The complete design matrix of the experiments and the results obtained are shown in Table 2.

Table 2. Results of orthogonal experiment.

No.	Symbol			Adsorption performance
	A	*B*	*C*	*Y* (mg·g^{-1})
1	2:1	500	40	130.09
2	2:1	600	60	110.04
3	2:1	700	80	118.03
4	3:1	600	40	88.60
5	3:1	700	60	115.43
6	3:1	500	80	105.64
7	4:1	700	40	120.67
8	4:1	500	60	77.83
9	4:1	600	80	119.28
K1	119.39	104.52	113.12	
K2	103.22	105.97	101.10	
K3	105.93	118.04	114.32	
R	16.17	13.52	13.22	

A weight ratio of activation agent to eucalyptus sawdust, *B* carbonization temperature (°C), *C* carbonization time (min), *Y* Cr(VI) adsorption value (mg·g^{-1}).

The experimental results(Table 2) show that the Cr(VI) adsorption value are large difference under different process conditions, the minimum is 77.83 mg·g^{-1}, the maximum is 130.09 mg·g^{-1}.

The concentration of Ca^{2+} on the composite adsorbent vary widely under different concentration of $CaCl_2$. However, the Cr(VI) adsorption mainly rely on the Ca^{2+} of the composite adsorbent, which can lead to Cr(VI) adsorption value vary widely.

From Table 2, it is noted that the affecting factors on Cr(VI) adsorption value followed the order: the weight ratio the carbonization temperature the carbonization time(A B C), the best conditions is A1B3C3 (2:1, 700 °C, 80 min).

3.4 Characterization of the adsorbent

3.4.1 Specific surface detection

The specific surface area of Ca-AC is 713 m^2·g^{-1} and the average hole diameter is 2.01 nm. This shows that the adsorption is mainly dependent on micropores.

3.4.2 FTIR Analysis

The FTIR spectra of the Ca-AC prepared under optimal conditions is shown in Figure 5.

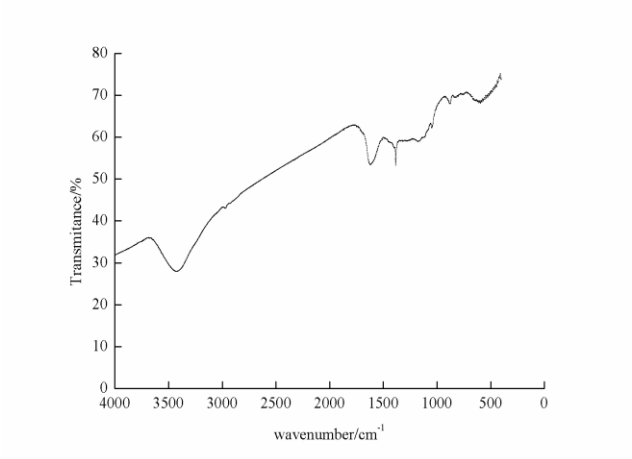

Figure 5. FT-IR spectra

It is noted that the absorption band at 3405.672 cm^{-1} is due to the O-H stretching vibration, the -NH stretching vibration absorption or carboxyl hydroxyl compounds, phenols, alcohols. The band at 1583.271 cm^{-1} is assigned to the scissoring vibration of the C=O group of lactones and C=C group of the aromatic ring skeleton. It may also be attributed either to the in-plane bending of the H-bonded hydroxyl group, an O-H deformation vibration in carboxyl groups or a C-H bending vibration[6]. The emergence of the hydroxyl group may also indicate a certain relationship in water. So the frederik southam balfour near 3400 cm^{-1} and the rush peak near 1600 cm^{-1} likely results from the peak of water. The band at 1384.639 cm^{-1} is O-H in-plane deformation vibration peak of phenolic hydroxyl[7,8]. The above analysis of the characteristic peak shows that the chemical state on the surface of Ca-AC changed during the process of carbonization. The carboxyl, hydroxyl, lactones groups and amino could be determined on the activated carbon surface.

4 Conclusions

In this study, composite adsorbent for Cr(VI) adsorption has been successfully from eucalyptus sawdust with $CaCl_2$ as load agent.

The best conditions for Ca-AC adsorbent were obtained: the carbonization temperature was 650 °C; the weight ratio of CaCl2 to eucalyptus sawdust was 2:1; the carbonization time was 80 min. The Ca-AC yield reached 28.88%; the Cr(VI) adsorption value was 131.03 $mg \cdot g^{-1}$.

The morphology and structure of the adsorbents were characterized. The results show that the specific surface area of Ca-AC can reach 713 $m^2 \cdot g^{-1}$. The carboxyl, hydroxyl, lactones groups and amino could be determined on the activated carbon surface.

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