Optimization of H$_2$O$_2$ Modification Conditions of Bamboo-based Activated Carbon by Response Surface Methodology

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**Abstract.** Using bamboo-based activated carbon as raw materials and H$_2$O$_2$ as modifying agent to enhance the Cr(VI) adsorption efficiency. Response surface methodology based on Box-Behnken design (BBD) was applied to investigate the effects and interactions of modified temperature, solid-liquid ratio, modified time and optimize the modification conditions. The optimum modification conditions for preparing bamboo-based activated carbon were modified temperature 38°C, solid-to-liquid ratio 1:10 and modified time 2 hours. The experimental and predicated results of the Cr(VI) adsorption value were 84.21% and 85%, respectively. This indicate the reliability of the model.

1. Introduction

In recent years, the damage to water resources from the rapid development of industrial technologies has become an important factor impacting economic and social development[1]. As defined by EPA, Chromium (Cr) is on the top priority list of toxic pollutants, and has been widely used as antifouling agent in cooling towers, chrome-plating, leather tanning, pigment, textile, and wood preservation[2]. In natural aquatic environments, Cr(VI) is one of the highly toxic metals and pose a serious threat to the environment and human health. To solve this problem, various methods have been developed to improve the removal efficiency of Cr(VI) from wastewater such as adsorption, chemical reduction and precipitation, coagulation, membrane filtration, and ion exchange. Among the various remediation technologies, absorption with activated carbons(ACs) was the most common method to removal Cr(VI) from effluents because of its high efficiency and low-cost process[3].

Cause the high specific surface area and well- modified surface, activated carbons are highly effective adsorbents for eliminating heavy metals from wastewater. A variety of carbonaceous materials such as biomass and their waster have been used to prepare ACs to removal of Cr(VI), for example Rai et al. prepared mango kernel with H$_3$PO$_4$ as activating agents[2] and Siboni et al. modified holly sawdust by using formaldehyde[4] .Bamboo as a tropical plant is widely distributed in Southern Asia such as China, Thailand and Vietnam[4]. With the increase demand of bamboo-based products, great deals of bamboo wastes were left and became to an environmental issues. The conversion from bamboos waste to ACs has attracted tremendous economic and ecologic attention.

Several researchers have been focus on the development of modification process for bamboo-based ACs. Zhang et al. used bamboo as raw materials to prepare high surface area ACs by steam activation[5] and modified bamboo based ACs by using humic acid to absorbed Cr(VI) [6] or used in
drink water[7]. H$_2$O$_2$ is a strong oxidant. Liu[8] et al. used H$_2$O$_2$ modified ACs to removal atrazine from water, Gao et al. modified ACs with H$_2$O$_2$ to adsorb sulfamethoxazole and ibuprofen[9]. H$_2$O$_2$ can change the pore structure to enhance the pore volume and specific surface area, modified ACs shows a high adsorb performance.

Response surface methodology (RSM) is useful for design of the experiments, for estimation the effects and interactions of process variables, and for predict the optimum operational conditions[10-12]. RSM can decrease the required experimental data to find the best operation conditions, and has been widely used in environmental science, biotechnology and chemical engineering fields.

No reports have been found by using RSM to optimize the modification conditions for bamboo-based ACs to removal Cr(VI) from waste water. Therefore, in the present study, RSM based on Box-Behnken design (BBD) has been used to optimize the modification process and determination the effects and interactions of the modification conditions (temperature, solid-fluid ratio and time) for the desirable response variable (Cr(VI) removal ratio). The main objectives were to optimize the modification process of bamboo-based ACs and investigate the influence of process variables on Cr(VI) removal ratio.

2. MATERIALS AND METHODS

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2.1. Materials

Commercial bamboo-based activated carbon from Guangshen (Xiamen, China) was used in this study. Hydrogen peroxide and potassium bichromate were provided from Runhe (Shanghai, China). Chromium(VI) standard was purchased from Sigma-Aldrich (St. Louis, MO, USA), all used chemical reagents in this study were of analytical grade. The stock solution of 1.0mg/L Cr(VI) was prepared by potassium dichromate and deionized water.

2.2. Modification of Bamboo-based ACs

Bamboo-based ACs was washed with deionized water and dried in an oven at 80℃ overnight. The washed ACs were treated by Hydrogen peroxide under modification variables including modification temperature, modification time and solid-liquid (AC/H$_2$O$_2$ ) ratio. Then the ACs were separated and washed with deionized water until the pH constant and dried in an oven at 80℃ for 24h.

2.3. Adsorption Experiments

The adsorption experiments were performed in 250ml Erlenmeyer flasks with 100ml of stock Cr(VI) solution, 0.1g modified ACs was added into the flasks. After shaking in an incubator at 298K to reach equilibrium, the adsorbent was isolated and the concentration of Cr(VI) solution was determined by measuring with 1.5-diphenylcarbodihydrazide spectrophotometric method using a UV-vis spectrophotometer at 540nm. The calibration curve was prepared by measured of standard solution of potassium dichromate, and the adsorption efficiency of Cr(VI) on modified ACs was calculate by using the difference from Cr(VI) before/after adsorption and it was expressed by Eq. (1):

$$\text{Adsorption} = \frac{C_0 - C_e}{C_0} \times 100\%$$

Where $C_0$(mgL$^{-1}$) and $C_e$(mgL$^{-1}$) are the initial and equilibrium concentration of Cr(VI),

2.4. Characterization of ACs

The surface area and pore volume were determined by using the Brunauer-Emmet-Teller (BET). Boehm titration was performance to calculation the total acidic and basic groups.

2.5. Experimental Design
The modification process was optimization by using the response surface method (RSM). The experimental design and variances analysis were performed with Stat-Ease software (Design-Expert 8.0 version). A three-levels three-factors Box-Behnken design (BBD) was employed and to optimized the modification conditions. Three variables are presented in Table 1.

| Factor                  | unit | symbol | Coded level |
|-------------------------|------|--------|-------------|
| Modification temperature| ℃    | A      | -1 0 +1     |
| Solid-Fluid ratio       | -    | B      | 0.2 0.15 0.1 |
| Modification time       | h    | C      | 2 3.5 5     |

Each variable was determined by preliminary experiments. An analysis of variance (ANOVA) table was generated to presented the effect and interaction of factors. The significances were judged by calculating the F-value at a probabilities (P-value) of 0.0001, 0.001 and 0.05.

3. RESULTS AND DISCUSSION

3.1. Characterization

It is generally verified that the porous structure of the ACs play an important role in their absorption process. Therefore, the specific surface area and pore volumes of the bamboo-based activated carbon before and after modification with H₂O₂ were characterized using N₂ adsorption-desorption analysis. The results are presented in Table 2.

| ACs                | Specific surface area (m²/g) | Pore volumes (cm³/g) |
|--------------------|-----------------------------|----------------------|
| Before             | 867.2                       | 0.513                |
| After              | 1021.5                      | 0.602                |

Based on the results, the surface area and pore volume of modified ACs are much higher than it before. Modification with H₂O₂ can efficiently increase the porous structure performance and enhance the adsorb ability of ACs.

Total acidic and basic groups were determined by using Boehm-titration and shows in Table 3. The content of total acidic groups was increased after modification process, H₂O₂ modification shows a effective ability to enhance the acidic groups for ACs and depress the basic groups.

| ACs                | Total acidic groups (mmol/g) | Total basic groups (mmol/g) |
|--------------------|------------------------------|-----------------------------|
| Before             | 1.365                        | 0.224                       |
| After              | 1.575                        | 0.126                       |

3.2. Analysis of Variances (ANOVA) Characterization

The experiments (17 runs) were designed by using BBD method. The Adsorption of Cr(VI) in % varies between 33% and 81%, respectively.

The analysis of variance (ANOVA) shows in Table 4, the model F-value of 33.72 and P-value is lower than 0.0001, which indicates that the model terms are highly significant, and there is only a 0.01%
chance that a model F-value this large could due to noise. The P-value of factors A and A^2 are lower than 0.0001 shows highly significant effect. Values of P great than 0.0001 and less than 0.005 indicate model terms are significant, in this case B and C^2 are significant model terms. Lack of fit is determining how well the model fits the data, in this study, the Lack of fit (P>0.05) is insignificant, the response were sufficiently represented.

| Table 4 Variances analysis of the models |
|-----------------------------------------|
| source       | Sum of squares | df^a | mean square | F-value | P     |
|---------------|----------------|------|-------------|---------|-------|
| model         | 3663.50        | 9    | 407.06      | 33.72   | < 0.0001 |
| A             | 1984.50        | 1    | 1984.50     | 164.40  | < 0.0001 |
| B             | 98.00          | 1    | 98.00       | 8.12    | 0.0247 |
| C             | 50.00          | 1    | 50.00       | 4.14    | 0.0831 |
| AB            | 16.00          | 1    | 16.00       | 1.33    | 0.0287 |
| AC            | 1.00           | 1    | 1.00        | 0.083   | 0.7818 |
| BC            | 0.186          | 1    | 0.192       | 0.061   | 0.8765 |
| A2            | 1216.84        | 1    | 1216.84     | 100.80  | < 0.0001 |
| B2            | 9.47           | 1    | 9.47        | 0.78    | 0.4051 |
| C2            | 206.32         | 1    | 206.32      | 17.09   | 0.0044 |
| residual      | 84.50          | 7    | 12.07       |         |        |
| Lack of fit   | 66.50          | 3    | 22.17       | 4.93    | 0.0788 |
| Pure error    | 18.00          | 4    | 4.50        |         |        |
| Cor total     | 3748.00        | 16   |             |         |        |

^a Degree of freedom

3.3. The Effect of Modification Conditions

In order to study the effect of modification conditions, the three dimensional (3D) surface responses plots were utilized to evaluate the relationship between the modification variables and responses. Figure 1(a-c) illustrate the fitted response surface plots of A_{Cr(VI)} versus modification variables (modification temperature, solid-fluid ratio, modification time).

As show in Figure 1a, the modification temperature demonstrates quadratic effects on the response. It is observed that the A_{Cr(VI)} increase with temperature to obtain a maximum at 38°C and thereafter decrease with a further increase in temperature for a given solid-fluid ratio. Modification temperature at about 38°C is preferable for achieving a higher Cr(VI) adsorption efficiency. The increase in Cr(VI) adsorption efficiency as the modification temperature increase can be explained by the increase in specific surface area and pore volume. In contrast, the decrease in the Cr(VI) adsorption efficiency at higher temperature might attribute to the collapsing of pore structure.
Figure 1b presented the effects of modification temperature and modification time of A$_{\text{Cr(VI)}}$. As seen here, the Cr(VI) adsorption efficiency increase slightly with modification time, with modification time of about 3h, the A$_{\text{Cr(VI)}}$ reach maximum of above 81%. Followed the A$_{\text{Cr(VI)}}$ decreased with increase modification time.

The interaction between solid-fluid ratio and the modification time shows in Figure 1c. There is less interaction between solid-fluid ratio and modification time. Combine with the results of Boehm titration Table 3 and the analysis of variances Table 5, modification with H$_2$O$_2$ enhance only lightly the total acidic groups of ACs, the interaction is insignificant.

\textbf{Figure 1-a.} Response surface plots for A and B.

\textbf{Figure 1-b.} Response surface plots for A and C

\textbf{Figure 1-c.} Response surface plots for B and C

\textbf{3.4. Optimized Studies for Maximizing Cr(VI) Adsorption Efficiency}

The Optimum modification conditions of the adsorption of Cr(VI) was carried out by using the Design-Expert software. According to the results above, the optimization equation shows in follow: \[ Y=79.00+15.75A+3.50B-2.50C+2.00AB+0.50AC+0.000BC-17.00A^2-1.50B^2-7.00C^2 \]

Where A is the modification temperature ,B is the solid-fluid ratio and C is the modification time.

In addition, the modification temperature and time variables were selected as "minimize" to reduce the cost of the process and its energy demand. The optimal modification variables are presented in Table 5.
Table 5. Optimization Results of the Modification variables

| Modification variable | Optimum value |
|-----------------------|---------------|
| Modification temperature | 38℃           |
| Solid-Fluid ratio     | 1:10          |
| Modification time     | 3             |

Three additional experiments were carried out under the optimal conditions, the average values of the triplicate experiments 84.61% are close to the predicted results 85.12, it indicate that the proposed model can well correlate the modification variables to the Cr(VI) adsorption efficiency.

4. Conclusion

In this work, modification conditions with H₂O₂ of bamboo-based activated carbon to improve the absorption of Cr(VI) were investigated and the modification variables have been optimized with response surface methodology. According to the BET and Boehm titration results, modification of ACs with H₂O₂ can increase the pore structure and total acidic groups. The influence of the modification variables including modification temperature, solid-fluid ratio and modification time on the adsorption efficiency of Cr(VI) was investigated using BBD combined with RSM. According to the obtained results, RSM model was an adequately application method for optimizing the variables for the bamboo-based activated carbon modification process. And the term for modification temperature shows the most significant effect to the absorption efficiency of Cr(VI). With the optimized modification condition (modification temperature 38 ℃, solid-fluid ratio 1:10 and modification time 3h) reach the absorption efficiency of Cr(VI) of 84.615, because of its high adsorption efficiency and low process cost, modification with H₂O₂ of bamboo-based activated carbon has a potential application in the treatment of Cr(VI) pollutant.

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