

INVESTIGATION OF FACTORS AFFECTING REMOVAL OF NICKEL BY PRE-TREATED WALNUT SHELLS USING FACTORIAL DESIGN AND UNIVARIATE STUDIES*

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Abstract– The main objective of this study was to identify the operating conditions which influence Ni(II) adsorption onto pre-treated walnut shell. For this purpose, in the first step, a series of experiments were planned according to a full 2^4 factorial experimental design. The factors investigated here were solution pH, adsorbent dose, the initial concentration of nickel, and temperature. The results predicted using the factorial regression model showed high values of regression coefficient ($R^2=99.55\%$), indicating good agreement with the experimental data. It was observed that the main effect of all the factors, besides the interaction of pH and metal concentration, were significant within a 95% confidence level, while for the conditions tested in this study, the pH of the solution was the most influential parameter in the removal of nickel.

In the second stage, univariate studies were conducted to validate the results obtained in the first part and also to find the conditions that would give the highest removal of nickel from aqueous solutions. The univariate experimental results provided evidence supporting the sorption data obtained in the factorial design phase of this study. Under the optimal conditions obtained, the nickel ion adsorption equilibrium could be satisfactorily described by the Langmuir isotherm model. The maximum pre-treated walnut shell adsorption capacity for Ni(II) was 8.57 mg/g. The kinetics of Ni(II) adsorption onto pre-treated walnut shell followed the pseudo second-order model.

Keywords– Adsorption, experimental design, isotherm, Ni(II), kinetic, pre-treated walnut shell

1. INTRODUCTION

Industrial activity generates large volumes of aqueous effluents containing high levels of hazardous species. The species with the most toxicological relevance in the industrial effluents are the heavy metals, which do not biodegrade over time, being accumulated in the human body [1]. Nickel is toxic and carcinogenic at relatively low concentrations. It is not self degradable and can accumulate in living organisms, causing lung cancer and embolism, respiratory failure, birth defects, asthma, chronic bronchitis, pulmonary fibrosis and renal edema, allergic reactions and hurt disorders [2]. The maximum allowable discharge concentration of Ni(II) is 2 mg/L. Therefore, an efficient and economic treatment technology for the removal of heavy metals from aqueous solutions is needed. Adsorption processes using various adsorbents have been employed for this purpose. Since agricultural wastes have shown potential sorption capacity for heavy metals, attention has been focused on these cost-effective adsorbents in recent years. Various studies have reported the successful removal of Ni(II) using low-cost sorbents such as sawdust [3-6], sugarcane bagasse [7,8], rice husk ash [9], green coconut shells [10], lotus stalks [11], peat moss [12] and nettle ash [13]. However, the search for more efficient, cheaper and freely available adsorbents continues.

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Iran ranks fourth in walnut production, producing about 290,000 metric tons of walnut per year. Consequently, walnut shells, as agricultural by-products, are available in large quantities in Iran. Walnut shell, in its natural form, has been used for the removal of heavy metals in previous works [14,15]. However, the application of untreated agricultural wastes as adsorbents carries several disadvantages, such as their low adsorption capacity, while also posing several problems, such as releasing soluble organic compounds contained in their materials into the aqueous solution [16-18]. Therefore, in this study pre-treated walnut shell was used as an adsorbent for the removal of Ni(II) ions. Despite the numerous studies regarding the use of agricultural wastes as adsorbents, to the best of our knowledge, there has been no published work using NaOH pre-treated walnut shell as an adsorbent for Ni(II) removal.

Many parameters were found to influence the adsorption process of heavy metals. Familiarity with the individual and interactive effects of the involved parameters could facilitate the better understanding of the complexity of adsorption processes. Most of the existing studies have focused on the individual effects [11,19,20], while in some researches the combined effects of several parameters may have been investigated without the use of any statistical design framework to obtain certain knowledge about the existence of significant interactions between these parameters [6,21,22]. Only in recent years, statistical experimental design methods such as factorial design and response surface analysis have been used in adsorption systems [23-26].

In this study, the effect of a number of operating parameters, such as pH, adsorbent dose, the initial metal concentration, and temperature, on the removal of nickel ions by the pre-treated walnut shell was studied by using a full factorial design method, which yields a mathematical model that shows the influence of each variable as well as its interactions. The results obtained from the factorial design experiments were further validated by the various univariate studies, and the optimum values of these variables were also determined. To the best of our knowledge, in this study for the first time, univariate studies have been used to validate the results obtained from the factorial design experiments.

2. MATERIALS AND METHODS

a) Preparation of adsorbent

Walnut shell obtained from a nearby garden was first grounded and sieved to get a fraction with a uniform particle size of 0.6-2.0 mm. Subsequently, the grounded walnut shell was washed with distilled water to remove the impurities. Afterwards, it was soaked in 1.0 mol/L NaOH for 24 hours and then rinsed with distilled water until there was no color in the filtrate. Finally, this walnut shell was air-dried for 24 h and stored in a container for further use.

b) Preparation of adsorbate solution

The Ni(II) stock solution containing 1000 mg Ni/L was prepared by dissolving nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) powders (analytical reagent grade) in distilled water. Ni(II) working solutions in different concentrations were prepared by diluting the Ni(II) stock solution with distilled water. Before the adsorption experiments, the pH value of the Ni(II) solutions was adjusted to the desired value with diluted HCl or NaOH.

c) Batch adsorption experiments

Batch adsorption studies were carried out by varying solution pH, adsorbent dose, the initial nickel concentration and temperature. In each experiment, a certain amount of pre-treated walnut shell was added to 200 mL of nickel solution taken in a 250 mL glass flask, and the pH was adjusted to the required value. Next, the mixture was agitated at 65 rpm in an incubated orbital shaker at a constant temperature. The

suspension was then filtered and the residual nickel in the solution was measured by using the atomic absorption spectrophotometry technique (SHIMADZU AA 680, air/C₂H₂ gas mixture). The measurements were done in duplicate for each individual solution to check repeatability, and the mean values were used in the analysis of the data. The percentage of Ni(II) removal from aqueous solution (%R) was calculated by using the following equation:

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

where C_i and C_f are the initial and final concentrations of nickel ions, respectively.

d) Statistical design of experiments

The factorial design helps to develop a statistical model of reaction and to determine the most important individual process parameters and their combined effects by performing a minimum number of well-chosen experiments [27].

In this study, the effect of solution pH (pH), adsorbent dose (m), the initial concentration of nickel ions (C), and solution temperature (T) on the removal percentage of nickel ions was investigated. For this purpose, a 2⁴ full factorial design was employed. 16 experiments were required, all of which were conducted in duplicate. Each of the independent variables was coded as pH, m, C, and T at two levels: -1 (low) and 1 (high). The experimental range and levels of independent variables considered in this study are presented in Table 1.

Table 1. Independent variables and their levels used for 2⁴ factorial design

Variable	Symbol	Range and level	
		-1	+1
Solution pH	pH	2	10
Adsorbent dose (g/L)	m	1	20
Nickel concentration (mg/L)	C	10	90
Temperature (°C)	T	15	45

The relationship between the experimental variables and corresponding responses is explained by the following equation.

$$\begin{aligned} \%R = & X_0 + X_1pH + X_2m + X_3C + X_4T + X_5pHm + X_6pHC + X_7pHT + X_8mC + X_9mT + X_{10}CT \\ & + X_{11}pHmC + X_{12}pHmT + X_{13}pHCT + X_{14}mCT + X_{15}pHmCT \end{aligned} \quad (2)$$

where X_0 represents the global mean and X_i represents the regression coefficient corresponding to the main factors' effects and interactions.

The results of the experimental design were interpreted by the use of Minitab Statistical Software, Release 15.1, to estimate the effects, coefficients, and statistical parameters of the fitted model along with the statistical plots.

3. RESULTS AND DISCUSSIONS

a) Characterization of adsorbent

Scanning Electron Microscopy (SEM) investigations of the natural and pre-treated walnut shell were conducted to evaluate the morphological changes as well as changes in surface characteristics brought about by the alkali treatment of the walnut shell. Fig. 1 depicts the SEM image of the natural and NaOH pre-treated walnut shell. It is evident from these figures that alkali treatment has affected the walnut's morphology. As is shown in Fig. 1, the pre-treated walnut shell has a comparatively irregular and porous

surface which makes it more appropriate for adsorption purposes. The specific surface area of the NaOH pre-treated walnut shell was $118 \pm 5 \text{ m}^2/\text{g}$, which was determined according to the technique described by Araujo and Jaroniec (2000) [28], using a lab-made thermogravimetric (TG) analyzer.

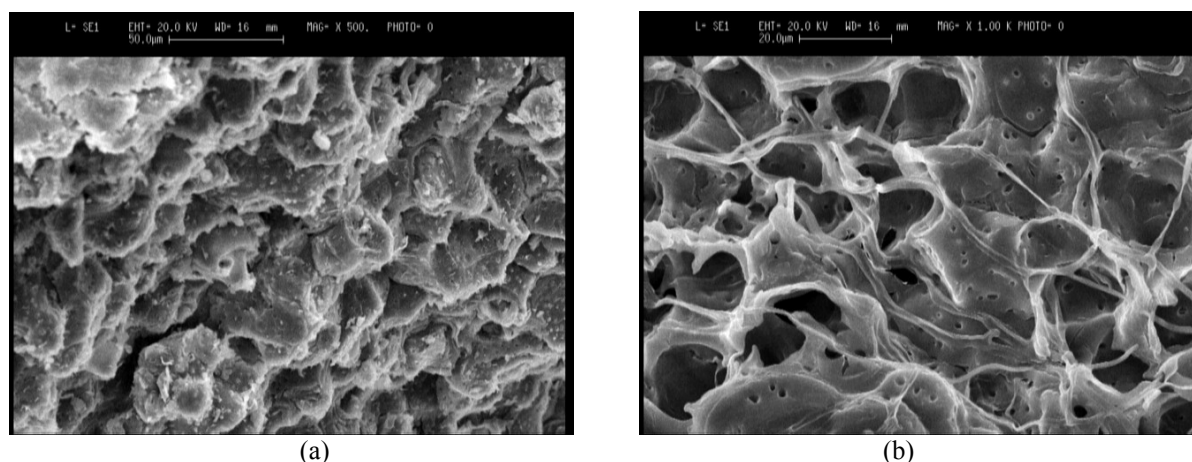


Fig. 1. SEM image of natural (a) and NaOH modified (b) walnut shell

b) Comparison of raw and NaOH pre-treated walnut shells

A comparison of the Ni(II) uptake capacities of the raw and pre-treated walnut shells was performed. Metal uptake capacities were measured by adding 2 g of adsorbent into 250 mL flasks containing 200 mL Ni(II) solution with an initial concentration of 50 mg/L. The pH values of the solutions were adjusted to 6, and the flasks were agitated at 65 rpm for 24 h. A comparison of the removal capacity of the two sorbents revealed that pre-treated walnut shell has a higher Ni(II) uptake of 4.5 mg/g (88.3% removal) than raw walnut shell, which stood at 1.2 mg/g (24.5% removal).

Agricultural crop residues such as walnut shell consist of lignin, cellulose and hemicelluloses. These major constituents of agricultural wastes contain methyl esters that do not bind metal ions significantly in their natural form. However, by treating the adsorbent with a base, these methyl esters can be modified to form carboxylate ligands, thereby increasing the metal-binding potential of the adsorbent [16]. In addition, the penetration of NaOH into cellulose transforms cellulose I into cellulose II, which reduces crystallinity, increases porosity and surface area, makes the hydroxyl groups of cellulose macromolecules more easily accessible, causes the liberation of new adsorption sites on the adsorbent, and finally improves the adsorption capacity of the adsorbent [29]. The effects of alkali pre-treatment on the adsorption capability of heavy metals have been previously reported by a number of researchers [16, 29].

In order to investigate the effect of the alkali treatment of walnut shell on the amount of organic matter released from this adsorbent, the chemical oxygen demand (COD) was measured for 200 mL Ni(II) solutions which contained 2 g of raw and NaOH treated walnut shell for 24 h. The results indicated that the COD of the solution containing raw walnut shell (45 mg/L) was higher than the one containing alkali treated walnut shell (27 mg/L). This indicates that in addition to enhancing the metal removal capacity, NaOH pretreatment of walnut shell can also extract soluble organic compounds from raw adsorbent.

c) Effect of contact time on Ni(II) removal

Initial experiments were conducted to determine the contact time needed to reach equilibrium. These experiments were performed following the general procedure described above (section 2.3), and samples were taken at predetermined time intervals ranging from 5 to 360 min. The initial metal concentration was approximately 50 mg/L, and the pH was adjusted to 8.0.

The results are shown in Fig.2. The removal of Ni(II) demonstrated an upward trend up to a reaction time of 5 h beyond which adsorption appeared to have approached equilibrium. However, it can be seen

that the Ni(II) sorption occurred in two stages: an initial fast phase which lasted for 15 min, followed by the slower second phase which continued until the equilibrium was reached. Initially, the concentration gradient between the liquid phase and the solid surface was large and, as such, the solute movement to the solid surface was faster. This fast stage can also be attributed to the rapid utilization of the most readily available adsorbing sites on the adsorbent surface. That is why it took only 15 min to reach a percentage removal of about 80%. As contact time increased, intra-particle diffusion become predominant. Therefore, the solute took more time to diffuse into the internal sorption sites through the pores. Taking into account these results, a contact time of 5 h was chosen for further factorial and univariate experiments.

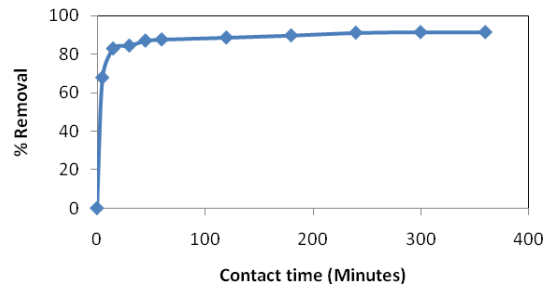


Fig. 2. Effect of contact time on % removal of Ni(II)

d) Screening of variables by statistical evaluation

The design matrix and experimental results obtained in the factorial adsorption tests are presented in Table 2. The design matrix was analyzed statically to determine the main and interaction effects quantitatively through the analysis of variance. As a result of this statistical analysis, the following regression equation was developed for the prediction of nickel removal efficiency.

Table 2. Factorial design experimental data

Run no.	Coded values of independent variables				Ni(II) removal (%)		Ni(II) removal (%) Average
	pH	m	C	T	Trial 1	Trial 2	
1	-1	-1	-1	-1	1.15	1.51	1.33
2	+1	-1	-1	-1	74.24	87.52	80.88
3	-1	+1	-1	-1	5.06	4.88	4.97
4	+1	+1	-1	-1	91.32	78.68	85
5	-1	-1	+1	-1	1.72	1.30	1.51
6	+1	-1	+1	-1	84.64	94.48	89.56
7	-1	+1	+1	-1	5.65	4.69	5.17
8	+1	+1	+1	-1	95.05	94.92	94.98
9	-1	-1	-1	+1	3.25	6.31	4.78
10	+1	-1	-1	+1	86.05	85.47	85.76
11	-1	+1	-1	+1	13.00	7.36	10.18
12	+1	+1	-1	+1	91.32	90.30	90.81
13	-1	-1	+1	+1	4.26	5.56	4.91
14	+1	-1	+1	+1	95.09	94.51	94.8
15	-1	+1	+1	+1	8.54	14.92	11.73
16	+1	+1	+1	+1	95.27	95.89	95.58

$$\begin{aligned} \%R = & 47.62 + 42.05pH + 2.18m + 2.16C + 2.20T - 0.26pHm + 1.90pHC - 0.13pHT \\ & - 0.10mC + 0.08mT - 0.22CT - 0.28pHmC - 0.54pHmT - 0.38pHCT - 0.26mCT - 0.44pHmCT \end{aligned} \quad (3)$$

The determination coefficient (R^2) was used to check how fit the model was. The model yielded a high determination coefficient ($R^2 = 99.55\%$), denoting that only 0.45% of the total variations could not be accounted for by the regression model.

The student's t -test and Fischer F -test were applied to evaluate the significance of the regression coefficients. If a given model is a good predictor of the experimental results, the calculated F and t -values should be greater than the tabulated F and t -values at a particular level of significance and a certain number of degrees of freedom. With a 95% confidence level and sixteen degrees of freedom, the values of F and t were equal to 4.49 and 2.12, respectively. The P -value was used to check the significance of each of the process effects. In all analyses an alpha (α) level of 0.05 was applied to determine the statistical significance. Values of P less than or equal to 0.05 indicate statistically significant model terms.

The results of the analysis of variance are presented in Table 3. According to the F -ratio, t -value and P -value, it seems that the effects of pH, adsorbent dose (m), the initial concentration of metal ion (C), and temperature (T) are statistically significant. Fig. 3 illustrates the main effects of the process parameters.

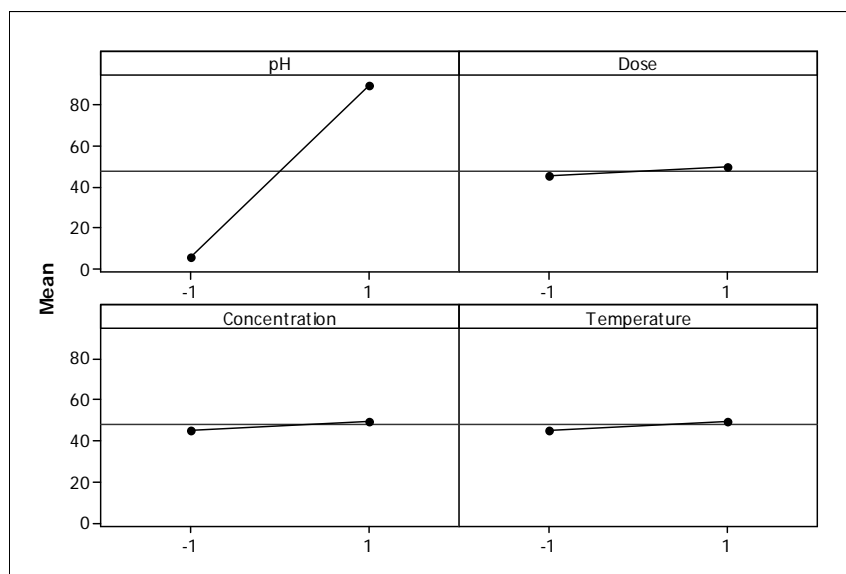


Fig. 3. Main effects plot for Ni(II) removal

Table 3. Statistical parameters for 2^4 factorial design

Term	Effect	Coefficient	t -value	P -value	DF	SS	MS	F -value
Constant (X_0)		47.62	66.83	0.000	1			
pH	84.10	42.05	59.01	0.000	1	56581.6	56581.6	3482.65
m	4.36	2.18	3.06	0.007	1	152.2	152.2	9.37
C	4.32	2.16	3.03	0.008	1	149.1	149.1	9.18
T	4.39	2.20	3.08	0.007	1	154.4	154.4	9.50
pHm	-0.52	-0.26	-0.36	0.721	1	2.1	2.1	0.13
pHC	3.80	1.90	2.67	0.017	1	115.6	115.6	7.12
pHT	-0.26	-0.13	-0.18	0.857	1	0.5	0.5	0.03
mC	-0.19	-0.10	-0.13	0.895	1	0.3	0.3	0.02
mT	0.15	0.08	0.11	0.917	1	0.2	0.2	0.01
CT	-0.44	-0.22	-0.31	0.759	1	1.6	1.6	0.10
pHmC	-0.55	-0.28	-0.39	0.704	1	2.4	2.4	0.15
pHmT	-1.08	-0.54	-0.76	0.460	1	9.3	9.3	0.57
pHCT	-0.77	-0.38	-0.54	0.597	1	4.7	4.7	0.29
mCT	-0.52	-0.26	-0.37	0.719	1	2.2	2.2	0.13
pHmCT	-0.87	-0.44	-0.61	0.549	1	6.1	6.1	0.37
Error					16	259.9	16.2	
Total					31	57442.4		

Standard error coefficient for all cases = 0.7125

Analyzing the data in Table 3, it can be inferred that the solution pH was the most important variable of the overall adsorption procedure since its coefficient was the largest at 42.05. The positive sign of this coefficient shows that Ni(II) removal was enhanced at higher pH values. Increasing the solution pH from 2 to 10 increased the removal efficiency by 84.1%. By comparison, adsorbent dose (m), the initial concentration of Ni(II) ions (C) and temperature (T) had almost the same small positive effects on Ni(II) removal efficiency. An increase in the adsorbent dose from 1 to 20 g/L resulted in a 4.36% increase in Ni(II) removal. Behavior similar to the aforementioned adsorbent dose effect had also been detected earlier [30]. Furthermore, an increase in the ion concentration from 10 to 90 mg/L increased removal efficiency by 4.32%. The obtained results for the effect of initial concentration on the removal efficiency of Ni(II) ions using pre-treated walnut shell are in agreement with the previous search on the adsorption of Ni(II) onto natural kaolinite clay [19], and activated carbon derived from lotus stalks [11]. Moreover, when temperature was increased from 15 to 45°C, Ni(II) removal efficiency increased by 4.39%.

According to the student's t -test, F -test and P -value, at the 95% confidence level the interaction effect between solution pH and initial metal concentration was statistically important for the nickel removal process, while the other two-, three- and four-variable interaction effects were statistically insignificant compared to the other effects. Discarding the insignificant parameters from Eq. (3) leads to the following equation:

$$\%R = 47.62 + 42.05pH + 2.18m + 2.16C + 2.20T + 1.90pHC \quad (4)$$

In addition to statistical tests, the adequacy of the model was also evaluated through the residuals (the difference between the observed and predicted values). A comparison of the model predictions calculated using Eq. (4) with the experimental responses, as well as the residual values and percent error of responses, appears in Table 4. A satisfactory correlation between the observed and predicted values of nickel removal efficiency is depicted in the parity plot shown in Fig. 4. As can be seen in this figure, the points cluster around the diagonal line, indicating a good fit of the regression model.

Table 4. Observed and predicted values of Ni(II) removal efficiency with residuals and errors

Run no.	Coded values of independent variables				Ni(II) removal efficiency (%)		Residuals ($Y_o - Y_p$)	Error (%)
	pH	m	C	T	Observed (Average), Y_o	Predicted, Y_p		
1	-1	-1	-1	-1	1.33	0.93	0.4	30.08
2	+1	-1	-1	-1	80.88	81.23	-0.35	0.43
3	-1	+1	-1	-1	4.97	5.29	-0.32	6.44
4	+1	+1	-1	-1	85	85.59	-0.59	0.69
5	-1	-1	+1	-1	1.51	1.45	0.06	3.97
6	+1	-1	+1	-1	89.56	89.35	0.21	0.23
7	-1	+1	+1	-1	5.17	5.81	-0.64	12.38
8	+1	+1	+1	-1	94.98	93.71	1.27	1.34
9	-1	-1	-1	+1	4.78	5.33	-0.55	11.51
10	+1	-1	-1	+1	85.76	85.63	0.13	0.15
11	-1	+1	-1	+1	10.18	9.69	0.49	4.81
12	+1	+1	-1	+1	90.81	89.99	0.82	0.90
13	-1	-1	+1	+1	4.91	5.85	-0.94	19.14
14	+1	-1	+1	+1	94.8	93.75	1.05	1.11
15	-1	+1	+1	+1	11.73	10.21	1.52	12.96
16	+1	+1	+1	+1	95.58	98.11	-2.53	2.65

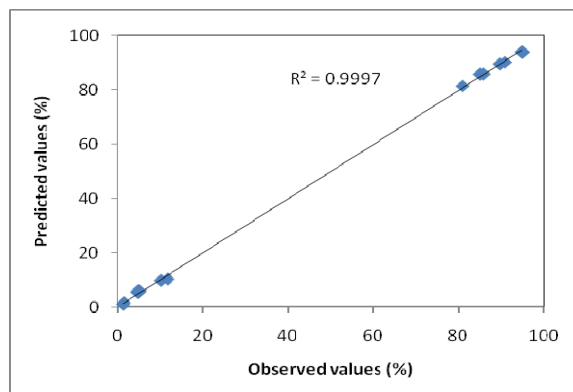


Fig. 4. Correlation between the experimental and predicted values

e) Significant parameters affecting the removal of nickel ions

The results of the factorial experiments were further validated by the various univariate studies conducted for nickel removal. In this section, the effects of the significant parameters influencing the nickel removal efficiency were studied via several one-variable-at-a-time tests and the optimum values of these parameters were determined.

1. Effect of initial solution pH: In the analysis of variance (section 3.4), pH was considered to be the most important parameter for the removal of nickel ions from aqueous solutions. This could be due to the fact that hydrogen ions themselves are strong competing sorbates and that solution pH influences the chemical speciation of metal ions as well as the ionization of functional groups onto sorbent surfaces. In addition, metal ion precipitation can enhance the metal removal at high pH values [31]. Furthermore, the interaction of pH and initial concentration of the solution also had a significant effect on nickel removal. For the optimization of the pH value, solutions containing 10 g/L pre-treated walnut shell were adjusted to various pH values ranging from 2.0 to 10.0. The resulting variations in nickel removal efficiencies with initial pH at different nickel concentrations are shown in Fig. 5. As can be seen, nickel removal increased hand in hand with solution pH and a maximum value was reached at initial pH values of 7.0, 8.0 and 9.0 for nickel concentrations of 10.22, 46.95 and 92.76, respectively. Thereafter, the metal removal efficiency decreased in each case with further increases in solution pH. At pH values higher than 8.0, metal ions hydroxides precipitation may account for metal ion removal [31]. However, the decrease of metal removal at higher pH values (i.e. pH=10) may be due to desorption from adsorbent which can offset the effect of precipitation. These observations were in accordance with the earlier results obtained in the factorial design experiments. The positive effect of pH and pH×C (the interaction of pH and initial concentration) on Ni(II) removal efficiency is evident in Fig. 5. In previous studies, the effect of pH on nickel removal efficiency was investigated [6, 19, 32]. Shukla et al. (2005) and Jiang et al. (2010) have reported the optimum pH values of 9.0 and 7.0 for Ni(II) ions adsorption onto sawdust and kaolinite clay, respectively. The initial concentration of the Ni(II) solution was 20 mg/L in the study by Jiang et al. (2010) [6, 19].

2. Effect of temperature: Based on the results obtained in section 3.4, higher temperatures result in an increase in nickel removal. The effect of temperature was studied more thoroughly using univariate analysis. Different temperatures were evaluated against the same pH (8.0), adsorbent dose (10 g/L) and nickel concentration (47.54 mg/L). Temperature variation between 15°C and 45°C slightly increased the metal removal efficiency (from 92.8 to 97.3%) and adsorption capacity (from 4.4 to 4.63 mg/g) and maximum removal was achieved at 45°C. The increase in the adsorption capacity of pre-treated walnut shell at higher temperatures denotes that some kind of endothermic interaction may be taking place during the adsorption process [33]. The increase in nickel removal resulting from a rise in temperature may be

due to either a change in the kinetic energy of Ni(II) cations leading to greater contact between Ni(II) ions and active sites of sorbent, or an enlargement of the pore size of the adsorbent causing intra particle diffusion within the pores. Furthermore, increasing temperature may also enhance the chemical affinity of the metal cations to the surface of the adsorbent leading to some kind of chemical interaction taking place during the adsorption process, which results in an increase in adsorption capacity [8]. Several studies have also reached the same conclusion with respect to the impact of temperature [4, 34].

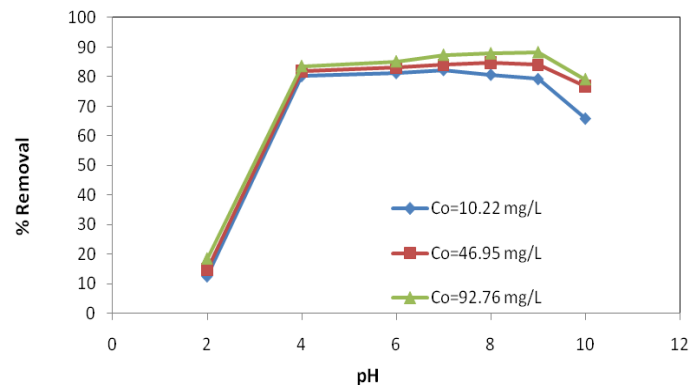


Fig. 5. Influence of pH on nickel removal efficiency

3. Effect of adsorbent dose: Based on the factorial experiments, adsorbent dose was the third statistically significant factor regarding Ni(II) uptake. Adsorbent dosage has been identified as an important parameter since it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. To determine the optimum dosage of pre-treated walnut shell as an adsorbent, a series of tests were conducted at 25°C and a solution pH of 8.0 by varying the sorbent dose from 1 to 20 g/L at a constant initial Ni(II) concentration of 44.68 mg/L. Fig. 6 presents the removal percentage and removal amount of nickel ions as a function of adsorbent dose. It is apparent that the Ni(II) removal efficiency increases with a rise in the amount of adsorbent. The increase in pre-treated walnut shell dosage from 1.0 to 10 g/L resulted in an increase in the removal of Ni(II) ions from 26.8% to 96.4%. However, further increasing the adsorbent dose (from 10 to 20 g/L) led to only a 2.2% improvement in removal efficiency. Hence, the optimum sorbent dose for nickel removal was found to be 10 g/L.

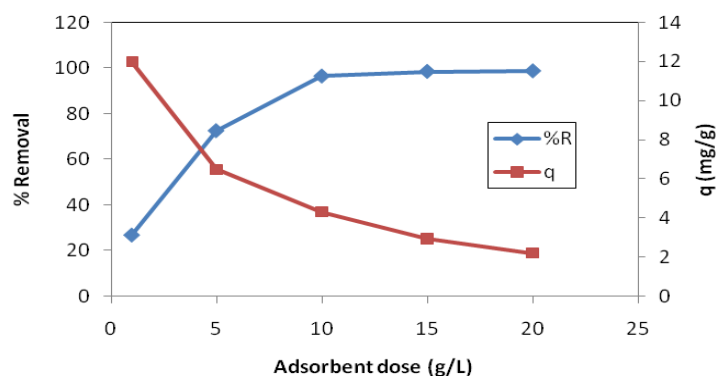


Fig. 6. Effect of adsorbent dose on nickel removal efficiency and adsorption capacity

On the other hand, unit adsorption capacity showed a reverse trend to the percentage of nickel removals. By increasing the adsorbent dose from 1.0 to 20 g/L, the removal of Ni(II) ion per unit mass of adsorbent decreased from 12.0 to 2.2 mg/g. This drop in adsorbed amount per unit mass of adsorbent is a commonly observed behavior which has also been reported by other researchers [22, 35, 36]. This effect may be due to the fact that some adsorption sites remain unsaturated during the adsorption process [29].

4. Effect of initial metal ions concentration: In the factorial design section (3.4), it was found that the initial concentration of metal ions was the least important individual variable for nickel ions uptake. A concentration dependency study was carried out by placing 2.0 g of pretreated walnut shell in a series of flasks containing 200 mL of metal ions at different concentrations (24-82.55 mg/L). The solution pH and temperature were fixed at 8.0 and 25°C, respectively. Figure 7 gives the nickel removal efficiency (%R) and amount of nickel ions adsorbed per gram of pre-treated walnut shell (q) as a function of Ni(II) ions concentration. As can be seen, a rise in initial metal ion concentration resulted in higher removal efficiencies. The amount of metal ions adsorbed at equilibrium appeared to follow the same upward trend as the initial Ni(II) ion concentration. Upon changing the initial concentration of nickel solution from 24.0 to 82.55 mg/L, the removal efficiency and amount adsorbed increased from 82.5 to 88.25% and 0.84 to 7.74 mg/g, respectively. These results are consistent with those obtained in the factorial design section. This behavior can be attributed to an increase in the driving force of the concentration gradient alongside a rise in the initial nickel concentration in order to overcome the mass transfer resistance of Ni(II) ions between the aqueous and solid phases. Therefore, a higher initial concentration of Ni(II) ions may improve removal efficiency and capacity [34]. Rafatullah et al. (2009) observed a similar behavior for the removal of nickel by means of meranti sawdust [4].

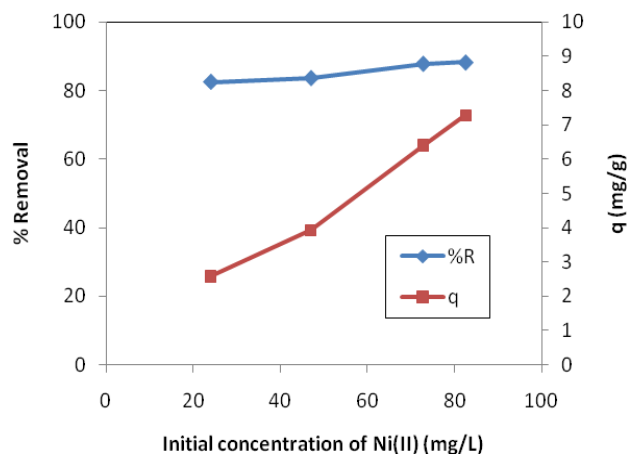


Fig. 7. Effect of initial concentration of Ni(II) ions on nickel removal efficiency and adsorption capacity

5. Adsorption isotherms: Adsorption isotherms were used to determine the affinity of pre-treated walnut shell for nickel. The isotherm study was carried out by varying initial metal ion concentration from 10 to 82.5 mg/L at a fixed temperature of 25°C. Both the Freundlich and Langmuir isotherm models have been shown to be suitable for describing the removal of metal ions by different adsorbents. Consequently, in order to investigate the sorption capacity of pre-treated walnut shell, these equilibrium models were fitted to the experimental data.

The Freundlich isotherm is an empirical equation which is used to describe multi-side adsorption isotherm for heterogeneous surfaces [37]. The linear form of the Freundlich isotherm can be represented as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

The isotherm constants K_f and n , which denote adsorption capacity and intensity, were calculated from the intercept and slope of the plot between $\log q_e$ and $\log C_e$ (Fig. 8).

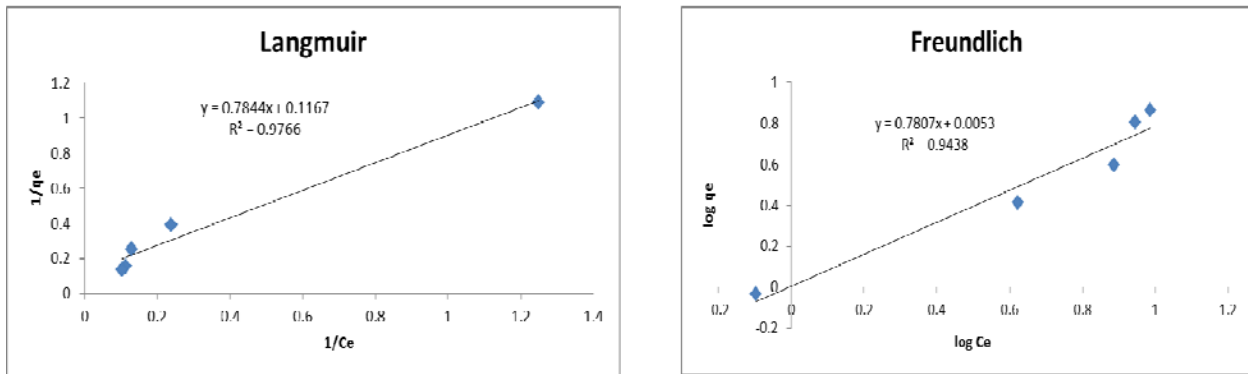


Fig. 8. Freundlich and Langmuir isotherm plot for the removal of Ni(II) on NaOH modified walnut shell

The Langmuir isotherm assumes a homogeneous surface for the sorbent and equivalent sorption energies for each site, with no interaction between the sorbed molecules. The linear form of the Langmuir equation is expressed as:

$$\frac{1}{q_e} = \left(\frac{1}{bQ} \right) \left(\frac{1}{C_e} \right) + \frac{1}{Q} \quad (6)$$

The isotherm constants b and Q were calculated from the intercept and slope of the plot $1/q_e$ versus $1/C_e$ (Fig. 8). The nickel adsorption data fitted with the linear form of the Freundlich and Langmuir models as well as the calculated constants have been summarized in Table 5 along with the regression coefficients. It can be observed from Table 5 that both models demonstrate a good representation of the experimental results. Even so, higher correlation coefficients indicate that the Langmuir model fit the adsorption data better than the Freundlich model. As shown in Table 5, the Q value, which is an indication of the monolayer adsorption capacity, was found to be 8.57 mg Ni(II) per gram of the adsorbent material, which is higher than the adsorption capacities of sugarcane bagasse (2 mg/g) [7], modified sawdust (3.37 and 6.43 mg/g), modified Jute fibers (5.26 mg/g), modified groundnut shells (7.49 mg/g) [17], modified bentonite clay (1.91 mg/g) [36] and natural kaolinite clay (0.9 mg/g) [19] for nickel ions.

Table 5. Parameters of the Freundlich and Langmuir models

Freundlich constants			Langmuir constants		
K_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$)	n	R^2	Q (mgg^{-1})	b (Lmg^{-1})	R^2
1.01	1.28	0.944	8.57	0.15	0.977

An important feature of the Langmuir isotherm model can be explained in terms of a separation factor or equilibrium constant (R_L) that gives a measure of the effectiveness of recovery of a solute: [21]

$$R_L = \frac{1}{1 + bC_i} \quad (7)$$

This dimensionless separation factor can predict the affinity between the adsorbate and adsorbent material. Equilibrium constants greater than 1 indicate that sorption is unfavorable, whereas values lying between 0 and 1 denote that sorption is favorable; an equilibrium constant of zero, on the other hand, means that the sorption process is irreversible [38]. Since the R_L value in this study (0.07-0.4) lies between 0 and 1, it can be concluded that the removal of nickel ions by pretreated walnut shell is favorable.

6. Adsorption kinetics: Kinetic studies were carried out by performing batch sorption experiments with an initial Ni(II) concentration of 50 mg/L at different time periods varying between 5 and 360 min. Four models, namely the pseudo first-order, pseudo second-order and intra-particle diffusion models, were used

to analyze the kinetics of the Ni(II) sorption onto pretreated walnut shell. The consistency between the experimental data and the model-predicted values was expressed using the correlation coefficient (R^2).

The pseudo first-order model is based on the assumption that the sorption process rate is proportional to the initial metal concentration and the number of free sites. The integral form of the pseudo first-order model is generally represented by the following expression:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (8)$$

where q_e and q_t (mg/g) are the amounts of adsorbed metal ions on the adsorbent at equilibrium and time t , respectively, and k_1 is the Lagergren rate constant of the pseudo first-order adsorption (min^{-1}).

A plot of $\log(q_e - q_t)$ versus t gives a straight line for the first-order adsorption kinetics from which k_1 and predicted q_e can be determined. It was observed from Table 6 that the first-order model failed to provide an estimate of the q_e of adsorbed Ni(II) ions onto pre-treated walnut shell, where the experimental value of q_e (4.47 mg/g) was higher than the fitted value (0.64 mg/g). Besides, the value of R^2 is well below 1, suggesting that the adsorption does not fit the pseudo first-order reaction. The insufficiency of the pseudo first-order model to fit the kinetics data could be due to the limitations of the boundary layer controlling the nickel sorption process. Moreover, functional groups existing on the surface of pre-treated walnut shell also contributed to the chemisorptions of Ni(II) on the adsorbent.

The pseudo second-order kinetic model is based on the assumption that the adsorption rate is proportional to the square of the uncovered adsorption sites [37]. The linear form of the pseudo second-order equation is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where k_2 is the pseudo second-order adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). The initial sorption rate (i.e., the rate at $t \rightarrow 0$) can be calculated using the constant k_2 as follows:

$$h = k_2 q_e^2 \quad (10)$$

The values of q_e and k_2 can be determined from the slope and intercept of the t/q_t versus t plot. The high R^2 values (~ 1) and good agreement between the predicted and experimental q_e values (Table 6) indicate that the adsorption system followed the pseudo second-order kinetic model, which suggests that the process controlling the rate may be a chemical sorption.

Table 6. Kinetic parameters for sorption of Ni(II) onto pre-treated walnut shell

$q_{e, \text{exp}}$ (mg g ⁻¹)	Pseudo first-order			Pseudo second-order		
	k_1 (min ⁻¹)	$q_{e, \text{cal}}$ (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e, \text{cal}}$ (mg g ⁻¹)	R^2
4.47	0.0154	0.64	0.885	0.0841	4.50	0.999

The adsorption data were also analyzed in terms of the intra-particle diffusion model in order to predict the rate-controlling step of the process. Based on this model, the mass transfer rate can be expressed as a function of the square root of time.

$$q_t = k_{id} t^{0.5} + C \quad (11)$$

where q_t is the fraction nickel uptake (mg/g) at time t , k_{id} is the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$) and C (mg/g) is a constant in the intra-particle diffusion model, which reflects the importance of the boundary layer or mass transfer effect.

If the plot of q_t versus square root of time gives a straight line, the only rate-controlling step is the intra-particle diffusion; however, if the data show multi-linear plots, then two or more steps are influencing the sorption process [39]. Figure 9 represents the q_t versus $t^{0.5}$ plot for Ni(II) adsorption. As seen from this figure, the plot was not linear over the entire time range, implying that more than one process had influenced the adsorption. The first initial step was governed by diffusion in the bulk phase to the exterior surface of the adsorbent. The second step seemed to refer to intra-particle diffusion. The third step pertained to the final equilibrium stage. This indicates that in the process of Ni(II) adsorption onto pretreated walnut shell, both surface adsorption and intra-particle diffusion contribute to the rate determining step.

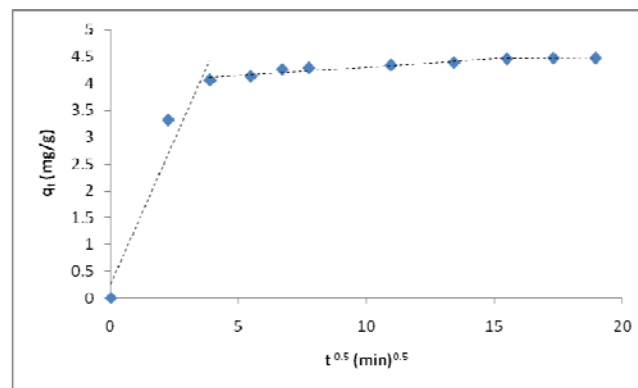


Fig. 9. Intra-particle diffusion plot for Ni(II) removal

7. The Gibbs free energy: The Gibbs free energy is the basic criterion to determine if a process occurs spontaneously. For a given temperature, a process is considered to be spontaneous if the value of free energy change (ΔG) has a negative value. The free energy change of the adsorption process is given by:

$$\Delta G = -RT \ln b \quad (12)$$

where ΔG is free energy change, R is the universal gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$), T is the solution temperature (K), and b is the Langmuir equilibrium constant (Liters per mole). The free energy change for the adsorption of Ni(II) at 25°C was -22.5 KJ/mol . The negative value of ΔG indicates the spontaneous nature of Ni(II) sorption on NaOH pre-treated walnut shell.

4. CONCLUSION

The pre-treated walnut shell was found to be a potential adsorbent for the removal of Ni(II) from aqueous solutions. The application of a four-factor, two-level full factorial experimental design helped in determining the significant factors affecting the removal of Ni(II) ions by pre-treated walnut shell. The proposed mathematical model also provided an analysis of the simultaneous interactive effects of the independent variables in order to better understand the Ni(II) removal process. The Ni(II) uptake was found to be sensitive to changes in all of the individual variables studied, viz., pH, adsorbent dose, Ni(II) concentration, and temperature, as well as the binary interaction of the solution pH and Ni(II) concentration. For the conditions applied in this study, the solution pH had the most significant effect on Ni(II) uptake, while other variables had a less significant effect.

In order to confirm the results obtained in the factorial experiments, as well as achieving the best conditions for Ni(II) uptake by pre-treated walnut shell, a series of univariate studies were also conducted. As a result of these studies, the best initial conditions were found to be: a pH value of 7.0-9.0, an

adsorbent dose of at least 10 g/L, an initial Ni(II) concentration of 70-90 mg/L, and a temperature of 45°C. The isotherm data fit both the Langmuir and Freundlich models well; however, higher R^2 values were obtained from the Langmuir model. The sorption capacity of pre-treated walnut shell was 8.57 mg/g at 25°C for the tested aqueous solution concentration range of 10.0-82.5 mg/L. The kinetics of Ni(II) adsorption onto pre-treated walnut shell followed the pseudo second-order model.

The results obtained in this study indicated that pre-treated walnut shell can be successfully applied for the removal of Ni(II) from aqueous solutions.

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NOMENCLATURE

b	Langmuir constants (L/mg)
C_i	initial metal concentration (mg/L)
C_f	final metal concentration (mg/L)
C_e	equilibrium liquid phase concentration (mg/L)
C^*	constant that gives idea about the thickness of the boundary layer (mg/g)
C	nickel concentration (mg/L)
F -value	Fisher test calculated value
DF	degree of freedom
ΔG	Gibbs free energy change (J/mol)
h	initial sorption rate (mg/(g min))
k_1	rate constants of the pseudo-first-order sorption (min^{-1})
k_2	rate constant of the pseudo-second-order sorption (g/(mg min))
K_f	Freundlich constant, sorption capacity (L/mg)
k_{id}	intra-particle diffusion rate constant (mg/(g min ^{1/2}))
m	amount of adsorbent (g)
MS	mean square
n	Freundlich constant, sorption intensity
P -value	probability
q_e	equilibrium solid phase concentration (mg/g)
q_t	amount of adsorbate adsorbed by adsorbent at time (mg/g)
Q	maximum adsorption capacity of adsorbent (mg/g)
R^2	coefficient of determination
R_L	separation factor, dimensionless
SS	sum of squares
t	time (min)
R	universal gas constant (8.314 J/mol K)
$\%R$	percentage metal removal
T	temperature (°C or K)
X_0	constant coefficient
X_i	regression coefficients in polynomial equation
Y_0	observed response
Y_p	predicted response

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