Journal of Materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 7, Page 2442-2454

http://www.jmaterenvironsci.com/

Response surface modeling of copper (II) adsorption from aqueous solution onto neem (*Azadirachta indica*) bark powder: Central composite design approach

B. Das*

Department of Chemistry, Kalna College, Kalna, Burdwan, West Bengal, India

Received 11 Mar 2016,
Revised 28 Mar 2017,
Accepted 01 Apr2017

Keywords

- ✓ Response surface methodology;
- ✓ Neem bark powder;
- ✓ Entropy;
- ✓ Adsorption;
- ✓ Desirability

B.Das
bchem1983@gmail.com
+9800230927

Abstract

In this work the individual and combined effect of four process parameters, i.e. initial copper (II) concentration, adsorbent dose, initial solution pH, and contact time on the adsorption of copper (II) from aqueous solution were studied by neem bark powder (NBP) using response surface methodology (RSM) approach based on central composite design (CCD). Copper (II) removal is maximum at the pH: 5, adsorbent dose: 0.9 g/50 ml, contact time: 90 min and initial copper (II) ion concentration: 62.5 mg/L. Analysis of variance (ANOVA) showed the relative significance of process parameters in removal process. The R^2, adjusted R^2 and predicted R^2 values showed a good agreement between the actual and the predicted values. Process variables were optimized by desirability function. Thermodynamic parameters such as Gibbs free energy (ΔG^o), the enthalpy (ΔH^o) and the entropy change of adsorption (ΔS^o) have also been evaluated and it has been found that the adsorption process was spontaneous, feasible and endothermic in nature.

1. Introduction

Heavy metals in water stream have been a major preoccupation for researchers for many years due to their toxicity, bio–accumulation tendency and persistency in nature [1-3]. The major toxic and hazardous heavy metals for humans as well as other forms of life are zinc, copper, nickel, mercury, cadmium, lead and chromium. Copper has been known as one of the most common toxic heavy metal, which finds its way to the water stream from industries like electroplating, mining, electrical and electronics, iron and steel production, the nonferrous metal industry, the printing and photographic industries and metal working and finishing processes [4, 5]. To maintain human body metabolism as a trace element, copper is essential, however excessive input of copper can cause serious health hazards such as damage to heart, kidney, liver, pancreas, brain, intestinal distress and anemia [6]. According to World Health Organization (WHO) maximum acceptable concentration of copper (II) in drinking water is 1.5 mg /L [7]. In India acceptable limit of copper in drinking water is 3 mg/L [8]. Therefore, the concentration of copper (II) ions must be reduced to levels that satisfy environmental regulations for various bodies of water. The common technologies for removing heavy metal ions from water and wastewater include chemical precipitation, ion-exchange, electrochemical deposition, solvent extraction, membrane filtration and adsorption. Among these, adsorption is one of the most economically favorable and technically simple methods [9]. Previously many heavy metal adsorption studies have been done by the application of activated carbons [10, 11]. However, due to its high cost and loss during the regeneration hamper its applicability. The discovery of alternative adsorbent to replace the costly activated carbon is highly encouraged. Nowadays, researchers are focusing more on the development of low cost and efficient adsorbents to remove heavy metals from aqueous solution. A number of researchers have utilized wide variety of adsorbents to remove heavy metal ions from aqueous solutions. Some of the recent developments include adsorbents like sawdust [12], chitosan hydrogel beads [13], fly ash [14], baggase [15], pumice [16], modified clay [17], cassava waste [18], sunflower hulls [19], Pine cone powder [20], spent coffee grains [21], alluvial soil of Bhagirathi river [22] etc. for the removal of copper ions from aqueous solution.

In the present study, a non-conventional finely ground neem bark powder (NBP) has been used as an adsorbent for the removal of copper (II) ions from aqueous solution. Lately, use of response surface methodology (RSM) has been accentuated for developing, improving and optimizing the complex processes and to find out the optimum operating conditions for a given system or the way in which a particular response is affected by a set of variables. RSM has been extensively used in the field of pharmacology [23], microbiology [24], food chemistry [25] and vehicle crash testing [26]. To date, there have been no reports regarding the optimization of process parameters for copper (II) adsorption onto NBP. The main aim of this study is to examine the combined effect of different operating parameters like initial copper (II) concentration, adsorbent dose, pH and contact time on the removal of copper (II) ions from aqueous solutions using neem bark powder. Thermodynamic parameters were also evaluated and reported.

2. Materials and methods

2.1. *Preparation of the synthetic copper solution*

A stock solution of copper (II) was prepared (100 mg/L) by dissolving 0.3929 g of analytical grade copper sulphate penta hydrate obtained from E. Merck Ltd., India in double distilled water. The working solutions of metal were prepared by diluting the stock solution to the desired concentrations (25-100 mg/L). Before mixing the adsorbent, the pH of each copper solution was adjusted to the required value by 0.1 M NaOH or 0.1 M HCl solution.

2.2 *Adsorbent collection and preparation*

The brown colored neem (*A. indica*) bark used in the present work was collected from local wood shop. The collected *A. indica* bark was washed thoroughly with deionised water to remove dirt particles and water soluble materials. The washing process was continued till the wash water contains no colour. The washed *A. Indica* bark was then initially sun–dried for 10 days followed by drying in hot air oven at 383 ± 1K for 24 h. The dried bark was then cut into small pieces and powdered using local mixer grinder and sieved to give a fraction of 150 mesh screen and then stored in sterile, closed glass bottles and directly used as adsorbent without any pretreatment. The developed powder is designated as NBP (neem bark powder).

2.3 *Analysis*

The physico-chemical properties of NBP were obtained from previous studies [27]. Unadsorbed copper (II) concentration was determined by atomic absorption spectrophotometer (Model No. GBC HG3000). Magnetic stirrer (TARSONS, Spinot digital model MC02, CAT No. 6040, S. No. 173) was used for stirring purpose. In order to gain better insight into the surface functional groups available on the surface of the adsorbent, the Fourier transform infrared (FTIR) spectra of NBP was recorded with Fourier transform infrared spectrophotometer (PERKIN-ELMER, FTIR, Model-RX1 Spectrometer, USA) in the range of 400–4,000 cm^{-1}. To study the surface morphology of the adsorbent, scanning electron microscopy (SEM) analysis was carried out with the help of a scanning electron microscope (HITACHI, S-530, Scanning Electron Microscope, ELKO Engineering, B.U., BURDWAN).

2.4 *Batch adsorption experiments*

In this investigation, 29 batch adsorption experiments designed by central composite design (CCD) approach using RSM were conducted by NBP as an adsorbent to study the effect of initial copper concentrations (25-100 mg/L), NBP dosage (0.05-0.9 g/50 ml), pH (2.0-8.0) and contact time (5-90 min) on the removal of copper (II). Samples were collected from the flasks at predetermined time intervals for analyzing the residual copper (II) concentration in the solutions. The amount of copper (II) ions adsorbed in milligram per gram was calculated using the following mass balance equation:

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (1)$$

Where q_e is the metal uptake (mg/g), C_i and C_e are the initial and equilibrium concentrations of copper (II) (mg/L). V is the volume of solution in liter and m is the mass of adsorbent (g). The percentage of removal of copper (II) ions was calculated from the following equation:

$$Removal(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (2)$$

All the experiments were performed in duplicate and the average values were recorded.

2.5 *Experimental design and optimization*

RSM was used in this study to find out the optimum condition for copper (II) adsorption. The central composite design (CCD) model with four independent variables i.e., initial copper (II) concentration (x_1), adsorbent dose

(x_2), pH (x_3) and contact time (x_4) were used as the experimental design model. The number of experiments can be calculated by using equation (3):

$$N = k^2 + k + cp \qquad (3)$$

Where k is the factor number and cp is the number of centre point replicates.

The process variables were coded by the following equation:

$$\text{Coded value} = x_i = \frac{X_i - X_0}{\Delta X} \text{ (i=1,2,3,...K)} \qquad (4)$$

Where x_i is the dimensionless value of a process variable, X_i is the real value of the i^{th} factor of an independent variable, X_o is the value of X_i at the centre point and ΔX is the step change. In order to get true functional relationship between independent variables and the response, a second order polynomial regression model equation (Equation 5) was used to describe the effect of variables in terms of linear, quadratic and cross product terms

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i,j=1(i \neq j)}^{n} \beta_{ij} x_i x_j + \varepsilon \qquad (5)$$

where, Y is the response variable, β_o is the offset term, β_i the coefficient of linear effect, β_{ii} the coefficient of square effect, β_{ij} the coefficient of interaction effect and x_j is the coded value of variable j. To describe the coefficients of the quadratic equation analysis of variance (ANOVA) was carried out. The significance and adequacy of the model were justified from Fisher variation ratio (F), probability value (prob>F) and adequate precision ratio [28]. Furthermore, each variable is investigated for individual and interactive effect on removal process. Equation (5) can be written for four independent variables with Y as ultimate response in their coded values in the following equation:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 \qquad (6)$$

CCD design consist of a 2^n factorial (coded to the usal ±1 notation), 2n axial points ($\pm\alpha$, 0, 0....,0), (0, $\pm\alpha$, 0,......,0), ...(0,0...........,$\pm\alpha$) and n_c center points (0, 0, 0,....0). In the present work, four process variables i,e initial concentration, pH, adsorbent dose and contact time were studied using CCD models with the help of design–expert software (Stat–Ease, Inc., version 8.0.7.1, Minneapolis, USA). The range of α lies between 1 and $\sqrt{n}$.

3. Results and Discussion

3.1. Characterization of adsorbent

The physico–chemical properties of neem bark powder (NBP) are summarized in Table 1.

Table 1: Physico–chemical characteristics of adsorbent.

Analysis	Value
Ash content (%)	12.70
Bulk density (g/cm^3)	0.563
pH$_{zpc}$	6.80
Surface area (m^2/g)	328.1
Volatile matter (%)	87.28
C (%)	43.23
H (%)	4.39
N (%)	0.93

The FTIR spectrum of NBP is shown in Figure 1. The broad and strong band at 3305 cm^{-1} indicates the presence of –OH stretching. The peak at 2924 cm^{-1} could be assigned to methylene C–H asymmetric stretching. The peak at 1593 cm^{-1} was attributed to the presence of carboxylate group. The characteristic peaks at 1222, 1025 and 774 cm^{-1} corresponds to aromatic phosphates (P–O–C stretching), C–O stretching and C–Cl stretching vibration [29]. The above results suggested that copper ions may interact with –O–H, carboxylate group and phosphate group present on the NBP surface.

For morphological characteristics SEM of NBP was carried out. The SEM images for NBP surface before and after copper adsorption are shown in Figures. 2 and 3, respectively. It is evident from the micrograph that the adsorbent has an irregular surface structure, thus making it possible for the adsorption of copper (II) on different parts of the adsorbent.

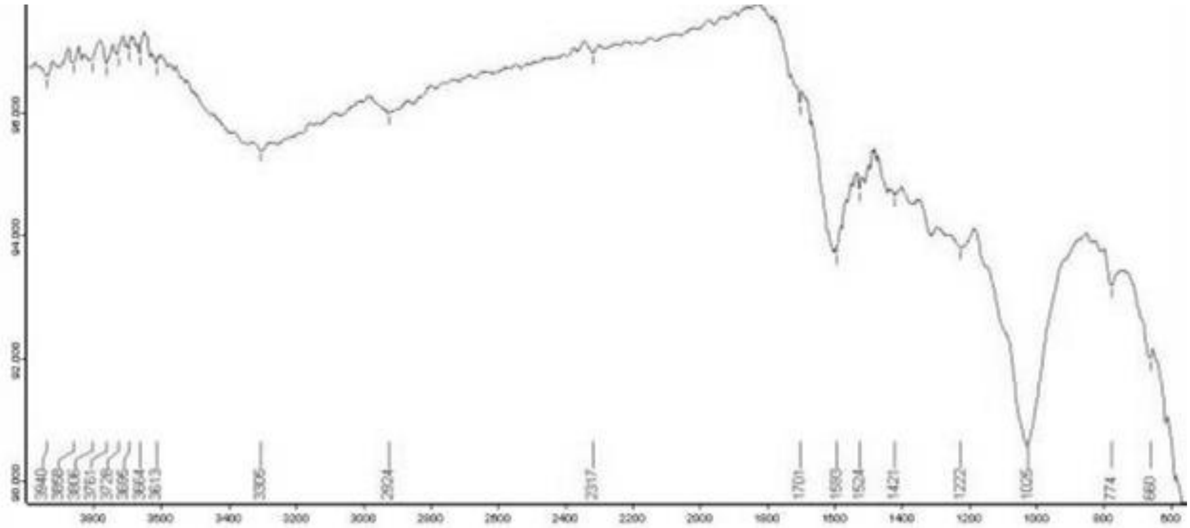


Figure 1: FTIR spectrum of NBP.

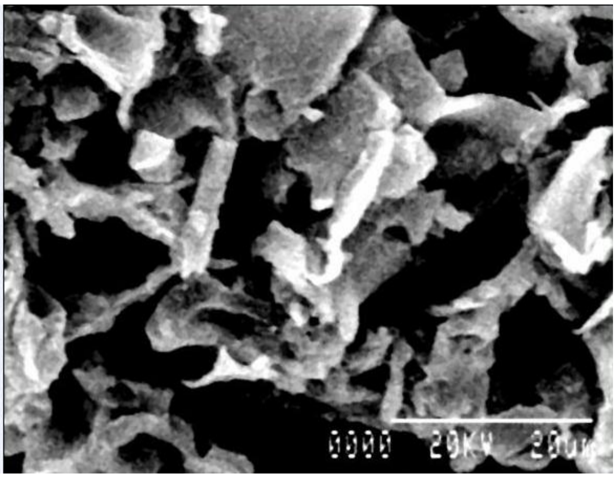


Figure 2: SEM image of NBP before treatment with copper (II).

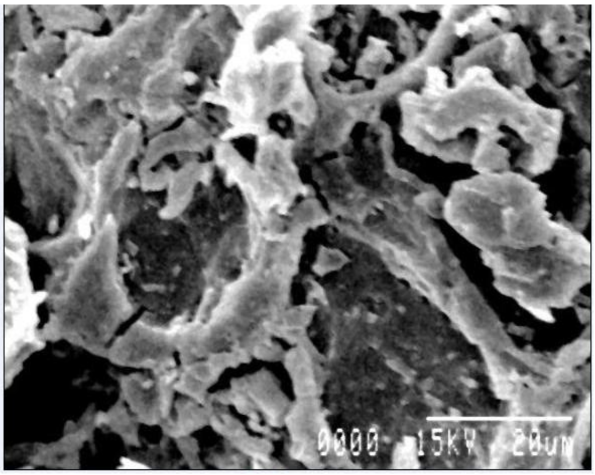


Figure 3: SEM image of NBP after treatment with copper (II).

3.2. Design of Experiments

The experimental design for optimization of copper (II) adsorption on NBP was done by applying response surface methodology (RSM) through central composite design (CCD). In order to investigate the effect of various independent process parameters such as initial concentration (x_1), adsorbent dose (x_2), pH (x_3), and contact time (x_4) on % removal of copper (II), 29 batch experiments were conducted based on the central composite design (CCD) for the optimization of process parameters. The coded values of the independent variables were determined by equation (4). The range and levels of independent process variables were summarized in Table 2. The behavior of the percentage removal of copper (II) was explained by the second order polynomial equation (Equation 6).

Table 2: Experimental factor levels used in factorial design.

Independent variable	Factor	Coded levels		
		–1	0	+1
Initial concentration (mg/L)	x_1	25	62.5	100
Adsorbent dose (g)	x_2	0.05	0.475	0.9
pH	x_3	2	5	8
Contact time (min)	x_4	5	47.5	90

3.3. Evaluation of model

In order to ascertain the validity of the different models such as linear, 2Fl, quadratic and cubic, evaluation was done on the basis of scores obtained from the sequential model sum of squares (Table 3), and it shows that the quadratic model has a high score. The larger magnitude of F (5105.41) and smaller value of p (< 0.0001) indicates that the quadratic model is highly significant and was found to be good.

Table 3: Sequential model sum of squares.

Source	Sum of squares	*df*	Mean square	*F*–value	*p*–value, prob>*F*	
Mean vs Toal	93617.77	1	93617.77			
Linear vs Mean	8241.29	4	2060.32	6.69	0.0009	
2Fl vs Linear	761.06	6	126.84	0.34	0.9040	
Quadratic vs 2Fl	6624.15	4	1656.04	5105.41	< 0.0001	Suggested
Cubic vs Quadratic	1.83	8	0.23	0.51	0.8156	Aliased
Residual	2.71	6	0.45			
Total	1.092E+005	29	3767.20			

3.4. Quadratic model for copper (II) adsorption process

To examine the combined effect of four different independent process parameters on percentage removal of copper (II), 29 experiments were performed. The experimental design is given in Table 4, along with experimental data and predicted responses. Regression analysis was performed to fit the response functions, i.e. percentage removal of copper (II).

Table 4: CCD matrix for the experimental design and predicted responses for Copper (II) removal.

Run order	Coded Value				Copper (II) removal (%)	
	x_1	x_2	x_3	x_4	Observed	Predicted
1	100.00	0.05	5.00	47.50	41	40.81
2	62.50	0.90	8.00	47.50	69	69.44
3	62.50	0.48	5.00	47.50	85	83.64
4	62.50	0.90	2.00	47.50	40	39.94
5	62.50	0.05	2.00	47.50	17	16.52
6	62.50	0.48	8.00	90.00	73	72.73
7	25.00	0.48	5.00	90.00	87	86.44
8	25.00	0.48	5.00	5.00	48	48.19
9	62.50	0.90	5.00	5.00	39	38.75
10	62.50	0.48	5.00	47.50	83.3	83.64
11	62.50	0.48	5.00	47.50	83.3	83.64
12	100.00	0.90	5.00	47.50	76	75.73
13	25.00	0.48	2.00	47.50	45	45.25
14	62.50	0.48	2.00	5.00	21	20.98
15	62.50	0.48	2.00	90.00	46	46.23
16	62.50	0.05	8.00	47.50	22	22.02
17	62.50	0.48	5.00	47.50	83.3	83.64
18	100.00	0.48	2.00	47.50	43	43.08
19	62.50	0.05	5.00	5.00	26	26.08
20	25.00	0.05	5.00	47.50	44	43.98
21	25.00	0.48	8.00	47.50	64	64.25
22	100.00	0.48	5.00	90.00	79	78.77
23	62.50	0.48	5.00	47.50	83.3	83.64
24	62.50	0.90	5.00	90.00	95.5	95.75
25	25.00	0.90	5.00	47.50	80	79.90
26	100.00	0.48	8.00	47.50	59	59.89
27	100.00	0.48	5.00	5.00	48	48.52
28	62.50	0.05	5.00	90.00	37	37.58
29	62.50	0.48	8.00	5.00	30	29.48

The second order polynomial equation developed represent responses as functions of initial metal concentration (x_1), adsorbent dose (x_2), pH (x_3), and contact time (x_4). An empirical relationship between the response and the input test variables in coded units can be expressed by the following equation:

$$\% R_{Copper\,(II)} = 83.64 - 1.83\,x_1 + 17.71\,x_2 + 8.75\,x_3 + 17.13\,x_4 - 0.25\,x_1x_2 - 0.75\,x_1x_3 - 2.00\,x_1x_4 + 6.00\,x_2x_3 + 11.38\,x_2x_4 + 4.50\,x_3x_4 - 3.80\,x_1^2 - 19.74\,x_2^2 - 26.92\,x_3^2 - 14.36\,x_4^2 \quad (7)$$

The above equation describes how copper (II) adsorption onto NBP was affected by the individual variables (linear and quadratic) or double interaction. Negative coefficient values indicated that individual or double interactions factors negatively affect copper (II) adsorption while positive coefficient values represents that factors increase copper (II) removal percentage. For instance, among all linear factors initial concentration had a negative effect but adsorbent dose, pH and contact time had a positive effect on copper (II) removal. The graphical representation of the regression equation (Equation 7) is shown by the 3D response surface plots [Figures (4)–(9)].

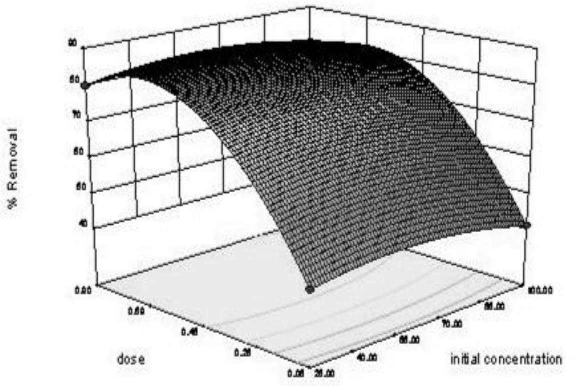


Figure 4: Effect of the interaction between adsorbent dose and initial concentration on copper (II) removal.

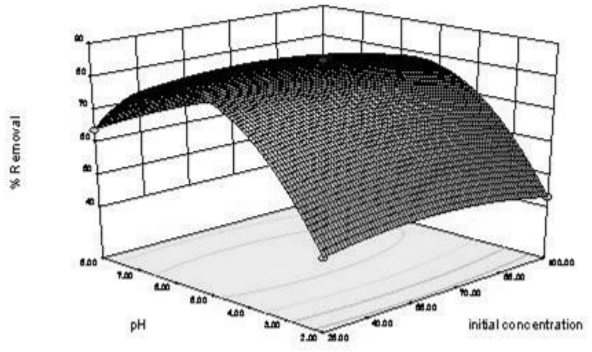


Figure 5: Effect of the interaction between pH and initial concentration on copper (II) removal.

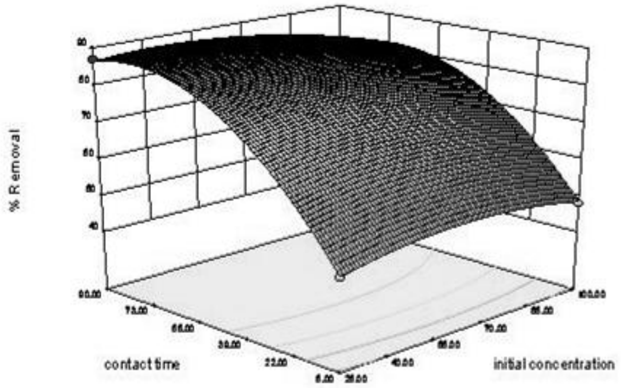


Figure 6: Effect of the interaction between initial concentration and contact time on copper (II) removal.

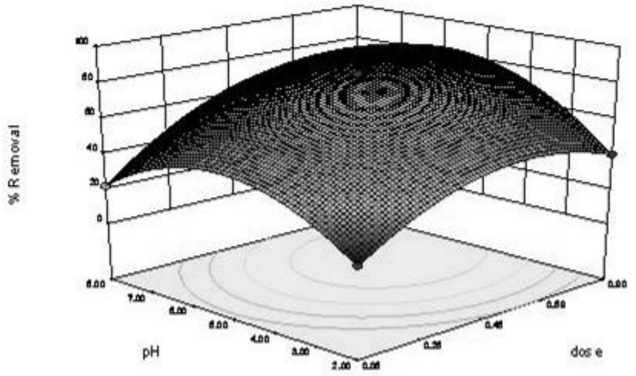


Figure 7: Effect of the interaction between adsorbent dose and pH on copper (II) removal.

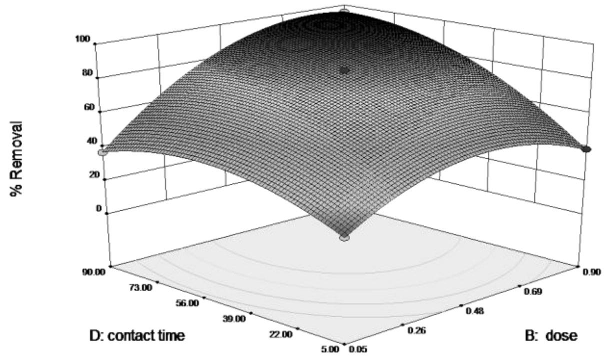


Figure 8: Effect of the interaction between contact time and adsorbent dose on copper (II) removal.

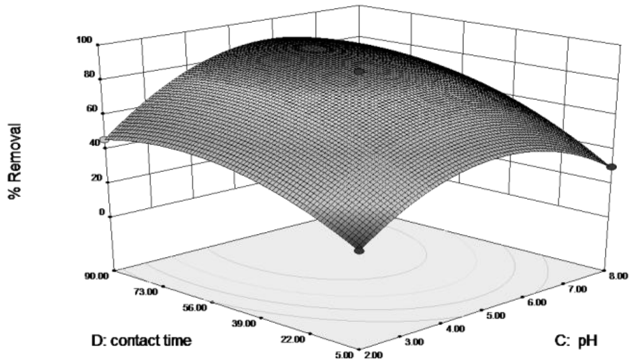


Figure 9: Effect of the interaction between pH and contact time on copper (II) removal.

It was evident from the above figures that the percentage removal of copper (II) ion decreased with increase of the initial copper (II) ions concentration. This can be explained by the fact that all adsorbents have a limited number of active sites and at a certain concentration the active sites become saturated [30]. However a sharp increase in the copper ion removal occurred when the pH value of the solutions changed from 2.0 to 6.0. From pH 6 onwards, a steady decrease of adsorption of copper ions was recorded. The percentage of copper ion removal increased with increase in adsorbent dose. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the adsorbent [31]. Furthermore, rate of adsorption increased with contact time.

The adequacy and significance of the quadratic model can be justified by the analysis of variance (ANOVA) (Table 5).

Table 5: Analysis of variance (ANOVA) for the quadratic model.

Variation source	Coefficient	Sum of squares	DF	Mean square	F	Prob>F
Intercept	83.64		1			
x_1	–1.83	40.33	1	40.33	124.34	<0.0001
x_2	17.71	3763.02	1	3763.02	11601.05	<0.0001
x_3	8.75	918.75	1	918.75	2832.42	<0.0001
x_4	17.13	3519.19	1	3519.19	10849.33	<0.0001
x_1^2	–3.80	93.62	1	93.62	288.63	<0.0001
x_2^2	–19.74	2526.72	1	2526.72	7789.65	<0.0001
x_3^2	–26.92	4702.12	1	4702.12	14496.22	<0.0001
x_4^2	–14.36	1337.89	1	1337.89	4124.58	<0.0005
x_1x_2	–0.25	0.25	1	0.25	0.77	0.3948
x_1x_3	–0.75	2.25	1	2.25	6.94	0.0196
x_1x_4	–2.00	16.00	1	16.00	49.33	<0.0001
x_2x_3	6.00	144.00	1	144.00	443.94	<0.0001
x_2x_4	11.38	517.56	1	517.56	1595.60	<0.0001
x_3x_4	4.50	81.00	1	81.00	249.72	0.0062
Model		15626.50	14	1116.18	3441.08	<0.0001
Residual		4.54	14	0.32		
Lack of Fit		2.23	10	0.22	0.39	0.8989
Pure Error		2.31	4	0.58		
Cor Total		15631.04	28			
R^2 = 0.9997						
$R^2_{Adjusted}$ = 0.9994						
$R^2_{Predicted}$= 0.9989						
Adeq Precision =193.42						

The analysis was done by means of Fisher's 'F'–test. The model F–value was found to be 3441.08 enlightening that the model was significant. The parameters are said to be significant if an F–statistics probability value less than 0.05 [32]. In this case x_1, x_2, x_3, x_4, x_2x_3, x_2x_4, x_3x_4, x_1x_3, x_1x_4,x_2x_3, x_1^2, x_2^2, x_3^2 and x_4^2 are statistically significant ($P<0.05$) model terms at the 95% confidence level. The non-significant value of lack of fit (F–value of 0.39) for the model indicated that developed model is valid [33]. Furthermore, The R^2, adjusted R^2 and predicted R^2 values were found to be 0.9997, 0.9994 and 0.9989, respectively, which indicates that there was a good agreement between the actual and the predicted values. The adequate precision ratio of 193.428 indicates an appropriated signal to noise ratio. The ratio determined was greater than 4, representing that the quadratic model can be used to navigate the design space and to find the optimal conditions for the removal process. Furthermore, the relationship between actual values and predicted values (Figure 10) showed that the actual values are distributed relatively near to the straight line, indicating good fitness of the model. The normal residual plot (Figure 11) between probability and internally studentized residuals showed that the residuals were distributed normally with minimum deviations. This was an indication of better agreement of the model with the experimental data.

From diagnostic case statistics the value of leverage, internally studentized residuals, externally studentized residuals, DFFITS and Cooks distance of the data can be obtained (Table 6). The result indicated that the leverage value was within 0 to 1. The number of standard deviation separating actual and predicted values can be measured by internally studentized residuals. It was observed that the limit of the internally studentized residuals is ±3 sigma. Furthermore, the influence of the observed value on its predicted value was measured by DFFITS analysis whose limit lies in between +2 and –2. Cook's distance actually measures the change in regression and must be in the range of ±1. The analysis of diagnostic case statistics of data showed that the model fits well to optimize the independent variables for the removal of copper (II) from aqueous solution.

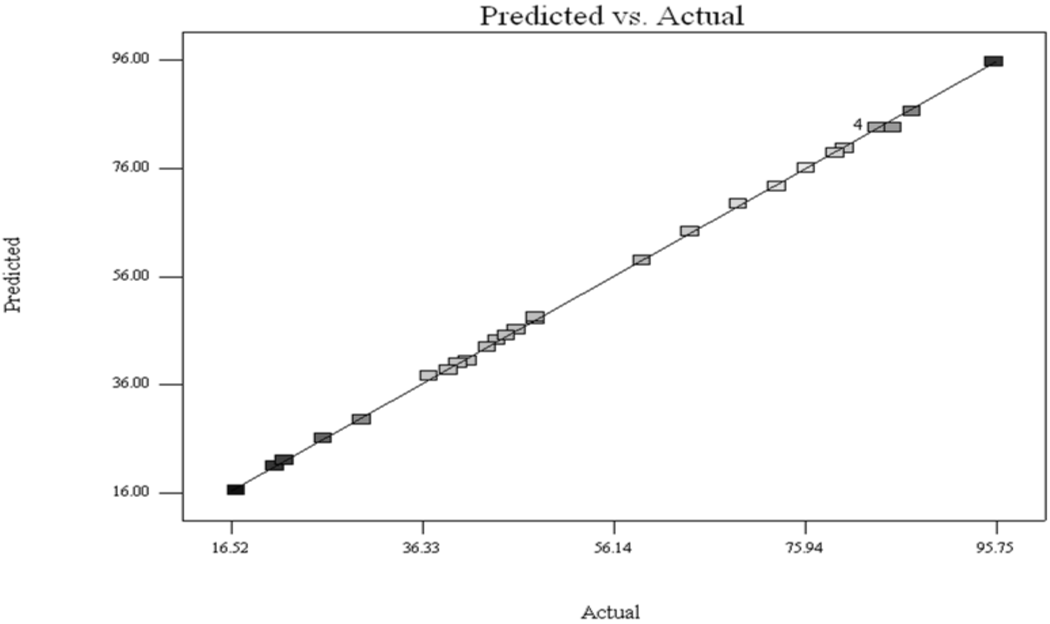


Figure 10: Comparison between the actual values and the predicted values of RSM model for adsorption of copper (II).

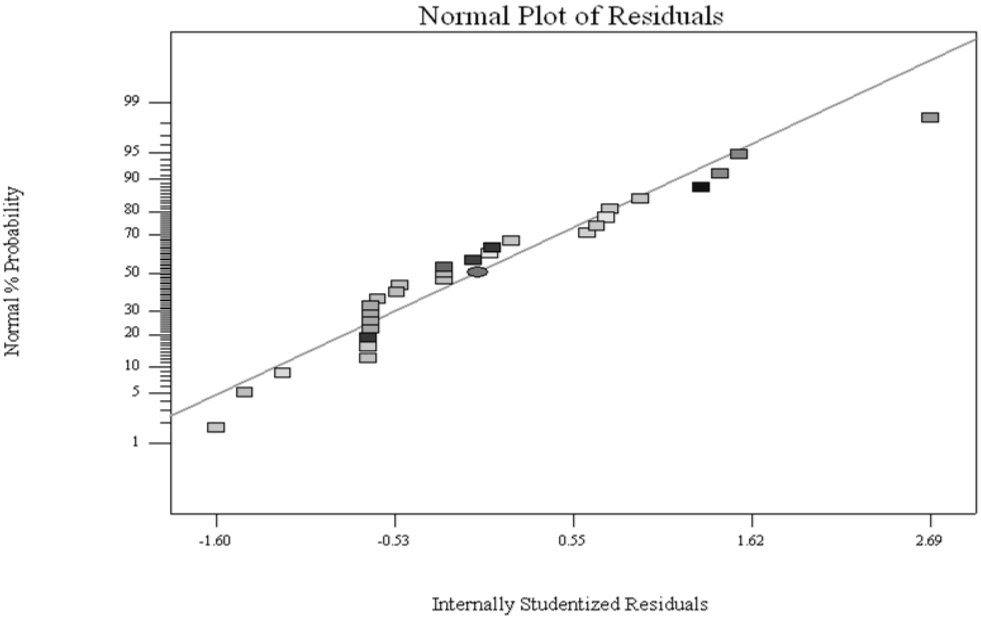


Figure 11: Plot of Studentized residuals versus experimental run number.

3.5. Comparative effect of individual variables

Perturbation plot is used in order to compare the effect of all the factors at a particular point in the design space. In perturbation plot the response was plotted by changing only one factor over its range while keeping all the other factors constant. Copper (II) removal efficiency was introduced as each variable move from preferred reference with all other factors held constant at the coded zero level. It shows the deviation of the factorial level from the adjusted reference point of all the variables. The comparative effects of all the independent variables for copper (II) adsorption are shown in Figure 12. The sharp curvature of all the independent variables indicated that the copper (II) removal efficiency was very much sensitive to all the process variables.

Table 6: Diagnostics case statistics.

Standard order	Actual value	Predicted value	Residual	Leverage	Internally studentized residuals	Externally studentized residuals	Influence on fitted values DFFITS	Cook's distance
1	44.00	43.98	0.021	0.583	0.057	0.055	0.065	0.000
2	41.00	40.81	0.19	0.583	0.510	0.496	0.587	0.024
3	80.00	79.9	0.10	0.583	0.283	0.274	0.324	0.007
4	76.00	75.73	0.27	0.583	0.737	0.724	0.857	0.051
5	21.00	20.98	0.021	0.583	0.057	0.055	0.065	0.000
6	30.00	29.48	0.52	0.583	1.417	1.475	1.745	0.187
7	46.00	46.23	–0.23	0.583	–0.623	–0.609	–0.721	0.036
8	73.00	72.73	0.27	0.583	0.737	0.724	0.857	0.051
9	48.00	48.19	–0.19	0.583	–0.510	–0.496	–0.587	0.024
10	48.00	48.52	–0.52	0.583	–1.417	–1.475	–1.745	0.187
11	87.00	86.44	0.56	0.583	1.530	1.616	1.912	0.219
12	79.00	78.77	0.23	0.583	0.623	0.609	0.721	0.036
13	17.00	16.52	0.48	0.583	1.303	1.340	1.585	0.159
14	40.00	39.94	0.062	0.583	0.170	0.164	0.194	0.003
15	22.00	22.02	–0.021	0.583	–0.057	–0.055	–0.065	0.000
16	69.00	69.44	–0.44	0.583	–1.190	–1.210	–1.431	0.132
17	45.00	45.25	–0.25	0.583	–0.680	–0.666	–0.788	0.043
18	43.00	43.08	–0.083	0.583	–0.227	–0.219	–0.259	0.005
19	64.00	64.25	–0.25	0.583	–0.680	–0.666	–0.788	0.043
20	59.00	59.08	–0.083	0.583	–0.227	–0.219	–0.259	0.005
21	26.00	26.08	–0.083	0.583	–0.227	–0.219	–0.259	0.005
22	39.00	38.75	0.25	0.583	0.680	0.666	0.788	0.043
23	37.00	37.58	–0.58	0.583	–1.587	–1.688	–1.998	0.235
24	95.50	95.75	–0.25	0.583	–0.680	–0.666	–0.788	0.043
25	83.30	83.64	–0.34	0.200	–0.667	–0.654	–0.327	0.007
26	83.30	83.64	–0.34	0.200	–0.667	–0.654	–0.327	0.007
27	83.30	83.64	–0.34	0.200	–0.667	–0.654	–0.327	0.007
28	83.30	83.64	–0.34	0.200	–0.667	–0.654	–0.327	0.007
29	85.00	83.64	1.36	0.200	2.670	3.672	1.836	0.119

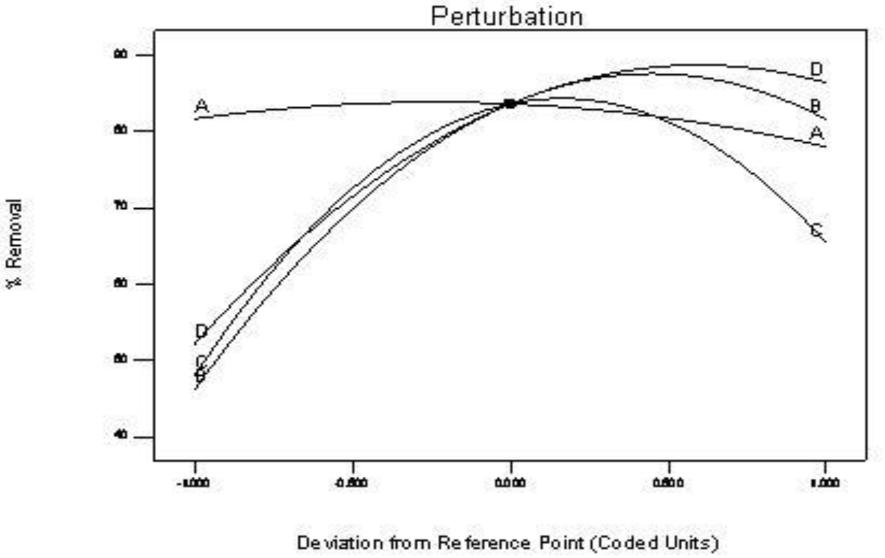


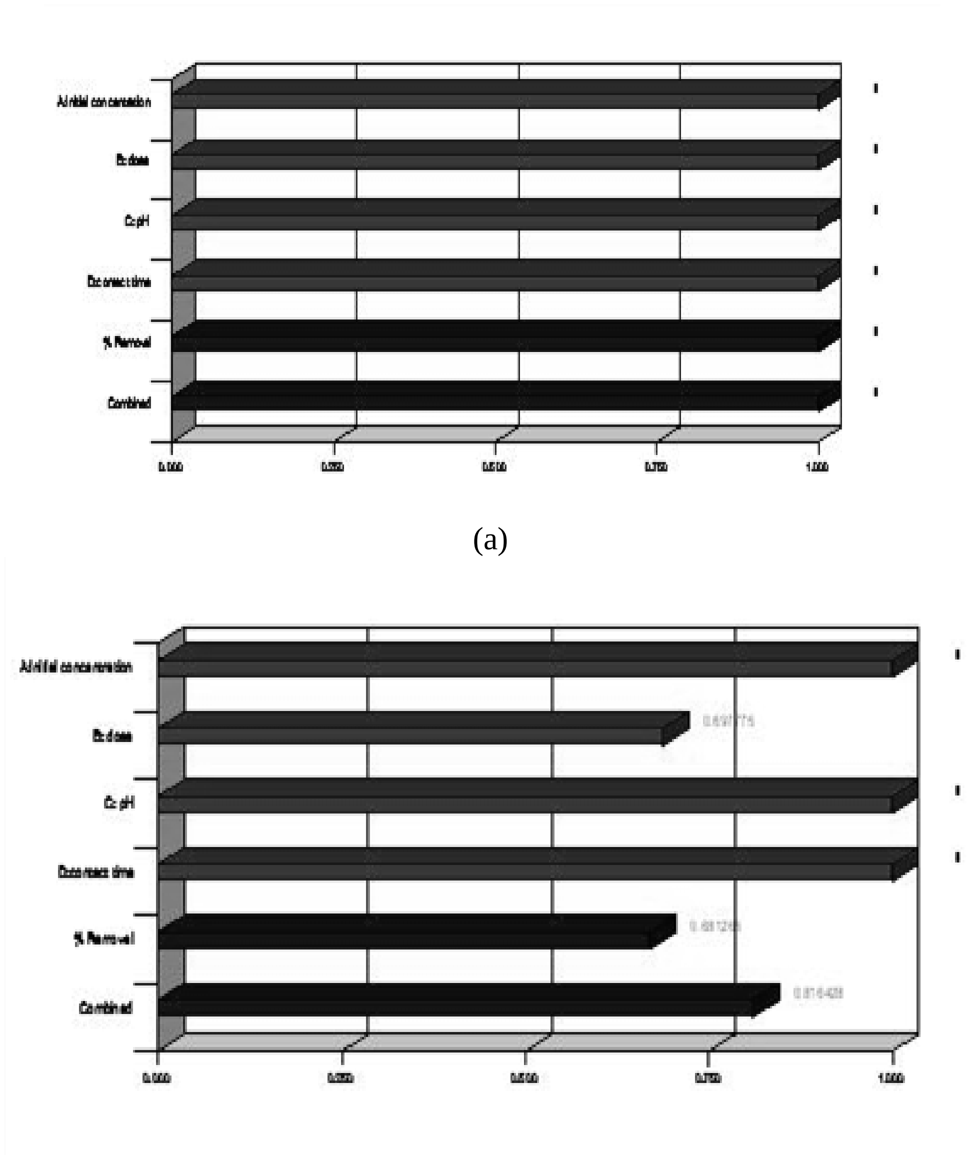
Figure 12: Perturbation plot (A, B, C and D factors are equivalent to factors x_1, x_2, x_3 and x_4).

3.6. Optimizing the process variables by desirability function

Desirability is an objective function. The ranges of this function lies from zero (outside the limits) to one (at goal). A multiple response method was used for optimization of any combination of five goals, namely, initial concentration, adsorbent dose, pH, contact time and copper (II) removal efficiency. In the numerical optimization procedure, a point was found that maximizes the desirability function in the design space [34]. The optimization was carried out in two different ways by setting different criteria. The desirability for each factor and response individually and collectively was discussed by the histogram plots. Histogram plots for the present study are depicted in Figure 13 a, b respectively. The optimum experimental conditions for the removal of copper (II) at maximum desirability is represented by RAMP plot (Figure 14 a, b).

3.7. First optimization procedure

The desirability values of first optimization procedure is shown in Figure 13 a. The criterion of this procedure was set as "in range" for independent variables (initial copper (II) concentration, adsorbent dose, pH and contact time) and "maximum" for dependent variable (removal of copper (II) (R_1, in percent). The desirability value was found to be 1 for individual and combination of all these variables. Figure 14 a shows 95.96 % as optimum removal efficiency of copper (II) when the independent variables were 32.99 mg/L (initial copper (II) concentration), 0.81 g/50 ml (NBP dose), 4.87 (pH), and 76.52 minute (contact time) at maximum desirability value.



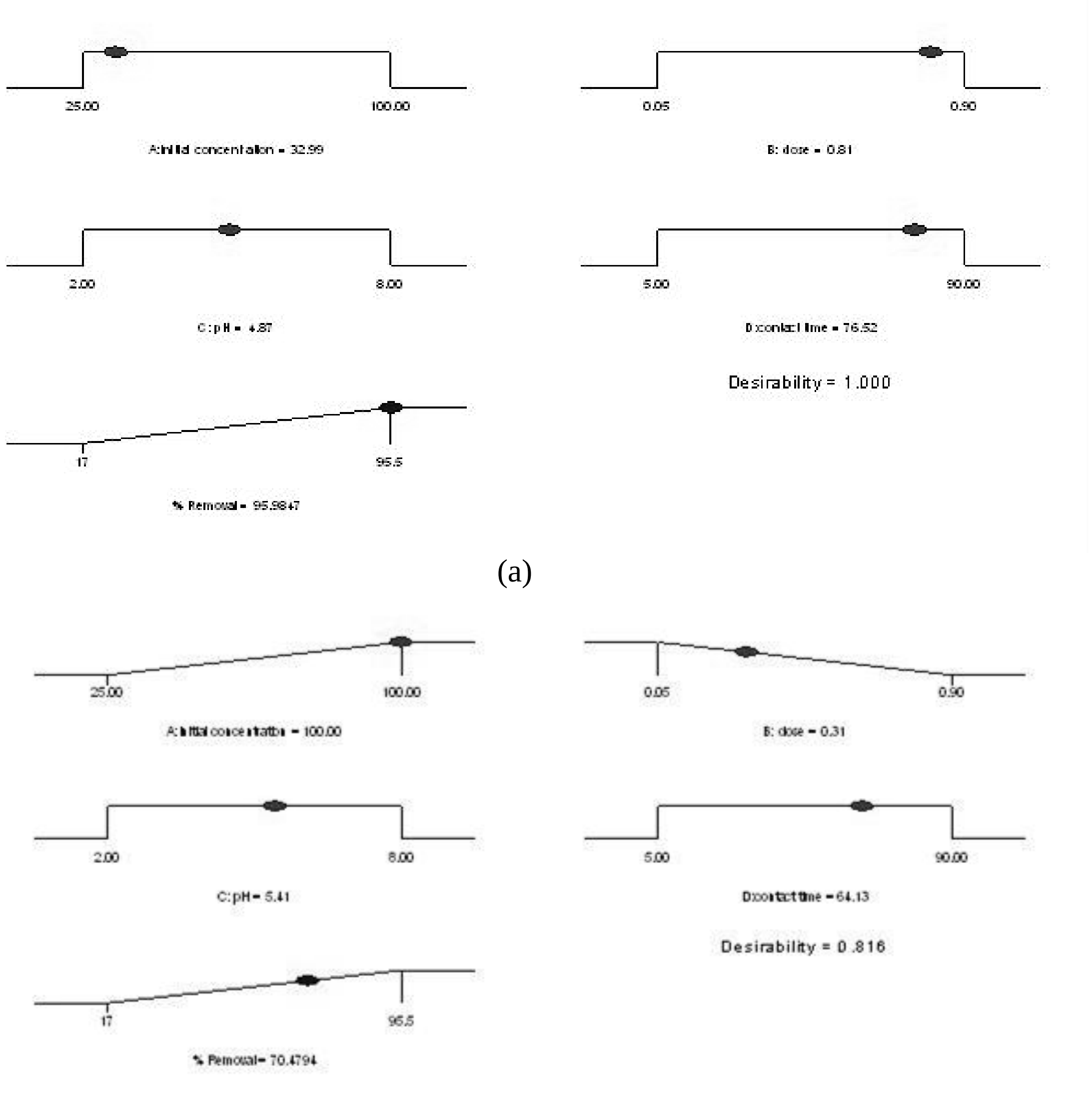
(a)

(b)

Figure 13: Bar graph for (a) first optimization procedure and (b) second optimization procedure (A, B, C and D factors are equivalent to factors x_1, x_2, x_3 and x_4).

3.8. Second optimization procedure

The desirability values of second optimization procedure are shown in Figure 13 b. The criterion of this procedure was set as “minimum” for adsorbent dosage, “maximum” for initial copper (II) concentration; “in range” for pH and contact time and the goal was set as “maximum” to analyze economically viable optimal condition. The objective of this process was to find the maximum removal percentage by utilizing minimum adsorbent dosage. In this, for individual variables the desirability value ranges from 0.68 to 1 and 0.816 for combination of all the variables. Figure 14 b portrays 70.47 % as the optimal response when the independent variables are 100 mg/L (initial copper (II) concentration), 0.31 g/50 ml (adsorbent dose), 5.41 (pH), and 64.13 minute (contact time) at maximum desirability value.



(a)

(b)

Figure 14: RAMP plots for (a) first optimization procedure and (b) second optimization procedure (A, B, C and D factors are equivalent to factors x_1, x_2, x_3 and x_4).

However, second optimization procedure was preferred for the removal of copper (II) by NBP on the basis of uptake capacity and economical usage of adsorbent. Furthermore, confirmatory experiments were performed on the two approaches obtained from the software to validate the accuracy of the predicted results. By applying the above said conditions, it was observed that predicted percentage removal of copper (II) matches with the experimental values well (Table 7). Similar optimization result has been previously reported by other investigator [34].

3.9. Thermodynamic parameters and sticking probability

The thermodynamic parameters such as free energy, enthalpy and entropy changes for the adsorption process can be computed from the following equations [35]:

$$\mathrm{K_C} = \frac{\mathrm{C_{Ae}}}{\mathrm{C_e}} \qquad (8)$$

$$\Delta\mathrm{G^0} = -\mathrm{RTlnK_C} \qquad (9)$$

$$\mathrm{logK_C} = \frac{\Delta\mathrm{S^0}}{2.303\,\mathrm{R}} - \frac{\Delta\mathrm{H^0}}{2.303\,\mathrm{RT}} \qquad (10)$$

Where C_e (mg/L) is the equilibrium concentration of copper in solution and C_{Ae} (mg/L) is the equilibrium concentration on the biosorbent and K_c is the equilibrium constant. The Gibbs free energy (ΔG^o) for the adsorption of copper onto NBP at all temperatures was obtained from equation 9 and is presented in Table 8. ΔH^o and ΔS^o were obtained from the slope and intercept of the plot $\log K_c$ against 1/T (Figure not shown) and are also listed in Table 8.

Table 7: Optimized results from model and experimental verification for copper (II) removal.

Initial concentration (mg/L)	pH	NBP dose (g/50 mL)	Contact time (min)	Removal (%)		Remarks
				Predicted	Experimental	
32.99	4.87	0.81	76.52	95.96	93.45	First procedure
100.00	5.41	0.31	64.13	70.47	68.25	Second procedure

In order to support that physical adsorption is the predominant mechanism, the value of sticking probability (S^*) was calculated from the experimental data. It was calculated using modified Arrhenius type equation related to surface coverage (θ) and activation energy (E_a) as follows [36]:

$$\theta = \left(1 - \frac{C_e}{C_i}\right) \qquad (11)$$

$$S^* = (1-\theta)e^{\frac{-Ea}{RT}} \qquad (12)$$

$$lnS^* = \ln(1-\theta) - \frac{E_a}{RT} \qquad (13)$$

$$ln(1-\theta) = \ln S^* + \frac{E_a}{RT} \qquad (14)$$

The sticking probability, S^*, is a function of the adsorbate/adsorbent system under consideration but must satisfy the condition $0 < S^* < 1$ and is dependent on the temperature of the system. The values of E_a and S* can be calculated from slope and intercept of the plot of ln (1–θ) versus1/T respectively (Figure not shown).

From Table 8 it is clear that the adsorption is spontaneous and feasible as ΔG^o values are negative at all the studied temperature. Again positive ΔH^o value confirms that the sorption is endothermic in nature. The positive value of ΔS^o reflects the affinity of the adsorbent towards the copper (II) ions. The values of E_a was found to be 12.445 kJ/mol for the adsorption of copper (II) onto NBP. The positive value of E_a indicates the endothermic nature of the adsorption process which is in accordance with the positive values of ΔH^o. The result as shown in Table 8 indicates that the probability of the copper (II) ions to stick on surface of NBP is very high as $S^* << 1$.

Table 8: Thermodynamic parameters for adsorption of copper (II) onto NBP.

Temperature (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o(kJ/mol)	E_a (kJ/mol)	S^*
		46.24	0.172	12.445	$1.573\mathrm{x}10^{-9}$
313	–7.949				
323	–9.155				
333	–11.403				

Conclusions

This study was focused on the adsorption of copper (II) ions onto NBP from aqueous solution. Response surface methodology based CCD model was used to determine the optimum reaction conditions. According to the ANOVA analysis, all the interaction (except interaction of $x_1$and x_2) terms are statistically significant. The quadratic model represents adequately the response surface space based on the adjusted determination coefficient (R^2_{Adj} = 0.9994) and the adequate precision ratio (193.428). The high similarity between the experimental value and the predicted ones suggested that the model was a good fit. The FT–IR analysis showed the role of various functional groups for copper (II) adsorption. The optimized result obtained from RAMP plots revealed that the use of NBP is an economically viable option for the removal of copper (II) from aqueous solution. The calculated thermodynamic parameters showed the endothermic and spontaneous nature of the adsorption of copper onto NBP. Furthermore calculated sticking probability indicates excellent sticking of metal ions on to NBP. The present findings suggest that NBP may be used as an inexpensive and effective adsorbent without any treatment or any other modification for the removal of copper (II) ions from aqueous solutions.

Acknowledgements-The authors are grateful to Dr. Alak Ghosh, Professor, Department of Chemistry, Burdwan University, West Bengal, India for recording FTIR data and they also extend their gratitude to Dr. Srikanta Chakraborty, Incharge of SEM, USIC, University of Burdwan, West Bengal for SEM study.

References

1. Friberg L., Elinder C.G., Encyclopedia of Occupational Health, third ed. International Labor Organization, Geneva, 1985.
2. Garg U.K., Kaur M.P., Garg V.K., Sud, D., *J. Hazard. Mater.* 140 (2007) 60.
3. Randall J.M., Hautala E., Waiss Jr. A.C., In: Proceedings of the Fourth Mineral Waste Utilization Symposium, Chicago, 1974.
4. Mukhopadhyay M., Noronha S.B., Suraishkumar G.K., *Bioresour. Technol.* 98 (2007) 1781.
5. Zhu B., Tongxiang F., Zhang D., *J. Hazard. Mater.* 153 (2008) 300.
6. Abu Al-Rub F.A., El-Naas M.H., Ashour I., Al-Marzouqi M., *Process Biochem.* 41 (2006) 457.
7. Ayhan I.Ş., Özacar, M., *J. Hazard. Mater.* 157 (2008) 277.
8. Maheswari P., Venilamani N., Madhavakrishnan S., Syed Shabudden P.S., Venckatesh R., Pattabhi, S., *E-journal Chem.* 5 (2008) 233..
9. Ahmad A., Rafatullah M., Sulaiman O., Ibrahim M.H., Chii Y.Y., Siddique B.M., *Desalination* 247 (2009) 636
10. Kikuchi Y., Qian Q., Machida M., Tatsumoto H., *Carbon*, 44 (2006) 195.
11. Malik D.J., Strelko Jr. V., Streat M., Puziy A.M., *Wat. Res.* 36 (2002) 1527.
12. Shukla S.R., Roshan S.P., *Separ. Purif. Technol.* 43 (2005) 1.
13. Yan H., Dai J., Yang Z., Yang H., Cheng R., *Chem. Eng. J.* 174 (2011) 586.
14. Panday K.K., Prasad G., Singh V.N., *Wat. Res.* 19 (1985) 869
15. Aly H.M., Daifullah A.A.M., *Adsorp. Sci. Technol.* 16 (1998) 33
16. Turan N.G., Mesci B., Ozgonenel O., *Chem. Eng. J.* 171 (2011) 1091.
17. Vengris T., Binkiene R., Sveikauskaite A., *Appl. Clay Sci.* 18 (2001) 183.
18. Abia A.A., Horsfall Jr. M., Didi O., *Bioresource Technol.* 90 (2003) 345.
19. Anna W.K., *Chem. Eng. J.* 192 (2012) 13.
20. Ofomaja A.E., Naidoo E.B., Modise S.J., *J. Hazard. Mater.* 168 (2009) 909.
21. Cerino-Cordova F.J., Diaj-Flores P.E., Garcia-Reyes R.B., Soto-Regalado E., Gomez-Gonzalez R., Garza-Gonzalez M.T., Bustamante-Alcantara E., *Int. J. Environ. Sci. Technol.* 10 (2013) 611.
22. Das B., Mondal N.K., Bhaumik R., Roy P., Pal K.C., Das C.R., *J. Mater. Environ. Sci.* 4 (2013) 392.
23. Belloto R.J.Jr., Dean A.M., Moustafa M.A., Molokhia A.M., Gouda M.W., Sokoloski Td., *Ind. J. Pharm.* 23 (1985) 195.
24. Kalathenos P., Baranyi J., Sutherland, J.P., Roberts T.A., *Int. j. Food Microbiol.* 25 (1995) 63.
25. Liyana-Pathirana C., Shahidi F., *Food Chem.* 93 (2005) 47.
26. Forsberg J., Nilsson L., *Int. J. Impot. Eng.* 32 (2006) 759.
27. Srivastava R., Rupainwar D.C.A., *Ind. J. Chem. Technol.* 18 (2011) 67.
28. Myers R.H., Montgomery D.C., Response surface methodology. 2nd edn.Wiley, New York, 2001.
29. Coates J., Interpretation of infrared spectra, A practical approach, Encyclopedia of Analytical Chemistry, R.A. Meyers (Ed.), John Willy and Sons Ltd, Chichester, 2000, 10815–10837.
30. Tsai W.T., Chen H.R., *J. Hazard. Mater.* 175 (2010) 844.
31. Abdel–Ghani N.T., Hefny M., El–Chaghaby G.A.F., *Int. J. Environ. Sci. Tech.* 4 (2007) 67.
32. Bagheri H., Alinejad S., Bastami K.D., *Iran Res. J. Environ. Toxicol.* 5 (2011) 147–151.
33. Hamsaveni D.R., Prapulla S.G., Divakar S., *Process Biochem.* 36 (2001)1103.
34. Bhuvaneshwari S., Sivasubramanian V., Sarkar K., Aswathi M., Harish B., *Indian J. Chem. Technol.* 22 (2015) 283.
35. Sujana M.G., Pradhan H.K., Anand S., *J. Hazard. Mater.* 161 (2009) 120.
36. Nevine K.A., *J. Hazard. Mater.* 165 (2009) 52.

(2017) ; http://www.jmaterenvironsci.com