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Optimization of biosorption parameters of Hg(II) from aqueous solutions by the buckwheat hulls using respond surface methodology

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ABSTRACT

The buckwheat hulls in the region of Jiaodong were used as the potential adsorbents for the removal of heavy metal ions from wastewater. The experimental results showed that the buckwheat hulls with 120 meshes had good adsorption capability for Hg(II) ions. Moreover, the adsorption process optimization of the buckwheat hulls for Hg(II) ions was performed through Central Composite Rotary Design using response surface methodology (RSM) by Design Expert Version 8.0.6.1 (Stat-Ease, Inc., Minneapolis, MN, USA). For the maximum biosorption of mercury ions from aqueous solutions by the buckwheat hulls, a total of 20 experimental runs were set and the experimental data fitted to the empirical second-order polynomial model of a suitable degree. The quantitative relationship between the mercury removal and different levels of the factors (initial pH, adsorbent dosage, and initial Hg(II) concentration) was used to work out optimized levels of these parameters by a full factorial design (2^3). The analysis of variance (ANOVA) of the quadratic model demonstrated that the model was highly significant, and initial pH of 4.0, initial Hg(II) concentration of 802.36 mg/L, and adsorbent dosage of 2.0 g/L were found to be the optimum conditions for the maximum uptake of mercury ions of 110.07 mg/g in batched mode.

Keywords: Biosorption; Mercury(II); Aqueous solutions; Buckwheat hulls; Optimization; Response surface methodology

1. Introduction

The pollution of environment with toxic heavy metals is spreading through the world along with industrial progress. Heavy metal ions, such as Hg(II), Cd(II), and Cr(III), are the major metal ion pollutants in water, and they can accumulate in the food chain, which posed a severe danger to human health [1]. Mercury, known as a kind of remarkably toxic and nonbiodegradable metal, is ubiquitous in the global environments and derives from both natural sources and industrial activities. The presence of mercury in fish, waste water, dental amalgams, vaccine preservatives, and in the atmosphere has made this particular toxic metal an increasing focus of health authorities and interest groups [2–6]. Hence, the removal of mercury from effluents has been a significant concern in

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most industrial branches due to the economic and environmental factors.

In the recent years, attention was focused on the methods for recovery and reuse of metals rather than disposal, and adsorption is highly effective and economical, and is a promising and widely applied method [7–11]. Therefore, effective adsorbents with strong affinities and high loading capacity for the targeted heavy metal ions have been subsequently studied. Recently, the search for low-cost adsorbents that have metal-binding capacities has intensified. Materials locally available in large quantities, such as natural materials, agricultural waste or industrial byproducts, can be utilized as low-cost adsorbents. A large number of low-cost adsorbents, such as coal ash, tea waste, spent grain, waste iron oxide, spent active clay, wood sawdust, seaweeds, etc., have been reported in the literature for the removal of heavy metals [12–19]. Especially, certain types of biomass, such as agricultural residuals, are efficient adsorbents for heavy metal ions [20–22]. It is well known that agricultural residuals, such as rice hull, peanut hull etc., are one kind of the rich sources for low-cost adsorbents. Because of abundant availability, agricultural wastes pose little economic value and create serious disposal problems. Moreover, when an adsorbent from agricultural waste gets saturated, regeneration of the spent adsorbent has become one of the most cost effective and sound environmental option, since no solid waste will be generated and disposed of. In fact, regeneration and desorption could be done to recover valuable metal from the spent adsorbent [23]. Buckwheat has become popular as a kind of healthy food, since it was reported that its seeds contain many biologically active compounds [24]. As one kind of agricultural residuals, buckwheat hull is rich in cellulose, which has carboxyl and hydroxyl functional groups, and it could be used as biosorbent for heavy metals. Until now, to the best of our knowledge, only a few reports are available on adsorption investigation of buckwheat hulls. Wu et al. used thiol-functionalized buckwheat hull to facilitate adsorption of Pb(II) from glucose solution, and its adsorption capacity could reach 44.84 mg/g [25]. Li et al. reported the biosorption of chromium(VI) ions by buckwheat hull from water, and removal ratio was 99.87% of 100 mg/L at pH 2.0 and loading of 5.0 g/L [26].

Because optimization of biosorption parameters by classical method involving changing one independent variable while keeping others at a fixed level is extremely time consuming and expensive for a large number of variables, recently, response surface methodology (RSM) is always employed to optimize the reaction parameters for production process , and it allows users to gather large amounts of information from a small number of experiments. It is also possible to observe the effects of individual variables and their combinations of interactions on the response by using RSM [27]. Then, the experimental factorial design and RSM can be employed to optimize the biosorption of heavy metals. Therefore, the purposes of the present study were to optimize the biosorption process of Hg(II) from stimulated wastewater by the buckwheat hulls in region of Jiaodong using RSM.

2. Experimental details

2.1. Materials and methods

The buckwheat hulls used in adsorption were obtained from a buckwheat production site in the suburbs of Yantai, China; they were washed with distilled water, dried at 50°C, and then ground in a mill to pass through different mesh sieves (30, 60, 90, 120 mesh) for further processing. All the reagents were of analytical grade and used without any further purification; they were purchased from Sinopharm Chemical Reagent Co., Ltd., China and all solutions were prepared with deionized water. Stock solutions of Hg(II) ($0.1\,mol\,L^{-1}$) were prepared by dissolving $Hg(NO_3)_2{\cdot}H_2O$ in 3% HNO_3 to avoid hydrolysis, and ammonium acetate/nitric acid buffer solution was used for pH adjustment.

Infrared spectra (FT-IR) of samples were reported in the range of 4,000–400 cm^{-1} with a resolution of 4 cm^{-1}, by accumulating 32 scans using a Nicolet MAGNA-IR 550 (series II) spectrophotometer. KBr pellets were used for solid samples. The morphology of the adsorbents was examined through JEOL JSF5600LV scanning electron microscope (SEM), JEOL Co., Japan. The EDXAS was performed on a NORAN LEVER-2 EDX analytical instrument. Before observation, the sample was placed on a specimen stub covered with a conductive adhesive tab and provided with a sputtered 15-nm gold coating. The concentration of metal ions were determined using a 932-model atomic absorption spectrometer (GBC-932A, made in Australia), equipped with air–acetylene flame.

2.2. Adsorption experiments for metal ions

Static adsorption experiment was employed to determine the adsorption capacities of the buckwheat hulls for different kinds of metal ions. The static adsorption experiments were carried out with shaking 0.02 g of adsorbents with 20 mL of metal ion solution (2 mmol/L). The mixture was equilibrated for 24 h on a thermostat-cum-shaking assembly at 25°C. The adsorbent was filtered and the concentrations of transition metals in solutions were determined using atomic adsorption spectrophotometer (GBC-932A).

The adsorption amount was calculated according to the Eq. (1):

$$q = \frac{(C_o - C_e)V}{W} \tag{1}$$

where q is the adsorption amount (mmol/g); C_o and C_e are the initial and equilibrium concentrations of metal ions (mmol/ml) in solution, respectively, V is the volume of the solution (mL), and W is the weight of the buckwheat hulls (g).

2.3. RSM

The effects of three independent variables: initial pH, initial Hg(II) concentration, and adsorbent dosage were investigated by means of central composite design (CCD). For statistical calculation, the variables were coded according to Eq. (2):

$$X_{\mathrm{Coded}} = \frac{X_{\mathrm{Actual}} - (X_{\mathrm{High}} + X_{\mathrm{Low}})/2}{(X_{\mathrm{High}} - X_{\mathrm{Low}})/2} \tag{2}$$

where X_{Coded} is the dimensionless coded value of the independent variable, X_{Actual} is the actual value of the independent variable and X_{High} and X_{Low} are the high and low independent variables (at 1 and −1 levels, respectively). The range and levels are given in Table 1. In this study, for a rotatable design, α is equal to 2. In order to ensure the feasibility of factors at ±α level, factor levels were entered in terms of α for the CCD. The quadratic equation for predicting the response was expressed according to Eq. (3):

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i x_i^2 + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{3}$$

where Y is the predicted response, x_i and x_j are the input variables, β_0 is the intercept term, β_i is the linear effect, β_{ii} is the squared effect, β_{ij} is the interaction effect, and ε is a random error. The number of tests required for the CCD includes the standard $2n$ factorial with its origin at the center, $2n$ points fixed axially at a distance say α from the center to generate the quadratic terms, and replicate tests at the center. For three variables, the recommended number of tests at the center is six. Hence, the total number of tests (N) required for the three independent variables is

$$N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 6 = 20 \tag{4}$$

All the 20 runs (Table 2) were conducted in duplicate in 100-mL Erlenmeyer flasks with 10 mL of metal solution at 130 rpm, 25℃ for 24 h. The data obtained were analyzed by the software Design Expert 8.0.6.1 (Stat-Ease, Inc., Minneapolis, MN, USA).

3. Results and discussion

3.1. Static adsorption of the buckwheat hulls for transition metal ions

Fig. 1 showed the static adsorption capacities of the buckwheat hulls with different sizes (30, 60, 90, and 120 mesh) for Hg(II), Cu(II), Pb(II), Ni(II), Cd(II), Cr(III), Zn(II), and Co(II) metal ions. It is clear from the figure that the buckwheat hulls (120 mesh) usually had the higher adsorption capacities for heavy metals than those of the buckwheat hulls with other particle sizes, which may be due to the higher specific surface area of the buckwheat hulls with smaller particle size. The research result also displayed the static adsorption capacities of the buckwheat hulls (120 mesh) for Hg(II) and Cu(II) were 0.806 and 0.262 mmol/g, respectively. However, those for Pb(II), Ni(II), Cd(II), Cr(III), Zn(II), and Co(II) metal ions were 0.157, 0.146, 0.148, 0.105, 0.0708, and 0.0154 mmol/g, respectively. Obviously, the adsorbent buckwheat hulls in the region of Jiaodong had good adsorption capability for Hg(II) and Cu(II) metal ions, especially for Hg(II) ion. According to the theory of hard and soft acids and bases defined by Pearson, metal ions will have a preference for coordinating with ligands that have more or less same electronegative donor atoms. The buckwheat

Table 1
Coded levels for independent factors used in the experimental design

Factors	Symbol	Coded levels				
		−2	−1	0	+1	+2
Initial pH	X_1	1	2	3	4	5
Adsorbent dosage (g/L)	X_2	1	2	3	4	5
Initial Hg(II) concentration (mg/L)	X_3	200.59	401.18	601.77	802.36	1002.95

Table 2
Experimental design and results of the response surface design

Std	Run no.	Independent values						Equilibrium adsorption capacity (q), mg/g		
		Coded values			Real values			Observed values	Predicted value	Residual
		X_1	X_2	X_3	X_1	X_2	X_3	q_{obs}	q_{pred}	$q_{obs}-q_{pred}$
16	1	0	0	0	3	3	601.77	71.75845	69.95117	1.807282
15	2	0	0	0	3	3	601.77	86.83582	93.01558	−6.17975
6	3	1	−1	1	4	2	802.36	46.16667	31.82232	14.34435
19	4	0	0	0	3	3	601.77	81.615	91.72371	−10.1087
13	5	0	0	−2	3	3	200.59	119.3381	108.5773	10.76075
5	6	−1	−1	1	2	2	802.36	96.37561	110.0679	−13.6923
14	7	0	0	2	3	3	1002.95	72.27317	65.44138	6.831794
1	8	−1	−1	−1	2	2	401.18	102.6137	103.7689	−1.15524
4	9	1	1	−1	4	4	401.18	51.4373	67.98337	−16.5461
7	10	−1	1	1	2	4	802.36	145.2694	129.3753	15.89403
9	11	−2	0	0	1	3	601.77	118.955	114.9769	3.978038
18	12	0	0	0	3	3	601.77	65.919	70.54908	−4.63008
12	13	0	2	0	3	5	601.77	50.06689	49.67246	0.394434
11	14	0	−2	0	3	1	601.77	99.29739	100.3439	−1.04647
20	15	0	0	0	3	3	601.77	70.625	70.73367	−0.10867
8	16	1	1	1	4	4	802.36	70.625	70.73367	−0.10867
3	17	−1	1	−1	2	4	401.18	70.625	70.73367	−0.10867
17	18	0	0	0	3	3	601.77	70.625	70.73367	−0.10867
10	19	2	0	0	5	3	601.77	70.625	70.73367	−0.10867
2	20	1	−1	−1	4	2	401.18	70.625	70.73367	−0.10867

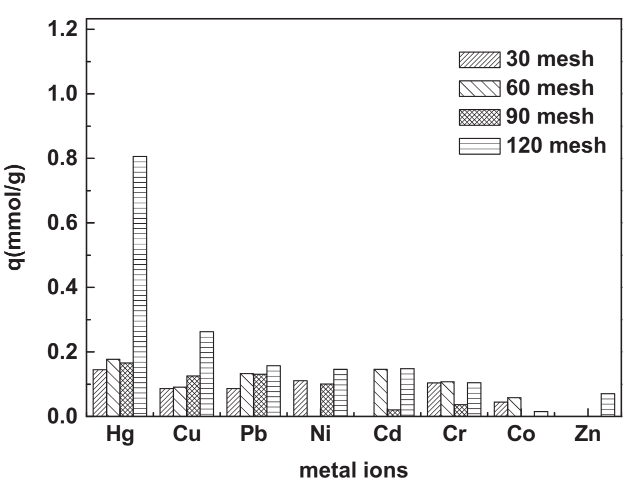
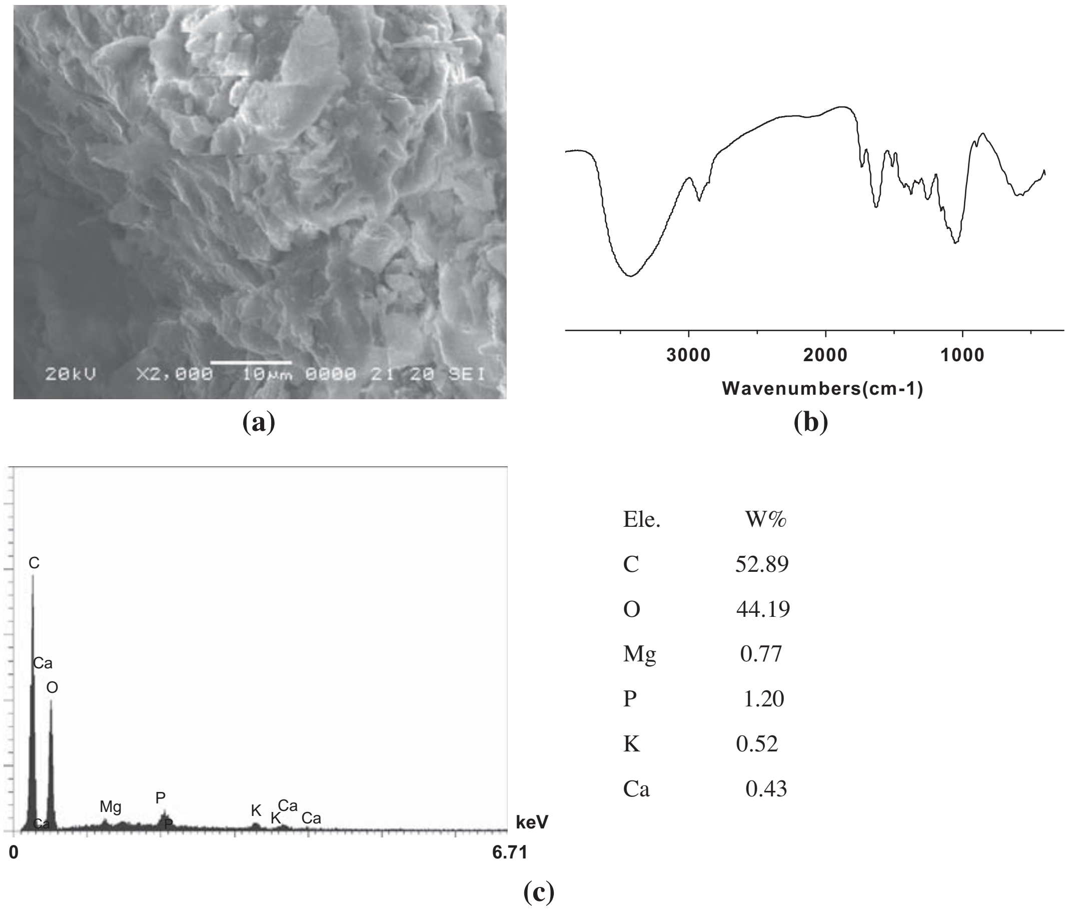


Fig. 1. The static adsorption capacities of buckwheat hulls with different meshes for transition metal ions (the initial solution concentration of transition metal ions: 2.0 mmol/L; pH=5.0; $T=25$℃).

hulls have surface functional groups, such as hydroxyl and carboxylic, that possess high affinity for mercury ions. Therefore, in the following part, the adsorption process of the buckwheat hulls for Hg(II) from aqueous solutions was investigated particularly.

3.2. Characterizations of the buchwheat hulls

The SEM image with ×2,000 magnification of the buckwheat hulls is shown in Fig. 2(a), which displayed the relevant surface characteristics. The surface layer of the buckwheat hulls appeared to be rough in nature, and might exhibit a microstructure porosity. Microporous active sites on the surface layer of the buckwheat hulls may proceed faster action of biosorption. Taking the adsorption mechanism into account, FT-IR analysis is considered to be a useful technology in exploring the adsorption behaviors of adsorbents. FT–IR spectrum of the buckwheat hulls is shown in Fig. 2(b). The band at 1637.17 cm^{-1} was assigned to the carboxyl groups in the buckwheat hulls. Moreover, The bands at 3428.26 and 1052.83 cm^{-1} were assigned to hydroxyl groups, which could coordinate with mercury ions in aqueous solutions. Fig. 2(c) shows the energy spectrum of the buckwheat; the relevant results of element percentage were C (52.89%), O (44.19%), Mg (0.77%), P (1.20%), and K (0.52%), while the EDX results of the buckwheat hull from Shanxi showed that it contained the elements of C, O, K, Al, S, Fe, etc. [26]. The buckwheat hulls in the region of Jiaodong are rich in cellulose, and have



Ele.	W%
C	52.89
O	44.19
Mg	0.77
P	1.20
K	0.52
Ca	0.43

Fig. 2. (a) SEM images of the buckwheat hulls; (b) FT–IR spectra of the buckwheat hulls; and (c) The energy spectra and element percentage of the buckwheat hulls.

carboxyl and hydroxyl functional groups. So, they had excellent adsorption capacities for Hg(II) due to their microstructure porosity and the functional groups on the surface.

3.3. RSM

RSM is an efficient statistical technique for optimization of multiple experimental variables to predict the best performance conditions with minimum numbers of synthesis experiments. RSM was applied to model the adsorption capacity of Hg(II) from aqueous solutions with three factors: initial pH, adsorbent dosage, and initial Hg(II) concentration. In the present study, CCD for the three variables was used as the experimental design model, and RSM enabled us to obtain sufficient information for statistically acceptable results using reduced number of experimental sets. A total of 20 experiments were required to be performed to calculate 10 coefficients of the second-order polynomial equation. The adsorption of mercury ion estimated as adsorption capacity of the buckwheat hulls was taken as the response of the system. The experimental design matrix derived from CCD and the adsorption amount has been shown in Table 2. All of the 20 designed experiments were performed, the results were multi-regression analyzed, and Table 2 lists the levels of the adsorption capacity at each of the 20 experimental sets generated by the principles of RSM used in this study. The application of RSM expressed in the following regression, Eq. (5), is an empirical relationship between adsorption capacity (q) and the tested variables take in coded unit.

$$\begin{aligned} q = {} & 70.73 + 15.35X_1 - 11.11X_2 + 12.67X_3 \\ & + 9.21X_1X_2 - 5.39X_1X_3 - 1.25X_2X_3 + 6.99X_1^2 \\ & + 5.01X_2^2 + 1.07X_3^2 \end{aligned} \quad (5)$$

where q is the response, i.e. adsorption capacity, and X_1, X_2, and X_3 are the coded values of the main effects of initial pH, adsorbent dosage, and initial Hg(II) concentration, respectively, whereas the variables X_1X_2, X_1X_3, and X_2X_3 represent the interaction effect of initial pH and adsorbent dosage, initial pH and initial Hg(II) concentration, and adsorbent dosage and initial Hg(II) concentration, respectively. X_1^2, X_2^2, X_3^2 are the measures of the main effect of initial pH, adsorbent dosage, and initial Hg(II) concentration, respectively. The central point was replicated six times. The results of the coefficients of the model and the analysis of variance (ANOVA) are shown in Table 3. The statistical significance of the modal equation was evaluated by the *F*-test ANOVA. The significance of each coefficient was determined by *F*-values and *P*-values. It was observed from Table 3, the coefficients for the main effects were highly significant ($p < 0.0027$) in comparison with the interactive and square effects. It is well known that the larger magnitude of the *F*-value and smaller the *P*-value, the more significant is the corresponding coefficient [28], then, this implies that the variable with the largest effect was initial pH value. Moreover, the interaction of initial pH and adsorbent dosage (X_1X_2) was highly significant ($p = 0.0431$), and the quadratic terms of initial pH X_1^2) was very insignificant ($p = 0.011$). The F_{model} value (9.5868) with a low probability value ($p = 0.0008$) demonstrates a high significance for the regression model. The goodness-of-the fit of the model was also checked by the multiple correlation coefficient (R^2). In this case, the coefficient of determination (R^2) of the model was 0.9861, which indicated that the model was suitable to represent the real relationships among the selected reaction parameters, and it revealed that this regression is statistically significant and 0.0139 of the total variations is not explained by the model. Moreover, a relatively lower value of the coefficient of variance indicates a better precision and reliability of the experiments that were carried out [29].

An attempt was made to improve the performance of the laboratory biosorption system with a view to understand better mercury ions removal efficiency. The adsorption capacity of the buckwheat hulls over different combinations of independent variables were

Table 3
Coefficients of the model and ANOVA

Terms	Coefficients estimate	Standard error		F-value	P-value
Intercept	70.73367	4.487259		9.586812	0.0008
X_1	15.34799	2.812538		29.77873	0.0003
X_2	−11.107	2.812538		15.59529	0.0027
X_3	12.66785	2.812538		20.28659	0.0011
X_1 X_2	9.209247	3.97753		5.360698	0.0431
X_1 X_3	−5.39346	3.97753		1.838687	0.2049
X_2 X_3	−1.25178	3.97753		0.099044	0.7594
${X_1}^2$	6.986418	2.243629		9.696321	0.011
${X_2}^2$	5.507331	2.243629		6.025321	0.034
${X_3}^2$	1.068621	2.243629		0.226853	0.6441
ANOVA					
source	Sum of squares	Degrees of freedom	Mean squares	*F*-value	*P*-value Prob > *F*
Model	10920.27	9	1213.364	9.586812	0.0008
X_1	3768.973	1	3768.973	29.77873	0.0003
X_2	1973.833	1	1973.833	15.59529	0.0027
X_3	2567.591	1	2567.591	20.28659	0.0011
X_1 X_2	678.4818	1	678.4818	5.360698	0.0431
X_1 X_3	232.7151	1	232.7151	1.838687	0.2049
X_2 X_3	12.53561	1	12.53561	0.099044	0.7594
X_1^2	1227.224	1	1227.224	9.696321	0.011
X_2^2	762.6003	1	762.6003	6.025321	0.034
X_3^2	28.71191	1	28.71191	0.226853	0.6441
Residual	1265.659	10	126.5659		
Lack of fit	1265.659	5	253.1319		
Pure error	0	5	0		
cor total	12185.93	19			
$R^2 = 0.9861$	CV = 0.1379				

visualized through three-dimensional view of response surface plots. The response surfaces and contour plots for the above-mentioned model were plotted with the adsorption capacity as a function of two variables, while keeping other variables at the optimum level. The effect of initial pH and initial Hg (II) concentrations on the mercury adsorption capacity is shown in Fig. 3(a). Clearly, the initial pH exerted stronger influence than initial metal concentration, which could also be deduced from the coefficients of factors in Eq. (5). It can be seen that the mercury removal increased with increase of initial solution pH, and on the other hand, metal uptake was increased with increasing of initial mercury ion concentration. At lower pH, the adsorbent surfaces might be highly protonated and the overall surface charge on the biomass adsorbent became positive or less negative, which would weaken the adsorption for mercury ions [4]. An increase of metal uptake by increasing initial metal ion concentration is a result of the increase in the driving force of the concentration gradient, rather than increase in the initial metal ion concentration [27]. Under the same conditions, if the concentration of mercury ions in the solution was higher, the active sites of the buckwheat hull would be surrounded by more mercury ions, and the adsorption process would be conducted more sufficiently. Moreover, it is found that a relatively strong interaction existed between initial pH and initial mercury concentration (X_1 and X_3), which was reflected by the corresponding P value ($p = 0.2049$) and it was deduced from the curvature of the contour. Furthermore, as mentioned above, the initial pH played an important role in mercury ion uptake as it was evident from the equation and plot, and the effect of biosorbent dosage and initial pH on mercury uptake is shown in Fig. 3(b). It was observed that the metal uptake decreased with increasing the amount of biomass. Though increasing the buckwheat hulls dosage can be attributed to increased biomass surface area and the availability of more adsorption sites, the values of metal uptake decreased with increasing the adsorbent dosage [30]. This means that the higher values of mercury ion uptake could be obtained by the decrease in biomass dosage and increase in initial solution pH simultaneously, which may be explained by the increase in availability of binding sites at higher initial solution pH and this improved in the access of metal ions to the metal-binding sites of cell wall [31]. Moreover, the curved contour lines showed that there was an interaction between adsorbent dosage and initial pH. It has been found that the interaction between adsorbent dosage and initial pH concentration (X_1 and X_2) was very significant ($p = 0.0431$) and found to be responsible for achieving a relative high mercury ions uptake, as predicted by the model and the response contour plot. The relationship between initial metal ion concentration and biomass dosage is shown in Fig. 3(c) which shows the effect of initial Hg(II) ion concentration, the buckwheat hulls dosage, and their reciprocal interaction on the adsorption capacity. It is clear that a moderate interaction was found between adsorbent dosage and initial metal concentration ($p = 0.7594$). As seen from Fig. 3(c), a higher ratio of the surface binding site on the buckwheat hulls to the mercury ion concentration could be obtained at lower biomass dosage and higher initial mercury ions concentration. Similar observations were found in studies on cadmium ions biosorption using *Saccharomyces cerevisiae* [27]. With the dosage of the buckwheat hulls increasing, the adsorption capacity of Hg(II) ions per unit mass of biosorbent was decreased. Increasing biosorbent

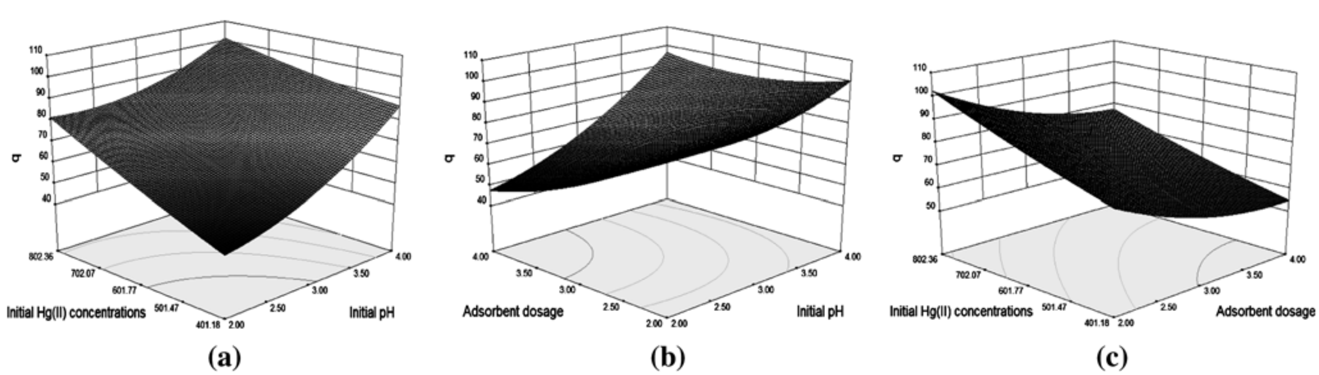


Fig. 3. (a) Response surface plot showing the effect on initial Hg(II) ions concentration and initial solution pH and their mutual effect on the metal biosorption capacity (q); (b) response surface plot showing the effect on the buckwheat hulls dosage and initial solution pH and their mutual effect on the metal biosorption capacity (q); and (c) response surface plot showing the effect on initial Hg(II) ions concentration and the buckwheat hulls dosage and their mutual effect on the metal biosorption capacity (q).

Table 4
Adsorption capacities of different adsorbents

Adsorbents	References	Adsorption capacities (mg/g)
The buckwheat hulls in the region of Jiaodong with 120 meshes	Our work	110.07 mg/g
TCF (the modified thiol cotton fiber)	[32]	60–70
SG-HO-pD	[33]	104.31
SG-HE-pD	[33]	36.11
SG-HO-dD	[33]	44.13
SG-HE-Dd (where SG means silica-gel; HE means heterogeneous, HO means homogeneous, d means direct, p means protected and D means diethylenetriamine)	[33]	28.08
GLA (cross-linking with glutaraldehyde)–chitosan	[34]	22.3–75.5
ECH (epichlorohydrin)–chitosan	[34]	16.3–30.3

dosage can be attributed to increased biosorbent surface area and the availability of more adsorption sites. However, the values of adsorption capacity decreased with increasing the buckwheat hulls dosage. The problem of high biomass dosage resulted in aggregates of the buckwheat hulls and may cause interference between binding sites at higher adsorbent dosage or insufficiency of mercury ions in aqueous solutions with respect to available binding sites.

3.4. Optimization of the adsorption conditions

As we know, it is of general interest for developing industrial process of the mercury adsorption from wastewater. Based on the discussion above, it was possible to obtain a high degree of adsorption capacity through searching for the optimum point. The maximum predicted adsorption capacity for optimum adsorption variables was obtained through point prediction method and response surface plots. The optimum values of selected variables were obtained by solving the regression equation (Eq. (5)). The optimal conditions for mercury adsorption using the buckwheat hulls were initial pH of 4.0, initial Hg(II) concentration of 802.36 mg/L, and adsorbent dosage of 2.0 g/L, and the theoretical maximum adsorption capacity was 110.07 mg/g. To confirm the prediction by the model, three independent experiments for the mercury biosorption over the buckwheat hulls were conducted under the established optimal conditions. The average experimental adsorption capacity reached 107.44 mg/g and was close to the predicted value. Thus, demonstrating that RSM with appropriate experimental design can be effectively applied to optimize the process of factors in the adsorption process, it was clear that the adsorption capacity of the buckwheat hulls in the region of Jiaodong with 120 meshes was relatively high when compared to several other adsorbents, such as the modified thiol cotton fiber, silica-gel supported diethylenetriamine, GLA (cross-linking with glutaraldehyde)–chitosan, etc. [32–34], and the adsorption capacities of different adsorbents are listed in Table 4. The above-mentioned research results showed that this low-cost adsorbent material was very useful for the removal of Hg(II). The buckwheat hulls are rich in carboxyl groups providing good ion exchange capacity, moreover, the hydroxyl and amino groups on buckwheat hulls can also interact with mercury (II) ions due to their electron donating nature. From the practical point of view, the high adsorption capacity and efficiency should make buckwheat hulls a kind of potential adsorbent, which can be used as low-cost adsorbent with high efficiency for water purification, would improve economic value, helping industries reduce the cost of waste disposal and providing a processing of mercury uptake.

4. Conclusions

The buckwheat hull is a kind of agriculture residues, and it is nontoxic and biodegradable biomass. This study demonstrated that buckwheat hulls with 120 meshes could be a kind of potential adsorbent for removing Hg(II) from aqueous solutions. The buckwheat hulls are rich in carboxyl groups providing good ion exchange capacity, moreover, the hydroxyl and amino groups on buckwheat hulls can also interact with mercury (II) ions due to their electron donating nature. From the practical point of view, the high adsorption capacity and efficiency should make buckwheat hulls a kind of potential adsorbent, which can be used as low-cost adsorbent with high efficiency for water purification, would improve economic value, helping industries reduce the cost of waste disposal and providing a processing of mercury uptake.

Moreover, it is evident that RSM can be used successfully to gain knowledge to explain the relative performance of the adsorbent buckwheat hulls for Hg (II) adsorption. The optimum values for maximum adsorption capacity could be obtained by RSM with a minimum of experimental work. Under the optimal conditions (pH of 4.0, initial Hg(II) concentration of 802.36 mg/L and adsorbent dosage = 2.0 g/L), the predicted value of the adsorption capacity was 110.07 mg/g. Validation experiments were also carried out to verify the availability and the accuracy of the model, and the result showed that the predicted value was in agreement with the experimental value (107.44 mg/g) well.

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