Optimization of Heavy Metal Cu(II) Adsorption by Cotton Straw Biochar Using Response Surface Methodology

Xuefei Hu1,*, Chong Liu1, Shengru Yue1, Fayong Li1, Yongjun You1 and Shan Wang1

1College of Water Resources and Architecture Engineering, Tarim University, Xinjiang, China

*Corresponding author email: 120150030@taru.edu.cn

Abstract. Box–Behnken response surface optimization design was used to improve the process of Cu(II) removal from water by cotton straw biochar (CSBC). The pH of the solution, and the dosage and temperature of the CSBC were set as the three influencing factors. The Cu(II) equilibrium adsorption amount was taken as the response value. The quadratic polynomial model between the equilibrium adsorption amount and the above factors was established, optimal adsorption conditions were determined, and model fitting on the thermodynamic adsorption process was conducted under optimal conditions. The results showed that the amount and temperature of CSBC were the significant factors. When the pH was 6.00, the amount of CSBC was 0.20 g/l, the temperature was 45 ℃, and adsorption capacity of CSBC to Cu(II) was the largest. The adsorption model conformed to the Freundlich isotherm equation. The adsorption of Cu(II) by CSBC belonged to a multimolecular layer adsorption, and the adsorption effect was significant. As a green, efficient, and cheap adsorbent, CSBC can be used to remove Cu(II) from wastewater.

Keywords: Cotton straw; Biochar; Adsorption; Response surface analysis.

1. Introduction
With industrialization and urbanization, many heavy metal ions have been released to the environment via discharge of industrial waste and household garbage. Heavy metal ions have the characteristics of high toxicity, difficult biodegradation, easy accumulation, and easy migration; they can enter human bodies through many ways, thereby posing a serious threat to human health [1]. Exposure to heavy metal ions of copper, Cu(II), can corrode the skin or damage the liver, kidney, spleen, and other vital organs, and cause acute renal failure and even cancer [2]. Traditionally, the heavy metal ions are removed from the wastewater by approaches such as precipitation, electrolysis, ion exchange, membrane separation, adsorption, and flocculation [3]. Among them, the adsorption method is widely used due to the easy operation, low energy consumption, great efficiency, and low investment requirement. During adsorption, adsorbent selection has been the critical issue, because surface characteristics of the adsorbent affect the adsorption efficiency. Biochar has porous structure, abundant surface functional groups, and strong adsorption capacity for heavy metals [4]. As an efficient adsorbent, the application of biochar in wastewater has attracted extensive attention. Recent studies have shown that biochar prepared through high-temperature pyrolysis of agricultural wastes (such as straw from wheat, rice, corn, soybean, and rapeseed; branches of fruit trees such as jujube, pine needles), residues of food and drug processing (residue of sea buckthorn fruit separation; residue of gallnut, brewer's grains, etc.), livestock excrement (cow excrement, chicken excrement), kitchen organic waste, and other biomass exhibits better adsorption of water environmental pollutants[4]. However, there are significant differences in the
adsorption efficiency and removal mechanism of biochar for water environmental pollutants due to differences in precursor materials and pyrolysis conditions used in the preparation of the biochar. Xinjiang is the main cotton planting area in China. The cotton planting in south Xinjiang promotes the development of the regional economy to a certain extent. However, efficient utilization of cotton straw biomass is required. The carbonization of cotton straw as a water adsorption material can not only alleviate a series of agricultural and ecological problems caused by straw returning[5], the common practice in this region, but also result in the resource utilization of agricultural straw waste in south Xinjiang. Currently, there are several studies on the kinetics and thermodynamics of heavy metal adsorption by biochar, but only few focus on the response surface analysis of heavy metal adsorption by cotton straw biochar (CSBC). Therefore, in this study, cotton straw biomass was used as raw material to prepare CSBC, and the adsorption effect of CSBC on Cu(II) was studied. In particular, the effects of adsorption time, temperature, pH, and biochar dosage on the adsorption capacity of CSBC were examined by single factor experimental analysis. The Box–Behnken response surface optimal experiment was performed to analyze those best conditions for adsorption. Our findings in this study lay a certain foundation to apply CSBC in treating wastewater polluted by heavy metals.

2. Experimental Setup and Methods

2.1. Materials
The experimental cotton straw was collected from the 10th regiment of Alar city, the first division of Xinjiang Production and Construction Corps. The cotton straw was washed to remove the surface adhesion, dried and crushed, and sealed in brown bottles for reserve.

2.2. Preparation of Cotton Straw Biochar
An oxygen-limited, temperature-controlled carbonization method was used to prepare the CSBC. The specific operation was as follows: the cotton straw powder was soaked; 50 g cotton straw biomass powder was weighed and screened with a 0.250 mm mesh sieve, put into a closed crucible, and put in a muffle furnace; the temperature of the muffle furnace was raised slowly (up to 200, 400, or 600 °C), so as to carbonize the biomass straw powder for 4 h (this was the carbonization time, and the early heating time was not included); the temperature was slowly reduced below 200 °C, and the carbonized material was taken out. The biochar sample numbers were CSBC200, CSBC400, and CSBC600, according to the pyrolysis temperatures used during production; their pH and ash content were 6.15 and 5.13%, 9.06 and 13.22%, and 10.52 and 14.09%, respectively.

2.3. Adsorption Experiment Method
The prepared CSBC was adopted for examining the adsorption performance on Cu (II) in aqueous solution, to explore the effect of adsorption time, temperature, pH, and dosage of CSBC on the adsorption of Cu(II). Certain amounts of the biochar samples were accurately weighed and added to 50.00 ml centrifuge tubes, respectively. Afterwards, 50.00 ml Cu(II) solution with a certain mass concentration was added to each tube. 0.1000 mol·L⁻¹ NaOH or HNO₃ solution was used to adjust adsorption solution pH. The supernatant was subsequently filtered with a 0.22 μm living water filtration membrane. Each experiment was repeated three times, and a blank control sample was set. The background adsorption solution was 0.0100 mol·L⁻¹ NaNO₃.

The adsorption capacity qₑ (mg/g) at equilibrium was calculated as follows:

\[ qₑ = \frac{(C₀ - Cₑ) \times V}{m} \]  \hspace{1cm} (1)

In the formula, C₀ and Cₑ (both in mg/L) stand for the original and equilibrium contents, separately. V (L) represents Cu(II) solution volume, while m (mg) indicates total CSBC amount.
2.4. Response Surface Methodology to Optimize Reaction Conditions

Three levels were selected for the central composite experimental design. The main effect and interaction of pH, adsorbent dosage and temperature on the adsorption of Cu(II) by CSBC were studied. The determination of experimental factors are given in table 1.

Table 1. Factors and levels of Box-Behnken design.

| Factors       | No. | Units | Levels   |
|---------------|-----|-------|----------|
| pH            | A   | --    | 5.00 5.50 6.00 |
| Adsorbent dosage | B   | g/L   | 0.20 0.25 0.30 |
| Temperature   | C   | °C    | 25 35 45 |

3. Results and Discussion

3.1. Single Factor Experimental Results and Discussions

3.1.1. Effects of pH on the adsorption performance of CSBC. Solution pH has a certain effect on the way that heavy metal ions exist as well as distribution of biochar (BC) surface charges, which consequently affects heavy metal adsorption into solution [3]. Under alkaline conditions, a large amount of -OH is ionized out of the solution; it forms precipitation with heavy metal ions, thus affecting the adsorption process, so the pH was set at 2.00-6.00. Fig.1 shows how pH affects CSBC adsorption for Cu(II) under 25 °C. When the Cu(II) solution pH increased, the CSBC adsorption elevated accordingly, which might be related to the elevated negative charges on CSBC surface with the increase in solution pH, thus resulting in the increased electrostatic effect while improving adsorption capacity.

Figure 1. Effect of Single factors on the Cu(II) adsorption by cotton straw biochars.

3.1.2. Effects of adsorption time on the adsorption performance of CSBC. figure 1. shows the adsorption trend of the three kinds of CSBC. The trend was almost consistent in the three samples: the initial adsorption capacity of CSBC to Cu(II) increased rapidly, and reached equilibrium at 120 min later. The adsorption reached more than 60% of the total adsorption capacity within 30 min, likely because of the driving force of mass transfer caused by original Cu(II) content difference at water–BC phase, together with those adsorption sites on CSBC surface. When adsorption time increased, those adsorption sites on CSBC surface were saturated, and the diffusion effect in the particles was gradually weakened. The adsorption reached more than 96% of the total adsorption capacity within 120 min.

3.1.3. Effects of adsorbent dosage on adsorption performance of CSBC. As shown in figure 1. As the dosage increased, the CSBC removing efficiency was enhanced accordingly, along with the decreased adsorption capacity for each unit of adsorbent, which was mainly because the specific surface area and adsorption sites in the solid–liquid adsorption system were not fully utilized.

3.1.4. Effects of temperature on the adsorption performance of CSBC. The isothermal adsorption test was performed for testing how temperature affected the CSBC adsorption performance, as observed
from figure 2. When temperature elevated, adsorption capacities for those biochars were remarkably enhanced, which indicated the endothermic process of CSBC adsorption for Cu(II). Under the high temperature condition, the degree of disorder of the system increased, resulting in the increase of the collision probability between molecules and adsorption sites, consequently, in the increase of the adsorption capacity. The order of adsorption capacity was as follows: CSBC600 > CSBC400 > CSBC200, with the adsorption capacity of CSBC600 much higher than the others, indicating that different pyrolysis temperatures determine the surface structure characteristics of biochar, which directly affect the adsorption performance.

Table 2. Experimental design and results.

| No. | A     | B     | C     | q(mg/g) |
|-----|-------|-------|-------|---------|
| 1   | 5.00  | 0.20  | 35    | 47.190  |
| 2   | 5.00  | 0.25  | 25    | 32.436  |
| 3   | 5.00  | 0.25  | 45    | 40.352  |
| 4   | 5.00  | 0.30  | 35    | 31.600  |
| 5   | 5.50  | 0.20  | 25    | 43.220  |
| 6   | 5.50  | 0.20  | 45    | 50.570  |
| 7   | 5.50  | 0.25  | 35    | 38.960  |
| 8   | 5.50  | 0.25  | 35    | 38.244  |
| 9   | 5.50  | 0.25  | 35    | 37.668  |
| 10  | 5.50  | 0.25  | 35    | 37.472  |
| 11  | 5.50  | 0.25  | 35    | 37.864  |
| 12  | 5.50  | 0.30  | 25    | 29.967  |
| 13  | 5.50  | 0.30  | 45    | 34.567  |
| 14  | 6.00  | 0.20  | 35    | 49.940  |
| 15  | 6.00  | 0.25  | 25    | 35.148  |
| 16  | 6.00  | 0.25  | 45    | 40.708  |
| 17  | 6.00  | 0.30  | 35    | 31.877  |

A: pH, B: adsorbent dosage (g/L), C: temperature (°C).

Table 3. Regression model variance analysis.

| Source | Seq SS | df | Mean Square | F Value | P-value |
|--------|--------|----|-------------|---------|---------|
| Model  | 608.14 | 9  | 67.57       | 115.715 | <0.0001 |
| A-A    | 4.64   | 1  | 4.64        | 7.951   | 0.0258  |
| B-B    | 494.71 | 1  | 494.71      | 847.182 | <0.0001 |
| C-C    | 80.81  | 1  | 80.81       | 138.386 | <0.0001 |
| AB     | 1.53   | 1  | 1.53        | 2.619   | 0.1496  |
| AC     | 1.39   | 1  | 1.39        | 2.376   | 0.1671  |
| BC     | 1.89   | 1  | 1.89        | 3.238   | 0.115   |
| A²     | 1.00   | 1  | 0.10        | 0.173   | 0.6899  |
| B²     | 21.60  | 1  | 21.60       | 36.99   | 0.0005  |
| C²     | 2.22   | 1  | 2.22        | 3.798   | 0.0923  |
| Residual | 4.09 | 7  | 0.58        |         |         |
| Lack of Fit | 2.71 | 3  | 0.90        | 2.616   | 0.1879  |
| Pure Error | 1.38 | 4  | 0.34        |         |         |
| Cor Total | 612.23 | 16 |             |         |         |

R² = 0.9933   R²Adj = 0.9847

Notes: ** indicates that the difference is extremely significant (P < 0.01).
* indicates a significant difference (P < 0.05).

3.2. Analysis on Response Surface Optimization Experimental Results

3.2.1. Experimental results. The central composite design and experimental results of response surface methodology are shown in table 2.

Design-expert was employed for conducting regression analyses on those response values for the 17 samples used for experiment, and the binary regression response surface model of equilibrium adsorption capacity was established as:

\[ Y = 38.04 + 0.76A - 7.86B + 3.18C - 0.62AB - 0.59AC - 0.69BC - 0.15A^2 + 2.26B^2 - 0.73C^2 \] (2)
Where Y represents the predicted value of equilibrium adsorption capacity; A, B, and C represent pH, adsorbent dosage, and temperature coding values, respectively. According to the variance analysis of the regression model in equation (2), P < 0.01 shows that the model has a high significance and can be applied to the optimization of parameters in this adsorption experiment. The optimal adsorption conditions calculated by regression equation (2) are as follows: pH as 6.00, CSBC dosage as 0.2 g/l, and temperature as 45 °C. In our experiment, the lack of fit term had the p-value of 0.1879 > 0.05, which suggested the great model fitting degree and creditable fitting results.

Table 3 shows that dosage and temperature significantly affect the adsorption capacity at equilibrium. The three interaction terms make no difference to the adsorption capacity at equilibrium, however, for the quadratic terms, dosage does have a significant impact on the equilibrium adsorption capacity. The model has a F-value of 115.715, which suggests obvious interactions of pH, adsorbent amount with temperature. The correlation coefficient of the model is 0.9933, indicating that 98.47% of the experimental data could be explained by the model. The correction coefficient (R²Adj) is 0.9847, indicating that 98.47% of the experimental data variability could be explained by this regression model. The Cv value is 1.97%, far less than 10%, showing that the experiment has strong stability. Adequate Precision is 37.68 (much more than 4), indicating that the model has high reliability and precision. In conclusion, this model may be adopted for the accurate prediction of CSBC adsorption for Cu(II).

3.2.2. 3D graphic analysis. The interaction between the 3D stereogram of the model and the variables is shown in figure 3. Increasing the pH, the CSBC adsorption capacity for Cu(II) at equilibrium increased gradually, but the trend was slow at pH > 4.00. In addition, increasing the pH o, the degree of protonation on the surface of CSBC decreased, and a large number of effective adsorption groups began to react. In the process of depolarization, CSBC showed negative charge, which was more conducive to the adsorption of the positively charged Cu(II). Temperature had a significant effect on the adsorption of Cu(II) by CSBC. Increasing the temperature improved the diffusion coefficient of Cu(II), increasing the conduciveness of Cu(II) diffusion in the CSBC channel, and, thus, improving the equilibrium adsorption capacity of Cu(II). Increasing the CSBC dosage, the total adsorption sites of the adsorption system increased, which led to increased adsorption. However, increasing the CSBC dosage, numerous adsorption vacancies appeared, and the equilibrium adsorption capacity per unit adsorbent decreased.

3.3. Adsorption isothermal Model

As shown in table 4, using Langmuir and Freundlich equation fitting Cu (II) on the CSBC isothermal adsorption. The isothermal adsorption process of Cu(II) by CSBC can be well described by the Freundlich model. In the Freundlich model, a 1/n less than 0.5 indicates that the adsorbate is easily adsorbed, whereas a 1/n more than 2 indicates that the adsorbate is difficult to adsorb. In this study, the adsorption factor 1/n of CSBC on Cu(II) was less than 0.5 under all tested conditions, indicating that CSBC is a good adsorbent of Cu(II).
Table 4. Constants of Langmuir and Freundlich isotherms.

| Temperature | Adsorbent  | Langmuir model | Freundlich model |
|-------------|------------|----------------|-----------------|
|             |            | $q_m$  | $k_L$ | $r_L^2$ | $1/n$  | $k_F$  | $r_F^2$  |
| 25°C        | CSBC200    | 68.9655 | 0.0821 | 0.8758 | 0.3726 | 12.9968 | 0.9402   |
|             | CSBC400    | 69.9301 | 0.1153 | 0.9137 | 0.3215 | 17.2515 | 0.9756   |
|             | CSBC600    | 80.0000 | 0.1447 | 0.9246 | 0.3039 | 22.1780 | 0.9819   |
| 35°C        | CSBC200    | 69.4444 | 0.0959 | 0.8935 | 0.3561 | 14.6128 | 0.9548   |
|             | CSBC400    | 76.3359 | 0.1251 | 0.9235 | 0.3236 | 19.2056 | 0.9540   |
|             | CSBC600    | 86.2069 | 0.2484 | 0.9771 | 0.2994 | 28.2361 | 0.9932   |
| 45°C        | CSBC200    | 72.9927 | 0.1226 | 0.8934 | 0.2832 | 20.3850 | 0.9558   |
|             | CSBC400    | 81.9672 | 0.1554 | 0.9335 | 0.3018 | 23.3828 | 0.9921   |
|             | CSBC600    | 90.9091 | 0.2709 | 0.9738 | 0.2887 | 31.0625 | 0.9682   |

4. Conclusion
The results of Box-Behnken experimental design showed that in the adsorption process of cotton straw biochar on Cu(II), both temperature and dose significantly affected the adsorption capacity at equilibrium; Among the interaction terms, the interaction of the three factors had no significant impact on the equilibrium adsorption capacity; Among the quadratic terms, the dosage had a significant effect on the equilibrium adsorption capacity. The order of influence of single factor on the adsorption of Cu(II) by cotton straw biochar was adsorbent dosage $>$ temperature $>$ pH; when pH was 6.00, CSBC dosage was 0.2g/l and temperature was 45°C, the adsorption of Cu(II) by cotton straw biochar was the largest. The adsorption model conforms to Freundlich isotherm equation. The adsorption of Cu(II) by cotton straw biochar belongs to a multi-molecular layer adsorption, with significant adsorption effect which can be used as a good adsorbent for heavy metals.

Acknowledgments
This work was financially supported by the National Natural Science Foundation of China (No. 21767025) and President’s foundation of Tarim university (TDZKQN201707). Xuefei Hu and Chong Liu are contribute equally on this work.

References
[1] Shen Z, Zhang Y and Jin F Qualitative and quantitative characterisation of adsorption mechanisms of lead on four biochars 2017 Sci. Total Env. 609 1401–1410.
[2] Lee M E, Park J H and Chung J W Comparison of the lead and copper adsorption capacities of plant source materials and their biochars 2019 J. Environ. Manage. 236 118–124.
[3] Deng J, Liu Y, Liu S, et al. Competitive adsorption of Pb (II), Cd (II) and Cu(II) onto chitosan-pyromellitic dianhydride modified biochar. 2017 Journal of colloid and interface science, 506 355-364.
[4] Chen H, Xie A, You S. A review: advances on absorption of heavy metals in the waste water by biochar. 2018 IOP Conf. Ser.: Mater. Sci. Eng. 301 12160.
[5] Liu H F, Tang G M and Sun N C Effects of different ways of returning cotton straw to the field on the growth and yield of cotton 2018 Xinjiang Agricultural Sciences 55 1710–1716.