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Optimization of process variables for a biosorption of nickel(II) using response surface method

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Abstract−The biosorption of nickel(II) was studied by using crab shell particles of diameter (d_p=0.012 mm) under different initial concentrations of nickel(II) in solution (0.01-5.0 g/*l*), temperature (20-40 °C), pH (2-6.5), and biosorbent dosages (0.5-10 g/*l*). The maximum removal of nickel(II) occurred at pH 6.5 and temperature 40 °C for a biosorbent dosage of 6 g/*l*. The results were modeled by response surface methodology (RSM), which determines the maximum biosorption of nickel(II) as a function of the above four independent variables, and the optimum values for the efficient biosorption of nickel(II) were obtained. The RSM studies were carried out using Box-Behnken design and the analysis of variance confirms the adequacy of the quadratic model with coefficient of correlation R^2 to be 0.9999. The quadratic model fitted the data well with Prob>F to be <0.0001, indicating the applicability of the present proposed model.

Key words: Biosorption, Biosorbent, Box-Behnken Design, Crab Shell, Nickel(II), RSM Modeling

INTRODUCTION

Nickel(II) is an inorganic pollutant discharged mainly from metal finishing processes whose concentrations range up to 10 mg/*l* [1,2], whereas the nickel(II) concentrations in potable water for human consumption must be ≤0.04 mg/*l* [3]. Ni(II) present in waste water cannot be successfully degraded into harmless end products [4], and hence the metallic species released into the environment tend to persist indefinitely, eventually accumulating throughout the food chain and thus posing a serious threat to animals and humans [5]. The conventional methods for removal of heavy metals include precipitation, filtration and ion exchange, oxidation-reduction, which are highly expensive and ineffective particularly when the metal concentration is low [6].

Biosorption is an effective alternative process to the conventional treatment methods [7,8] under various conditions of operation. The natural materials that are available in large quantities of certain waste from agricultural operations have the potential to be used as low cost adsorbents as they represent untapped resources available widely and are environmentally friendly [9]. The processing wastes of aquatic species such as shrimps, prawns, and crabs contain ≈10-55% of chitin on a dry weight basis. Although not all of the potentially applicable biosorbents are systematically examined, a substantial body of evidence has been collected identifying ion exchange as the principal mechanism of metal biosorption [5,10].

Biosorption is the term that describes passive binding of metal ions to either living microorganisms (bacteria, fungi, algae etc.) or to biomasses such as crab shell, egg shell, yeast, seaweeds etc. Of the various biosorbents available, chitin has been recognized as an effective and naturally abundant biomass identified for its high sorption capacity for metal ion removal. Even though, a well known adsorbent such as activated carbon has proved its sorption capacity with respect to the heavy metal ion removal, its high cost promotes the usage of readily available cheap biomasses such as chitin present in the crab shell. Chitin is a natural polysaccharide consisting of (1-4)-2-acetamido-2-deoxy-D-glucose units and its de-acetylated derivative chitosan is responsible for the sorption of metal ions from aqueous solution. These acetamido groups are non-specific chelators and form hydrogen bonds with heavy metals [11].

Many researchers have attempted to establish the kinetics or the isotherms of the biosorption process of nickel(II). In the present work, an attempt was made to study the biosorption of nickel(II) by using crab shell as biosorbent, at different biosorbent dosages (0.5-10 g/*l*) and optimize the process by the RSM approach. The influence of the biosorbent (crab shell) at different concentration of nickel(II) (0.01-5 g/*l*) was also analyzed under different pH (2-6.5) and temperature (20-40 °C) conditions in a batch mode. The optimization of these four factors on the percentage removal of nickel(II) was statistically analyzed by using a Box-Behnken design, and the interaction of these four factors on the biosorption of nickel(II) was studied at three levels (−1,0 and +1).

MATERIALS AND METHODS

1. Crab Shells

The crab shells (biosorbent) were collected from Marina Beach, Chennai, India and were washed with distilled water, dried, crushed and sieved to an average particle size of 0.012 mm. The shell particles were then washed with 0.1 M HCl for 5 h and then washed with distilled water and then again dried. The resulting shell particles were used for biosorption experiments.

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2. Chemicals

Analytical grades of $NiSO_4 \cdot 6H_2O$ were purchased from Merck, India. Ni(II) solution was prepared by dissolving its corresponding sulphate salt in distilled water. The pH of the solutions was adjusted by using 0.1 M HCl and 0.1 M NaOH. All the experiments were performed in triplicate and an average value is reported.

3. Batch Experiments

The experiments were carried out using the biosorbent crab shell (d_p=0.012 mm) at dosages (0.5 g/*l*-10 g/*l*). The batch experiments were performed in Erlenmeyer flasks of capacity 250 ml with a working volume of 100 ml in an orbit shaker at 180 rpm. The experiments were carried out at different initial nickel(II) concentrations (X_1), pH (X_2) and temperature (X_3) with varying amounts of biosorbent dosages (X_4). The samples were collected at fixed intervals of time and analyzed for nickel content by photometric method at a λ_{max} of 440 nm [12].

4. Experimental Design

Response surface methodology (RSM) is a statistical technique used for multiple regression analysis of quantitative data obtained from statistically designed experiments by solving the multivariable equations simultaneously. The graphical representation of these equations is called as response surfaces, which determines the mutual interaction between the test variable and their subsequent effect on the response [13,14]. The percentage removal of nickel(II) was statistically modeled and designed by RSM and a four factor 3-level Box-Behnken design as shown in Table 1 was used for the optimization procedure.

This design consists of replicated center points and the set of points lying at the mid point of each edge of the multidimensional cube that defines the region of interest. The aim of the present study was to correlate the response, namely the percentage removal of nickel (II) as a function of the factors such as initial concentration of nickel (II) (X_1), pH (X_2), temperature (X_3), and biosorbent dosage (X_4). The quadratic response surface models have been explored and second order polynomial models have been constructed. The second order quadratic equation to predict the maximum percentage removal of nickel(II) is given below:

$$Y=A_0+A_1X_1+A_2X_2+A_3X_3+A_4X_4+A_{11}X_1^2+A_{22}X_2^2+A_{33}X_3^2+A_{44}X_4^2 +A_{12}X_1X_2+A_{13}X_1X_3+A_{14}X_1X_4+A_{23}X_2X_3+A_{24}X_2X_4+A_{34}X_3X_4 \quad (1)$$

where,

Y=Predicted percentage sorption of nickel(II)

A_0=Constant

X_1=Concentration of nickel(II) (g/*l*)

X_2=pH

X_3=Temperature (°C)

Table 1. Design variables in three levels

Levels	Factor 1	Factor 2	Factor 3	Factor 4
	Concentration of nickel(II) in solution (C_0) (g/*l*)	pH	Temperature (T °C)	Biosorbent dosage (B_{SD}) (g/*l*)
−1	0.01	2	20	0.5
0	2.505	4.25	30	5.25
+1	5	6.5	40	10

Table 2. Experimental design

Run	X_1 (g/*l*)	X_2	X_3 °C	X_4 (g)	Response (Y)
1	0.01	2	30	5.25	87.1
2	5	2	30	5.25	40.9
3	0.01	6.5	30	5.25	98.1
4	5	6.5	30	5.25	76.3
5	2.505	4.25	20	0.5	52.1
6	2.505	4.25	40	0.5	60.8
7	2.505	4.25	20	10	60.8
8	2.505	4.25	40	10	70.3
9	0.01	4.25	30	0.5	85.8
10	5	4.25	30	0.5	51.4
11	0.01	4.25	30	10	94.5
12	5	4.25	30	10	60.8
13	2.505	2	20	5.25	49.2
14	2.505	6.5	20	5.25	68.2
15	2.505	2	40	5.25	54.2
16	2.505	6.5	40	5.25	80.9
17	0.01	4.25	20	5.25	84.3
18	5	4.25	20	5.25	50.2
19	0.01	4.25	40	5.25	93.2
20	5	4.25	40	5.25	59.8
21	2.505	2	30	0.5	48.6
22	2.505	6.5	30	0.5	71.3
23	2.505	2	30	10	57.1
24	2.505	6.5	30	10	80.8
25	2.505	4.25	30	5.25	59.2
26	2.505	4.25	30	5.25	59.2
27	2.505	4.25	30	5.25	59.2
28	2.505	4.25	30	5.25	59.2
29	2.505	4.25	30	5.25	59.2

X_4=Biosorbent dosage (g/*l*)

A_1, A_2, A_3, A_4=Linear Coefficients

A_{12}, A_{13}, A_{14}, A_{23}, A_{24}, A_{34}=Cross product coefficients

A_{11}, A_{22}, A_{33}, A_{44}=Quadratic coefficients

A total of 29 experiments (Table 2) were necessary to estimate the model coefficients of the equation. The experimental data were analyzed by using "Design Expert 7.1.2" from Stat Ease.

RESULTS AND DISCUSSION

Although many biological materials bind heavy metals, only those with sufficiently high metal binding capacity and selectivity for heavy metals are suitable for use in a full scale biosorption process. The chemical makeup of a biosorbent and its structure is such that metals can be deposited either on its surface or within its structure. The natural source of chitin is the shell of crustacean lobsters, crab and shrimps and the de-acetylated chitin is chitosan, which is highly selective for metal ions and it only uptakes the transition and post transition metals but does not adsorb alkali and alkaline earth metals [15]. The formation of a coordination complex between the metal and the chitin as well as ion exchange mechanism has also been

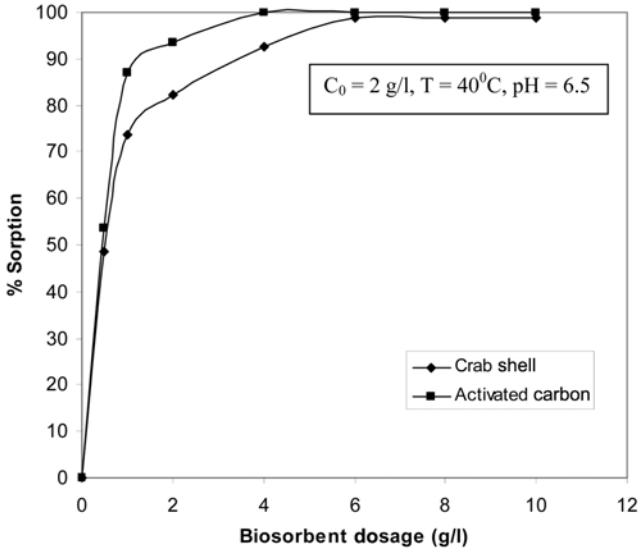

Fig. 1. Effect of biosorbent dosage on the % sorption of nickel(II).

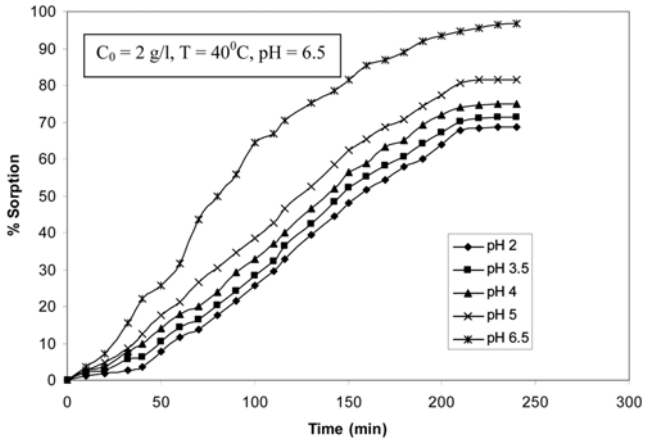

Fig. 2. Effect of pH on the % sorption of nickel(II) using crab shell as biosorbent.

suggested as a process that may be active in certain metal uptake by chitin or chitosan. The biosorbent crab shell can be regarded as an assorted floor of different functional groups such as -COOH, -NH_2, -SH, -PO_4^{3-}, -OH etc., wherein coordination complexes with metals can be formed. In crab shells, the metal ions can bind either to the amino groups of chitin (R_2-NH) or chitosan (R_2-NH_2). The associated proteins such as aspartate, glutamate and cysteine present in the crab shell are also believed to play an important role in metal chelation.

1. Effect of Biosorbent Dosage

The variation in the nickel(II) sorbed at different concentrations of the crab shell dosage (0.05-10 g/*l*) was analyzed at an initial concentration of Ni(II) at 2 g/*l*, pH 6.5 and temperature 40 °C. It was observed from Fig. 1 that the maximum removal of nickel(II) occurred at a crab shell dosage of 6 g/*l* beyond which the increase in the biosorbent dosage did not have any effect. Biosorption of nickel (II) by crab shell is proportional to the specific area, which is the total area available for biosorption. The increase in the biosorption capacity from 0.5-6 g/*l* is due to an increase in sorbent surface and pore volume [16-18]. Further, for comparative purpose the adsorption of Ni(II) by activated carbon at an initial Ni(II) concentration of 2 g/*l* is also shown in Fig. 1. Although activated carbon shows equally good sorption of Ni(II) from aqueous solution, its high cost promotes the usage of such efficient cheap and efficient biosorbent such as crab shell.

2. Effect of pH

The solubility of the metal ions and the solubility of $CaCO_3$ in the crab shell are greatly influenced by pH. The medium pH affects the solubility of metals and the ionization state of functional groups [4, 19,20] present in the biosorbent (crab shell). Experiments for Nickel (II) sorption were carried out at different pH values ranging from 2-6.5 (Fig. 2) at an initial concentration of Ni(II) at 2 g/*l*, biosorbent dosage of 6 g/*l* and temperature 40 °C. The studies were not performed above pH 6.5 since the precipitation of nickel hydroxide occurred. The nickel(II) biosorption capacity increased with increasing pH up to a pH of 6.5. This indicates the passive interaction of the biosorbent binding sites with protons, and with an increase in pH the percentage sorption of nickel(II) increases as the degree of ionization of negative functional groups (-COOH, -NH_2, -SH etc.) present in the crab shell increases. It is also suggested that the amine nitrogen on each chitin monomer unit acts as the active site for metal coordination [21,22]. At lower pH values <6.5 the amino groups present in the crab shells become protonated, and hence the biosorption capacity decreases (Al-Qodah, 2006). Further, pH effects may be explained on the basis of competition effect between hydronium $(H_3O)^+$ and Ni(II) to the active sites for biosorption. At low pH values, the concentration of $(H_3O)^+$ far exceeds that of Ni(II) ions, and they get bound onto the surface of biosorbent, i.e., crab shells in preference to the biosorption of nickel(II) ions, whereas the reverse binding of nickel(II) ions in preference to hydronium ions occurs at higher pH values [23,24]. The results are in consistent with the results reported for chitosan [25] from lobster and crab which is in the range of 6.4-7.2.

3. Effect of Temperature

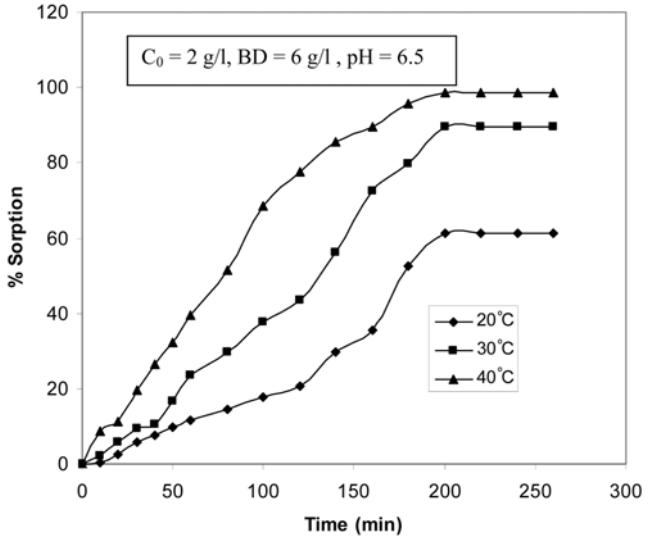

Fig. 3. Effect of temperature on the % sorption of nickel(II) using crab shell as biosorbent.

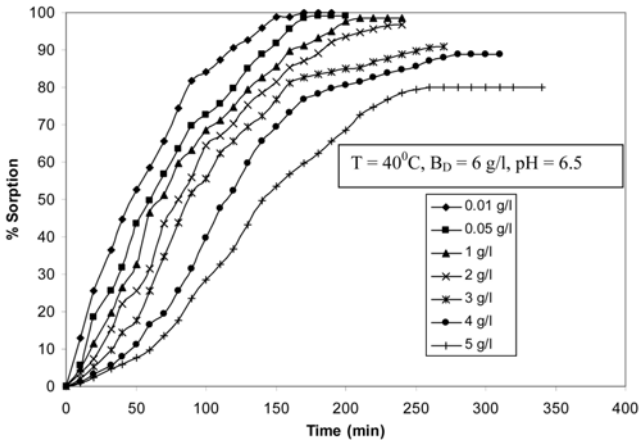

Fig. 4. Effect of various initial concentration of nickel(II) on the % sorption of nickel(II) using crab shell as biosorbent.

The effect of temperature on the removal of nickel(II) was studied at various temperatures, namely (20 °C, 30 °C and 40 °C) at an initial concentration of Ni(II) at 2 g/*l*, pH 6.5 and biosorbent dosage of 6 g/*l* as shown in Fig. 3. The biosorption of nickel(II) was found to increase with increase in temperature from 20-40 °C. The biosorption of Ni(II) increases with increasing temperature indicating an endothermic process [26] and the increase in biosorption with temperature may be attributed to either increase in the number of active sites available for biosorption due to bond rupture or decrease in the thickness of the boundary layer surrounding the biosorbent with temperature [18].

4. Effect of Initial Concentration of Nickel(II)

The effect of various initial concentrations of nickel(II) on crab shell was carried out at concentrations ranging from (C_0=0.01-5.0 g/*l*) at a pH of 6.5, crab shell dosage of 6 g/*l* and temperature of 40 °C, and the results are shown in Fig. 4. The results indicate that the percentage sorption of nickel(II) decreased with an increase in initial nickel(II) concentrations, and the surface saturation is dependent on the initial concentration of the metal. The decrease in percentage sorption of Ni(II) at higher concentrations is due to the rapid saturation of metal binding sites of the biosorbent. For nickel(II) concentrations of up to 2.0 g/*l*, the ratio of initial moles of nickel(II) ions to the available surface area was low, and subsequently the fractional sorption became independent of initial concentration. However, at higher concentrations of nickel(II), i.e., >2.0 g/*l*, the available sites for sorption became less compared to the moles of nickel ions present, and hence the percentage sorption of nickel(II) was dependent upon the initial metal ion concentration. The results are in agreement with those reported in the literature [17].

5. RSM Optimization of Nickel(II) Biosorption

Each contour in the response surface plot represents one variable maintained at zero levels and a number of combinations of the other two variables, and these studies reveal the best optimal values for the biosorption process. The three-dimensional response surface plot (Fig. 5) shows the biosorption of nickel(II) versus the variation of pH with initial nickel(II) concentration. It is observed from Fig. 5 that the percentage sorption decreases as the concentration of nickel (II) increases. The concentration of nickel(II) varied from 0.01 to 5 g/*l* with the temperature at 30 °C and biosorbent dosage at 5.25 g/*l*. The percentage sorption decreased from 88.37% to 50.31% on increasing the concentration of nickel(II) from 0.01 to 5 g/*l*. Similarly, Fig. 6 shows the response surface plot showing the effect of temperature with initial nickel(II) concentration at a pH of 4.25 and biosorbent dosage of 5.25 g/*l*. At an optimum temperature of 30 °C, the removal of nickel(II) was found to be 85.88% at a nickel(II) concentration of 0.01 g/*l*, whereas the percentage removal was found to be 56.37% at a nickel(II) concentration of 2.5 g/*l*. The 3-D graph showing the variation of concentration of nickel(II) with respect to biosorbent dosage at a pH of 4.25 and temperature of 30 °C is given in Fig. 7. At an optimum biosorbent dosage of 5.25 g/*l*, the percentage removal of nickel(II) increased from 57.66% to 87.16%

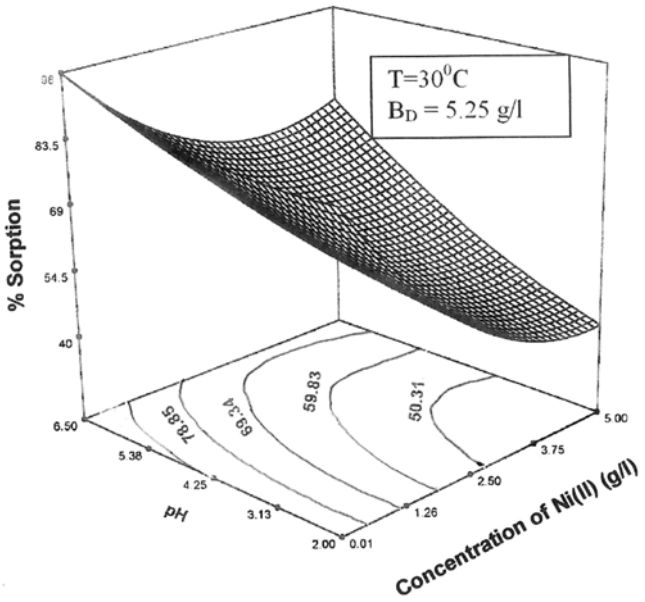

Fig. 5. Response surface plot showing the effects of pH with initial concentration of nickel(II).

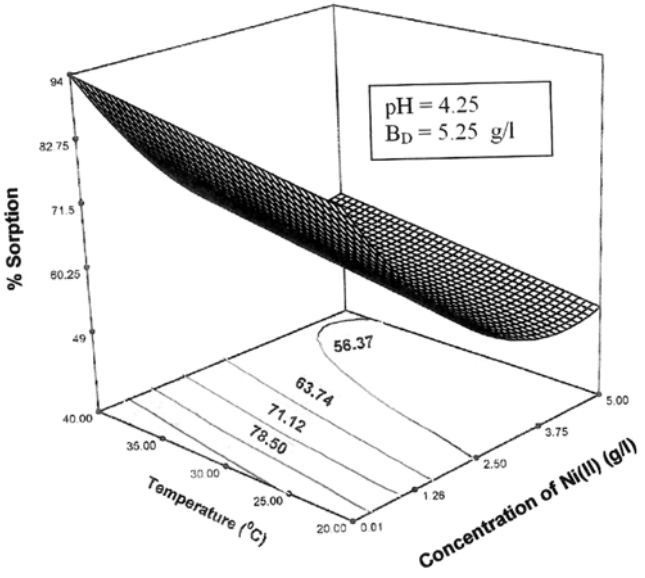

Fig. 6. Response surface plot showing the effects of temperature and initial concentration of nickel(II).

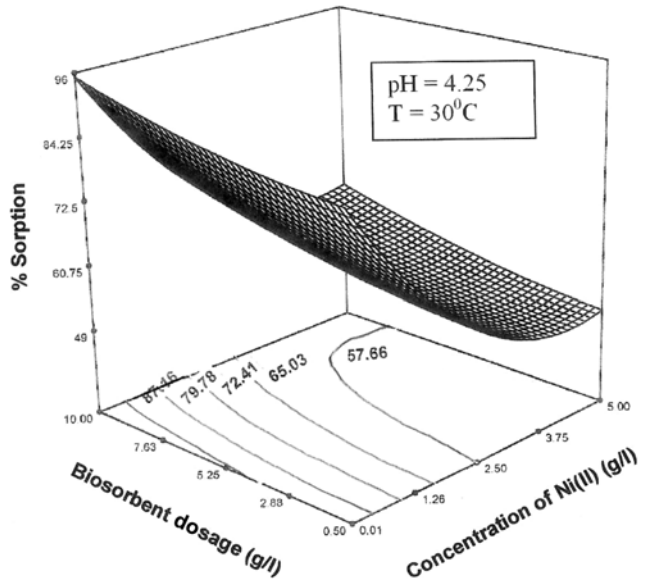

Fig. 7. Response surface plot showing the effects of biosorbent dosage and initial concentration of nickel(II).

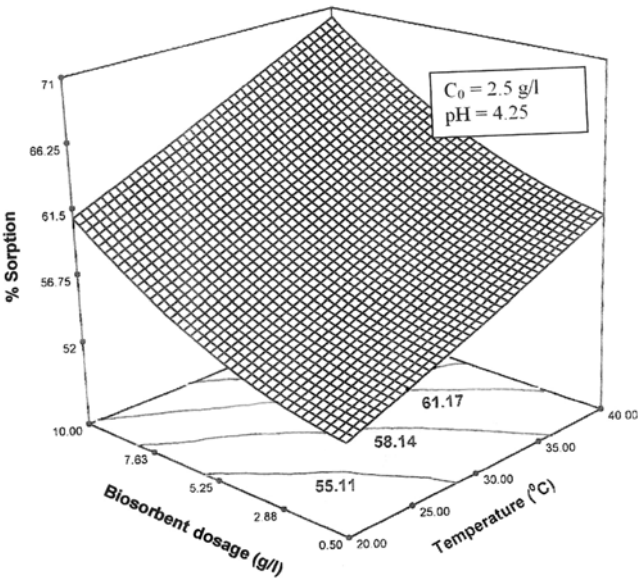

Fig. 9. Response surface plot showing the effects of biosorbent dosage and temperature.

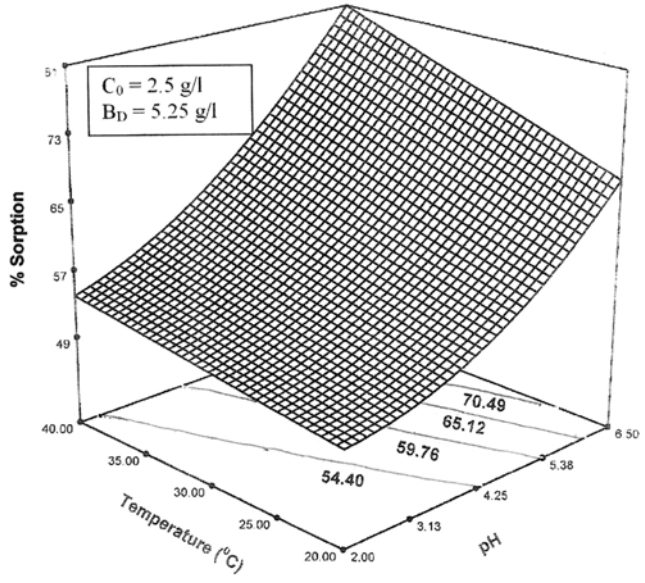

Fig. 8. Response surface plot showing the effects of temperature and pH.

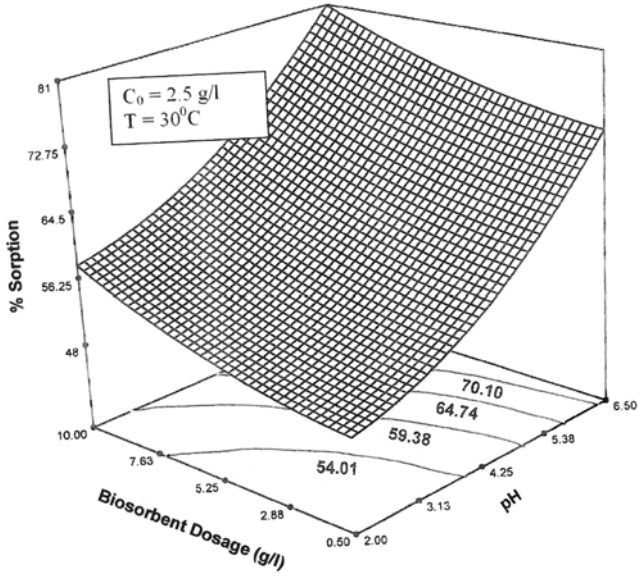

Fig. 10. Response surface plot showing the effects of biosorbent dosage and pH.

as the concentration of nickel(II) was decreased from 5 g/*l* to 0.01 g/*l*. Fig. 8 shows the 3-D graph showing the variation between pH and temperature at an optimum concentration of nickel(II) at 2.5 g/*l* and biosorbent dosage of 5.25 g/*l*. It is observed from the graph that the percentage removal increases on increasing the pH from 2 to 6.5. However, at an optimum pH of 4.5 and temperature 30 °C, the maximum percentage removal of nickel(II) was found to be 54.40%. Similarly, Fig. 9 shows the 3-D graph between temperature and biosorbent dosage at a fixed concentration of nickel(II) at 2.5 g/*l* and pH at 4.25. At an optimum temperature of 30 °C and biosorbent dosage of 5.25 g/*l*, the percentage removal of nickel(II) was found to be 55.11%. The 3-D response surface graph between pH and biosorbent dosage at a nickel(II) concentration (Fig. 10) of 2.5 g/*l* and temperature 30 °C, respectively, were analyzed. and at an optimum pH of 4.25 and at a biosorbent dosage of 5.25 g/*l*, the maximum percentage removal of nickel(II) was found to be 54%.

The results of the analysis of variance (ANOVA) for the proposed statistical model and their model coefficients are given in Table 3 and Table 4, respectively. The polynomials were estimated by the method of least squares. The experimental data were analyzed with "Design Expert 7.1.2" from Stat Ease. The ANOVA for the systems confirms the adequacy of the quadratic model since the Prob>F was found to be <0.0001, indicating the significance of the proposed model.

The second order equation for the estimation of percentage re-

Table 3. ANOVA of the quadratic model

Source	Sum of squares	Degrees of freedom	Mean square	F-Value	Prob>F
Model	6781.02	14	484.36	19056.72	< 0.0001
Residual	0.36	14	0.025	---	---
Lack of fit	0.36	10	0.036	---	---
Pure error	0.000	4	0.000	---	---
Correlation total	6781.37	28	---	---	---
Std. Dev	0.16		R^2	0.9999	
Mean	66.64		Adjusted R^2	0.9999	
CV %	0.24		Predicted R^2	0.9999	
PRESS	2.05				

Table 4. Coefficients for the Quadratic model

Factor	Coefficient estimate	Degrees of freedom	Error	Mean square	F Value	Prob>F
Intercept	59.20	1	0.071	---	---	---
Concentration of nickel(II) (C_0) (g/*l*)	−16.97	1	0.046	3454.41	1.359E+005	<0.0001
pH	11.54	1	0.046	1598.52	62892.62	<0.0001
Temperature (T) °C	4.53	1	0.046	246.61	9702.82	<0.0001
Biosorbent Dosage (B_D) g/*l*	4.53	1	0.046	245.71	9667.18	<0.0001
C_0 x pH	6.10	1	0.080	148.84	5856.00	<0.0001
C_0 x T	0.17	1	0.080	0.12	4.82	0.0455
C_0 x B_D	0.17	1	0.080	0.12	4.82	0.0455
pH x T	1.93	1	0.080	14.82	583.18	<0.0001
pH x B_D	0.25	1	0.080	0.25	9.84	0.0073
T x B_D	0.20	1	0.080	0.16	6.30	0.0250
C_0^2	12.50	1	0.063	1014.19	39902.53	<0.0001
pH^2	3.79	1	0.063	93.25	3669.03	<0.0001
T^2	0.20	1	0.063	0.27	10.64	0.0057
B_D^2	1.49	1	0.063	14.43	567.85	<0.0001

moval of nickel(II) (Y) in terms of initial concentration of nickel(II) (X_1), pH (X_2), temperature (X_3), and biosorbent dosage (X_4) is represented in terms of coded factors (−1,0 and +1) as follows.

$$Y=59.20-16.97\,X_1+11.54\,X_2+4.55\,X_3+4.54\,X_4+6.10\,X_1X_2+0.17\,X_1X_3+0.17\,X_1X_4+1.93\,X_2X_3+0.25\,X_2X_4+0.25\,X_3X_4+12.50\,X_1^2+3.78\,X_2^2+0.22\,X_3^2+1.51\,X_4^2 \quad (2)$$

Eq. (2) represents the quantitative effect of the process variables (X_1, X_2, X_3 and X_4) and their interactive effects on the response (Y). A positive sign in the equation represents a synergistic effect of the variables, while a negative sign indicates an antagonistic effect of the variables.

The analysis of variance shows a Model F value to be 19056.72, and the model is significant with Prob>F to be <0.0001. It is further observed that the Prob>F was found to be <0.05 for all the four interactive factors, indicating good significance between all the factors. The experimental values and the predicted values according to Eq. (2) show good agreement with each other and are shown in Fig. 11. The RMS error was found to be <1%, and this proves the reliability of the Box-Behnken design for the biosorption of nickel(II) from aqueous solutions using crab shell as the biosorbent.

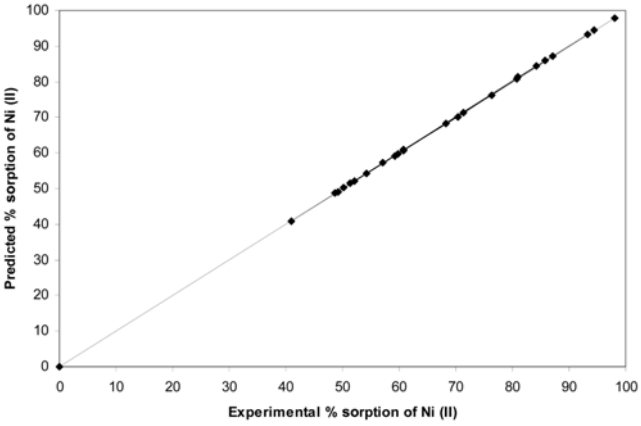

Fig. 11. Plot of experimental values versus predicted values according to Eq. (2).

6. Effect of Factor Plot

The behavior of the response (Y), i.e., percentage sorption of nickel (II) using crab shell in three levels, −1, 0 and +1, with respect to the four factors (initial concentration of nickel(II) (X_1), pH (X_2), temperature (X_3), and biosorbent dosage (X_4)) can be studied by

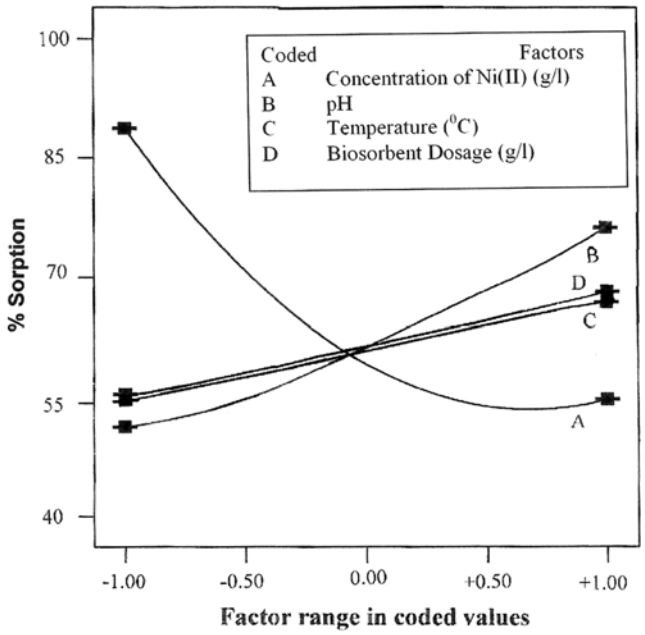

Fig. 12. Factor plot representing the individual variable effect on the biosorption of nickel(II) according to Table 1.

using the factor plot. This plot is shown in Fig. 12, which shows how the response moves as the level changes. The gradual decrease (line A) in the percentage removal of nickel(II) was observed as the concentration of nickel(II) was increased from coded value −1 (0.01 g/*l*) to coded value +1 (5 g/*l*). However, a steep increase in the percentage sorption of nickel(II) (line B) was observed as the pH was increased from coded value −1 (2) to coded value +1 (6.5). Lines C and D show a gradual increase in the percentage removal of nickel(II) as the temperature is increased from coded value −1 (20 °C) to coded value +1 (40 °C) and the biosorbent dosage is increased from coded value −1 (0.5 g) to coded value +1 (10 g).

CONCLUSION

The use of cheap and efficient biosorbents to remove and recover metal ions from industrial wastes is an effective method that has been applied in the present work to remove Nickel(II) from aqueous solution. The objective of the present work was to find and optimize the Nickel(II) biosorption by using a biosorbent, namely crab shell, on the basis of the RSM approach. Using these composite designs, the parameters--initial Ni(II) concentration (X_1), pH (X_2), temperature (X_3), biomass dosages (X_4)--were studied. The biosorption of nickel(II) by using the Box-Behnken Model revealed the optimum values for the process as initial concentration of Ni(II) as 2.5 g/*l*, pH 4.5, temperature as 30 °C and the biosorbent dosage at 5.25 g/*l*. This work has emphasized the use of the composite designs to determine the optimum conditions for the biosorption. The close agreement of the experimental value with the predicted values confirms the applicability of the RSM to optimize the above process parameters involved in biosorption.

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