Preparation of activated carbons from a kind of Chinese herbal medicine wastes by phosphoric acid and CO$_2$ activation

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Abstract. The effects of parameters on the adsorption capacity of activated carbons (AC) prepared from Chinese Herbal Medicines Wastes (CHMWs) by phosphoric acid and CO$_2$ activation were studied. Response surface methodology (RSM) was used to optimize the process parameters for preparing activated carbon from CHMWs. The results showed that the optimal conditions were as follows: impregnation ratio of 2.61, activation temperature of 700 $^\circ$C, activation time of 2.5 h and the CO$_2$ flow rate was 50mL/min. The adsorption value of iodine and methylene blue of the resultant activated carbon was 626.83 mg/g, 278.99 mg/g, respectively. The Activated Carbon prepared from Chinese Herbal Medicines Wastes (CHMWs) shows high adsorption capacity and well-developed pore structure.

1. Introduction
Chinese herbal medicine wastes (CHMWs) are the by-product of Chinese medicine industry, commonly discarded as a waste that have potentially harmful to the environment [1]. Hence, upcycle of CHMWs is of significance based on the environmental and economic concerns [2].

Activated carbon (AC) is a carbon-containing material with abundant pores, large specific surface area, and strong adsorption ability [3]. Converting the CHMWs into valuable activated carbon is better ideas. However, little information regarding the activated carbon prepared from CHMWs is available.

The study is to evaluate the feasibility of preparing activated carbon from a kind of CHMWs. Phosphoric acid and CO$_2$ were selected as the activation agent. The effects of the process parameters, such as activation temperature, impregnation ratio and activation time and the flow rate of CO$_2$ on absorption characteristics of prepared activated carbon were evaluated. In addition, response surface methodology (RSM) was used to optimize the preparing conditions.

2. Experimental procedure

2.1. Material
A kind of CHMWs from *Evodia rutaecarpa* was obtained from Lishizhen Medical group in Hubei, China. The CHMWs were dried at 80 $^\circ$C, and then ground and sieved by a 20 mesh sieve (approximate 0.9mm).

2.2. Preparation and characterization of activated carbon
The CHMWs were weighed, mixed with phosphoric acid solution and continuously stirred for 2h, the mixtures were dehydrated at 105 $^\circ$C for 24h, and pyrolyzed in a tubular furnace under nitrogen flow.
When temperature reaches designed value, the sweep gas was changed from N\textsubscript{2} to CO\textsubscript{2}. The resultant activated carbon was firstly washed with 1M NaOH solution (90℃), and then with distilled water until neutral pH, finally dried at 105℃ for 12h and the yield of activated carbon was weighed.

The adsorption capacities of activated carbon were characterized by the adsorption values of iodine and methylene blue (GB/T12496.8-1999, GB/T12496.10-1999, respectively). The surface morphology, specific surface area of activated carbon were measured by scanning electron microscopy (SEM), nitrogen adsorption at 77K (Micromeritics ASAP2020), respectively.

3. Results and discussion

3.1. Effect of impregnation ratio

Figure 1 shows the effect of impregnation ratio on adsorption capacity of AC prepared from CHMWs. It can be seen that the impregnation ratio influenced the adsorption capacity of AC greatly. The iodine adsorption value increased firstly and then decreased with increase impregnation ratio. However, the methylene blue adsorption value showed a continuous increase. This was attributed to that the activation reaction was accelerated with the increase of impregnation ratio. As a result, some micro pores of AC were expanded to mesopores when the content of phosphate increased [4]. Form the above analysis, it shows that the optimal impregnation ratio for preparing AC was about 2.

![Figure 1. Effect of impregnation ratio on adsorption capacity of AC from CHMWs.](image)

![Figure 2. Effect of activation temperature on adsorption capacity of AC.](image)
3.2. Effect of activation temperature

Figure 2 shows the effect of activation temperature on adsorption capacity of AC. When the temperature was lower than 600°C, it can be seen that the adsorption value of iodine and methylene blue are both decreased with increase of temperature. It meant that activation temperature has a negative effect on the adsorption capacity. However, the adsorption value increased with the temperature high than 600°C. Researchers found that the adsorption performance of AC activated by phosphoric acid was the best at 400°C and the surface of AC was eroded as temperature increase [5]. Therefore, the adsorption capacity of AC was lowered with increase of activation temperature. When the activation temperature was higher than 600°C, the phosphoric acid inside the carbon skeleton was evaporated, carbon could be reacted with CO₂ and more pores were formed. As a result, the adsorption value increased.

3.3. Effect of activation time

The effect of activation time on the adsorption capacity was showed in Figure 3. It can be seen that activation time exhibited significant impact on the adsorption capacity. The adsorption value of iodine and methylene blue were increased with the increase in activation time and reached 685mg/g and 480mg/g, respectively. Studies found that the pores within the AC increased rapidly with prolonging the activation time [6]. Therefore, the result shows that the optimal AC could obtain as the activation time was longer than 2.0 h under 700°C and 2.5 h.

3.4. Effect of the flow rate of CO₂

![Figure 3. Effect of activation time on adsorption capacity of AC from CHMWs.](image1)

![Figure 4. Effect of the flow rate of CO₂ on adsorption capacity of AC from CHMWs.](image2)
Effect of the CO\(_2\) flow rate on adsorption capacity of CHMWs based AC was given in Figure 4. It clearly shows that CO\(_2\) flow rate has different effect on the adsorption of AC. When CO\(_2\) flow rate was lower than 100mL/min, the adsorption value of iodine and methylene blue were both increased continuously. However, the adsorption value began to decrease with the further increase of CO\(_2\) flow rate. Low flow rate of CO\(_2\) might be helpful for the formation of pores in AC, while high flow rate would lead to the ablation of the surface of AC and the adsorption capacity decreased. Therefore, the optimal flow rate of CO\(_2\) was determined as 100mL/min.

3.5. Response surface methodology (RSM) analysis

The RSM method was used to study the interactions between different variables on the adsorption capacity of activated carbon based on the single factor experiment. The objective of this experiment was to find out the parameters that activated carbons prepared has the optimal adsorption capacity on both iodine and methylene blue. The optimal parameters, the predicted and experimental adsorption values of iodine and methylene blue at optimum conditions and the three-dimensional response surface curves representing the interactions between impregnation ratio and activation time on iodine adsorption were given in Table 1, Figure 5, respectively. The experimental values are in good agreement with the predicted values obtained by the RSM models.

| Impregnation ratio | Activation temperature (°C) | Activation time (min) | CO\(_2\) flow rate (mL/min) | Iodine adsorption (mg/g) | Methylene blue adsorption (mg/g) |
|-------------------|-----------------------------|-----------------------|-----------------------------|--------------------------|---------------------------------|
|                   |                             |                       |                             | Pred. | Exp. | Pred. | Exp. |
| 2.61              | 700                         | 90                    | 50                          | 640.8 | 626.8 | 283.9 | 279.0 |

**Figure 5.** Effect of interactions between impregnation ratio and activation temperature on iodine adsorption.

**Figure 6.** SEM images of the activated carbon. (Magnifications: 2500×).
3.6. Characterization of the activated carbon

3.6.1. Surface morphology. Figure 6 shows the surface morphology of the AC at optimum conditions. It can be seen that numerous regular pores were formed after activation. The results indicated that the reaction between the carbon and CO₂ occurred during the activation process, which is effectively contributed to the formation of micro and mesopores.

3.6.2. Surface area and pore volume. The BET surface area, total pore volume and average pore diameter of the AC were 887.44 m²/g, 0.6 cm³/g and 3.07 nm, respectively. The datum indicated that the pores in AC were mainly mesopores, according to the IUPAC classification. The high surface area, pore volume and well developed porosity of the AC was attributed to the role of CO₂ in activation process.

4. Conclusions
The effects of the process parameters on the adsorption capacity of AC prepared from CHMWs were evaluated. By RSM, the optimum preparation conditions were impregnation ratio of 2.6, activation temperature of 700°C and activation time of 90 min, resulting in 626.8 mg/g of iodine adsorption value and 279 mg/g of methylene blue adsorption. Characterization analyses show that the AC has high surface area and well-developed porosity.

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