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Optimization of Cd(II) removal from aqueous solution with modified corn straw biochar using Plackett–Burman design and response surface methodology

Xiao Deng[a], Hang Zhou[a], Xiao-Ning Qu[b], Jian Long[a], Pei-Qin Peng[a,*] , Hong-Bo Hou[a], Ke-Lin Li[a], Ping Zhang[a], Bo-Han Liao[a]

[a]*College of Environmental Science and Engineering, Central South University of Forestry and Technology, Changsha 410004, China, Tel. 86-0731-85623459; Fax: 86-0731-85623459; emails: pengpeiqin123@163.com (P.-Q. Peng), xiaotimex@163.com (X. Deng), zhouhang4607@163.com (H. Zhou), longjianking@163.com (J. Long), 814699489@qq.com (H.-B. Hou), csfuklli@163.com (K.-L. Li), zhyp2008@163.com (P. Zhang), liaobohan1020@163.com (B.-H. Liao)*
[b]*Commerce & Tourism College, Changsha 410116, China, email: 2508556567@qq.com*

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ABSTRACT

Statistical optimization designs were used to optimize Cd(II) removal from aqueous solution with modified corn straw biochar in this study. Based on the results of a single-factor experiment under a Plackett–Burman design (PBD), we screened three main influencing factors for the Cd(II) adsorption process: pH, initial Cd(II) concentration, and biochar dosage. With the Cd(II) adsorption percentage as the response target, the Box–Behnken design optimization was performed for the three main factors of pH (3–7), the initial concentration (20–120 mg·L^{-1}), and dosage (2–8 g·L^{-1}). Then, with the obtained second-order model of the adsorption percentage, we determined the optimal conditions for Cd(II) adsorption experiments. The optimization results indicated that biochar dosage showed a significant interaction with initial Cd(II) concentration. With considering the cost, the optimal adsorption percentage was obtained under the following conditions: pH 5.52, the initial concentration of 20.00 mg L^{-1}, and the dosage of 3.05 g·L^{-1} according to the importance weight setting. The experimentally obtained maximum adsorption percentage was 90.05%, which was more economical and reasonable than the obtained conditions without taking the cost into consideration. The combined PBD and BBD method could be applied in the optimization of Cd^{2+} adsorption conditions and provide more reasonable and effective results.

Keywords: Biochar; Adsorption; Cd(II); Plackett–Burman design (PBD); Response surface methodology (RSM); Importance weight

1. Introduction

Water pollution related to toxic and hazardous heavy metals has been widely concerned [1]. Cadmium (Cd) pollution has adverse effects on human health by causing various diseases, such as hypertension, liver insufficiency, bone lesions, and cancers [2]. Cadmium in the environment mainly comes from fossil fuels, mining, smelting, phosphate fertilizers, electroplating, batteries, and pigments [3]. The maximum permissible level of Cd^{2+} in drinking water is 5.0 μg·L^{-1} in the standard of World Health Organization (WHO) [4]. Due to the pervasive contamination of Cd^{2+}, various Cd removal techniques, such as chemical precipitation, ion exchange, adsorption, membrane filtration, and electrochemical treatment, had been evaluated [5,6]. In these techniques, adsorption has attracted high attention due to its good removal effect, low investment, and low operating cost [7].

In adsorption, the adsorbent type largely determines the Cd removal effect. Recently, different materials, such as activated carbon [8], agricultural and industrial wastes [9,10], biochar [11], ore materials [12], nanomaterials [13], and microorganisms [14], had been developed into adsorbents to remove heavy metals such as Cd from wastewater.

As a fine-grained porous substance, biochar has a similar appearance as charcoal produced by the pyrolysis of biomass

* Corresponding author.

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under oxygen-limited conditions. It has the structured carbon matrix with the high porosity and large specific surface area, suggesting that it may act as a surface adsorbent to remove contaminants [15]. Various biochar produced with plant residues or agricultural wastes had been developed to adsorbents to adsorb heavy metals [16–18]. Corn is one of the main food crops in northern China, and its annual planting area is approximately 2.33 × 10^7 hm^2. Every year, 100 million tons of corn straw are burned directly in the fields in China, causing energy waste and air pollution [19]. Recently, some researchers made biochar and then modified the prepared biochar with potassium permanganate solution to improve its adsorption effect. The modified biochar was used to adsorb heavy metal ions from aqueous solution. Previous experimental results showed that the adsorption capacity of modified biochar was higher than unmodified biochar [20,21]. The adsorption capacities of different types of low-cost adsorbents for Cd removal are compared in Table 1. It is found that the modified corn straw biochar may have great potential for the removal of Cd from water.

The traditional single-factor experimental method is time-consuming and cannot provide the reliable optimization results of adsorption conditions because the interactions among the adsorption factors are not considered in the method [29]. The Plackett–Burman design [30,31] (PBD) is a statistical optimization method of experimental conditions developed in the mid-twentieth century and has been widely used to optimize microbial culture conditions and fermentation processes. The PBD method is an effective two-level experimental design. In the design method, the orthogonal experimental design is firstly adopted to study principal factors, and then the main factors with the most significant effects on the response target are screened by statistical experimental designs and data analyses. The design method can decrease the number of factors to be optimized as well as the number of subsequent experiments greatly and is widely used to estimate the main effects of factors. Response surface methodology (RSM) is the combination of mathematical and statistical methods [32,33] and is used in the modeling and response analysis of multiple factors to optimize the response target. The RSM methods include central composite design, Box–Behnken design (BBD), and Doehelrt Design. The BBD [34] is a common response surface optimization method to determine the effects of experimental factors and their interactions on the response index. Currently, BBD has been applied to optimize adsorption processes. Han et al. [35] adopted BBD to optimize As(V) removal by mesoporous alumina adsorption and obtained the maximum adsorption capacity of 39.06 $mg \cdot g^{-1}$. Tripathi et al. [36] utilized BBD to optimize the adsorption process of methyl orange by using commercial grade activated carbon and realized the removal rate of 99.11%. Jain et al. [37] adopted BBD to optimize Cr(VI) removal by using chemically treated *Helianthus annuus* flowers and reached the removal rate of 90.8%. Compared with the traditional single-factor and orthogonal experiments, RSM possesses the following advantages: less experimental data, high accuracy, straightforward results, and high prediction performance.

The combination of PBD and RSM has so far not been applied to optimize heavy metal adsorption. The combination of PBD and RSM can be used to analyze the effect size of each factor of the adsorption process and screen the main factors. In this way, the combined PBD and RSM method can efficiently and precisely provide optimal adsorption conditions. Moreover, statistically designed experiments can effectively solve optimization issues and minimize the error in determining the effects of factors and their interactions [38]. In this study, combining PBD with BBD, we optimized the adsorption process of Cd from solution with modified corn straw biochar. We analyzed the main influencing factors of the adsorption process (pH, temperature, adsorbent dosage, the initial concentration, adsorption time, and shaking speed) and screened the main influencing factors. Furthermore, we established the second-order response surface model for the main factors, explored the interactions among various factors, and predicted the optimum adsorption conditions.

2. Methods and materials

2.1. Preparation of adsorbents

Corn straws were collected from a cultivated field in Changsha of Hunan Province, China. Corn straws were washed and then dried in a constant-temperature oven, cut into small pieces with scissors, pulverized with a small-sized pulverizer, and finally sieved through a 100-mesh nylon sieve. The obtained powder was then placed in a crucible,

Table 1
Comparison of adsorption capacities of Cd^{2+} with some low-cost adsorbents

Adsorbents	Modification reagent	Cd^{2+} adsorption capacity ($mg \cdot g^{-1}$)	Reference
Grape stalk residue	Not modified	21.5	[22]
Hickory wood biochar	Potassium permanganate solution	28.1	[20]
Raphanus sativus peels biomass	Not modified	19.8	[1]
Bamboo charcoal	Not modified	12.1	[23]
Saponified mangosteen pericarp	Alkaline solution of calcium hydroxide and sodium hydroxide	39.3	[24]
Pine bark	Hydrochloric acid solution	10.5	[25]
Rice husk	Sodium carbonate	16.2	[26]
Peels of banana	Not modified	5.7	[27]
Peanut shells	Epichlorohydrin and ethylenediamine	14.2	[28]
Corn straw biochar	Potassium permanganate solution	28.6	This study

which was put in a box-type resistance furnace, carbonized at 300°C for 2 h, and cooled down to room temperature. The carbonized product was washed with 3 M hydrochloric acid to remove lime and surface residue, then washed with deionized water to the neutral pH value, and dried in an electric incubator at 70°C. Then corn straw biochar was placed into 0.1 M $KMnO_4$ solution (solid–liquid ratio of 1:100). After stirring, corn straw biochar was soaked for 24 h, filtered, washed with deionized water, and dried in an oven at 70°C to obtain modified corn straw biochar.

2.2. Design of screening experiments

The PBD method allows the study of (N – 1) variables through N experiments, where N is generally a multiple of 4 [39]. According to the general adsorption rules of heavy metals and previous single-factor experiment results, six factors (pH, initial Cd concentration, adsorption time, adsorbent dosage, shaking velocity, and temperature) were selected for the screening experiments. Moreover, five virtual factors were added for error analysis. High and low levels (–1 and 1) were arranged for each factor. According to the requirements of PBD, the high level was generally 1.25 to 1.5 times of the low level. The reasons for selecting the range were as follows: taking pH as an example, it is well known that cadmium ions exist in the form of precipitation of $Cd(OH)_2$ in the solution when pH value is higher than 7; if pH value is too low, cadmium ions cannot be adsorbed by the adsorbent either because of the competition between cadmium ions and hydrogen ion. On the other hand, the results of single-factor experiments showed that the optimum pH value of adsorption is 6; it is better to keep the pH value equal to or below 6. So considering the practical situation and the results of the pre-experiment, the range of different factors investigated by the PBD is shown in Table 2. With the Cd^{2+} adsorption percentage as the response factor, 12 experiments involving eleven factors were conducted to determine the effect size of each factor. In the experimental design, a linear function was adopted, and the interactions among factors were ignored [40]. The linear model equation is provided below:

$$Y = \beta_0 + \Sigma\beta_i X_i \quad (i = 1, 2 \ldots k), \tag{1}$$

where Y is the response value of the adsorption percentage of Cd^{2+}; X_i is the actual value of the factor to be investigated; β_i is the regression coefficient reflecting the influencing degree of X_i. The effect size of each factor is calculated as:

$$E(X_i) = \frac{2\Sigma(M_{i+} - M_{i-})}{N} \tag{2}$$

where $E(X_i)$ is the effect size of main factors and can measure the significant level of the effect; M_{i+} and M_{i-} are maximum and minimum adsorption percentages obtained in the Cd^{2+} adsorption experiment of the ith factor; and N is the number of the experiments.

Table 2
Range of different factors investigated by the PBD

Symbol	Factors	Low (–1)	High (+1)
X_1	pH	3	5
X_2	Temperature (°C)	20	30
X_3	Adsorbent dose (g·L^{-1})	2	3
X_4	Initial concentration (mg·L^{-1})	80	120
X_5	Time (h)	1.5	2
X_6	Stirring speed (rpm)	150	200
X_7, X_8, X_9, X_{10}, X_{11}	Dummy factors	–	–

2.3. Design of optimization experiments

Based on the results of the PBD experimental design, we designed BBD experiments to optimize the three factors (pH, initial concentration, and dosage) screened by PBD (Table 3). Three levels (–1, 0, and 1) were arranged for each factor and labeled. Polynomial regression analysis was adopted to fit the experimental data, and the quadratic polynomial was obtained. The obtained model can describe the relationship between the response factor and the influencing factors [41]:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{j-1}\sum_{j=1}^{k}\beta_{ij}X_iX_j + \sum_{i=1}^{k}\beta_{ii}X_i^2 \tag{3}$$

where Y is the system response value; β_0, β_i, and β_{ii} are, respectively, the offset item, linear offset, and second-order offset coefficients; β_{ij} is the interaction coefficient; and X_i is the value of each factor. According to the main effects and interactions of various factors, the optimum values were finally obtained within a certain range for each main influencing factor.

2.4. Adsorption experiments

Adsorption experiments were conducted according to the results obtained in subsections 2.3 and 2.4. First, 100 mL of $CdCl_2$ solution with a certain concentration was placed into a 250-mL conical flask, and then the pH value was adjusted to the desired value. After adding a certain amount of adsorbents, the conical flask was shaken in a constant-temperature shaker. After adjusting the shaking velocity, the adsorption process was completed. Then the adsorption solution was filtered, and the Cd concentration in the filtered solution was measured with a flame atomic adsorption spectrometer. The Cd adsorption percentage was calculated as below:

$$R = \left(1 - \frac{C}{C_0}\right) \times 100\% \tag{4}$$

Table 3
Factors and levels of the Box–Behnken design

Symbol	Factors	Level		
		–1	0	+1
X_1	pH	3	5	7
X_3	Adsorbent dose (g·L^{-1})	2	5	8
X_4	Initial concentration (mg·L^{-1})	20	70	120

where R is the Cd adsorption percentage; C_0 is the initial Cd^{2+} concentration before adsorption ($mg \cdot L^{-1}$); and C is the Cd^{2+} concentration in the solution after adsorption ($mg \cdot L^{-1}$).

2.5. Sample determination and data analysis

All samples were analyzed with a flame atomic adsorption spectrometer (ThermoFisher ICE 3000). The pH value was measured with a pH meter (PHS-3C). The chemical reagents used in this study were of analytical or ultrapure grade. All glassware and polyethylene bottles were soaked in 10% HNO_3 solution overnight before their uses. The analytical data were the averages of the measured values. Data processing and mapping was performed in Design Expert 8.0.

3. Results and discussion

3.1. PBD experimental results and analysis

The PBD experimental results are presented in Table 3. Independent variables X_1–X_6 are the six influencing factors on the adsorption percentage, and X_7–X_{11} are the five virtual factors. The regression analysis was performed with the adsorption percentage data in Table 4 to obtain partial regression coefficient and the significant level of each factor (Table 5).

In the regression results, the effect sizes of various factors on the adsorption percentage are decreased in the following order: pH > initial concentration > dosage > shaking speed > adsorption time > temperature according to their contribution rates. The pH, initial concentration, and dosage are the main influencing factors of the adsorption process ($p < 0.05$ is considered to be significant). According to the regression coefficients and the values of $E(X_i)$, the positive or negative effect of each factor on the adsorption percentage can be obtained. In Table 5, the regression coefficient and $E(X_i)$ of the factor X_1 (pH) are 6.91 and 13.82, respectively; the regression coefficient and $E(Xi)$ of the factor X_3 (dosage) are 6.59 and 13.19, respectively. These values are above 0, indicating that both pH and dosage have positive effects on the adsorption percentage. However, the factor X_4 (initial concentration) shows negative effect. These results indicated that enhancing the pH, increasing adsorbent dosage, or decreasing the initial concentration could increase the Cd adsorption percentage of modified corn straw biochar.

The pH, dosage, and the initial concentration were selected for BBD response surface optimization. However, other factors without significant effect may also affect the adsorption process. The design conditions of these insignificant factors adopted in the PBD experiments may be the optimum adsorption conditions, so the insignificant results are obtained. Based on the positive or negative values in Table 5, in the subsequent BBD response surface optimization, three insignificant factors were set as the fixed values as follows: shaking velocity of 200 $r \cdot min^{-1}$, temperature of 30°C, and adsorption time of 1.5 h. The small effect sizes of five virtual factors (X_7, X_8, X_9, X_{10}, and X_{11}) on the response target were 0.17%, 0.14%, 0.68%, 0.55%, and 0.13%, respectively, which indicated the applicability of a linear model.

Table 5
Partial regression coefficients and analyses of significance of PBD

Factors	Regression coefficient	E(Xi)	Contribution (%)	
Intercept	40.41			
X_1	6.91	13.82	33.17	Significant
X_2	0.32	0.64	0.072	–
X_3	6.59	13.19	30.23	Significant
X_4	–6.75	–13.50	31.70	Significant
X_5	–0.69	–1.39	0.34	–
X_6	2.01	4.03	2.82	–
X_7	–0.5	–0.99	0.17	–
X_8	–0.45	–0.89	0.14	–
X_9	0.99	1.97	0.68	–
X_{10}	0.89	1.77	0.55	–
X_{11}	0.43	0.86	0.13	–

Note: R^2 – 0.9511; Adjusted R^2 – 0.9327; CV – 8.04%; Adeq precision – 21.60; 95% significant level.

Table 4
PBD experimental design and response values

Run order	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}	Adsorption percentage (%)
1	1	1	–1	1	1	1	–1	–1	–1	1	–1	31.00
2	–1	1	1	–1	1	1	1	–1	–1	–1	1	47.00
3	1	–1	1	1	–1	1	1	1	–1	–1	–1	46.30
4	–1	1	–1	1	1	–1	1	1	1	–1	–1	21.52
5	–1	–1	1	–1	1	1	–1	1	1	1	–1	44.32
6	–1	–1	–1	1	–1	1	1	–1	1	1	1	24.80
7	1	–1	–1	–1	1	–1	1	1	–1	1	1	48.86
8	1	1	–1	–1	–1	1	–1	1	1	–1	1	46.07
9	1	1	1	–1	–1	–1	1	–1	1	1	–1	66.08
10	–1	1	1	1	–1	–1	–1	1	–1	1	1	32.73
11	1	–1	1	1	1	–1	–1	–1	1	–1	1	45.61
12	–1	–1	–1	–1	–1	–1	–1	–1	–1	–1	–1	30.66

By stepwise multivariate regression analysis, the optimal linear regression equation is obtained as below:

$$Y = 40.41 + 6.91X_1 + 6.59X_3 - 6.75X_4 \tag{5}$$

p Value of the model is <0.0001, indicating a significant level and the good fitting result within the regression range. The correction coefficient (R^2) is 0.9511, indicating the high correlation of the model. The corrected correction coefficient (Adjusted R^2) is 0.9327, indicating that 93.27% of the variations in the experimental data can be interpreted by the regression model. The coefficient of variation (CV) is 8.04%, which is less than 10%, indicating that the experiment can be reproducible. The precision (Adeq Precision) is the ratio of valid signal to noise. If Adeq Precision is >4.0, the experimental results are believed to be reasonable [42]. The Adeq Precision of this experiment was 21.60.

3.2. BBD experimental results and analysis

Based on the PBD experimental results, the Cd^{2+} adsorption performance of the modified corn straw biochar was experimentally optimized with the pH, initial concentration, and dosage as the influencing factors and Cd^{2+} adsorption percentage as the response value. The experimental design and results are shown in Table 6.

Through BBD response surface design of the pH, initial concentration, and dosage, the corresponding quadratic model was obtained as:

$$Y = 83.66 + 2.47X_1 + 20.95X_3 - 17.87X_4 - 0.10X_1X_4 - 1.85X_1X_3 + 11.71X_3X_4 - 7.29X_1^2 - 11.43X_3^2 - 0.68X_4^2 \tag{6}$$

As shown in Table 7, the F value of the above model is 23.81 ($p < 0.0001$), indicating a significant correlation of the regression model. The correction coefficient (R^2) is 0.9684, indicating that the equation allows the good fitting result [39]. Therefore, the model is applicable for the prediction of Cd adsorption percentage. The CV is 8.16%, and Adeq Precision is 17.106, which is >4.0, indicating that the model can reasonably reflect the experimental results. A significance test of the regression coefficients of the quadratic model showed that the linear effects of the factors (X_3 and X_4) on the adsorption percentage were significant. The curvature effect of X_4^2 and the interaction of X_3 and X_4 on the adsorption percentage were also significant.

Before accepting a model as a statistically correct model, the model should be validated. The data were also analyzed to check the normality of residuals. As shown in Fig. 1, the residuals are close to the straight line and scattered randomly around it without particular pattern, which indicated that the data did not show any abnormal behavior

Table 6
Box–Behnken design and response result

Experimental run	pH (X_1)	Adsorbent dose (X_3)	Initial concentration (X_4)	Adsorption percentage, % (Y)
1	0	1	1	79.86
2	0	0	0	82.92
3	–1	0	–1	91.01
4	1	1	0	92.51
5	–1	1	0	89.03
6	1	0	–1	93.91
7	0	0	0	83.65
8	1	0	1	59.17
9	0	0	0	83.27
10	0	0	0	83.25
11	0	–1	1	25.3
12	1	–1	0	43.55
13	–1	0	1	56.68
14	–1	–1	0	32.65
15	0	0	0	82.72
16	0	1	–1	93.39
17	0	–1	–1	85.66

Table 7
Analysis of variance (ANOVA) for the response surface quadratic model

Source	Sum of squares	Degrees of freedom	Mean square	F value	p Value (Prob > F)	
Model	7,504.19	9	833.80	23.81	0.0002	Significant
X_1	48.86	1	48.86	1.39	0.2762	–
X_3	2,554.70	1	2,554.70	72.94	<0.0001	Significant
X_4	3,512.48	1	3,512.48	100.28	<0.0001	Significant
X_1X_3	0.042	1	0.042	0.0012	0.9733	–
X_1X_4	13.76	1	13.76	0.39	0.5506	–
X_3X_4	548.26	1	548.26	15.65	0.0055	Significant
X_1^2	223.98	1	223.98	6.39	0.0393	–
X_3^2	1.92	1	1.92	0.055	0.8214	–
X_4^2	550.42	1	550.42	15.71	0.0054	Significant
Residual	245.18	7	35.03	–	–	–
Corr. Total	7,749.47	16	–	–	–	–

Note: R^2 – 0.9684; Adjusted R^2 – 0.9277; CV – 8.16%; Adeq Precision – 17.11; 95% significant level.

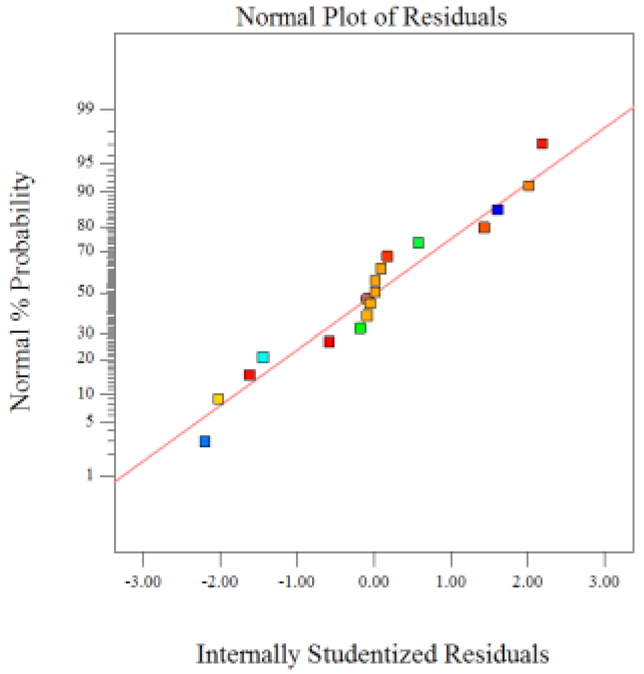

Fig. 1. Normal probability plot of the studentized residual for Cd^{2+} adsorption.

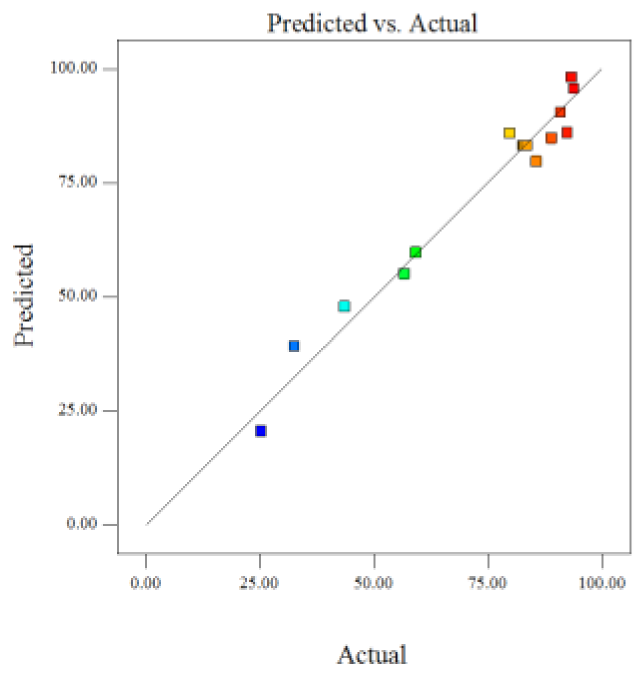

Fig. 2. Correlation of actual and predicted removal.

[43]. Fig. 2 shows the relationship between the actual and predicted values of Y for the adsorption percentage of Cd^{2+} by modified corn straw biochar. These figures indicated that there was a good fit between the observed and the predicted values, and also displayed that the residuals distributed normally on a line [44].

3.3. Response surface analysis

3.3.1. Effects of pH and dosage on the adsorption process

Fig. 3 shows the 3D simulation diagram and contour plot of the effects of pH and dosage on the adsorption percentage. The encoded value of initial concentration is 0, and the encoded value ranges of pH and dosage are -1 and 1. With an increase in the dosage, Cd^{2+} adsorption percentage increased but the increase rate was gradually decreased. When the dosage reached 8.0 $g \cdot L^{-1}$, the adsorption percentage showed a downward trend. The change might be interpreted as follows: When the adsorbent concentration was too high, the adsorbent was stacked together, thus reducing the effective surface area, generating the interaction among adsorption sites on the adsorbent surface, and decreasing the binding effect between the adsorption sites and Cd^{2+}. At the same time, when the adsorbent concentration increased, Cd^{2+} concentration in the solution was decreased. The diffusion trend of Cd^{2+} to the adsorbent surface was decreased, while the desorption trend of Cd^{2+} from the adsorption surface was enhanced [45]. When the pH rose from 3.0 to 5.5, the adsorption percentage increased gradually. When the pH rose further from 5.5 to 7.0, the adsorption percentage decreased. The adsorption process of Cd^{2+} has the suitable pH range. When the pH was too low, H^+ in the solution will compete with Cd^{2+} for adsorption sites, thus resulting in the lower adsorption percentage. When the pH rose, H^+ ions decreased, and the competitive effect with Cd^{2+} decreased. The probability of the combination between functional groups and Cd^{2+} increased, and thus the adsorption percentage increased. When the pH rose to 5.5, the adsorption percentage decreased due to the formation of soluble hydroxyl radicals [45]. When the pH rose above 7, OH^- reacted with Cd^{2+} to form micro-precipitate, thus affecting the adsorption process [46].

As shown in a contour plot, when the encoded value of initial concentration was 0, the optimal pH was between 5.0 and 6.0, and the optimal dosage was between 7.0 and 8.0 $g \cdot L^{-1}$. The shape of the contour plot can reflect the intensity of the interaction of the investigated factors. The circular shape indicates the insignificant interaction, while the oval shape indicates the significant interaction [47]. The contour plot and significance tests indicated that the interaction between pH and dosage was not significant, but the interaction still existed. According to the effect sizes of PBD experimental factors and the coefficients of various items in Eq. (6), pH, dosage, and other items showed the positive effects, but the coefficient of X_1X_3 was negative (–1.85). This phenomenon might be interpreted as follows: the pH value not only affected the state of Cd^{2+} but also changed the active functional groups on the adsorbent surface, especially the functional groups directly related to adsorption, such as alcoholic hydroxyl group and carboxyl group [48]. For the adsorbent of modified corn straw biochar, with the pH rising, the number of active groups on the surface of modified corn straw biochar was increased, and the adsorption sites were decreased. In general, the combined effect of pH and dosage on the adsorption percentage was negative.

3.3.2. Effects of pH and initial concentration on the adsorption process

Fig. 4 shows the 3D simulation diagram and contour plot of the effects of pH and the initial concentration on the

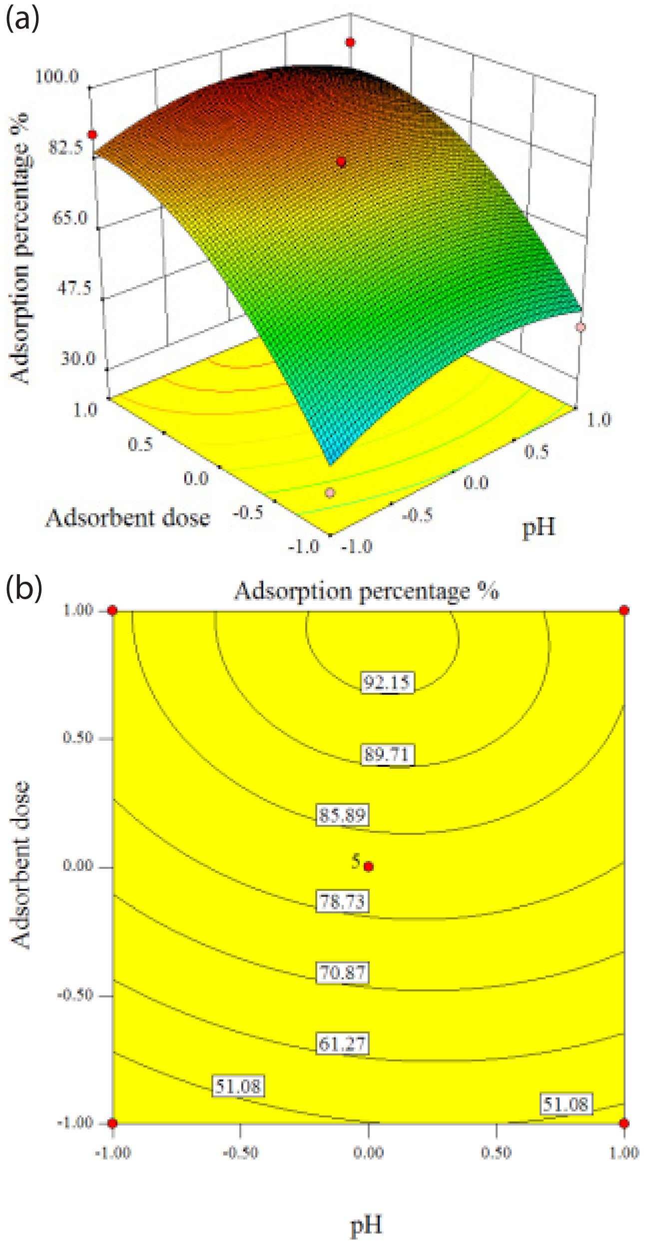

Fig. 3. Response surface and contour plot for the effect of pH and adsorbent dosage on Cd^{2+} removal.

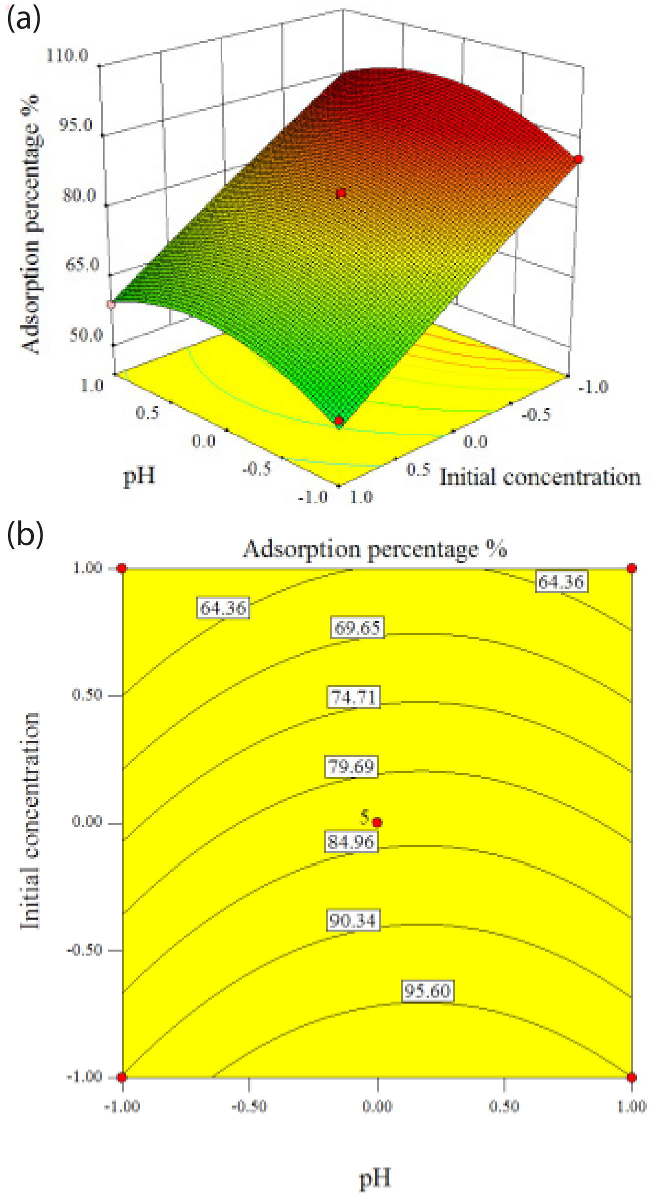

Fig. 4. Response surface and contour plot for the effect of pH and initial concentration on Cd^{2+} removal.

adsorption percentage. The encoded value of dosage is 0. The change trend of the adsorption percentage with pH is similar to that shown in Fig. 1. With the pH rising, the adsorption percentage decreased. When the pH rose to 5.5, the adsorption percentage decreased gradually; when the initial concentration decreased, the adsorption percentage increased. As indicated by the coefficients in Eq. (6), pH showed a positive effect, while the initial concentration showed a negative effect. The coefficient of X_1X_4 was –0.10, indicating a negative effect. Therefore, under the combined effect of pH and initial concentration, the positive effect of pH rise was weaker than the negative effect of the increase in the initial concentration. In order to improve the adsorption percentage, the preferred option is to reasonably reduce the initial concentration. The contour plot indicated that the interaction between pH and the initial concentration was not significant. The optimal pH was between 5.0 and 6.0, and the optimal initial concentration was 20 $mg \cdot L^{-1}$.

3.3.3. *Effects of dosage and initial concentration on the adsorption process*

Fig. 5 shows the 3D simulation diagram and contour plot of the effects of the initial concentration and dosage on the adsorption percentage. The encoded value of pH is 0. In general, the adsorption percentage increased with the decrease in the initial concentration and the increase in dosage. However, when the initial concentration was low, the adsorption percentage increased with the increase in the dosage; when the

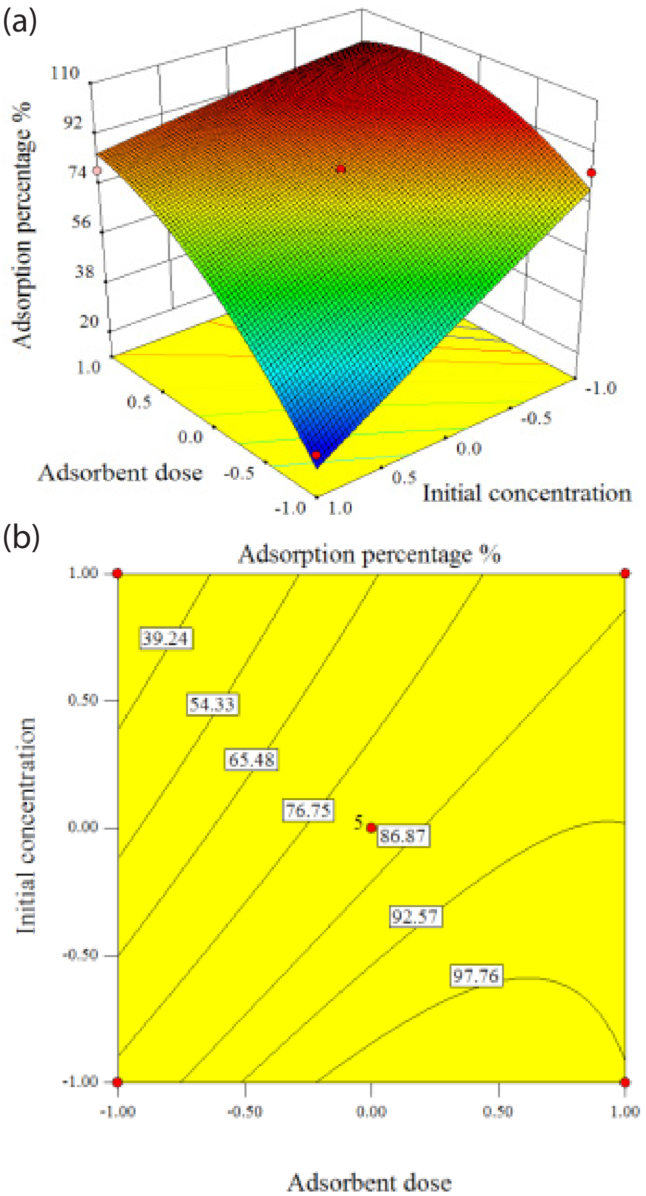

Fig. 5. Response surface and contour plot for the effect of initial concentration and adsorbent dosage on Cd^{2+} removal.

dosage was increased to 6.5 g·L^{-1}, the adsorption percentage declined. This phenomenon might be the same as that shown in Fig. 1. In Table 6, significant analysis and contour plot indicated that the interaction between the initial concentration and dosage was significant. Al-Asheh and Duvnjak [49] found that a proper ratio of metal ion concentration and the adsorbent concentration might yield a higher adsorption percentage. The coefficients in Eq. (6) indicated that the initial concentration and dosage, respectively, showed the positive and negative effects. The coefficient of X_3X_4 was 11.71, indicating a positive effect. Therefore, the positive effect of the increase in the dosage was greater than the negative effect of the increase in the initial concentration. Therefore, a reasonable increase in dosage is the preferred option to improve the adsorption percentage.

3.3.4. Confirmation experiments

In summary, under the low initial concentration and the high dosage, pH 5.5 allowed the higher adsorption percentage. The optimization results by Design Expert software indicated that the adsorption percentage was predicted to be 100% under the following conditions: pH 5.73; the initial concentration of 20.33 mg·L^{-1}; and the dosage of 6.41 g·L^{-1}. Under the obtained conditions, the experimentally obtained adsorption percentage was 99.03%. The predicted results obtained with the model were basically consistent with the experimentally measured adsorption percentage. The study indicated that it is feasible to adopt the combination of PBD and BBD to remove the heavy metal from wastewater.

3.3.5. Process optimization

Cost is an issue that must be considered in remediation of heavy metal contamination. In this study, dosage of modified corn straw biochar is the key factor of cost that cannot be neglected. When determining the best adsorption conditions, Cd adsorption percentage was the main yardstick for optimization at first (depending on the software settings, the highest value of 5 was given to the importance weight), which was to reach the maximum; meanwhile, dosage tended to be used less which importance weight set to be value of 3; the optimal adsorption process parameters was obtained under the following conditions: pH = 5.52, the initial concentration of 20.00 mg·L^{-1}, and the dosage of 3.05 g·L^{-1}. Under the obtained conditions, the experimentally adsorption percentage was 90.05%, which was close to the predicted value of 90.56%. Compared with the obtained conditions neglected the cost, the pH value and the initial concentration in this condition changed little; although the removal rate decreased, there were still more than 90%; what more important is that 52.4% of dosage reduced. It was more significance in practice that the cost had been considered. It was known that the increase of adsorption percentage needs much more dosage while there was a little cadmium ions in the solution; optimization results in this study indicated that more than half of biochar must be dosed to increase the adsorption percentage from 90% to 99%, which is obviously uneconomical.

Currently, the adsorption conditions were optimized by the traditional single-factor experiments and orthogonal experiments [50,51]. In single-factor experiments, single factor was explored under the conditions that the other factors were fixed and the gradient range was set for the single factor to determine the optimal value. We previously optimized the adsorption process of Cd by using modified corn straw biochar through single-factor experiments. In the single-factor experiment of pH, the other adsorption conditions remained unchanged, and pH values were, respectively, set to be 2, 3, 4, 5, 6, and 7 to determine the highest adsorption percentage at each pH value. The pH 6 allowed the highest adsorption percentage. The results obtained with the single-factor experiment method were not reliable because the results were obtained under the set pH values. However, the optimal adsorption percentage might be obtained under the pH between two pH values. For example, the optimal pH was 5.73, which could not be obtained through single-factor experiments. Moreover, the interactions among various factors were ignored in single-factor experiments, thus leading to the unreliable results. In orthogonal experiments, based on the results of single-factor experiments, the representative values of various factors were selected for further optimization. Although the results of orthogonal experiments were more precise than those of single-factor experiments, the interactions among various factors were ignored. Compared with traditional optimization methods, RSM is more precise and intuitive, and can provide more reasonable optimal conditions.

Compared with RSM, the combined method of PBD and BBD is faster and more efficient, and can provide more accurate optimal conditions. First, PBD can quickly obtain the effect size of each factor to screen the main factors, thus largely decreasing the number of the factors to be explored and experiment times. Therefore, the combined method can reduce the experimental errors and increase the experimental efficiency. In the six factors in the study, three main factors were screened through 12 experiments for subsequent BBD optimization. The subsequent BBD optimization of three factors required 17 experiments, but the direct BBD optimization of six factors required 54 experiments. Moreover, the PBD experiments could provide the positive/negative effect of each factor. According to the values and the positive/negative effects of the factors, the ranges of various factors might be adjusted more reasonably in BBD optimization experiments, thus providing the more precise model. Therefore, the optimal conditions obtained with the BBD experiments were more reliable and accurate.

4. Conclusions

The study aims to determine important influencing factors for the adsorption process of Cd^{2+} onto modified corn straw biochar and achieve the maximum removal percentage of Cd^{2+}. The PBD experimental results showed that the main influencing factors for the adsorption process of Cd^{2+} onto modified corn straw biochar included pH, initial Cd^{2+} concentration, and biochar dosage. With taking the cost into consideration, BBD response surface analysis results indicated that the optimal adsorption percentage could be obtained under the following conditions: pH 5.52, the initial concentration of 20.00 mg·L^{-1}, and the dosage of 3.05 g·L^{-1} according to the importance weight setting. The experimentally obtained adsorption percentage was 90.05%, which was close to the predicted value of 90.56%. The results indicated the feasibility of the combined PBD and BBD method, and proved the accuracy and reliability of this statistical and experimental design method. Therefore, the combined PBD and BBD method could be applied in the optimization of Cd^{2+} adsorption conditions and provide more reasonable and effective results.

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References

[1] M.A. Ashraf, M.A. Rehman, Y. Alias, I. Yusoff, Removal of Cd(II) onto *Raphanus sativus* peels biomass: equilibrium, kinetics, and thermodynamics, Desal. Wat. Treat., 51 (2013) 4402–4412.

[2] Q.H. Zhu, D.Y. Huang, S.L. Liu, Z.C. Luo, H.H. Zhu, B. Zhou, M. Lei, Z.X. Rao, X.L. Cao, Assessment of single extraction methods for evaluating the immobilization effect of amendments on cadmium in contaminated acidic paddy soil, Plant Soil Environ., 58 (2012) 98–103.

[3] Y.C. Sharma, Thermodynamics of removal of cadmium by adsorption on an indigenous clay, Chem. Eng. J., 145 (2008) 64–68.

[4] U. Guyo, T. Makawa, M. Moyo, T. Nharingo, B.C. Nyamunda, T. Mugadza, Application of response surface methodology for Cd(II) adsorption on maize tassel-magnetite nanohybrid adsorbent, J. Environ. Chem. Eng., 3 (2015) 2472–2483.

[5] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, J. Environ. Manage., 92 (2011) 407–418.

[6] Y. Feng, J.L. Gong, G.M. Zeng, Q.Y. Niu, H.Y. Zhang, C.G. Niu, J.H. Deng, M. Yan, Adsorption of Cd (II) and Zn (II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents, Chem. Eng. J., 162 (2010) 487–494.

[7] J. Song, H. Kong, J. Jang, Adsorption of heavy metal ions from aqueous solution by polyrhodanine-encapsulated magnetic nanoparticles, J. Colloid Interface Sci., 359 (2011) 505–511.

[8] H.C. Tao, H.R. Zhang, J.B. Li, W.Y. Ding, Biomass based activated carbon obtained from sludge and sugarcane bagasse for removing lead ion from wastewater, Bioresour. Technol., 192 (2015) 611–617.

[9] H.A. Hegazi, Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents, HBRC J., 9 (2013) 276–282.

[10] R.C. Sahu, R. Patel, B.C. Ray, Adsorption of Zn(II) on activated red mud: neutralized by CO_2, Desalination, 266 (2011) 93–97.

[11] T.Y. Jiang, J. Jiang, R.K. Xu, Z. Li, Adsorption of Pb(II) on variable charge soils amended with rice-straw derived biochar, Chemosphere, 89 (2012) 249–256.

[12] E. Padilla-Ortega, R. Leyva-Ramos, J. Mendoza-Barron, Role of electrostatic interactions in the adsorption of cadmium(II) from aqueous solution onto vermiculite, Appl. Clay Sci., 88 (2014) 10–17.

[13] F. Yuan, C. Song, X. Sun, L. Tan, Y. Wang, S. Wang, Adsorption of Cd(II) from aqueous solution by biogenic selenium nanoparticles, RSC Adv., 6 (2016) 15201–15209.

[14] J. Wang, C. Chen, Biosorption of heavy metals by *Saccharomyces cerevisiae*: a review, Biotechnol. Adv., 24 (2006) 427–451.

[15] X. Chen, G. Chen, L. Chen, Y. Chen, J. Lehmann, M.B. McBride, A.G. Hay, Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution, Bioresour. Technol., 102 (2011) 8877–8884.

[16] A.A. Abdelhafez, J. Li, Removal of Pb(II) from aqueous solution by using biochars derived from sugar cane bagasse and orange peel, J. Taiwan Inst. Chem. Eng., 61 (2016) 367–375.

[17] D. Mohan, H. Kumar, A. Sarswat, M. Alexandre-Franco, C.U. Pittman, Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars, Chem. Eng. J., 236 (2014) 513–528.

[18] Q. Cheng, Q. Huang, S. Khan, Y. Liu, Z. Liao, G. Li, Y.S. Ok, Adsorption of Cd by peanut husks and peanut husk biochar from aqueous solutions, Ecol. Eng., 87 (2016) 240–245.

[19] X. Liyou, Z. Zhili, Z. Mingzhu, L. Yan, Characteristics analysis of hydro-mechanical continuously variable transmission of tractor, J. China Agric. Univ., 11 (2006) 70–74 (in Chinese).

[20] H. Wang, B. Gao, S. Wang, J. Fang, Y. Xue, K. Yang, Removal of Pb(II), Cu(II), and Cd(II) from aqueous solutions by biochar derived from $KMnO_4$ treated hickory wood, Bioresour. Technol., 197 (2015) 356–362.

[21] Z. Yu, L. Zhou, Y. Huang, Z. Song, W. Qiu, Effects of a manganese oxide-modified biochar composite on adsorption of arsenic in red soil, J. Environ. Manage., 163 (2015) 155–162.

[22] M. Erdem, H. Duran, M. Şahin, I. Ozdemir, Kinetics, thermodynamics, and isotherms studies of Cd(II) adsorption onto grape stalk, Desal. Wat. Treat., 54 (2015) 3348–3357.

[23] F.Y. Wang, H. Wang, J.W. Ma, Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent—bamboo charcoal, J. Hazard. Mater., 177 (2010) 300–306.
[24] K. Huang, Y. Xiu, H. Zhu, Removal of heavy metal ions from aqueous solution by chemically modified mangosteen pericarp, Desal. Wat. Treat., 52 (2014) 7108–7116.
[25] M.E. Argun, S. Dursun, M. Karatas, Removal of Cd(II), Pb(II), Cu(II) and Ni(II) from water using modified pine bark, Desalination, 249 (2009) 519–527.
[26] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk, Bioresour. Technol., 97 (2006) 104–109.
[27] J. Anwar, U. Shafique, M. Salman, A. Dar, S. Anwar, Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana, Bioresour. Technol., 101 (2010) 1752–1755.
[28] Y. Liu, X. Sun, B. Li, Adsorption of Hg^{2+} and Cd^{2+} by ethylenediamine modified peanut shells, Carbohydr. Polym., 81 (2010) 335–339.
[29] D. Weuster-Botz, Experimental design for fermentation media development: statistical design or global random search? J. Biosci. Bioeng., 90 (2000) 473–483.
[30] R.L. Plackett, J.P. Burman, The design of optimum multifactorial experiments, Biometrika, 33 (1946) 305–325.
[31] P.C. Giordano, A.J. Beccaria, H.C. Goicoechea, Significant factors selection in the chemical and enzymatic hydrolysis of lignocellulosic residues by a genetic algorithm analysis and comparison with the standard Plackett–Burman methodology, Bioresour. Technol., 102 (2011) 10602–10610.
[32] A. Maher, M. Sadeghi, A. Moheb, Heavy metal elimination from drinking water using nanofiltration membrane technology and process optimization using response surface methodology, Desalination, 352 (2014) 166–173.
[33] A.I. Khuri, S. Mukhopadhyay, Response surface methodology, WIREs Comput. Stat., 2 (2010) 128–149.
[34] S.L.C. Ferreira, R.E. Bruns, H.S. Ferreira, G.D. Matos, J.M. David, G.C. Brandao, E.G.P. da Silva, L.A. Portugal, P.S. Dos Reis, A.S. Souza, W.N.L. Dos Santos, Box-Behnken design: an alternative for the optimization of analytical methods, Anal. Chim. Acta, 597 (2007) 179–186.
[35] C. Han, H. Pu, H. Li, L. Deng, S. Huang, S. He, Y. Luo, The optimization of As(V) removal over mesoporous alumina by using response surface methodology and adsorption mechanism, J. Hazard. Mater., 254 (2013) 301–309.
[36] P. Tripathi, V.C. Srivastava, A. Kumar, Optimization of an azo dye batch adsorption parameters using Box–Behnken design, Desalination, 249 (2009) 1273–1279.
[37] M. Jain, V.K. Garg, K. Kadirvelu, Investigation of Cr(VI) adsorption onto chemically treated *Helianthus annuus*: optimization using response surface methodology, Bioresour. Technol., 102 (2011) 600–605.
[38] N.K. Sahoo, K. Pakshirajan, P.K. Ghosh, A. Ghosh, Biodegradation of 4-chlorophenol by Arthrobacter chlorophenolicus A6: effect of culture conditions and degradation kinetics, Biodegradation, 22 (2011) 275–286.
[39] A.S. Guzun, M. Stroescu, S.I. Jinga, G. Voicu, A.M. Grumezescu, A.M. Holban, Plackett-Burman experimental design for bacterial cellulose-silica composites synthesis, Mater. Sci. Eng. C Mater. Biol. Appl., 42 (2014) 280–288.
[40] S.S. Patil, H.M. Jena, Statistical optimization of phenol degradation by *Bacillus pumilus* OS1 using Plackett–Burman design and response surface methodology, Arab. J. Sci. Eng., 40 (2015) 2141–2151.
[41] M. Amini, H. Younesi, N. Bahramifar, A.A.Z. Lorestani, F. Ghorbani, A. Daneshi, M. Sharifzadeh, Application of response surface methodology for optimization of lead biosorption in an aqueous solution by *Aspergillus niger*, Arab. J. Sci. Eng., 154 (2008) 694–702.
[42] M. Mourabet, A. El Rhilassi, H. El Boujaady, M. Bennani-Ziatni, R. El Hamri, A. Taitai, Removal of fluoride from aqueous solution by adsorption on hydroxyapatite (HAp) using response surface methodology, J. Saudi Chem. Soc., 19 (2015) 603–615.
[43] W. Daoud, T. Ebadi, A. Fahimifar, Optimization of hexavalent chromium removal from aqueous solution using acid-modified granular activated carbon as adsorbent through response surface methodology, Korean J. Chem. Eng., 32 (2015) 1119–1128.
[44] A.M. Ghaedi, M. Ghaedi, A. Vafaei, N. Iravani, M. Keshavarz, M. Rad, I. Tyagi, S. Agarwal, V.K. Gupta, Adsorption of copper (II) using modified activated carbon prepared from Pomegranate wood: optimization by bee algorithm and response surface methodology, J. Mol. Liq., 206 (2015) 195–206.
[45] A.K. Meena, K. Kadirvelu, G.K. Mishraa, C. Rajagopal, P.N. Nagar, Adsorption of Pb(II) and Cd(II) metal ions from aqueous solutions by mustard husk, J. Hazard. Mater., 150 (2008) 619–625.
[46] A.H. Hawari, C.N. Mulligan, Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass, Bioresour. Technol., 97 (2006) 692–700.
[47] R.V. Muralidhar, R.R. Chirumamila, R. Marchant, P. Nigam, A response surface approach for the comparison of lipase production by *Candida cylindracea* using two different carbon sources, Biochem. Eng. J., 9 (2001) 17–23.
[48] Y. Göksungur, S. Üren, U. Güvenç, Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass, Bioresour. Technol., 96 (2005) 103–109.
[49] S. Al-Asheh, Z. Duvnjak, Adsorption of copper and chromium by *Aspergillus carbonarius*, Biotechnol. Prog., 11 (1995) 638–642.
[50] J. Zolgharnein, N. Asanjarani, T. Shariatmanesh, Taguchi L_{16} orthogonal array optimization for Cd (II) removal using *Carpinus betulus* tree leaves: adsorption characterization, Int. Biodeterior. Biodegrad., 85 (2013) 66–77.
[51] M. Feizi, M. Jalali, Removal of heavy metals from aqueous solutions using sunflower, potato, canola and walnut shell residues, J. Taiwan Inst. Chem. Eng., 54 (2015) 125–136.