

Response surface methodology optimization of nickel (II) removal using pigeon pea pod biosorbent

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Abstract Pod of pigeon pea (*Cajanus cajan*), a cellulose-rich agricultural residue, was investigated for its nickel binding efficiency. The influence of key physicochemical parameters such as contact time, initial metal ion concentration, adsorbent dosage and pH on nickel (II) removal was studied. The equilibrium time was found to be 45 min. The optimum Ni (II) removal was obtained at an initial metal ion concentration of 80 mg/l, pH of 9.0 and an adsorbent dose of 400 mg/100 ml. A search for optimal combination of key variables was studied by response surface methodology for maximum removal of nickel. The experiment encompassing 17 runs was established with the aid of Box–Behnken design. Owing to the reasonable agreement between predicted and adjusted R^2 value (0.9714), the corresponding quadratic model gives the most appropriate relationship between the variables and response. The optimal point obtained was located in the valid region and the optimum adsorption parameters were predicted as an initial Ni (II) concentration of 60 mg/l, pH value of 9.0 and contact time of 75 min. Under these adsorption conditions, a maximum removal of 96.54 % of initial metal concentration was demonstrated.

Keywords Agricultural residue · Box–Behnken design · Nickel · Optimization

Introduction

Industrial effluents from mining, electroplating, tanning, manufacture of fertilizers, etc., resulted in huge deposits of toxic heavy metals in the environment. Owing to their persistence, bio-magnification, toxicity and consistently increasing applications, they contribute to the major environmental concern (Das et al. 2007). Among these heavy metals, nickel exhibits remarkable toxicity, thereby causing irreversible damage to environment and human health. Uptake of large doses of nickel affects human health adversely: High incidence of lung cancer, nose cancer, larynx cancer and prostate cancer; lung embolism; respiratory failure; birth defects; asthma and chronic bronchitis; allergic reactions such as skin rashes; heart disorders (Rao and Prabhakar 2011). Moreover, prolonged exposure to nickel may result in genotoxicity, neurotoxicity, nephrotoxicity, immunotoxicity and reproductive toxicity. Conventional technologies for removal of metal ion from industrial effluents are less efficient, very costly and generate toxic sludge. The search for new techniques for the removal of toxic metals directed attention toward biosorption (Ahalya et al. 2003). Due to the presence of surface functional groups such as acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulfhydryl groups, cellulosic agricultural waste materials act as an important source for metal biosorption. Effective metal biosorption was demonstrated by microalgae, sea weeds, bacteria, fungi, animal residues and agricultural residues (Can et al. 2006; Kirbiyik et al. 2012; Xu et al. 2013; Din and Mirza 2013; Zhao et al. 2012; Farnad et al. 2012).

Agricultural wastes are characterized by ready availability, affordability, eco-friendliness and high uptake capacity for heavy metals. The husk of grains such as rice,

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wheat, Bengal gram and corn had been studied extensively in the past, for their adsorption efficiency. The results showing high efficiencies at low cost triggers further study to estimate the adsorption characteristics of similar low cost agricultural waste products. In this regard, a novel biosorbent was examined for nickel binding traits and the combination of key physical parameters that influence the extent of nickel removal. Dry matter yield of pigeon pea in pod shells is almost equal to the seed yield. The protein content in pods is also negligible. This contains low levels of digestible energy and sulfur and hence not a preferred livestock feed (Whiteman and Norton 1981). The physical parameters that influence the Ni (II) uptake in a batch system like pH, contact time, initial metal ion concentration and adsorbent dosage were optimized. The combined effect of these factors was determined by experiments that conducted for different combinations of the physical parameters using statistically designed experiments (Zolgharnein et al. 2008).

Traditionally optimization of experimental condition is done by varying one-factor-at-a-time (OFAT) while keeping the other factors at a constant level. This method is feasible and practical when only a limited number of variables are involved in the experiment, but when the variables involved are large then this method becomes laborious and necessitates a daunting number of trials compounded with a drawback as it fails to incorporate the interaction effects between the variables on the process (Kanmani et al. 2013).

Response Surface Methodology (RSM) a fraction factorial design involves a set number of designed experiments to obtain an optimal response enable effective medium optimization using a limited number of trials and eliminate the limitations and drawbacks of the traditional optimization processes. There are nowadays widely employed for the optimization of a number of processes including adsorption studies (Goyal et al. 2008; Rene et al. 2007) and have been successfully applied for metal removal (Can et al. 2006; Cordova et al. 2011). Box–Behnken design is part of RSM, where each experimental variable is taken at three levels and the experimental outcome (actual) is compared with the predicted response (Box and Wilson 1951; Box and Behnken 1960; Ferreira et al. 2007).

In this article, we report the adsorption of nickel on to a novel natural material pigeon pea pod (PPP) screening for their nickel removal efficiency based on important process parameters such as pH, contact time and initial metal concentration that have a significant impact on adsorption capability of pigeon pea pod.

The present study was carried out in Coimbatore, India, during the period of December 2011 to April 2012.

Materials and methods

Preparation of biosorbent from pigeon pea pod

Pigeon pea (*Cajanus cajan*) pod was collected from land near Kovilur village of Dindigul district in southern part of Tamilnadu, India. The pigeon pea pod was washed extensively in running tap water to remove dirt and other particulate matter. It was dried at 40 °C for 24 h and was then finely ground and sieved with a mesh size of 150 µm. FTIR analysis was carried out to obtain qualitative information on surface functional groups responsible for metal uptake. The spectra of the adsorbent were measured within the range of 500–4,000 cm⁻¹. The finely powdered biosorbent was pretreated using 1 M sodium hydroxide (NaOH) solution. The mixture was filtered, and the powdered residue was washed with distilled water, several times to remove any base contents. This filtered biomass was dried in an oven at 60 °C for 6–8 h. The dried biomass was stored in air tight containers to protect it from moisture.

Preparation of synthetic single metal solution

An aqueous stock solution (1,000 mg/l) of Ni (II) ions was prepared using NiCl₂ salt (analytical reagent). pH of the solution was adjusted using 0.5 N HCl or NaOH. Fresh dilutions of 100 mg/l were used for each study.

Batch adsorption studies

The biosorption capacity of pigeon pea pod was evaluated by varying initial metal ion concentration, pH, contact time and adsorbent doses while fixing the volume of metal solution as 100 ml. While varying one parameter, the others were maintained constant. The mixture was agitated in a thermostatic orbital shaker at 120 rpm followed by filtration using Whatman filter paper (No. 1). The filtrate containing the residual concentration of Ni was determined spectrophotometrically at 465 nm after complexation with dimethylglyoxime (DMG) (Krishna and Swamy 2011).

Metal analysis

Spectrophotometric analysis was adopted to estimate nickel (II), using dimethylglyoxime (DMG). Different standard solutions containing less than 100 mg/l of nickel (II) were prepared and 2 ml of 20 % w/v potassium sodium tartrate solution, 10 ml of 4 % w/v ammonium per sulfate, 2.5 ml of 5 M sodium hydroxide solutions 15 ml of (1 + 30) HCl and 0.5 ml of 1 % DMG solutions were added. The absorbance was measured after 30 min using UV–visible spectrophotometer at 465 nm. A reagent blank



was also prepared for nickel (II) solution. The amount of nickel present in the sample was obtained from the calibration curve.

Removal efficiency

The percentage nickel removal, R (%), was determined after each run as follows:

$$\text{Removal Efficiency (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i and C_e were the initial and final concentration of nickel in the solution in mg/l.

Process optimization

The appropriate combination of optimum conditions for maximum adsorption of Ni(II) by pod of *Cajanus cajan* was determined by means of a three-factor, three-level Box–Behnken experimental design combining with response surface modeling and quadratic programming. As the initial step of RSM, a suitable approximation is introduced to find true relationship between the dependent variable (response) and the set of independent variables (factors). If knowledge concerning the shape of true response surface is insufficient, the preliminary model (generally a first-order model) is upgraded by adding high-order terms to it. In the next step, the behavior of the system is explained by the following quadratic equation:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where Y is the predicted response, i.e., the percentage removal for Ni (II), β_0 is the constant coefficient, β_i is the i th linear coefficient of the input factor x_i , β_{ii} is the i th quadratic coefficient of the input factor x_i , β_{ij} is the different interaction coefficients between the input factors x_i and x_j , and ε is the error of the model (Box and Behnken 1960). For this study, the independent variables were coded as A , B and C , and thus, the equation could be described as follows:

$$Y = \beta_0 + \beta_i A + \beta_j B + \beta_k C + \beta_{ii} A^2 + \beta_{jj} B^2 + \beta_{kk} C^2 + \beta_{ij} AB + \beta_{jk} AC + \beta_{ik} BC \quad (3)$$

It is important to include the second-order model to provide good prediction throughout the region of interest. The second-order response surface design is rotatable; this means that the variance of the predicted response is the same at all points. Rotatability is a reasonable basis for the selection of response surface design. Because the purpose of response surface methodology (RSM) is optimization and as the location of the optimum is unknown prior to running the experiment, it makes sense to use design that

provides equal precisions of estimation in all directions (Montgomery 2001; Yetilmesoy et al. 2009; Zolgharnein et al. 2008).

Results and discussion

Characterization of biosorbent

The changes in the vibrational frequencies of the functional groups in the adsorbent were analyzed using FTIR spectra. The spectra of the pretreated and loaded adsorbent measured within the range of 4,000–400 cm^{-1} wave number are presented in Fig. 1, and their corresponding fundamental peaks are given in Table 1. FTIR studies of various adsorbents have identified the presence of several surface functionalities with C=O (carboxylic, anhydride, lactone and ketone) at 1,750–1,630 cm^{-1} ; C=C at 1,600–1,450 cm^{-1} ; C–O stretching and O–H bending (lactonic, ether, phenol, etc.) at 1,440–1,000 cm^{-1} ; C–H (900–600 cm^{-1}); OH, NH, CH stretching in alkyl or aryl at 3,488–3,100 cm^{-1} (Anirudhan and Sreekumari 2011).

It is shown in Table 1 that the absorbance of peaks in Ni (II) loaded biosorbent is subsequently lower than those in pretreated biosorbent. This indicates that bond stretching occurs to a lesser extent due to presence of nickel and subsequently peak absorption is attenuated. Thus, the major functional groups involved in efficient removal of nickel are attributed to the presence of C=O, C–O, O–H and C–H bond, which can coordinate with nickel.

Fereidouni et al. (2009) have observed that Ni (II) biosorption on to *Ralstonia eutropha* cells which involved hydroxyl (OH), amine (NH) and carboxylate ions (COO[−]) groups of the bacterial cell wall peptidoglycan layer's polysaccharides, and similarly, Qu et al. (2011) also observed Ni (II) biosorption FTIR spectral bands, shifting at 3,303 and 1,654 cm^{-1} , indicating the binding of Ni (II) with amino and hydroxyl groups. They also noted peak shift at 1,064 cm^{-1} , indicating the role played by carboxyl group of the biomass in Ni (II) biosorption. They also reported the interactions between the Ni (II) and the functional group's hydrogen atoms in (−COOH), hydroxyl (−CH−OH) and amine (−NH₂) groups.

Batch adsorption studies

Effect of contact time

To establish an appropriate contact time between the pretreated adsorbent and metal ion solution, percentage removal of metal ion were measured as a function of time. The graph in Fig. 2a indicates that the rate of the percentage of Ni (II) removal is higher at the beginning,



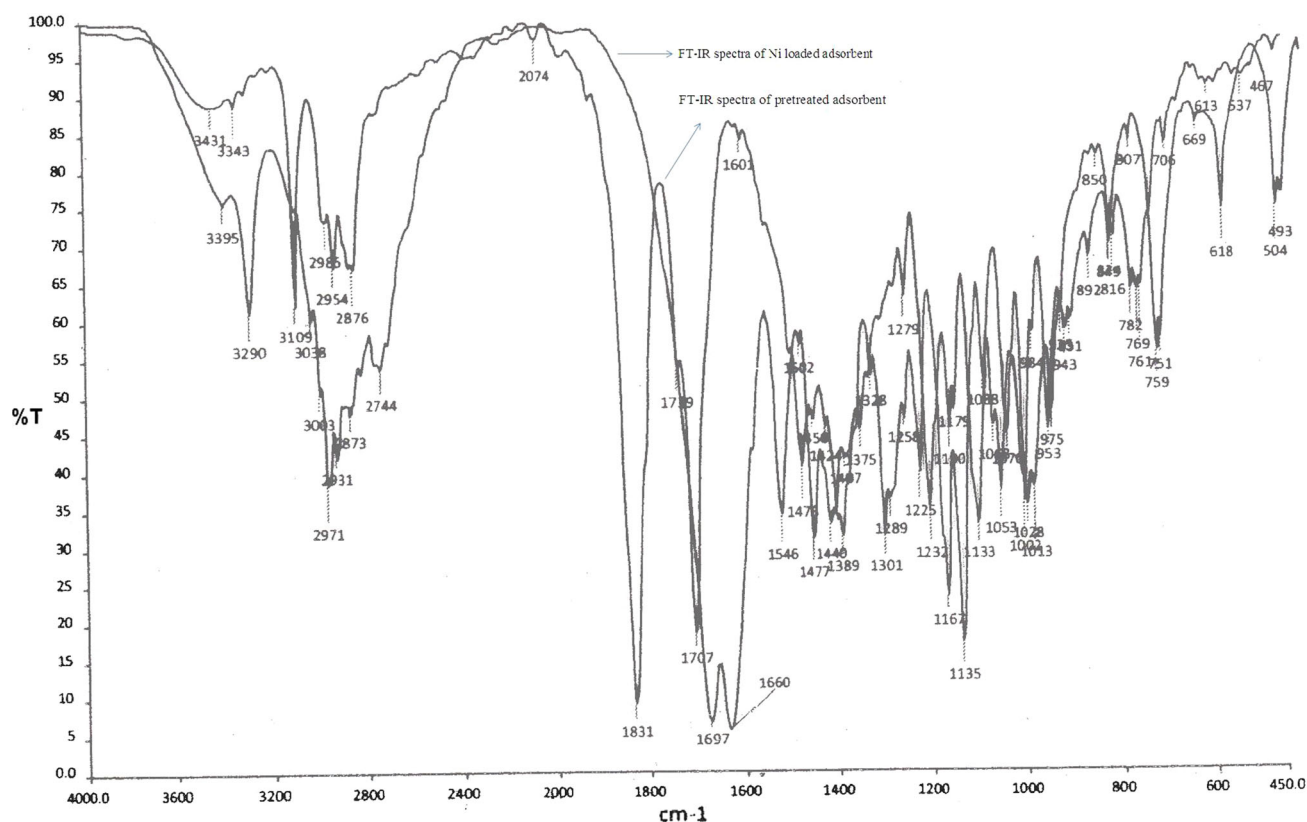


Fig. 1 FTIR spectra of pretreated adsorbent and Ni-loaded adsorbent

Table 1 FTIR frequencies of adsorbent before and after adsorption

Adsorbent	O–H stretch	C=C bond	C=O bond	C–O stretch	C–H bond
Pretreated	3,431	1,546	1,697	1,440	892
Ni (II) loaded	3,395	1,473	1,631	1,424	850

probably due to the larger surface area of the adsorbent being available at beginning for the adsorption of metals. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The equilibrium rate of Ni (II) removal was attained after agitating for 45 min. This is in agreement with the results reported in the literature where the maximum removal was demonstrated at a contact time of 30 min (Kehinde et al. 2009). Therefore, equilibrium time of 45 min was selected for all further studies.

Effect of metal concentration

To investigate the effect of various initial concentrations of Ni (II) on biosorption, batch experiments were carried out by agitating 100 ml of different concentrations of Ni (II)

solutions ranging from 20 to 100 mg/l which are maintained at pH 8.0 and with 100 mg of adsorbent. After equilibrating for different time periods from 15 to 90 min, the solutions were filtered and analyzed for Ni (II) content and the percent adsorption in each case was determined. The effect of initial nickel concentration on biosorption is shown in Fig. 2b. The increase in initial Ni (II) concentration from 20 to 100 mg/l decreased the percentage of adsorption from 95 to 85 % at the equilibrium contact time of 45 min. A further increase in the contact time has a negligible effect on Ni (II) removal. The decrease in percentage removal of Ni (II) is due to the saturation of metal-binding sites of the biosorbent. This indicates that the initial metal concentration has an influence on percentage sorption of Ni (II). A similar trend was observed for the adsorption of Ni (II) on crab shell particles (Murugesan et al. 2009) where the percentage sorption decreased with increase in initial nickel ion concentrations within the experimental operating conditions.

Effect of adsorbent dosage

The dosage of adsorbent is a key parameter to control both availability and accessibility of adsorption sites. The results are shown in Fig. 2c as follows: Percentage of removal for

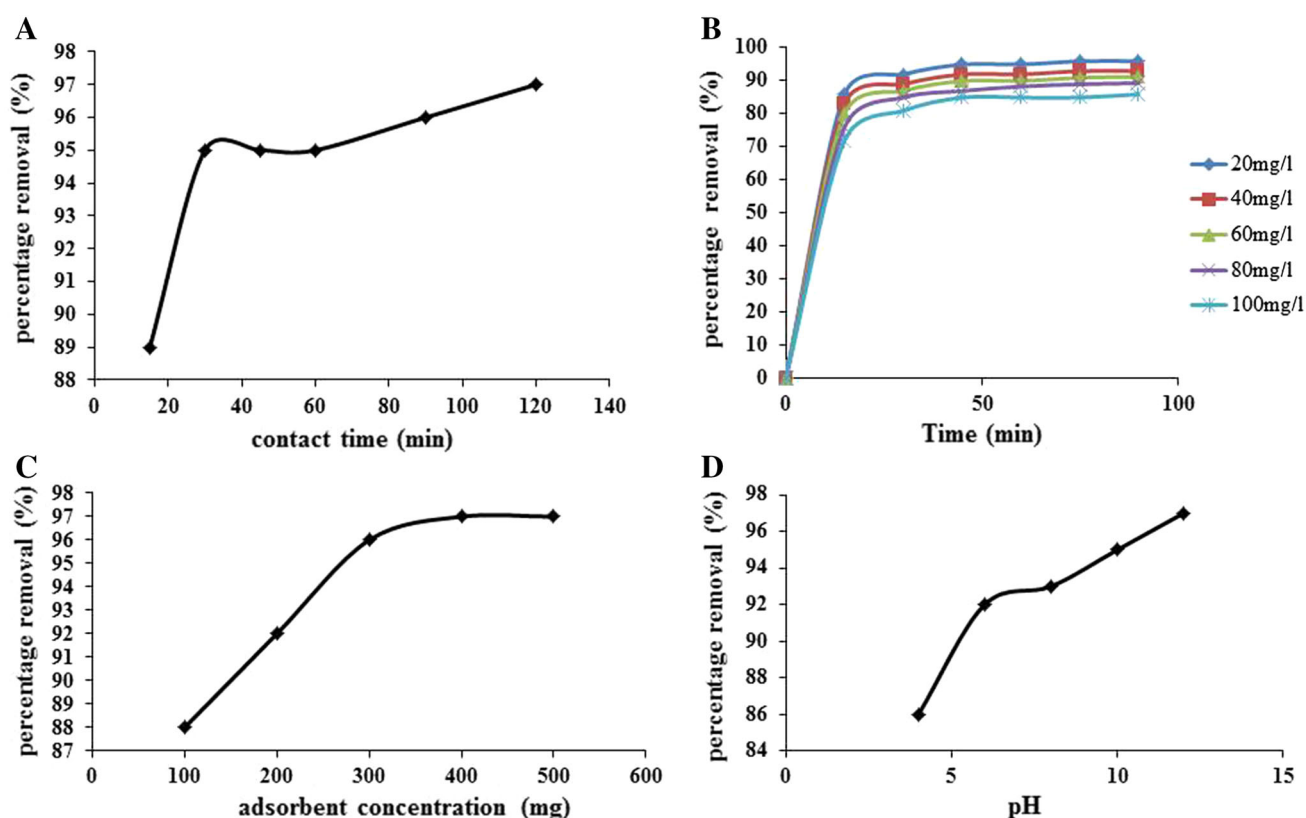


Fig. 2 **a** Effect of contact time, **b** effect of metal ion concentration, **c** effect of adsorbent dosage, **d** effect of pH

100 mg/L Ni (II) was observed to increase gradually from 88 to 97 % with the increase in adsorbent dosage from 0.1 to 0.5 g, and maximum removal was achieved at a dosage of 0.4 g. This is comparable to the results obtained by Krishna and Swamy (2011) where maximum removal was demonstrated at a dose of 0.2 g/50 ml of metal solution. The observed trend may be due to the fact that higher the dosage of adsorbent greater the availability of surface area and functional groups for metal ions. These chemical groups play an important role in the formation of van der Waals bonding as the functional groups play the main role in binding metals to the adsorbent during adsorption process. This provides more possibilities for adsorption to occur since there was less competition between metals for the binding sites.

Effect of pH

In heavy metal biosorption, pH is the most important parameter. The speciation of metals in the solution and the state of chemically active sites is pH dependent. The effect of pH on Ni (II) biosorption is shown in Fig. 2d. For biosorption of Ni (II), maximum removal was achieved at pH of 9.0. This could be due to an increasing negative charge density on the adsorbent surface. It is apparent that Ni (II)

is strongly adsorbed at higher pH values. At pH greater than 8, Ni (II) removal was mostly due to precipitation and not by sorption. Similar results were obtained when Mosambi fruit peels were used as biosorbent as investigated by Gaballah and Kilbertus (1998) and Salamatnia et al. (2006).

Experimental design for optimization

Box–Behnken analysis

The best performance of a Box–Behnken design depends on some prior knowledge of the system being optimized. If the values of all the system parameters to be studied are unknown, the projection of the results with the factorial design cannot be optimized. Besides this, the total number of experiments required will be excessively large, making the factorial design very complex. Optimization of biosorption of heavy metals by the classical method is time consuming and expensive for a large number of variables. To overcome this difficulty, the experimental Box–Behnken design under response surface methodology can be employed to optimize the biosorption of heavy metals.

Experiments are conducted according to the Box–Behnken experimental design as shown in Table 2 in order to



Table 2 Experimental design matrix with response

Std	Run	Factor1 A: pH	Factor2 B: contact time (min)	Factor3 C: metal concentration (mg/l)	% Removal experimental	% Removal predicted
16	1	9	75	60	96.23	96.23
3	2	6	120	60	85.26	85.53
12	3	9	120	100	92.71	93.11
15	4	9	75	60	96.23	96.23
6	5	12	75	20	92.67	93.33
14	6	9	75	60	96.23	96.23
17	7	9	75	60	96.23	96.23
1	8	6	30	60	79.96	79.43
8	9	12	75	100	95.74	94.82
2	10	12	30	60	96	95.73
13	11	9	75	60	96.23	96.23
4	12	12	120	60	90.41	90.94
7	13	6	75	100	88	87.34
11	14	9	30	100	91.11	92.29
10	15	9	120	20	89.28	88.09
5	16	6	75	20	78.19	79.11
9	17	9	30	20	88	87.6

Table 3 Selection of a satisfactory model for Ni (II) removal: sequential model sum of squares

Source	Sum of squares	df	Mean square	F value	p value prob > F
Mean versus total	1.41E+005	1	1.41E + 005		
Linear versus mean	283.53	3	94.51	4.98	0.0198
2FI versus linear	41.03	3	13.68	0.67	0.6191
Quadratic versus 2F	1,199.08	3	72.43	72.43	<0.0001 suggested
Cubic versus quadratic	6.41	3	2.14	6.3 + 007	<0.0001
Residual	0.0	4	0.0		

search for the optimum combination of parameters for the sorption of nickel using the pretreated adsorbent. The percentage removal of nickel is influenced by the individual effects of combinations of test variables and the results showed a significant variation for each combination.

Adequacy of the model for Ni (II) removal

A system or process with several variables is likely to be driven primarily by some principal factors and low-order interactions. In the present work, only two-way interactions were investigated. Linear, two-factor interaction (2FI), quadratic and cubic models were used to analyze the experimental data in order to obtain the appropriate regression equations. To determine the adequacy of the models depicting the removal of Ni (II) by pretreated biosorbent, three different tests, such as the sequential model sum of squares, lack of fit tests and the model summary statistics, are carried out, and the corresponding results are shown in Table 3.

It can be seen that *p* values for quadratic model was lower than 0.01 and Design Expert 8.0 suggested the model to be significant. As a natural log transformation was applied to the experimental data, the interaction of two factors (2FI) and the linear model was suggested to be insignificant using the response surface methodology. From the model summary statistics, it can be seen that the “Predicted R^2 ” of 0.877 was in reasonable agreement with the “Adjusted R^2 ” of 0.9714 for the quadratic model. Furthermore, the quadratic model had maximum “Predicted R^2 ” and “Adjusted R^2 ” values. The aforementioned results indicate that the quadratic model provide an excellent explanation for the relationship between the independent variables and the corresponding response (Table 4).

Regression analysis

Regression analysis was carried out to fit the response functions, i.e., percentage adsorption of Ni (II). The

Table 4 Model summary statistics

Source	SD	R^2	Adjusted R^2	Predicted R^2
Linear	4.35	0.53	0.43	0.26
2FI	4.53	0.61	0.38	0.008
Quadratic	0.96	0.98	0.97	0.877
Cubic	0.00	1.0	–	–

regression models developed represent responses as functions of pH (*A*), contact time (*B*), initial metal concentration (*C*). An empirical relationship between the response and input variables in coded terms is expressed by the following response surface reduced quadratic model equation:

$$Y = 96.23 + 5.43xA + 0.32xB + 2.43xC - 2.72xAxB - 1.69xAxC + 0.08xBxC - 4.97xA^2 - 3.35x * B^2 - 2.61xC^2 \quad (4)$$

This equation reveals how the individual variables or double interactions affected nickel biosorption from aqueous metal solution on pretreated pigeon pea pod as adsorbent. Negative coefficient values indicate that individual or double interaction factors negatively affect nickel biosorption (i.e., removal percentage decreases), whereas positive coefficient values mean that factors increase nickel removal in the tested range. From the equation, it is observed that all individual factors have a positive effect on nickel removal. This is compared to the study conducted by Murugesan et al. (2009) on nickel biosorption, where all factors (temperature, pH, biomass dose) had positive impact on nickel removal.

ANOVA for response surface quadratic model

The ANOVA suggests that the equation and the actual relationship between the response and the significant variables represented by the equation were adequate. The larger the value of *F* and the smaller the value of *p*, the more significant is the corresponding coefficient term (Kalavathy et al. 2009). The value of *p* was lower than 0.05, indicating that the model may be considered to be statistically significant. For the removal of Ni (II) by pretreated adsorbent, the ANOVA results (Table 5) indicated that the *F* value for the model was 63.51, implying that the model is significant. The probability $p < 0.0001$ also suggested that the model is significant. In this study, *A*, *C*, *AB*, *AC*, *A*², *B*², *C*² were significant factors. The other model terms whose *p* values are listed as being greater than 0.1000 in Table 5 are not significant factors.

Table 5 Analysis of variance

Source	Sum of squares	df	Mean square	<i>F</i> value	<i>p</i> value prob > <i>F</i>
Model	523.65	9	58.18	63.51	<0.0001
<i>A</i> -pH	235.55	1	235.55	257.11	<0.0001
<i>B</i> -contact time	0.84	1	0.84	0.92	0.37
<i>C</i> -metal conc	47.14	1	47.14	51.46	0.0002
<i>AB</i>	29.65	1	29.65	32.36	0.0007
<i>AC</i>	11.36	1	11.36	12.4	0.0097
<i>BC</i>	0.026	1	0.026	0.028	0.872
<i>A</i> ²	104.16	1	104.16	113.69	<0.0001
<i>B</i> ²	47.42	1	47.42	51.54	0.0002
<i>C</i> ²	28.6	1	28.6	31.22	0.0008
Residual	6.41	7	0.92		
Lack of fit	6.41	3	2.14		
Pure error	0.00	4	0.00		
Cor total	530.06	16			

Diagnostic plots

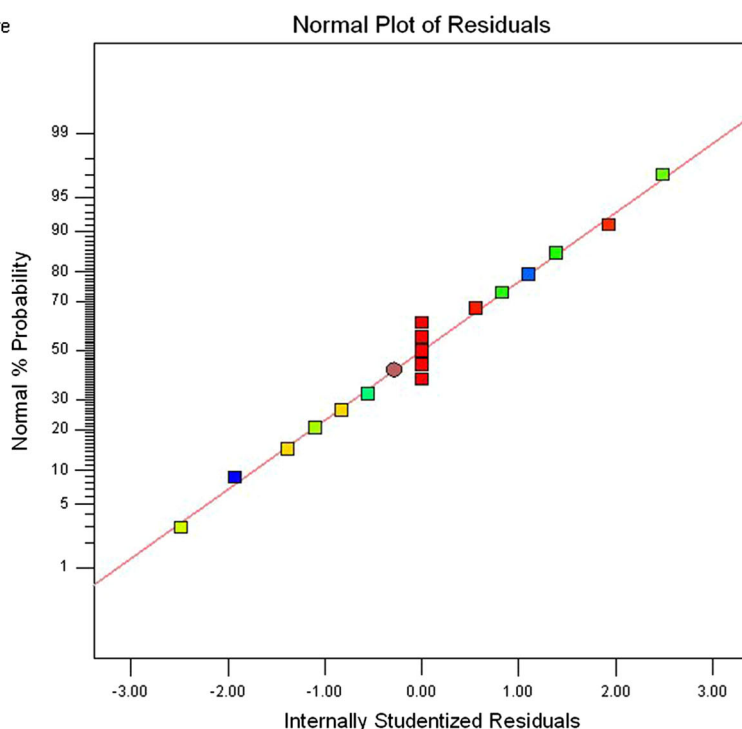
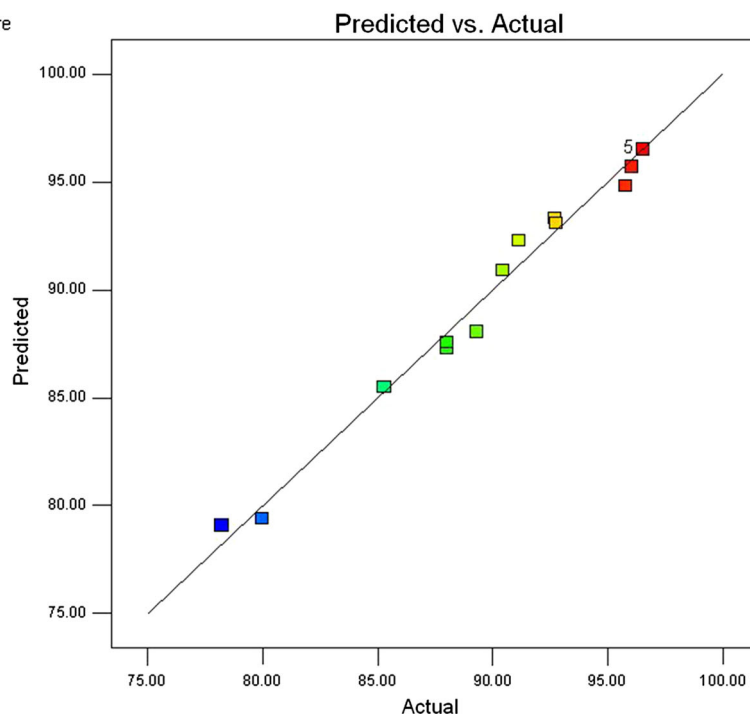
The data are analyzed to check the normal probability plot and a dot diagram of residuals correlation as shown in Fig. 3. The data points on this plot lie reasonably close to a straight line, lending support to the conclusion that *A* and *A*² were highly significant effects, *C*, *AB*, *AC*, *B*², *C*² were significant effects and that the underlying assumptions of the analysis were satisfied.

The data are also analyzed to check the correlation between the experimental and predicted percentage removal, as shown in Fig. 4. The experimental values were the result obtained, while the predicted values were obtained by calculation from the quadratic equation. It is shown in Fig. 4 that the data points on the plot are distributed near to the straight line, indicating a good relationship between the experimental and predicted values of the response. The result also suggests that the selected quadratic model was adequate in predicting the response variables for the experimental data.

Response surface contour plot

Contour plot is a two-dimensional representation of the response for selected factors. The contour plots, represented by the projection of the response surfaces in the *x*–*y* plane, provide a straightforward determination of the effects of the independent variables on the dependent variable. The response surface contour plots of percentage removal of nickel versus the interactive effect of pH, contact time and initial nickel ion concentration are shown



Fig. 3 Normal plot of residualsDesign-Expert® Software
%removalColor points by value of
%removal:**Fig. 4** Plot of experimental and predicted valuesDesign-Expert® Software
%removalColor points by value of
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in Fig. 5a–c. Each contour plot represents a number of combinations of two test variables with the other variable maintained at zero levels. The maximum percentage removal of nickel is indicated by the surface confined in the smallest curve (circular or elliptical) of the contour plot. In response surface contour plots, the optimum values of variable factors could be analyzed by the saddle point or by

determining the maxima formed by the x - and y -coordinates.

As evident from Fig. 5a–c, the percentage sorbed increases from 80 to 95 % with increasing values of pH, contact time and initial metal concentration. A similar trend was observed in the study conducted by Ismail et al. (2008) where the sorption percentage of Ni (II) reached



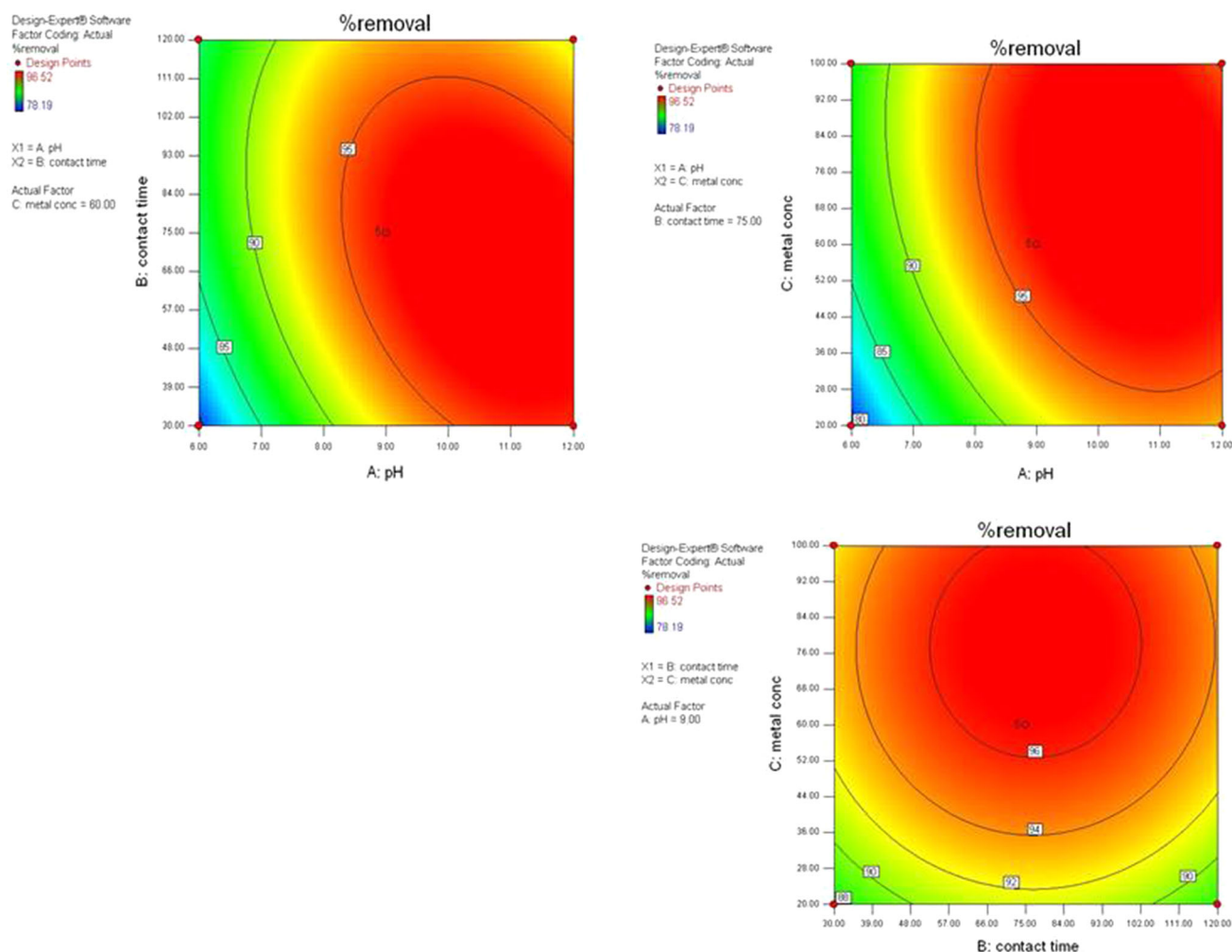


Fig. 5 **a** Response surface contour plot for the effects of pH and contact time on metal removal. **b** Response surface contour plot for the effects of pH and initial metal concentration on metal removal.

c Response surface contour plot for the effects of contact time and initial metal concentration on metal removal

100 % from 98.2 % as the pH, contact time and initial metal concentration was increased. The studies of the contour plots reveal the best optimal values of the process conditions, which are pH 7.5–9.5, contact time 65–85 min and initial nickel ion concentration 50–75 mg/l, which agrees with the batch adsorption studies investigated earlier.

Validation experiment

One of the primary objectives of the present study is to validate the result obtained for RSM-based optimized process parameters. An independent run was carried out using a pH value of 9.0, contact time of 75 min and an initial metal concentration of 60 mg/l. A maximum % removal of 96.23 was achieved which validated the design.

Conclusion

The adsorbent prepared from the pod of pigeon pea appears to be a promising adsorbent for removal of Ni (II) ions from aqueous solution. The study indicated that the pre-treated adsorbent produced through chemical activation using NaOH as an effective material for the removal of Ni (II). The maximum removal of Ni (II) is obtained at an alkaline pH of 8.0 for an equilibrium time of 45 min with a minimal dosage of adsorbent. The response surface modeling was successfully combined with the three-level factorial, Box–Behnken design to determine the influence of important process parameters, such as the initial metal concentration, the pH and contact time on Ni (II) removal by the adsorbent, over the experimental range was examined. The results indicated that a second-order polynomial regression model was capable of interpreting the



experimental data; it was shown that the initial metal concentration and pH had significant effects on metal adsorption. The pod of pigeon pea used to produce adsorbent is locally and abundantly available agricultural waste product. Hence, the adsorbent prepared from the pigeon pea pod would be an economically useful tool and alternative to the commercially available activated carbon in the treatment of effluent containing Ni (II) ions.

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