A method for the preparation of a compound adsorbent for Eucalyptus and CaCl₂

Shen Liu¹, Zhaoju He¹,³, Minjie Qin¹, Li Zhu¹,³, Yanqin Lu¹,²* Yanqin Lu¹,²*
¹ College of Environmental Science and Engineering, Guilin University of Technology, Guilin 541004, China
² Guangxi Colleges and Universities Key Laboratory of Heavy Metal Pollution Prevention Theory and Technology, Guilin 541004, China
³ Shenzhen Shenshui Water Resources Consulting Co., LTD, Shenzhen 518003, China
⁴ Guangxi Eco-engineering Vocational and Technical College, Liuzhou 545005, China
*Corresponding author: E-mail: luyanqin@glut.edu.cn; Tel: +86 13807736423; Fax: +86 773 5895330

Abstract. In this study, composite adsorbent of Eucalyptus and CaCl₂ has been prepared by carbonation method. The effects of the weight ratio, carbonation temperature and carbonation time were studied. The best conditions for composite adsorbent (Ca-AC) were obtained: the carbonation temperature was 650 °C; the weight ratio of CaCl₂ to the eucalyptus sawdust was 2:1; the carbonation time was 80 min. the iodine adsorption value was 529 mg·g⁻¹; the methylene blue adsorption value was 98.52 mg·g⁻¹; After carbonation, the activated carbon surface is smooth, no sediment, and filled with different size and shape of pore structure, the size and quantity are increased. The feasibility and characteristics of the preparation of Eucalyptus and CaCl₂ composite adsorbents by carbonization were verified by experiments.

1. Introduction
In recent years, several research have been study on the new type activated carbon using plant as raw material [1,2]. Eucalyptus is a kind of ideal adsorbent material on account of growth speed, high wood density and different scale of ordered porous special anatomical structure [3,4]. Activated carbon modified methods have physical activation method, chemical activation method and the load of metal ions [5]. It can improve the adsorption performance through loading the metal cation Ca²⁺ to the surface of activated carbon. In addition, CaCl₂ is a kind of chemical adsorbent, which can adsorb ammonia gas and other pollutants.

2. Methods

2.1 Preparation of the adsorbent

2.1.1 Materials
The following chemicals were used without further purification: CaCl₂, I₂, KI, Na₂S₂O₃·5H₂O, soluble starch, methylene blue, K₂Cr₂O₇, acetone, reagent grade, H₂SO₄, H₃PO₄, HCl, and NaOH. The raw
material of eucalyptus sawdust provided by the Guangxi Guilin Farm, China, with particles of 0.25~0.42 mm selected by sieving.

2.1.2 Making method
The 10.00g eucalyptus sawdust and different quantities of CaCl₂ (20, 30, 40, 50 g) were put into the cone bottle, and mixed with 100mL demonized water. The mixture was dipped in a thermostat oscillator at 80 °C for 5 h and vibration velocity is 120 r·min⁻¹. And the sample heated in a thermostatic drying oven until the water completely dried. in a muffle furnace, from room temperature to specified temperature (500, 600, 700, 800 °C (heating rate is 10°C·min⁻¹)) and maintained at this temperature for the specified time (40, 60, 80, 100 min). After cooling, the mixture was soaking in the hydroelectric acid(10%) for more than 12 hours and then washed with demonize water to pH=7.0. Separation of activated carbon by filtration, bake the washed sample in a thermostatic drying oven at 110 degrees to constant weight (about 12 h) and stored in tightly closed bottles until further analysis.

Scanning electron microscope (Japan, JSM-6380LV) was used to analyzed the surface morphology and distribution of samples. Microcrystalline structure was analyzed by powder X-ray diffraction (Germany, D8ADVANCE), and the scan range is 5~80°(2θ), CuKa as the radiation source, the wavelength is 0.15405 nm.

2.2 Analytical methods
The iodine adsorption value was determined by test methods of wooden activated carbon –Determination of iodine number (GB/T12496.7-1990 standard). The methylene blue adsorption value was determined by spectrophotometric method (GB/T12496.10-1999 standard).

2.3 Orthogonal test
According to the results of single factor experiment, three single factors of A, B and C were optimized orthogonal. Each factor was selected 3 levels. These parameters, their range and levels are summarized in Table 1.

| Levels | Symbol A weight ratio | Symbol B Carbonation temperature (°C) | Symbol C Carbonation 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 carbonation temperature on adsorption performance
The effect of carbon 60 minutes on absorption under different weight ratio and temperature condition is shown in Figs. 1-2.
The Figs. 1-2 showed that the highest adsorption was found the weight ratio of 2:1. When the weight ratio over 2:1, CaCl₂ excessively activates the sawdust of Eucalyptus, resulting in the continuous expansion of the micro-porous structure, the destruction of the micro-porous structure group and the decrease of the adsorption properties.

In a certain temperature range, the higher activation temperature is beneficial to the adsorption properties of the products. Because the higher temperature is beneficial to the production of rich pore structure, but the excessive activation temperature can ablate the pore structure into large void. And melting point of CaCl₂ is 772 °C, CaCl₂ is liable to be interbreed at higher carbonation temperature, which leads to the crystallization increased. Therefore, the carbonation temperature should not be too high, the best weight ratio is 2:1 and carbonation temperature is 650 °C.

3.2 Effect of carbonation time on adsorption performance

At the carbonation temperature of 650 °C and the weight ratio of CaCl₂ to the eucalyptus sawdust was 2:1, the effect of carbonation time on adsorption performance is shown in Figs. 3-4.

The Figs. 3-4 showed that the adsorption value was rising with the increase of activation time. Maximum adsorption at 80 mins, this is mainly because the activation time of 40~60 mins is shorter and the activation is not fully carried out. When the carbonation time is more than 80 mins, the adsorption began to decline, 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 mins.

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

| No. | Symbol | Adsorption performance |
|-----|--------|------------------------|
|     | A      | B          | C  | \(Y(\text{mg}\cdot\text{g}^{-1})\)  |
| 1   | 2:1    | 500        | 40 | 77.95 |
| 2   | 2:1    | 600        | 60 | 72.38 |
| 3   | 2:1    | 700        | 80 | 96.52 |
| 4   | 3:1    | 600        | 40 | 66.72 |
| 5   | 3:1    | 700        | 60 | 83.90 |
| 6   | 3:1    | 500        | 80 | 66.53 |
| 7   | 4:1    | 700        | 40 | 84.00 |
| 8   | 4:1    | 500        | 60 | 59.73 |
| 9   | 4:1    | 600        | 80 | 82.63 |

\(K_1\) 82.29  68.07  76.23  
\(K_2\) 72.38  73.91  72.00  
\(K_3\) 75.45  88.14  81.89  
\(R\) 9.90  20.07  9.89  

\(A\) weight ratio of activation agent to eucalyptus sawdust, \(B\) carbonation temperature (°C), \(C\) carbonation time (min), \(Y\) methylene blue adsorption value (\(\text{mg}\cdot\text{g}^{-1}\)).

The experimental results (Table 2) show that the methylene blue adsorption value are large difference under different process conditions, the minimum methylene blue adsorption value is 59.73 \(\text{mg}\cdot\text{g}^{-1}\), and the maximum is 96.52 \(\text{mg}\cdot\text{g}^{-1}\). The causes of the above phenomenon is that, the number of micro-pores and mesomorph of composite adsorbents were similar under different preparation condition.

From Table 2, it is noted that the affecting factors on methylene blue adsorption value followed the order: the carbonation temperature the weight ratio the carbonation time (\(B\ A\ C\)), the best conditions is \(B3A1C3\) (700 °C, 2:1, 80 min).

3.4 Characterization of the adsorbent

3.4.1 Surface morphology
Scanning electron microscope was employed to observe the surface physical morphology of the adsorbent. The SEM micrographs of raw material and Ca-AC are shown in Figure 5.
From Figure 5, it is noted that the activated carbon structure is still consistent with the eucalyptus raw material structure after carbonized, which illustrates that carbonation had not make a difference to eucalyptus fibre skeleton.

The Figure 5(a) shows the activated carbon produced a part of the new hole after activation, the white part of hole wall on the activated carbon is ash which generated in the process of carbonation. The Figure 5(b) shows the hole walls of Eucalyptus raw material contain lots of sediment such as water, organic matters and so on, these sediment were all removed during the process of carbonation. After carbonation, the activated carbon surface is smooth, no sediment, and filled with different size and shape of pore structure, the size and quantity are increased. Therefore, the specific surface area of Ca-AC is greatly increased after carbonized, making the contact area between adsorbent and adsorb significantly improved, which provides a more adsorption and improve the adsorption performance.

3.4.2 Micro crystalline structure analysis

The Figure 6 shows that there is a large wide peak namely amorphous diffraction peak (002) between 20° and 30°, which belongs to the amorphous structure. Between 40° and 50°, there is a medium width peak namely crystal plane diffraction peak (100), which belongs to the graphite structure. These characteristic peak shows that the composite adsorbent Ca-AC is amorphous carbon, but has the trend of local graphite.

4. Summary

In this study, composite adsorbent of eucalyptus and CaCl₂ has been successfully prepared with carbonation and activation method

The best conditions for Ca-AC adsorbent were obtained: the carbonation temperature was 650 °C; the weight ratio of CaCl₂ to eucalyptus sawdust was 2:1; the carbonation time was 80 min. The iodine
adsorption value was 529 mg·g⁻¹; the methylene blue adsorption value was 98.52 mg·g⁻¹. After carbonation, the activated carbon surface is smooth, no sediment, and filled with different size and shape of pore structure, the size and quantity are increased.

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