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Natural zeolite for nickel ions removal from aqueous solutions: optimization and modeling using response surface methodology based on central composite design

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ABSTRACT

Natural zeolite was tested as a low-cost adsorbent for Ni(II) removal from aqueous solutions. In order to reduce the total number of experiments necessary for achieving the best conditions of the batch sorption procedure, response surface methodology based on central composite design was carried out for the natural zeolite. Four independent variables, *viz.* initial nickel ion concentration (10–200 mg/L), adsorbent dose (0.1–0.7 g/L), contact time (5–120 min), and initial pH of solution (2–8) were transformed to coded values and the quadratic model was built to predict the responses. Very high regression coefficients between the variables and the response indicate excellent evaluation of experimental data using a second-order polynomial regression model. Three-dimensional plots demonstrate relationships between the nickel ion uptake with the paired factors (as the fourth factor was kept at its optimal level), which illustrate the behavior of the sorption system in a batch process. The model showed that nickel uptake in aqueous solution was affected by all four factors studied. An optimum nickel uptake was achieved at an initial nickel ion concentration of 10–15 mg/L, clinoptilolite dosage of 0.37–0.43 g/L, a contact time of 56–68 min, and a pH of 4.8–6. On the basis of experimental results and model parameters, it can be inferred that the adsorbent, which exhibits a relatively high adsorption capacity, can be utilized for the removal of nickel from aqueous solution.

Keywords: Nickel ion removal; Natural zeolite; Optimization; Central composite design; Response surface methodology

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1. Introduction

Nickel ions are among the most harmful pollutants in several industrial wastewaters. Nickel is being discharged into the environment as industrial wastes, causing serious soil and water pollution [1]. Nickel is employed in several industrial activities, including mineral processing, electroplating, production of paints and batteries, and manufacturing of sulfate and porcelain enameling [2–4]. Human exposure to this heavy metal at significant levels is associated with serious health effects. Nickel is associated with dermatitis, nausea, coughing, chronic bronchitis, gastrointestinal distress, reduced lung function, and lung cancer [5–10]. Therefore, removal of nickel from natural and industrial wastewater has been drawing more and more attention [11–15]. The optimization of water and wastewater purification processes requires the development of new operations based on low-cost raw materials with high pollutant removal efficiency. During the last few years, many techniques have been proposed to remove unwanted cations from wastewater, such as ion exchange, precipitation, adsorption, membrane processes, reverse osmosis, sedimentation, and electro-dialysis [16–18]. Among the different processes proposed, ion exchange is one of the most promising, since it allows good performances, reasonable costs and, sometimes, metal recovery [19].

The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently. Zeolite is a naturally occurring crystalline aluminosilicate mineral that are aluminosilicates consisting of a framework of tetrahedral molecules, linked with shared oxygen atoms. Natural zeolites are safe, environmentally friendly, low-cost, and has a large surface area and high cation exchange capacities [20] and are considered effective materials for the removal of heavy metals such as Cd^{2+}, Pb^{2+}, Mn^{2+}, and Zn^{2+} from wastewaters [21]. Natural zeolites have found widespread applications in molecular sieves, ion-exchangers, adsorbers, catalysts, detergent builders, and adsorption [22,23], due to their favorable structural characteristics and valuable properties. In Iran, large piles of zeolite exist with no disposal options. The zeolite samples from different regions show different characteristics in ion exchange and adsorption processes [24–26].

In this study, the uptake efficiency of Ni^{2+} from aqueous solution by western Azerbaijan natural clinoptilolite under batch conditions was investigated. In order to obtain the highest adsorption efficiency, it is necessary to consider and optimize several variables that affect the adsorption process. The parameters affecting the adsorption efficiency are initial heavy metal ion concentration, adsorbent dosage, contact time, and initial pH of solution. In most previous studies, optimization of these parameters involved repetitive changes of one independent variable while maintaining all others at fixed levels which is time consuming and expensive. In addition, this method did not allow the determination of the magnitudes of interactions among the process variables. To overcome this difficulty, a response surface methodology (RSM) based on central composite design (CCD) was employed to optimize the adsorption of nickel in aqueous solution onto natural clinoptilolite in a batch experiment. Batch experiments were carried out to establish how the initial nickel ion concentration, adsorbent dosage, contact time, and initial pH of solution interacted and ultimately affected the Ni(II) removal efficiency from aqueous solution. A total of 28 experiments were conducted in a study of the removal of Ni(II), which yielded mathematical models showing the influence of each variable and intervariable interactions.

2. Experimental

2.1. Reagents

All chemicals used were of analytical grade from Merck (Darmstadt, Germany) and the solutions were prepared with freshly double-distilled water.

2.2. Statistical software

Essential Regression and Experimental Design for chemists and Engineers (EREGRESS), as an MS Excel Add-in software [27,28], was used to design the experiments and to model and analyze the results. All calculations in the computing process were performed using MATLAB 7.8 and Microsoft Excel for windows.

2.3. Pretreatment of natural zeolite

The particular ion exchanger of interest in this study is clinoptilolite. As mentioned earlier, clinoptilolite is an abundant natural zeolite exhibiting a high cation exchange capacity (CEC) and stability to set attrition. The clinoptilolite used as an adsorbent in this experiment was obtained from Shahin Dezh City in the south of Western Azerbaijan, Iran. The chosen clinoptilolite was sieved into three particle sizes: 0.5, 1, and 2 mm, washed with hot distilled water to remove very fine particles, then dried in an oven at

110°C for 24 h before being used. Characterization of this clinoptilolite was reported earlier [29,30].

2.4. Nickel adsorption tests

A sorption study of nickel ions to clinoptilolite was carried out using a batch method. In this procedure, 0.1–0.7 g/L of adsorbent material was added to a 100 mL aqueous solution of 10–200 mg/L nickel ions. The suspension was shaken for a preselected period of time using a water bath shaker, then filtered and the amount of nickel ions was determined by inductivity coupled plasma (ICP) using an ICP-OES Varian Vista-Pro CCD spectrometer. The removal efficiency (%) was calculated using the relation.

$$\text{Removal efficiency}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where C_0 and C_e, are the initial and final nickel ion concentrations (mg/L) of solution.

2.5. Central composite design

CCD was employed to investigate and optimize the experimental variables in the removal of Ni(II) from aqueous solutions. Four independent factors, namely the concentration of nickel (F_1), the dosage of cliniptilolite (F_2), the contact time (F_3), and pH (F_4), were studied at five levels with four repeats at the central point, using a circumscribed CCD. For each of the four variables studied, a high (coded value: +1.607) and a low (coded value: −1.607) set points were selected as shown in Table 1.

Also, Table 2 shows the coded and real values of designed experiments achieved based on CCD methodology achieved using EREGRESS software.

Table 2
List of experiments in the CCD for model optimization (coded values)

Factor levels					
Design points	F_1	F_2	F_3	F_4	Response
1	0.8	−0.8	0.8	0.8	49.85
2	0.8	0.8	−0.8	−0.8	33
3$^{(cp)}$	0	0	0	0	69.58
4	−0.8	0.8	0.8	−0.8	61.56
5	0.8	0.8	0.8	0.8	44
6	0	0	0	1.6	22.17
7	0	−1.6	0	0	50
8	−0.8	−0.8	0.8	0.8	61.69
9	−0.8	0.8	−0.8	−0.8	48.73
10$^{(cp)}$	0	0	0	0	69.6
11	0	0	1.6	0	52.11
12	−0.8	−0.8	−0.8	0.8	48.87
13	−1.6	0	0	0	80
14	−0.8	−0.8	−0.8	−0.8	48.73
15	0	1.6	0	0	69.6
16	0.8	0.8	−0.8	0.8	30
17	0	0	0	−1.6	21.9
18	1.6	0	0	0	41
19	0.8	0.8	0.8	−0.8	49.71
20	0	0	−1.6	0	24
21	−0.8	0.8	0.8	0.8	61.69
22$^{(cp)}$	0	0	0	0	69.6
23	−0.8	−0.8	0.8	−0.8	61.56
24	0.8	−0.8	−0.8	0.8	37.02
25	−0.8	0.8	−0.8	0.8	48.87
26	0.8	−0.8	0.8	−0.8	49.54
27	0.8	−0.8	−0.8	−0.8	32
28$^{(cp)}$	0	0	0	0	69.6

Note: $^{(cp)}$indicates 4 repeat of center points.

Polynomial equations and a response surface, for a particular response, were produced using EREGRESS. For an experimental design with four factors, the model including linear, quadratic, and cross-terms can be expressed as:

$$\begin{aligned}\text{Response} = {} & b_0 + b_1 \times F_1 + b_2 \times F_2 + b_3 \times F_3 + b_4 \\ & \times F_4 + b_5 \times F_1 \times F_1 + b_6 \times F_2 \times F_2 + b_7 \\ & \times F_3 \times F_3 + b_8 \times F_4 \times F_4 + b_9 \times F_1 \\ & \times F_2 + b_{10} \times F_1 \times F_3 + b_{11} \times F_1 \times F_4 \\ & + b_{12} \times F_2 \times F_3 + b_{13} \times F_2 \times F_4 + b_{14} \\ & \times F_3 \times F_4\end{aligned} \tag{2}$$

Table 1
The variables and values used for CCD

Coded factor levels					
Variable name	−1.607 (low)	−0.8	0	0.8	+1.607 (high)
F_1 Concentration of Nickel (mg/L)	10	57.5	105	152.5	200
F_2 Dosage of Clinoptilolite (g/L)	0.095	0.247	0.4	0.553	0.705
F_3 Contact time (minutes)	5	33.75	62.5	91.25	120
F_4 pH	2	3.5	5	6.5	8

where F_1–F_4 are the variable parameters, and b_0–b_{14} are the coefficients whose values were obtained through multiple linear regression (MLR), using EREGRESS. The response surface plots were obtained through a statistical process that described the design and the modeled CCD data. The response surface methodologies graphically illustrate the relationships between parameters and responses, and represent the way to an exact optimum [30–33].

The statistical significance of the predicted models was evaluated by the analysis of variance (ANOVA) and least squares techniques. ANOVA indicates which of the factors significantly affects the response variables studied, using a Fisher's statistical test (*F*-test). The significance and the magnitude of the estimated coefficients of each variable, and all their possible interactions, on the response variables were determined. Such coefficients for each variable represent the improvement in the response, i.e. the variable setting is expected to change from low to high. Effects with less than 95% of significance (effects with a *p*-value higher than 0.05) were discarded, and pooled into the error term, and a new ANOVA was performed for the reduced model. Note that the *p*-value represents a decreasing index of the reliability of a result [31]. Replicates ($n = 4$) of the central points were performed to estimate the experimental error.

3. Result and discussion

3.1. Experimental design

The aims of the CCD strategy were: (i) study of the effect of pH, contact time, dosage of adsorbent, and initial concentration of nickel on the removal of Ni; (ii) identification of the variables that have a higher impact on the adsorption procedure; (iii) to give an insight into the robustness of the method close to the optimum conditions; and (iv) to eventually show the interactions between the variables. In order to find the important factors and build a model to optimize the procedure, we started with a full quadratic model including all terms of Eq. (2), To obtain a simple and realistic model, the insignificant terms ($p > 0.05$) were eliminated from the model through a "backward elimination" process.

The constructed model using all 15 terms of Eq. (2) showed a relatively good fit. For this model, a regression coefficient (R^2) for calibration close to 1 was achieved. Some of these 15 regression variables are insignificant, or at least have low significance, and should be eliminated from the model. Since (R^2) always decreases when a regression variable is eliminated from a regression model, in statistical modeling the adjusted R^2 (R^2_{adj}), which takes the number of regression variables into account, is usually selected [29–32]. Also R^2_{pred}, which indicates the predictive power of the model, is chosen for the same reason. This parameter was approximated using the prediction error sum of squares or PRESS that was calculated from residuals, which are based on a regression model with one data point removed. So, R^2, adjusted R^2 (R^2_{adj}), and R^2 for prediction (R^2_{pred}) together are very convenient to get a quick impression of the overall fit of the model, and the predictive power based on one data point removed. In a suitable model, these parameters should not be too different from each other. However, for small data sets, it is very likely that every data point is influential. In these cases, a high value for R^2 for prediction (R^2_{pred}) cannot be expected.

By the elimination of insignificant parameters from Eq. (2), calibration R^2 decreased finally to 0.958, but adjusted R^2 (R^2_{adj}), and R^2 for prediction (R^2_{pred}) increased nearly to 0.943 and 0.852, respectively. The reduced model using significant linear, quadratic, and interaction parameters was obtained finally (Table 3). For this case, the adjusted R^2 values were well within the acceptable limits and there were not large differences between R^2 values, which revealed that the experimental data show a good fit using the second-order- polynomial equation.

The magnitude of the coefficient in the above quadratic equation denotes the intensity, while the sign indicates nature of influence (positive or negative) of the particular variable on the response. A positive effect of a factor means that the response is improved when the factor level increases and a negative effect of the factor revealed that the response is inhibited when the factor level increases.

3.2. Response surface and selection of optimum conditions

3.2.1. Effect of pH

The pH of the solution has been recognized as the most important parameter governing adsorption of metal ions on different adsorbents [34–38]. This is partly due to the fact that hydrogen ions themselves are a strong competing sorbate and partly to the fact that the solution pH influences the chemical speciation of metal ions. The effect of pH on adsorption of nickel ions onto natural zeolite is presented in Fig. 1(c)–(f). As shown in these figures, by increasing the pH to around 5–6 the removal efficiency increases, but decreases beyond that [10,39].

At low pH values, the low adsorption observation can be explained due to increase in positive charge

Table 3
Some characteristics of the constructed models

Regression equation		Coefficient	Value	p-value
Removal (%) = $b_0 + b_1 \times \text{Dos} + b_2 \times \text{Time} + b_3 \times \text{pH} + b_4 \times \text{Conc} \times \text{Conc}$		b_0	−114.95	3.157E-09
$+ b_5 \times \text{Dos} \times \text{Dos} + b_6 \times \text{Time} \times \text{Time} + b_7 \times \text{pH} \times \text{pH}$		b_1	75.55	0.00993
		b_2	1.366	2.432E-10
		b_3	50.71	2.751E-12
		b_4	−0.0008	1.111E-09
		b_5	−85.10	0.01655
$\lvert R \rvert$	0.979	b_6	−0.0089	4.454E-09
R^2	0.958	b_7	−5.077	2.1616E-12
R^2 adjusted	0.943			
R^2 for prediction	0.852			
Standard error	0.2			
No. points	28			
PRESS[a]	0.35			

[a] Prediction error sum of squares.

density on the surface sites, and thus, electrostatic repulsion occurs between the nickel ions and the edge group with positive charge on the surface. Thus resulting surface charge developed at low pH is not suitable for adsorption of the nickel ions. When the pH was increased, the competing effect of H^+ ions decreased and the positively charged Ni^{2+} ions hook up the free binding sites. Hence, the nickel ion uptake was increased on the surface of the adsorbent with the increase in pH [40,41].

In the experiments, which were conducted at pH values higher than 6, metal precipitation occurred and adsorbent capacity was decreased with accumulation of nickel ions [42–44]. Therefore, the pH of 5.3 was selected to be the optimum pH for further experimental studies.

3.2.2. *Effect of initial nickel concentration and contact time and adsorbent dosage*

In order to gain insight into the effect of each variable, the three-dimensional (3D) plots for the predicted responses were also formed, based on the model function to analyze the change of response

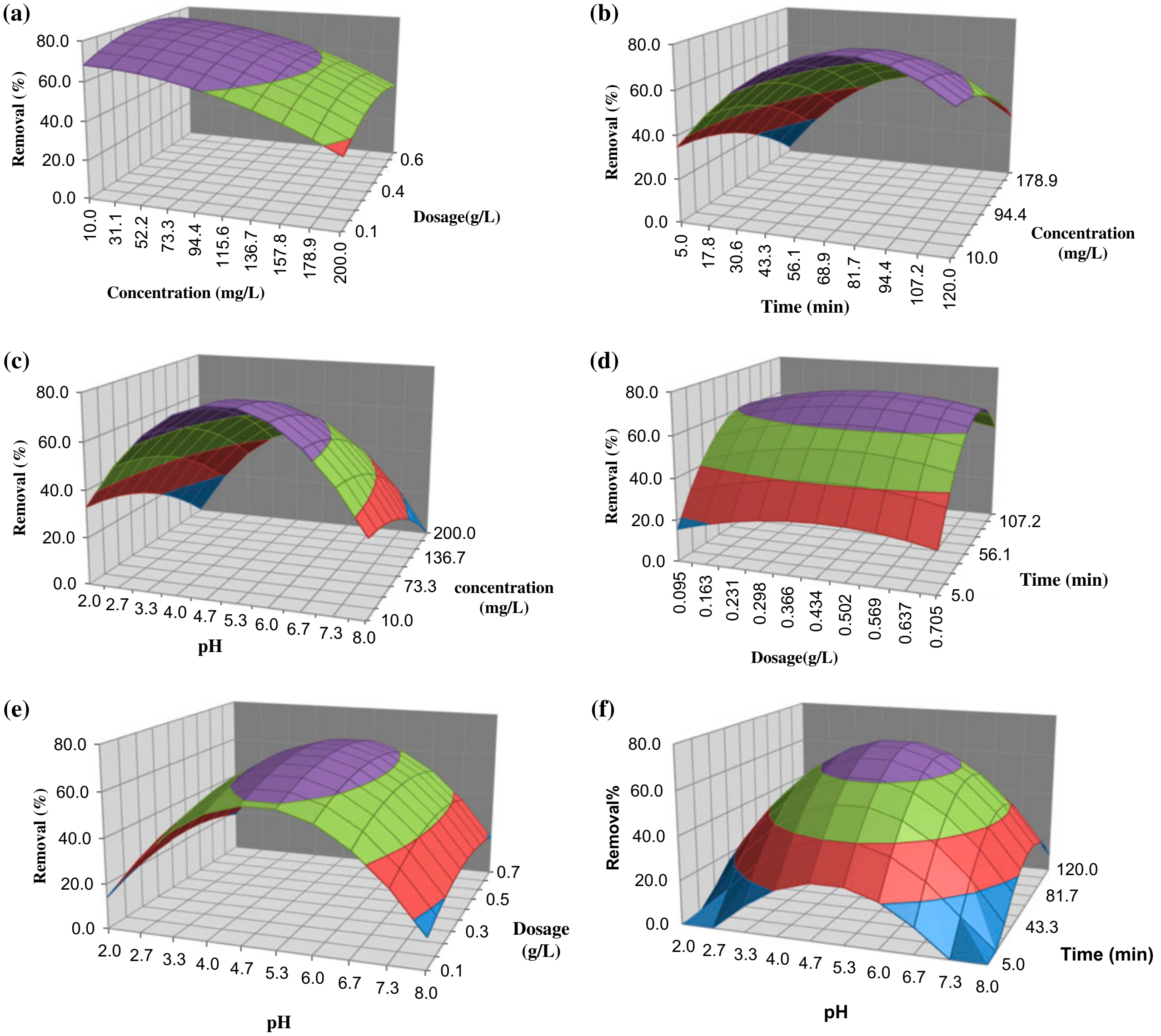

Fig. 1. Response surface showing the effect of concentration (mg/L) of nickel (F_1), dosage (g/L) of cliniptilolite (F_2), contact time in minutes (F_3) and pH (F_4), in addition to their mutual effects on the percent nickel removal from aqueous solutions: (a) concentration and dosage, (b) time and concentration, (c) pH and concentration, (d) dosage and time, (e) pH and dosage, and (f) pH and time.

Table 4
Optimum conditions obtained by response surface modeling

Variable name	Optimum values	Selected values
F_1 Concentration of nickel (mg/L)	10–15	12
F_2 Dosage of clinoptilolite (g/L)	0.37–0.43	0.4
F_3 Contact time (minutes)	56–68	59
F_4 pH	4.8–6	5.30

Table 5
Comparison of clinoptilolite sample studies on nickel ion adsorption process with some literature values

		Optimum condition				
Metal	Adsorbent	pH	Concentration of Nickel (mg/L)	Dosage of zeolite (g/L)	Contact time (min)	Refs.
Ni	Turkish clinoptilolite	7–8	12.5	30–40	60	[11]
Ni	Iranian clinoptilolite	6–7	25	2	1,440	[25]
Ni	Iranian clinoptilolite	4	10	0.2	1,440	[39]
Ni	Turkish clinoptilolite	7	25	15	45	[42]
Ni	Turkish clinoptilolite	6	50	8	80	[43]
Ni	Turkish clinoptilolite	–	50	8	50	[47]
Ni	Netherlands clinoptilolite	6	25	4	60	[48]
Ni	Iranian clinoptilolite	5.3	12	0.4	59	Present study

surface. For example, Fig. 1 shows some of response surface plots that depict the 3D plots relationship between the removal (%) of nickel and two of the variables, while the two other variables were kept in center levels.

As shown in Fig. 1, there was a non-linear relationship between response and each of the four variables F_1–F_4, because all the surface plots of response showed curvature. Table 3 lists several linear, squared, and interaction parameters, which are statistically significant. The selection of optimum conditions of the method is possible from the response surface plots (Fig. 1). These results demonstrate that the response surfaces have a flat optimum. The plots show the interaction between the mentioned factors when the remaining factors have been fixed using the constructed model by EREGRESS software. The results (Fig. 1) show a pronounced dependency of the absorbance on all of the investigated experimental variables.

Fig. 1(a)–(c) shows that by increasing the initial concentration of nickel (F_1), the removal efficiency decreases. This observation is logical because at low concentrations, metals are sorbed by specific active sites; while at higher concentrations absorption decreases due to saturation of the adsorption sites [45]. Fig. 1(a), (d) and (e) shows that the removal percentage is higher as the adsorbent dosage is within the range of 0.095–0.43 g/L, which correlates with the greater availability of the adsorbent surface. But from 0.43 to 0.705 g/L the efficiency decreases, which is attributed to the partial adsorbent aggregation taking place at high clinoptilolite dosage thus causing a corresponding decrease in active adsorption sites [8,46]. In Fig. 1(b), (d) and (f), it is seen that the metal removal increased in the first 60 min then reached equilibrium beyond that. The overall results are summarized in Table 4, which lists the optimized working conditions for the removal of nickel ions from aqueous solutions in terms of concentration of nickel ions, the dosage of clinoptilolite, the contact time, and solution pH.

The comparison of effective parameters for adsorption of nickel ions by zeolite from different regions is reported in Table 5. Based on the results, the maximum adsorption of nickel ions occurred at a pH of around 4.8–6. Although, other research groups reported different optimum pH values for nickel ions removal by natural clinoptilolite. However, the variation in optimum pH reported in these studies may be due to the different species and zeolite deposits used with different experimental conditions and procedures which require further investigation [6,49]. These results show that Iranian natural zeolite has remarkable potential for the removal of Ni(II) ions from aqueous solution and wastewater.

4. Conclusion

In this study, adsorption of Ni(II) on western Azerbaijan natural clinoptilolite was examined using a batch system. To determine the optimum operating conditions of the adsorption process for maximum efficiency, CCD based on RSM was applied. Factorial design gave important main and interaction effects. Using CCD, quadratic and interaction terms revealed the location of the optimum set of experimental conditions. The regression model proposed to predict the percent nickel removal was found to fit the experimental data very well. The equations describing the relation between the removal efficiency and the variables allowed identifying the statistically significant variables, and evaluating quantitatively the effect of each on the removal percentage, in addition to the interactions between each two variables. The plots of response surface clearly showed the interactions between main variables and their effects on the response. The western Azerbaijan natural clinoptilolite is stable, efficient, low cost, and hence environmentally safe. These results showed that the present adsorbent has a great potential for removal of nickel ions from aqueous solutions.

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