Efficient Removal of Cr (VI) with Biochar and Parameters Optimized by Response Surface Methodology

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Abstract: A highly efficient reduction process of Cr (VI) with biochar was conducted in this paper. The results showed that nearly 100% Cr (VI) was reduced at selected reaction conditions: the dosage of biochar at m(C)/m(Cr) = 3.0, reaction temperature of 90 °C, reaction time at 60 min and concentration of H2SO4 of 20 g/L, respectively. The reduction kinetics analysis demonstrated that the reduction of Cr (VI) fitted well with the pseudo-first-order model and the apparent activation energy was calculated to 40.24 kJ/mol. Response surface methodology confirmed that all the experimental parameters had positive effect on the reduction of Cr (VI). The influence of each parameter on the reduction process followed the order: dosage of biochar> Concentration of H2SO4 > Reaction Temperature > Reaction Time. This paper provided a versatile strategy for treatment of wastewater containing Cr (VI) and showed a bright tomorrow for wastewater treatment.

Keywords: Chromium; Response surface methodology; Reduction; Biochar

1. Introduction

Chromium pollution is a serious environmental problem and Cr (VI) has been classified in Group 1 by IARC (International Agency for Research on Cancer) [1-5]. Cr (VI) has many negative impacts on earthworms, plants, fish and so on. It will increase the reproduction and mortality of earthworms, and is toxic on kidney and cells for animals and humans, etc. In recent years, many technologies had been applied to treat the wastewater containing Cr (VI) [6]. The physicochemical technology (like ion exchange, membrane filtrate, chemical precipitation, etc.) were easy to conduct with high removing efficiency [7-10]. The so-called electrochemical technology associated with electricity showed high removal efficiency and being proud of clean and environmental-friendly [11-13]. Photocatalysis and nanotechnology were also developed for treatment of wastewater and showed great performance [14, 15]. While the problems like large scale application, secondary pollution, high cost were remained. Therefore, it is urgent to develop useful technologies for Cr (VI) treatment [16-18]. Recently, reduction of Cr (VI) to Cr (III) had attracted much more attention [12, 13, 19-21].

Biochar derived from plant and animal wastes was a typical adsorbent to remove inorganic and organic pollutants in water due to its low-cost and abundant feed stock availability [22-24]. In addition, the large surface area, high mineral content, and rich oxygen-containing functional groups of biochar were favorable for adsorption of wastewater contaminants such as antibiotics, dyes, and heavy metals [25-27]. Thus, biochar was applied to adsorb chromium (VI) in this paper (actually biochar was acted as a reductant and the adsorption process was proved to be a reduction process). The experimental parameters including the dosage of biochar, reaction temperature, reaction time and concentration of H2SO4 on the reduction process were investigated. Also, the reduction kinetics analysis was done.
2. Materials and Methods

2.1 Materials

K2Cr2O7, H2SO4 and biochar were of analytical grade and used as received without further purification, which were purchased from Kelong Co., Ltd, Chengdu, China. All solutions were prepared with deionized water with a resistivity greater than 18 MΩ/cm (HMC-WS10) [12, 13, 19, 28].

2.2 Experimental procedure

All the experiments were conducted in a beaker placed in a thermostatic water bath with a temperature precision of ± 0.1 °C [12, 13]. In the batch experiments, 100 mL 1000 mg/L Cr (VI) solution was prepared by dissolving amount of K2Cr2O7 in the deionized water, then the prepared biochar was added into the beaker as the solution was heated to a predetermined temperature. After a required reaction time, the solution with Cr (III) and retained biochar were separated by vacuum filtration. The concentration of Cr (VI) in the filtrate was determined by ICP-OES [12, 13, 21], and the reduction efficiency (η) of Cr (VI) was calculated following Equation (1):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$

(1)

Where, C0, is the initial concentration of Cr (VI) in the solution, mg/L; Ct, is the concentration of Cr (VI) in the solution at reaction time of t, mg/L.

2.3 Response surface optimization

The interactions between experimental parameters were important for the experimental results while it had been ignored during the single factor experiment, thus, RSM was applied to optimize the experimental process and order the significance of experimental parameters [13, 29, 30]. In this paper, the experimental parameters affected the reduction process were selected as A (m(C)/m(Cr)), B (Reaction Temperature), C (Reaction Time) and D (Concentration of H2SO4). The actual values for them were confirmed through the single factor experimental results and displayed in Table 1.

| Independent variable | Unit | Level |
|----------------------|------|-------|
|                      |      | -1    | 0    | 1    |
| A: m(C)/m(Cr)        | -    | 0.5   | 1.75 | 3.0  |
| B: Reaction Temperature | °C  | 30    | 60   | 90   |
| C: Reaction Time     | min  | 10    | 35   | 60   |
| D: Concentration of H2SO4 | g/L | 0     | 10   | 20   |

3. Results and Discussions

The dosage of biochar had a significant effect on the reduction of Cr (VI) as it was the main reaction reagent. A series of experiments were conducted to investigate the effect of the
dosage of biochar (m(C)/m(Cr)) on the reduction efficiency of Cr (VI). The m(C)/m(Cr) was set as m(C)/m(Cr)= 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0, respectively. The other reaction conditions were kept as constant: reaction temperature of 90 °C, reaction time of 60 min and concentration of H2SO4 at 10 g/L. The results shown in Figure 1a indicated that the reduction efficiency of Cr (VI) was increased with the increasing of m(C)/m(Cr). The reduction efficiency of Cr (VI) was increased from 40.32% to 97.74% as dosage of biochar increased from m(C)/m(Cr)=0.5 to m(C)/m(Cr)=3.0. Thus, the m(C)/m(Cr) =3.0 was selected for further experiments.

Reaction temperature played an important role in a standard chemical reaction. A series of experiments were conducted to investigate the effect of reaction temperature on the reduction efficiency of Cr (VI) and the reaction temperature was set as 30, 45, 60, 75, and 90 °C, respectively. The other reaction conditions were kept as constant: m(C)/m(Cr)=3.0, reaction time of 60 min and concentration of H2SO4 at 10 g/L. It could be seen from Figure 1b that the reduction efficiency was increased with the increasing of reaction temperature, and the increasing trend of reduction efficiency was similar with dosage of biochar, which indicated that both dosage of biochar and reaction temperature had significant effect on the reduction process. Higher temperature could intensify the activity of biochar molecule and Cr (VI) ion, promoted the extent of the reduction reaction and enforced the reduction of Cr (VI) [12, 13, 31]. Therefore, 90 °C was selected as the optimal reaction temperature for further experiments.

Recent study indicated that Cr (VI) was easy being reduced to Cr (III) in the strong acidic medium [12, 13, 21]. A series of experiments were conducted at the concentration of H2SO4 ranged from 0 g/L to 20 g/L at various dosage of biochar. Figure 1c displayed that the increase of concentration of H2SO4 could facilitate the reduction process of Cr (VI). In theoretical, the formation of HCrO4- was the main species of Cr (VI) at 0.8 < pH < 6.8, and CrO42- was the main species at pH > 6.8 (Figure 2a measured by software Visual MINTEQ [32]). Other way, HCrO4- was easier reduced into Cr (III) than CrO42- as HCrO4- the oxidation potential was higher according to the results showed in Figure 2b (E0(HCrO4-/Cr3+) = 1.35 V, E0(CrO42-/Cr3+) = 0.56 V). When the dosage of biochar was much high, the reduction efficiency had no obvious increase (when m(C)/m(Cr) was up 2.5, the reduction efficiency of Cr (VI) was nearly 100% at 10 g/L). Thus, concentration of H2SO4 at 10 g/L was enough for further experiments.

Figure 1d described the effect of reaction time on the reduction process at various reaction temperatures as other reaction conditions kept as m(C)/m(Cr)=3.0 and concentration of H2SO4 at 10 g/L. The results showed that the extend the reaction time could improve the reduction efficiency of Cr (VI) at all reaction temperature. And higher reaction temperature was beneficial for the reduction process, which was consistent with the analysis above.
3.2 Response Surface Methodology

3.2.1 Model fitting

The squares root was used to express the simulated results and it was presented in Equation (2):

$$\sqrt{\eta} = 8.38 + 0.55A + 0.38B + 0.27C + 0.52D - 0.17AB + 0.22AC + 0.25AD - 0.025BC + 0.25BD + 0.20CD - 0.03A^2 + 0.25B^2 + 0.02C^2 - 0.30D^2$$

(2)
The influence of each parameter on the reduction efficiency of Cr (VI) could be seen from the coefficients before them in the Equation (2). The coefficients of them were 0.55, 0.38, 0.27 and 0.52, respectively, which confirmed that all the parameters had a positive effect on the reduction efficiency. The results displayed in Figure 3 indicated that the influence of each parameter on the reduction efficiency followed the order: $A > D > B > C$, which was consistent with the results described in Equation (2). Above all, the dosage of biochar and concentration of H2SO4 had the greatest influence on the reduction process.

![Figure 3 Perturbation plot for the reduction efficiency of Cr (VI) in the design space. (A- (m (C)/m(Cr)); B- (Reaction Temperature); C- (Reaction Time) and D- (Concentration of H2SO4)).](image)

The analysis of variance of the reduction efficiency of Cr (VI) was shown in Table 2. The results showed that the p-value of the model was < 0.0001, which indicated that the selected model was significant and suitable for simulating the reduction process of Cr (VI) [30, 33]

**Table 2 Analysis of variance for the response**

| Source | Sum of Squares | Z | Mean square | F value | p-value Prob>F |
|--------|----------------|---|-------------|---------|---------------|
| Model  | 11.76          | 14| 0.84        | 14.47   | <0.0001       |
| A      | 3.60           | 1 | 3.60        | 62.00   | <0.0001       |
| B      | 1.76           | 1 | 1.76        | 30.29   | <0.0001       |
| C      | 0.87           | 1 | 0.87        | 15.05   | 0.0017        |
| D      | 3.31           | 1 | 3.31        | 56.94   | <0.0001       |
| AB     | 0.12           | 1 | 0.12        | 2.10    | 0.1690        |
| AC     | 0.19           | 1 | 0.19        | 3.36    | 0.0882        |
| AD     | 0.24           | 1 | 0.24        | 4.22    | 0.0591        |
| BC     | 2.54E-003      | 1 | 2.54E-003   | 0.044   | 0.8372        |
| BD     | 0.26           | 1 | 0.26        | 4.39    | 0.0547        |
### 3.2.2 Response surface analysis

To evaluate the fitting effect of the model on the experimental results, some other important diagnostic plots including Internally Studentized Residuals against Run Number, Predicted against Actual, Internally Studentized Residuals against Predicted and Normal Probability against Internally Studentized Residuals, respectively, were shown in Figure 4. All points showed in the Normal Probability against Internally Studentized Residuals plot shown in Figure 4a was concentrated in a straight line illustrated that the error was normally distributed. In a plot of Internally Studentized Residuals against Run Number and Internally Studentized Residuals against Predicted, the residuals were randomly distributed between +3.00 and -3.00, indicating that the Box-Behnken model was successfully established the relationship between the independent variable and the reduction efficiency. A plot of Predicted against Actual was shown in Figure 4b, the points were approximately distributed on a straight line with a slope of 1, which indicated that this model could accurately predict the actual value.
Figure 4 Diagnostic plots of the quadratic model. (a- Normal Probability against Internally Studentized Residuals; b- Predicted against Actual; c-Internally Studentized Residuals against Run Number; d- Internally Studentized Residuals against Predicted)

The contour plots were applied to analysis the interaction between experimental parameters. Figure 5 showed that the reduction efficiency of Cr (VI) was increased with the increase of all experimental parameters and the results were consistent with the analysis above.
3.3 Reduction Kinetics Analysis

In this paper, pseudo-first-order model as described as Equation (3) was applied to simulate the reduction behavior of Cr (VI) [33-36].

\[ \frac{dC}{dt} = -KC \]  

Integrate.

\[ -\ln C = Kt - \ln C_0 \]  

Figure 5 Response surface plots for factors
Where, $v$, is the reduction rate of Cr (VI); $C$, is the concentration of Cr (VI); $C_0$, is the initial concentration of Cr (VI); $K$, is the reduction reaction constant.

Figure 6a displayed the fitting results of experimental results fitted with Equation (4), which indicated that the reduction process of Cr (VI) was fitted well with the pseudo-first-order model. The reduction reaction apparent activation energy was obtained by simulating the experimental results with the Arrhenius Equation (Equation (5)). The apparent activation energy was calculated as 40.24 kJ/mol according to the results showed in Figure 6b, which was much larger than the apparent energy calculated for reduction with oxalic acid (22.49 kJ/mol) [21] and electrochemical reduction (4.74 kJ/mol) [12]. It meant that the reduction process with biochar was harder than oxalic acid and electrochemical reduction.

$$\ln K = \ln A - \frac{E_a}{RT}$$  

Where, $E_a$, is the apparent activation energy; $A$, is the pre-exponential factor; $R$, is the molar gas constant, 8.314 J/(mol K); $K$, is the reduction reaction constant at different reaction temperatures.

![Kinetics plots](image)

3.4 Removal of Chromium (III)

After the reduction process, the Cr (VI) was reduced to Cr (III) and it was removed by precipitation with sodium hydroxide [37] or adsorption with melamine [19, 20].

4. Conclusions

A highly efficient reduction process of Cr (VI) with biochar was investigated and the following conclusions could be obtained:

1. The Cr (VI) was easily being reduced by biochar at high reaction temperature with high dosage of biochar in strong acidic medium. Nearly 100% Cr (VI) was reduced at selected reaction conditions: the dosage of biochar at $m(C)/m(Cr)=3.0$, reaction temperature of 90 $^\circ$C, reaction time at 60 min and concentration of H2SO4 of 20 g/L, respectively.

2. The reduction kinetics analysis indicated that the reduction behavior of Cr (VI) fitted well with the pseudo-first-order model and the apparent activation energy was calculated as 40.24 kJ/mol.
Response surface methodology confirmed that all the experimental parameters had positive effect on the reduction of Cr (VI). The influence of each parameter on the reduction process followed the order: A (dosage of biochar (m (C)/m(Cr)) > D (Concentration of H2SO4) > B (Reaction Temperature) > C (Reaction Time). Especially, the dosage of biochar and concentration of H2SO4 had the greatest influence on the reduction process.

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