Original Article

Optimisation of nickel(II) ions removal from aqueous solutions by olive pulp

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Abstract : In this study, batch adsorption experiments were carried out for the removal of nickel ions from aqueous solutions using an agricultural waste biomass (olive pulp) as adsorbent. Response surface methodology was performed to optimize the adsorption process. Plackett-Burman design (PBD) was used in the first step to evaluate the effects of five independent variables on the yield adsorption of metal. Among these variables, initial pH of the medium, initial concentration of the nickel ions and the dose of the adsorbent were screened as significant variables and were then further optimized using response surface methodology based on a Box-Behnken design (BBD). Very high value of regression coefficient (R^2=0.9780) indicates excellent evaluation of experimental data by second-order polynomial regression model. The optimum conditions for maximum removal of nickel ions from aqueous solution were found to be as follows: pH (4.43), adsorbent dose (18.40 g/L) and initial concentration of nickel ions (15.76 mg/L).
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Keywords : Adsorption, nickel ions; Olive pulp; Optimization; Response surface methodology.

INTRODUCTION

Different industries release aqueous effluents containing heavy metals such as lead, chromium, copper, cadmium, zinc and nickel, which are very toxic even at low concentrations. Nickel is one of such toxic heavy metal present in effluents from industries of electroplating, mineral processing, nonferrous metals porcelain enamelling, battery and accumulator manufacturing and steam-electric power plants[1,2], etc. Many treatment methods have been developed for the decontamination of water and wastewater polluted with heavy metals. The most commonly used include chemical precipitation, solvent extraction, electrochemical treatment, membrane separation, reverse osmosis, ion-exchange, evaporation, cementation, filtration, flotation, flocculation, sedimentation[3,4]. However, these conventional processes may be ineffective and/or extremely expensive when concentrations of dissolved heavy metals in the wastewater are low[1,3].

Adsorption is an effective and promising treat-

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ment method, which is relatively easy to implement. In addition, this method can remove heavy metals ions from raw wastewater streams even at very low concentrations[4]. Activated carbon has been the most used adsorbent. Despite its excellent adsorbent properties, its use is usually limited due to its high cost and difficulties for regeneration[3]. In recent years, the low-cost agricultural wastes such as sugarcane bagasse[5,6], rice husk[6], waste tea[7], walnut shells[8], olive mill solid waste[4,9], loquat bark waste[10], etc., have been widely used and studied as unmodified or modified biosorbents by many researchers. The major advantages of biosorption over conventional treatment methods include: low-cost, high efficiency, minimization of chemical and/or biological sludge, regeneration of biosorbent, no additional nutrient requirement and possibility of metal recovery[11].

Batch adsorption studies have shown that the removal of metal ions is dependent upon process parameters such as initial pH of the metal solution, temperature, time of contact, liquid-solids/ratio, degree of agitation, ionic force and the parameters related to the state of the adsorbent and metal. Thus, it is difficult to determine for the main factors and to optimize them for such adsorption process as several factors are involved. Response surface methodology is an effective statistical technique for optimising complex processes. This methodology significantly reduces the number of experiments to be performed for evaluating of effects of many independent variables and their interactions on response variables, and for process modelling. Today, it is widely applied for product design, development and optimisation process in many industries, and more particularly for modelling and optimizing of adsorption process of heavy metal pollutants[8,12].

Among agricultural by-products, olive pomace is one of the most abundant in all areas of Mediterranean basin. In most countries, it is released into the environment while its potential uses are numerous and diverse. This solid waste can be used as natural fertilizer[13], nutrient additive for animal food[14], energy source[15], etc. There are also many studies related with this material as biosorbent of metallic ions. The removing of heavy metals such as lead, zinc, nickel are among the most recent stud-

ies[9,16,17]. On the other hand, olive stones and olive pulp are the solid components of olive pomace generated by olive-oil industry. Untreated and chemically treated olive stones have been successfully used as biosorbents for a wide variety of metallic pollutants in aqueous solutions[4,18]. However, to our knowledge, no work has been reported on the use of crude olive pulp regarding the optimisation of nickel(II) ions removal from aqueous solutions using the response surface methodological approach.

The purpose of the present study was to investigate the adsorption of nickel(II) ions using olive pulp (OP). Response surface methodology, based on a Box-Behnken design (BBD), was applied for modelling and optimizing the significant independent variables affecting the adsorption of Ni(II) ions on this agricultural waste adsorbent.

MATERIAL AND METHODS

Biosorbent material

Raw olive pomace issued from the three-phase centrifugation system was supplied by a local olive oil production plant. The pulp was separated from the stones, washed several times with boiling distilled water and then cold, in order to remove the organic compounds which could interfere in the results. The sample was then dried in an oven at 80 °C until a constant weight was achieved. After sieving, the <1.000 mm fraction was stored in a glass bottle prior to use as an adsorbent for biosorption of nickel(II) ions.

Experimental procedure

Metal solution of 1 g/L of nickel ions was prepared in distilled water using the metal salt $Ni(NO_3)_2 6H_2O$. The solution was diluted to prepare the different concentrations required. The solutions were then stored at room temperature. Batch adsorption experiments were conducted in a 250 ml glass reactor, which was placed in a thermostatic bath equipped with a mechanical stirrer. Adjustment of the initial pH value was performed using 0.1M NaOH and HCl solutions. For each experiment, the volume of the metallic solution and the stirring velocity were fixed to 50 ml and 150 rpm, respectively. After ad-

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sorption, the solid-liquid separation was carried out by filtration using filter paper (Whattman n°3). The Ni(II) concentrations in the filtrates were then determined according to the dimethylglyoxime method in an oxidizing medium[19]. All chemicals used were analytical reagent grade.

The absorbance measurements of the complex formed by the nickel ions with the dimethylglyoxime were made at 465 nm using the SHIMADZU UV-1601PC UV/visible spectrophotometer.

Experimental design and statistical analysis

Plackett-burman experimental design

A Plackett-Burman design, a fractional factorial design, was used to screen the most significant independent variables for the adsorption of nickel ions on the olive pulp. The design matrix in coded and actual values is given by TABLE 1. In this study, five independent variables (initial pH of solution (pH), temperature (T), initial concentration of Ni(II) in aqueous solution [Ni], dose of adsorbent (m) and time of contact (t_c)) in eight combinations were organized according to applied design. Each independent variable was represented at two levels, high and low symbolized by (+) and (-), respectively (TABLE 1). The studied response, denoted Y, is the adsorption yield of Ni(II) adsorbed from aqueous solutions computed as follows:

$$Y\ (\%) = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \qquad (1)$$

where C_i and C_f are the initial and final Ni(II) concentrations, respectively. All trials were performed in triplicates for the mean calculation.

The effect (E_{Xi}) of each variable on the yield was calculated using the equation:

$$E_{Xi} = \frac{2}{N}\left(\sum_{i=1}^{n} Y_{i+} - \sum Y_{i-}\right) \qquad (2)$$

where Y_{i+} and Y_{i-} are the responses of trials, in which the independent variable (X_i) was present at its higher and lower levels, respectively, and N is the number of trials. The significance of effect of each variable was determined according to Student's *t*-test and *p*-value. The larger the magnitude of the *t*-value and smaller the *p*-value, the more significant the corresponding coefficient[20]. The variables with confidence levels greater than 95% were considered to influence the yield of adsorption significantly.

Box–behnken experimental design

In this study, a three-level Box–Behnken design combining with a response surface methodology were applied for modelling and optimizing the most significant independent variables affecting the adsorption of Ni(II) on the olive pulp. The following second order polynomial model was fitted to correlate relationship between independent variables and response:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i x_i + \sum_{i=1}^{k}\beta_{ii} x_i^2 + \sum_{i<j}^{k}\beta_{ij} x_i x_j \qquad (3)$$

where Y is the response variable, β_0 the intercept, β_i the coefficient for the linear effect, β_{ii} the coefficient for the quadratic effect, β_{ij} the coefficient for the interaction effect, and x_i and x_j the coded level of independent variable X_i and X_j. The relation between the coded values and actual values is described according to the following equation:

$$x_i = \frac{(X_i - X_0)}{\Delta X} \qquad (4)$$

where x_i is the coded value of an independent variable, and X_i is the actual value of the ith independent variable, X_0 is the actual value of the X_i at the center

TABLE 1 : PBD (in coded and actual values) and experimental results

Run	pH	T (°C)	[Ni]²⁺(mg/L)	m (g)	t_c (min)	Y_e (%)
1	5(+1)	45(+1)	50(+1)	0.1(-1)	30(+1)	42.10
2	2(-1)	45(+1)	50(+1)	1.0(+1)	10(-1)	15.05
3	2(-1)	25(-1)	50(+1)	1.0 (+1)	30(+1)	11.14
4	5(+1)	25(-1)	10(-1)	1.0 (+1)	30(+1)	93.50
5	2(-1)	45(+1)	10(-1)	0.1(-1)	30(+1)	7.24
6	5(+1)	25(-1)	50(+1)	0.1(-1)	10(-1)	38.44
7	5(+1)	45(+1)	10(-1)	1.0(+1)	10(-1)	92.80
8	2(-1)	25(-1)	10(-1)	0.1(-1)	10(-1)	11.15

point, and ΔX_i is the step change value of an independent variable.

According to this design, the total number of treatment combinations was $2^k + 2k + n_0$, where k is the number of independent variables and n_0 is the number of repetition of experiments at the centre point. The goodness of fit of the second degree polynomial equation was checked using the determination coefficient (R^2) and the correlation coefficient (R). The statistical software package MODDE 6.0 (Umetrics AB, Emea, Sweden) was used for regression and graphical analysis of the experimental data.

RESULTS AND DISCUSSION

Screening of significant variables

The experimental results of the adsorption yield (Y_e) of nickel ions on the pulp of olive, obtained from an experimental Plackett-Burman design, are reported in the last column of TABLE 1. They showed a wide variation of adsorption yield in the eight trials (11.14 to 93.50%), which reflected importance of medium optimization to attain a higher adsorption yield.

TABLE 2 shows the statistical analysis of the studied variables on the adsorption process, which included the effects, t-values and p-values of the variables. Among the five variables investigated, initial pH of solution, initial concentration of metal ions, and adsorbent dose were identified as influencing the adsorption of Ni(II) on OP at the 5% significant level. Initial pH of solution had the most significant effect on the yield as it has the largest coefficient followed by adsorbent dose and initial concentration of Ni(II). The remaining variables, i.e. temperature and time of contact, had p-values greater than 0.05 and hence, were considered insignificants

within the range of variables studied. Thus, these two variables were not included in the next optimization experiment. On the other hand, initial pH of solution and adsorbent dose had positive effects on the yield of adsorption, whereas initial concentration of metal exerted a negative effect on the yield.

Modelling and optimizing of the significant variables

Based on the PBD, where initial pH of solution, dose of adsorbent and initial concentration of metal were selected for their significant effects on the adsorption yield, a BBD with three replicates at the center point was used for further optimization. The variables and the coded and uncoded values of these variables at various levels are given in TABLE 3.

The experimental design, along with the experimental yields, is shown in TABLE 3. A total of 15 experiments were conducted, and each experiment was performed in duplicate. The obtained results of yield varied markedly from 4.97 to 91.16% within the range of variables studied. By applying multiple regression analysis on the experimental data, the following quadratic polynomial equation was found to describe the adsorption of Ni(II) on COP:

$$Y_p = 77.673 + 34.596\,x_1 + 12.636\,x_2 - 7.470\,x_3 - 31.025\,x_1^2 \\ - 6.054\,x_2^2 - 0.885\,x_3^2 + 4.553\,x_1 x_2 - 0.221\,x_1 x_3 + 7.759\,x_2 x_3 \quad (5)$$

where Y_p is the predicted response variable and x_1, x_2, x_3 are the coded values of the independent variables of initial pH, dose of adsorbent and initial concentration of metal, respectively. The coefficient of determination R^2 was found to be 0.9790, indicating that only 2.20% of the total variations were not explained by the model. When R^2 approaches unity, the better the empirical model fits the experimental data. The smaller the value of R^2, the less relevant the dependent variables in the model have in ex-

TABLE 2 : Statistical analysis of PBD showing effects values, t-values and p-values of variables

Variables	Effects	t-value	p-value	Ranking
pH	55.565	25.104	0.0016	1*
T (°C)	0.740	0.334	0.7702	5
[Ni^{2+}] (mg/L)	-24.49	11.063	0.0081	3*
m (g)	28.39	12.828	0.0060	2*
t_c (min)	-0.870	0.393	0.7339	4

* Statistically significant at 0.05 level; Standard error =1.1067

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TABLE 3 : BBD variables [in actual (X) and coded (*x*) levels] and experimental results

un	Independent variables						Experimental Yield (%)
	X_1	x_1	X_2	x_2	X_3	x_3	
1	2	-1	0.1	-1	30	0	4.97
2	5	+1	0.1	-1	30	0	59.15
3	2	-1	1.0	+1	30	0	12.93
4	5	+1	1.0	+1	30	0	85.33
5	2	-1	0.55	0	10	-1	11.49
6	5	+1	0.55	0	10	-1	87.03
7	2	-1	0.55	0	50	+1	4.94
8	5	+1	0.55	0	50	+1	79.60
9	3.5	0	0.1	-1	10	-1	73.21
10	3.5	0	1.0	+1	10	-1	91.16
11	3.5	0	0.1	-1	50	+1	34.80
12	3.5	0	1.0	+1	50	+1	83.78
13	3.5	0	0.55	0	30	0	77.50
14	3.5	0	0.55	0	30	0	77.85
15	3.5	0	0.55	0	30	0	77.67

X_1: Initial pH; X_2: Dose of adsorbent (g); X_3: Initial $[Ni]^{2+}$ (mg/L) (1) indicates the low level; (0) indicates the basal level; (+1) indicates the high level

TABLE 4 : Results of regression analysis of BBD for adsorption of Ni(II) on the OP

Coded Variables	Coefficients	Standard Error	*t*-value	*p*-value
x_1	34.596	2.875	12.033	0.00007
x_2	12.636	2.875	4.395	0.00706
x_3	-7.470	2.875	2.600	0.04836
$x_1 \times x_1$	-31.025	4.232	7.331	0.00074
$x_2 \times x_2$	-6.054	4.232	1.431	0.21197
$x_3 \times x_3$	-0.885	4.232	0.209	0.84258
$x_1 \times x_2$	4.553	4.066	1.120	0.31373
$x_1 \times x_3$	-0.221	4.066	0.054	0.95880
$x_2 \times x_3$	7.759	4.066	1.908	0.11463

plaining the behavior variation[21]. Additionally, the high value of the correlation coefficient (*R*=0.9894) indicated a good agreement between the experimental and predicted values of the adsorption yield, thus suggesting a high significance for the model.

The coefficient estimates of Eq. (3), along with the corresponding standard errors, *t*-values and *p*-values are presented in TABLE 4. The obtained results revealed that the linear coefficients of pH, adsorbent dose and initial concentration of metal, as well as the quadratic coefficient of pH affect the yield of adsorption at the 5% significant level. They also suggested that both linear and quadratic effects of pH and linear effect of adsorbent dose displayed

highly significant effect ($p<0.0001$, $p<0.001$ and $p<0.001$, respectively), while the linear coefficient of initial concentration of metal with *p*-value slightly lower than 5% has relatively little impact on the yield within the range studied. The remaining quadratic and interaction coefficients showed no significant effect on the yield ($p>0.05$). Among them, the interaction between dose of adsorbent and initial concentration of metal presented the most important effect ($p<0.15$). On the other hand, positive coefficient of X_1 and X_2 indicated linear effect to increase the yield. However, linear term of X_3 along with quadric term of X_1 had negative effects that decrease Y.
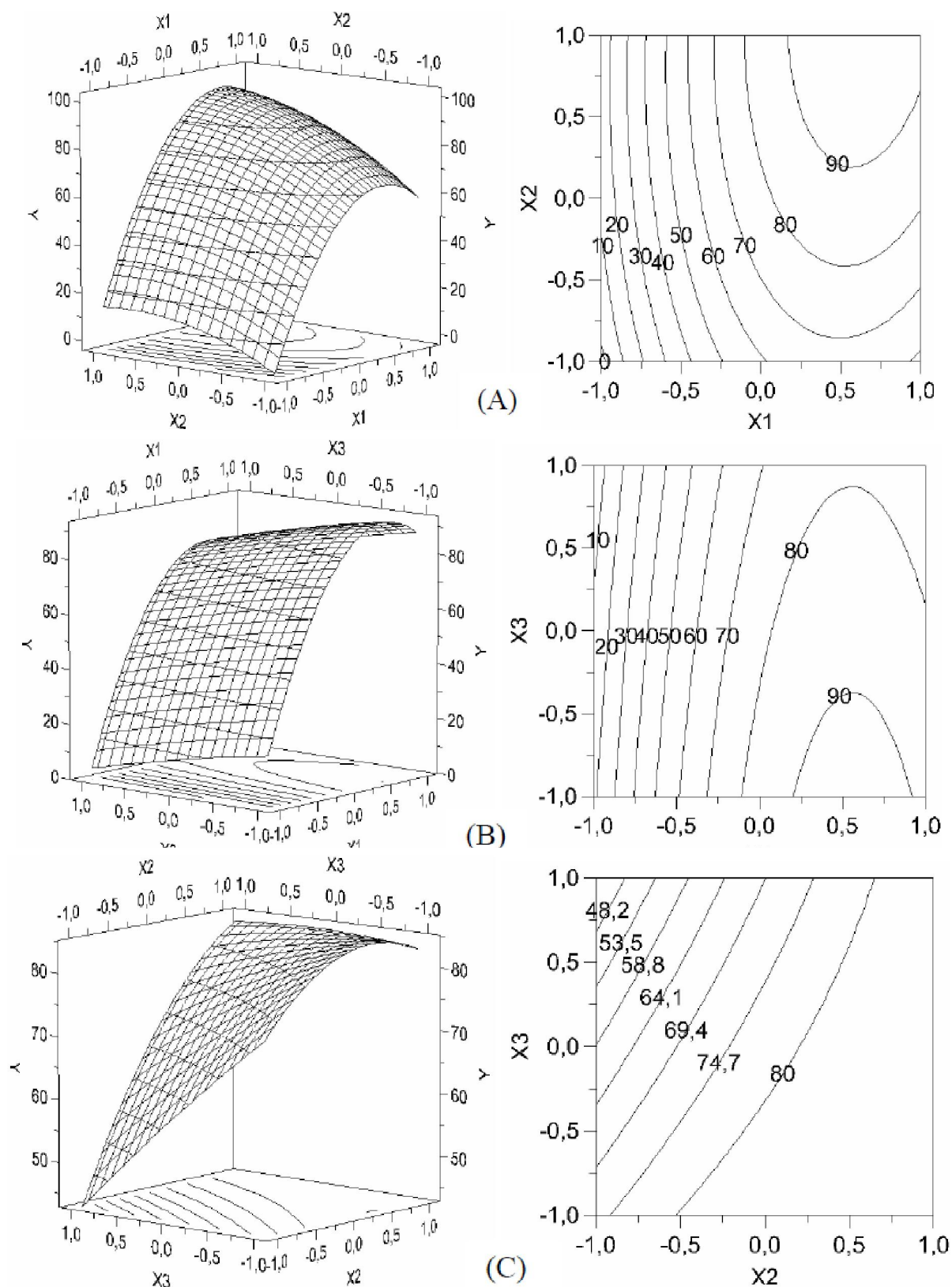
Figure 1 : Response surfaces and contour plots for the combined effects of variables on the adsorption yield of Ni(II) on OP: (A) pH (X_1) and adsorbent dose (X_2); (B) pH (X_1) and initial concentration of Ni(II) (X_3); (C) dose of adsorbent (X_2) and initial concentration of Ni(II) (X_3).

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Response surfaces and contour plots

To visualise the effect of the three independent variables on the adsorption yield, response surfaces and contour plots (Figure 1A-C) of the second-order polynomial model were generated by varying two of the independent variables within the experimental range, while keeping the third variable constant at its central level.

Figure 1A shows the response surface plot and corresponding contour curves based on independent variables initial pH (X_1) and adsorbent dose (X_2), while the third variable, initial concentration of the metal (X_3), was kept at its central level (30 mg/L). It can be seen that the adsorption yield was positively affected by both variables X_1 and X_2. A high initial pH of solution associated with a high dose of adsorbent had lead to a good yield of adsorption yield Figure 1B depicts the effect of variables X_1 and X_3 for the yield adsorption by maintaining dose of adsorbent constant at 1g. As can be seen from this figure, the yield of adsorption increased significantly with increasing initial pH of solution. High yields were obtained at low concentrations of Ni(II) ions and when the coded value of initial pH was within the range of 0.25–1.0. Indeed, at a high pH, relatively low concentration of H+ ions means less competition for the adsorption site on olive pulp particles, which results in high values of the yield for nickel ions. The effect of varying of adsorbent dose and initial concentration of metal on the adsorption yield, while maintaining the initial pH of solution constant at its central level (pH=3.5), is represented by Figure 1C. The removal of Ni(II) ions increases with increasing dose of adsorbent and decreasing initial concentration of metal. High yields were observed at low concentrations of the metal and for coded values of dose of adsorbent higher than (-0.5). Then, this result is expected because the higher adsorbent dose in the solution, the greater availability of exchangeable active sorption sites for the ions. It could be concluded that initial pH of medium and dose of adsorbent are the important variables affecting the adsorption of Ni(II) ions on the OP. Within the tested levels range, the adsorption yield is strongly favoured with increasing both these parameters. The same trend was observed by several authors that investigated Ni(II) sorption by different biomaterials[1,2,6,22].

From equations derived by differentiation of Eq. (5), the optimal values of X_1, X_2 and X_3 in the coded units were found to be: 0.621, 0.807 and -0.712, respectively. According to the relation between X_i and x_i, the uncoded values of these variables were as follows: 4.43, 18.40 g/L and 15.76 mg/L, respectively. The optimum pH for the adsorption of Ni(II) ions from aqueous solution was found to be at pH 4.0 for cone biomass of *Thuja orientalis*[1], tea factory waste[2] and waste pomace[17], at pH 4.85 for barley straw[22], at pH=6 for modified loquat bark waste[10] and at pH around 5 for sugarcane bagasse[5]. Bhattacharyya and al.[23] were found that the extent of Ni(II) biosorption on *Azadirachta indica* leaf powder increased in the pH range, 2.0–5.0.

The maximum of adsorption yield obtained by using the above optimized concentrations of the variables was 96.16%. The maximum of yield obtained experimentally was found to be 94.65% (average of four determinations), which is in good agreement with the theoretical prediction.

CONCLUSIONS

The present study demonstrated that the use of Plackett-Burman and Box-Behnken experimental designs can be used in combination to determine significant independent variables and optimal conditions for adsorption of Ni(II) ions on crude olive pulp. Among the variables tested using the Plackett–Burman design, initial pH of solution, dose of adsorbent and initial concentration of Ni(II) ions in aqueous solution were found to have significant effects on adsorption process. Based on the quadratic model, the optimal values of these variables in actual levels were found to be 4.43, 18.40 g/L and 15.76 mg/L, respectively, resulting in 96.16% of yield adsorption. This maximal value was found in perfect agreement with the experimental value (94.65%). These results may provide valuable data for pilot-scale and industrial applications.

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