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Removal of cadmium ions from aqueous solutions using nickel metal-organic framework: isotherm, kinetic studies, optimization, and modeling by response surface methodology (RSM)

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ABSTRACT

Metal-organic frameworks are among the methods that can effectively absorb a large volume of these heavy elements. The aim of this study was the investigation of nickel metal-organic framework potential in the removal of cadmium from aqueous solutions, and optimization using response surface methodology (RSM). This study was experimental and was performed in a laboratory-scale pilot. The effect of important operational parameters such as solution pH, adsorbent dose, and contact time at five levels ($-\alpha$, –1, 0, +1, + α) was studied. Optimization and analysis of the results were performed by Design Expert 11. The results showed that the quadratic model was suitable for the data ($P_{value} > 0.0001$) and the proposed model was confirmed with a high correlation coefficient (($R^2 = 0.98$), ($R^2_{Pre} = 0.91$), and ($R^2_{Adj} = 0.97$)). Under the optimal conditions for the process (pH of 5, adsorbent dose of 0.03 mg/L, and contact time of 15.0 min), the observed Cd removal efficiency was 81.5%. According to the result, absorption efficiency depends on pH due to the metallic nature of this element. On the other hand, the extreme increase of absorbent amount and its duration has a negative influence on the adsorption process. In addition, the Langmuir isotherm model has demonstrated the highest conformity with laboratory results and the increase in absorbent is shown due to an increase in the contact surface between absorbent and adsorbate. The results of the present study indicate that the application of nickel metal-organic frameworks is a cost-effective, practical, and suitable method to remove heavy metal ions like cadmium from an aqueous solution.

Keywords: Absorption; Cadmium ion; Aqueous solutions; Nickel metal-organic framework; Response surface methodology

1. Introduction

Nowadays, the environmental pollution by different types of heavy metals entering human and animal food Cycles has created serious challenges to the globe and its living organisms. The widespread industrial activities, excessive consumption of toxic materials, chemical fertilizer, and wastewater discharges into the environment are among the most important manifestations of this type of pollution [1,2]. Cadmium is a highly toxic metal that can cause death. The main toxic effects of cadmium are on the lungs, kidneys, and bones. Cadmium enters aquatic ecosystems through soil erosion and bedrock, atmospheric contaminated sediments from industrial plants, contaminated effluents, and

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the use of sludge and fertilizers in agriculture [3–5], which can be toxic and resistant, and its transmission in food chains can endanger the health of the aquatic environment and humans. These heavy metals have threatened the health of humans and aquatics living in the sea due to their toxicity, resistance, and the amount of their transfer into the food chain [6,7]. Additionally, they entered the sea through agricultural and industrial activities, excavations, and fossil fuel transportation [8,9].

Various methods have been used to remove heavy metals from contaminated waters. These methods can be generally divided into three physical, chemical, and biological categories. Among these methods, adsorption using a proper adsorbent, being a physical method to remove heavy metals, has brought about very favorable results. It has been influential in the removal of these elements from water and contaminated wastewaters. In this method, the surface area, and porosity of the adsorbent are considered effective elements in increasing the efficiency of the adsorption process. In the meantime, the porous nanostructures including nano adsorbent, and metal-organic frameworks have attracted the attention of researchers due to the large pore size, surface area, and selective adsorption of small molecules [10,11]. Additionally, too much little inaccessible concentrated volume in metal-organic is among the most important properties of these materials [12]. Although the large surface area has been reported for active carbon and zeolites, very little volume in frameworks with the highest porosity has been shown [13].

The results of different studies indicate the high efficacy of the metal-organic framework. For instance, the study of Sohrabi et al. [14] and Sohrabi [15] has indicated that porous metal-organic frameworks including Thiol-functionalized nanoparticles, copper, and trimestric acid compounds are useful for removing mercury. In another study carried out by Zhu et al. [16], it has been found that synthesis of Fe-BTC metal-organic framework using the simple solvothermal method can be used as a suitable adsorbent to remove arsenic from water samples. This group of materials, which is classified as coordination polymers are hybrid organic mineral crystals. They are formed by linking metal ions including metals accompanied by organic ligands such as carboxylate letrozole and sulphoxylate through coordination bonds. In fact, three-dimensional polymers which have permanent porosity known as metal-organic frameworks have gained more attention due to the inclusion of molecules with multiple functions inside their networks. In addition, metal ions with secondary structures or organic networks cannot only diversify the topology but also the pores in the walls can serve multiple functions including catalytic applications, hydrogen storage, mechanism separating molecules from gaseous or liquid compounds [17]. One of the main advantages of the adsorbents studied in this study, including low density and high surface area of these frameworks, having so many ions in their structure that these ions can interact with other chemical species. In addition, regular and large internal cavities with an average pore inlet size of less than 2 nm and a uniform size distribution increase the adsorption properties [18–20]. Perfectly regular and uniform cavities created by the repetition of the same units are other advantages of these adsorbents and are one of the important factors in increasing the selectivity of these materials, which makes this material different from carbon materials [19].

Given the intense necessity of heavy metals removal from aqueous solution and the high efficiency of metal-organic frameworks, the present study is carried out to investigate the application of these structures to remove toxic elements cadmium. It has been viewed as one of the most dangerous heavy metals for human health entering into the water bodies through various wastewater. For designing and analyzing the experiments of the present study, we employed the central composite design (CCD) along with the response surface methodology (RSM); this method has been introduced as appropriate statistical tools to design and optimize the studied process [21–23]. We also assessed the effect of variables, for example, contact time, solution pH, and adsorbent dose on the removal efficiency. Moreover, we employed the Langmuir and Freundlich isotherm models to determine the adsorption capacity and equilibrium time of cadmium metal adsorption and the pseudo-first-order kinetic and pseudo-second-order kinetic models to describe the adsorption process and to estimate kinetic coefficients.

Separation of heavy metals from the aquatic environment and synthesis of metal-organic frameworks, due to their importance, are some of the most important areas of research. In most studies, different frameworks have been used to separate heavy metal ions such as cadmium, lead, copper, and zinc. In recent research, the method of functionalization of the magnetic nanoparticles has been used to improve the surface properties in the adsorption reaction. According to the studies done so far, no study has been done on the synthesis of strong nickel metal-organic framework synthesized based on cyanoguanidin linker, and their effect on the separation of heavy metal ions from the aqueous medium. For this purpose, the process of separation of heavy metals in the presence of a synthesized metal-organic framework with a special structure was studied for the first time.

2. Materials and methods

In this study, the cadmium (Cd) was purchased from Sigma-Aldrich (St. Louis, MO, USA), and other chemicals required, such as H_2SO_4, NaOH, $Ni(NO_3)_2{\cdot}6H_2O$, $AlCl_3{\cdot}6H_2O$, HNO_3, and $Cd(NO_3)_2$ were provided from the Merck CO., Germany.

The present work was carried out to study the possibility of using nickel-based metal-organic frameworks in the adsorption of cadmium toxic elements in wastewater and to reduce the rate of heavy metals from aqueous solution. All synthesis phases of the framework and experimental studies were conducted in the Islamic Azad University of Tehran, North branch, environment lab. RSM was used to design the experiments. This method is used in cases where the desired response is influenced by multiple variables, and the main purpose is to optimize the response [24–26]. Additionally, the CCD method was used to do experiments on cadmium heavy metal adsorption. Thus, the main advantage of using RSM is the reduced number of experiments required to evaluate the effects of the process variable and their interactions and response [27,28]. The study

of cadmium adsorption on nanosorbents was investigated in discontinuous conditions. The initial concentration of cadmium ions was performed at different times. The stock solution of 1,000 mg/L was prepared by dissolving a suitable amount of lead nitrate in deionized water and then, by diluting the stock solution, solutions with suitable concentrations were obtained [29].

The specific parameters, that is, pH (4.0–6.0), adsorbent dose (0.02–0.04 g), and contact time (10.0–20.0 min) were thus optimized (Table 1). The optimization of cadmium removal using the adsorption process was accomplished by CCD. The design, modeling, and analysis of the experiments were exploited by Design Expert Software version 11, using a full five-level factorial (one of RSM family designs). Optimum variable values were calculated from the experimental response and coded at five levels from −α, −1, 0, +1, and +α as defined by Eq. (1) [30]:

$$X_i = \frac{X_i - X_0}{\Delta X_i} \tag{1}$$

where X_i symbolizes the coded value of variable X_i; X_0 reveals the actual value of X_i at the center point, and ΔX_i indicates the increment.

The quadratic equation model for predicting the optimal conditions can be defined as follows (Eq. (2)) [30,31]:

$$Y = \beta_0 + \beta_i X_i + \beta_j X_j + \beta_{ii} X_i^2 + \beta_{jj} X_j^2 + \beta_{ij} X_i X_j + \varepsilon \tag{2}$$

where Y embodies the variable of response (percentage cadmium removal); X_i and X_j are independent coded variables, and β_0, β_i, β_{ii}, and β_{ij} are related to intercept term, linear, quadratic, and interaction effects, respectively [31,32]. Random error (ε) articulates the measure of the difference between observed and predicted values.

Using analysis of variance (ANOVA), adequate data were gathered to check Eq. (2) for each response and the independent variables. Determination of the fitting level of the mathematical models to experimental data was evaluated using the coefficient of determination (R^2) and the adjusted coefficient of determination (R^2_{adj}). In addition, investigating the model consistency was carried out by Fisher *F*-test, and the model terms were assessed by *p*-value (probability) at a confidence level of 95% at five levels.

The number of experiments designed is obtained using Eq. (3), in which k is the number of variables and C_p the number of repetitions at the central point [32,33]:

$$N = k^2 + (2 \times k) + C_p \tag{3}$$

Given that, in this study, the design of the experiment was considered with three factors, for example, pH, adsorbent dose, and contact time, the number of experiments was calculated to be 20 runs, according to Eq. (1). The minimum and maximum values of the main factors, which are presented in Table 1, demonstrate the level of change of each design element obtained by the Design-Expert software, based on the change intervals of each variable. Levels of change for each variable included high and low axial levels (+α and −α), central levels (0), and high and low levels of factors (+1 and −1), which their actual values are shown in Table 1.

To better clarify CCD results, Pareto analysis was utilized to calculate the percentage effect of each independent variable (P_i) on the removal of cadmium (Eq. (4)) [34,35]:

$$P_i = \left(\frac{\beta_i^2}{\sum \beta_i^2} \right) \times 100 \qquad i \neq 0 \tag{4}$$

At first, to prepare cadmium standard solution, 1.6 g of cadmium nitrate powder was dissolved in 10 cc of 69% concentrated nitric acid and then the solution was brought up to the volume into a 1,000 mL volumetric flask. Therefore, 1,000 mg/L cadmium standard solution was synthesized and subsequent solutions were prepared at the desired concentration by diluting the certain volume of the original solution. In addition, Freundlich and Langmuir isotherm models were used to describe the experimental data and adsorbent–adsorbate behavior that shows the relationship between the amount of metal in solution and metal absorbed on adsorbent in a constant temperature. In addition, to determine the characteristics of the synthesized nickel metal-organic framework, X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) were used.

2.1. Synthesis of nickel metal-organic framework

In the present study, Ni-MOF was synthesized by dissolving 2.27 mmol cyanoguanidin linker and 3.56 mmol nickel nitrate hexahydrate in 25 mmol water, and the mixture was transferred to autoclave. Heating was carried out in a heating furnace at 110°C for 22 h. Then the solution was washed out by distilled water and finally, the resulting product dried in the oven at 60°C for 24 h.

3. Results and discussion

3.1. Characterization of synthesized nickel metal-organic framework

SEM which is a group of electron microscopes is one of the most popular microscopic methods that can be used for chemical analysis and other studies, in addition

Table 1
Examined levels of independent variables

Independent Variables	Symbol	Unit	−α	−1	0	+1	+α
pH	*A*	–	4.0	4.5	5.0	5.5	6.0
Time	*B*	min	10.0	12.5	15	17.5	20.0
Adsorbent dose	*C*	g	0.02	0.025	0.03	0.035	0.04

to providing magnified images. According to Figs. 1a–c, it is observed that the studied adsorbent surface before the adsorption process is heterogeneous and has an irregular and irregular surface, and has many cavities, which can be a suitable place for the adsorption of metal ions. These pores become almost dense in different adsorbents, especially on the adsorbent surface, which can lead to the bonding and adsorption of cadmium ions on the adsorbent surface. Fig. 1d shows the XRD pattern of the nickel metal-organic framework. By examining the XRD pattern of this sample, the intensity of the main peaks of the synthesized material was appropriate and its crystallinity was good at temperature and time. At this temperature and time, the organic metal framework appears to be fully formed. The main peaks appear at 2θ = 14.68°, 23.7°, and 40.85°. The strongest peak of impurity related to the linker appears at 2θ = 14.68°.

3.2. Experimental design and data analysis by RSM

After designing and determining the number of parameters and runs by the CCD, the results of the cadmium removal by the nickel metal-organic framework were obtained; these results can be seen in Table 2. One of the key and important steps in analyzing the results is to select and truthful model for accurate and precise prediction of the results. For this reason, the proposed quadratic model was used for the system, which includes three terms of single effects (*A*, *B*, and *C*), three terms of interaction effects (*AB*, *AC*, and *BC*), and three terms related to quadratic effects (A^2, B^2, and C^2).

By employing the ANOVA, the model was assessed and its significance was tested. The results of ANOVA related to the removal of cadmium using the nickel metal-organic framework are represented in Table 3. Based on this Table, the *p*-value for the proposed model was less than 0.0001. A *p*-value less than 0.05 is considered as a criterion for determining the effectiveness of single and interaction effects. Another parameter is the lack of fit (LOF) test. This test is significant if the *p*-value is greater than 0.05, which is based on the *p*-value represented in Table 3, the LOF is not significant for the removal of the cadmium. According to the residual parameters in the modeling system, Eq. (5) was proposed to predict the cadmium removal

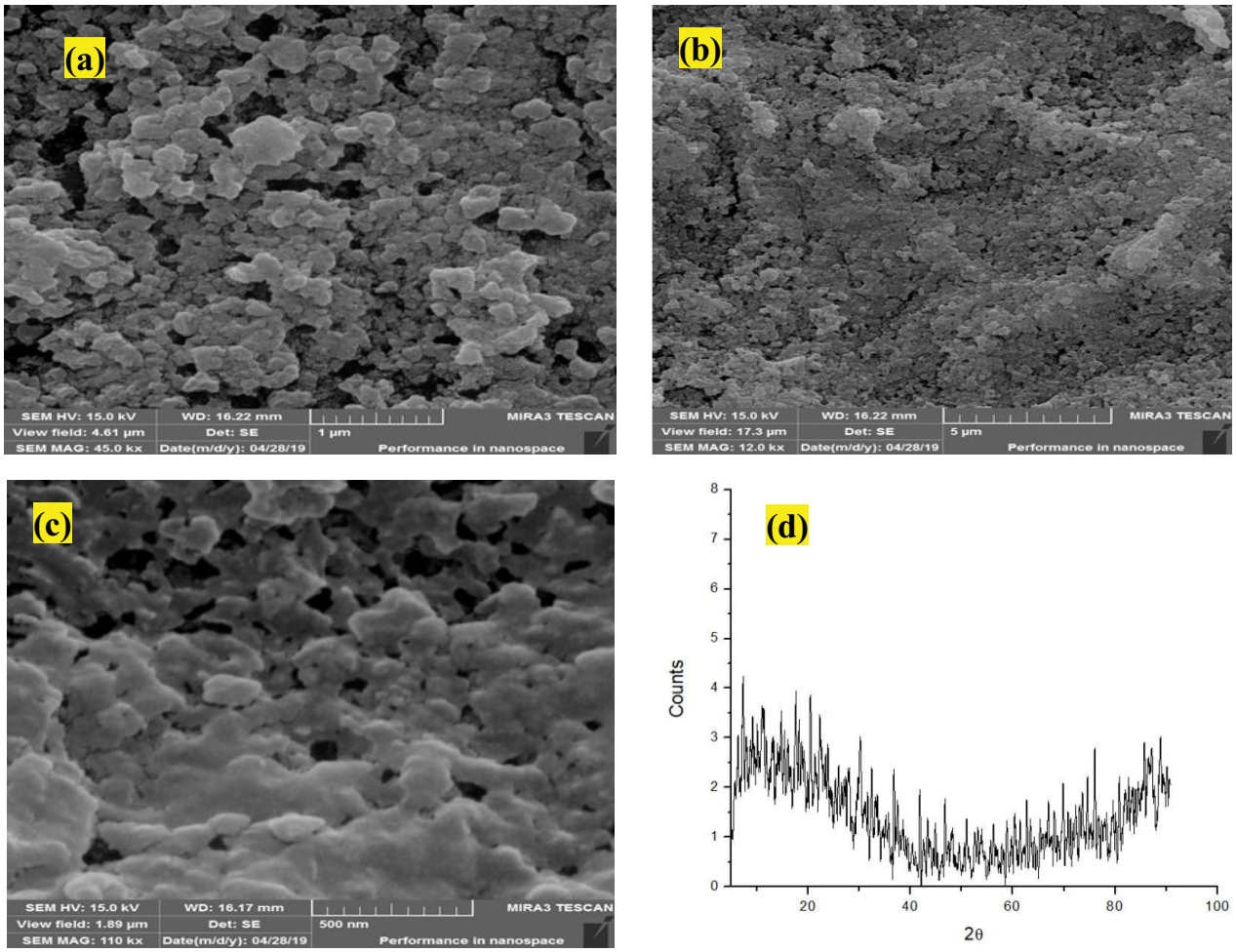

Fig. 1. SEM images of the surface morphology of the synthesized nickel metal-organic framework: magnification image (a) 1 µm and (b) 5 µm, and (c) 500 µm of the synthesized nickel metal-organic framework. (d) XRD diffractogram of the synthesized nickel metal-organic framework.

efficiency, which is a set of single, interactive, and quadratic effects:

$$\text{Cd removal\%} = 78.10 + 9.30A + 7.53B + 4.40C - 3.94AB + 4.58AC - 1.70BC - 10.51A^2 - 8.83B^2 - 9.33C^2 \quad (5)$$

where Y indicates the predicted response to the efficacy of cadmium by the nickel metal-organic framework. Moreover, the A, B, and C represent the parameters, that is, the solution pH, contact time (min), and adsorbent dose (g), respectively.

In Eq. (5), the positive effect of factor represents that factor level increase has a direct effect on removal efficiency, which develops its value. Even so, the negative effect of the factor is indicative of the fact that an enhancement in the factor level has no effect on efficiency. As well, in the above equation, the coefficients of the factors represent the importance of each parameter. Based on this equation, the highest importance in the removal of cadmium is related to the pH. Fig. 2 indicates the Pareto graphic analysis; it introduced the pH (A) variable as the most important factor in cadmium with 57.8.

The values of correlation coefficient R^2, predicted R^2, and adjusted R^2 are employed for the assessment of the suitability of the models. Desirable condition is observed when the R^2 value is close to 1, and a rational settlement with adjusted R^2 is required. The linear regression coefficient (R^2) between experiments and different response values in the model for cadmium removal was 0.9882. Nevertheless, the value of R^2 should be close to the R^2_{adj}; so that for the higher difference between these two, insignificant involvement of expressions in the model may be observed. The results of the present study revealed that there is a closeness between values of R^2_{adj} for cadmium removal (0.9738) and R^2. Based on previous studies, sufficient precision, which is employed to measure the signal-to-noise ratio, is suitable when its value is greater than 4 [36]; its value, in the present study, was higher than 4 for the response, which indicates a sufficient signal and a good fitting degree. The minimum values of coefficient of variation (C.V. of 6.27% for cadmium removal) represent the high accuracy and reliability of the test. The evaluation of the ability of models (linear, 2FI, quadratic, and cubic models) was carried out using the sequential model sum of squares, and the results were represented in Tables 3. The adequate models for removal efficiency of cadmium were chosen by the probability value ($p < 0.05$) and the Fisher's F-value along with the determination of coefficient (R^2). The fit summary for removal efficiency of cadmium proposed a quadratic relationship, where the additional terms were significant and the model was not aliased.

Inspection of the quality of the proposed models was carried out by drawing the graphs that corresponded to predicted response values vs. actual values and the graphs of the normal distribution of data, which is shown in Fig. 3. According to Fig. 3a, the points are allied in a straight line, and no deviation in the data distribution can be detected; this confirms the presence of a high correlation and normal distribution between the residual values. Moreover, in Fig. 3b, the scattering of the residuals against the given values has been represented; since no specific

Table 2
Results of central composite design (CCD) of experiment along with actual and predicted values of cadmium removal

Run	*A*: PH	*B*: Time (min)	*C*: dose (g)	Cadmium removal (%)	
				Actual	Predicted
1	4.5	17.5	0.025	62.92	56.69
2	4.5	12.5	0.035	37.35	36.41
3	5.0	15.0	0.03	78.68	80.19
4	4.5	12.5	0.025	40.28	32.90
5	5.5	17.5	0.025	53.90	53.00
6	4.5	17.5	0.035	54.15	53.39
7	5.5	17.5	0.035	67.62	68.03
8	5.5	12.5	0.035	66.90	66.81
9	4.0	15.0	0.03	34.58	39.24
10	4.5	20.0	0.03	66.24	65.74
11	4.5	15.0	0.03	73.24	80.19
12	4.5	15.0	0.03	74.89	80.19
13	6.0	15.0	0.03	62.42	61.69
14	4.0	15.0	0.04	67.14	61.60
15	5.0	15.0	0.03	82.24	80.19
16	4.5	10.0	0.03	41.27	44.70
17	5.0	15.0	0.02	40.38	46.01
18	5.0	15.0	0.03	77.29	80.19
19	5.5	12.5	0.025	50.64	44.96
20	5.0	15.0	0.03	76.98	77.29

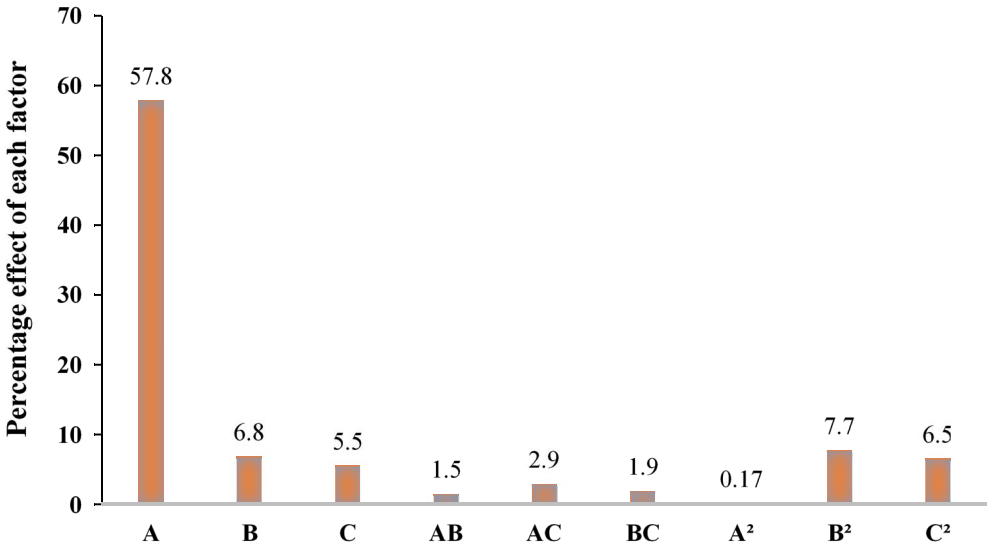

Fig. 2. Pareto chart of the main effects obtained from the screening experiments.

Table 3
Statistical models obtained from the analysis of variance for response surface reduced quadratic model for optimization of Cadmium removal

Source	Sum of squares	df	Mean square	*F*-value	*p*-value	
Model	11,300.09	13	869.24	20.71	<0.0001	Significant
A-PH	2,362.22	1	2,362.22	56.28	<0.0001	Significant
B-Time	1,549.27	1	1,549.27	36.91	<0.0001	Significant
C-dose	528.24	1	528.24	12.59	0.0016	Significant
AB	248.20	1	248.20	5.91	0.0229	Significant
AC	336.34	1	336.34	8.01	0.0092	Significant
BC	46.45	1	46.45	1.11	0.03033	Significant
A^2	3,015.62	1	3,015.62	71.85	<0.0001	Significant
B^2	2,128.04	1	2,128.04	50.70	<0.0001	Significant
C^2	2,376.49	1	2,376.49	56.62	<0.0001	Significant
Residual	1,007.36	24	41.97			
Lack of fit	868.96	16	54.31	3.14	0.0828	Not significant
Pure error	138.40	8	17.30			
Cor. total	12,307.46	37				

Standard deviation: 5.48; mean: 50.49; C.V.%: 6.27; R^2: 0.9882; adjusted R^2: 0.9738; predicted R^2: 0.9104; adeq precision: 10.953; PRESS: 1,949.07; adequacy of the model tested: linear, 2FI, quadratic and cubic; model suggested: quadratic.

trend related to variance changes (increase or decrease) is observed, the constancy of variance is approved. In addition, in Fig. 3c, the independent scattering of the residuals has been brought; as observed, there is no sinusoidal trend in the independence of the residuals, which is indicative of the suitability of the selected model for data analysis [37,38]. The effect of each of the studied factors (pH, contact time, and adsorbent dose) on the removal of cadmium is shown in Fig. 3d.

According to the results presented in Fig. 3d, with increasing the adsorbent dose and reaction time, the cadmium removal efficiency increased. As the amount of adsorbent increases, the number of available adsorption sites for cadmium ions increases, so the adsorbent efficiency increases, which is consistent with the results of the study of Salam et al. [39]. Also, with increasing the reaction time, more contact between cadmium ion with the functional groups in the adsorbent structure (adsorption sites) is provided and the adsorption rate increases, which is consistent with the results of the study of Gupta and Nayak [40]. Cadmium removal efficiency also increased with increasing pH to about 5 and then decreased, which is consistent with the results of the study of Shekari et al. [41]. In the study of Shekari et al. [41], the pH for cadmium removal from aqueous solutions was in the range of 3–9. The results showed that the highest cadmium removal efficiency was obtained at pH = 5, and at pH more than 5, removal efficiencies had

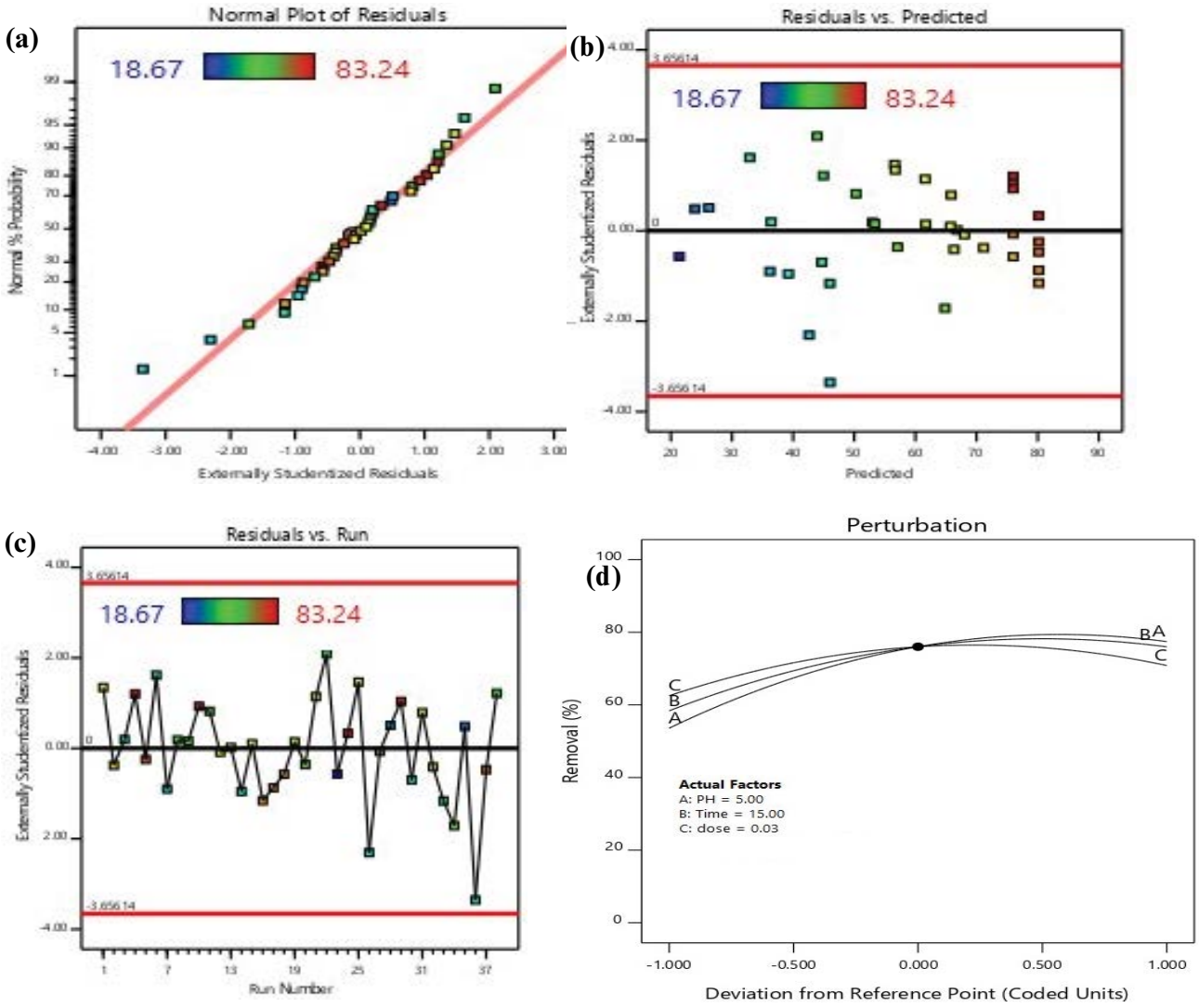

Fig. 3. (a) Normal probability distribution of residuals, (b) residuals vs. predicted, (c) externally studentized residuals vs. run, and (d) perturbation plot for Cd removal, respectively.

a descending trend. At pH above 6, the OH^- anions of the environment increase, which leads to their competition with the adsorbent for the adsorption of cadmium ions, and thus the rate of cadmium adsorption by the adsorbent decreases [42].

3.3. Optimization using desirability functions

To discover the specific point that can improve the desirability function, the numerical optimization of the software was selected. The intended goal was chosen by changing the weight of importance, which may change the characteristics of the goal. Five points including none, maximum, minimum, target, and within range were considered the goal fields for the response. The criteria for optimizing the studied factors related to removal percentage included pH (in range), contact time (in range), adsorbent dose (in range), and cadmium removal (maximize). Employment of this desirability function with all pre-selected goals for each factor could facilitate the assumption of the specific value for all responses; its results are shown in Fig. 4. It was observed that the software can optimize 81.5% removal of cadmium through the calculation of the optimized model factors, for example, pH of 5.0, contact time of 15.0 min, and nickel metal-organic framework dose of 0.03 g. Finally, duplicate confirmatory experiments were used to validate them by the optimized parameters. It was detected that results are narrowly linked to the data achieved from optimization analysis using desirability functions, which is representative of successful cooperation of CCD design and desirability functions in the optimization of the adsorption parameters for the removal of cadmium by used nickel metal-organic framework. In Table 4, the results of the experiments in optimal areas have been compared. Examination of the truthfulness of the desired conditions was done through DOE software using standard deviation for each response. Our results were also indicative

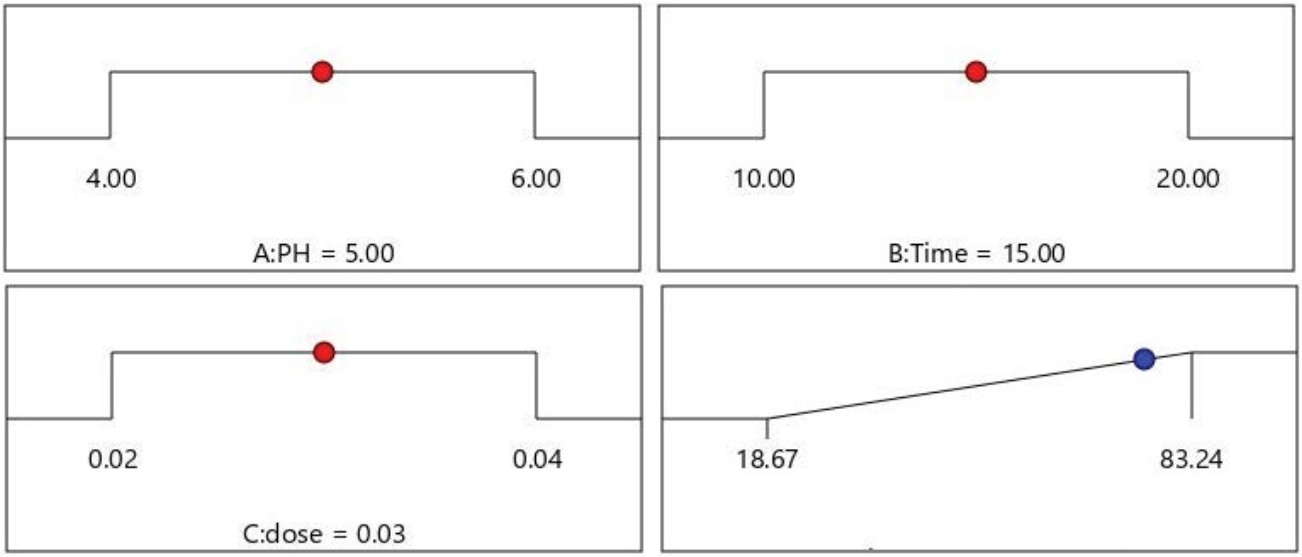

Fig. 4. Desirability ramp for numerical optimization of four selected goals.

Table 4
Verification of experimental results at optimum conditions

Optimum condition	Diazinon degradation (%)
Experimental results	78.68%
Model response	CI low: 65.81, CI high: 88.19
Error	5.87
Standard deviation	±5.47

of the remarkable vicinity of actual values to the predicted values of the model. Considering the response, the optimum region for the cadmium removal using nickel-metal organic framework was 81.5%.

3.4. Effect of independent variables

3.4.1. Effect of pH and contact time

The results of the study have been evaluated as interactions between non-numerical variables. Therefore, an interaction between the two factors is reported. If one factor acted on the other factor levels, the response is changed. The existence of this interaction indicated that factors would influence response independently and simultaneously. However, the simultaneous effects of factors on response were different from that of an independent factor on response [43,44]. Moreover, nonparallel lines and curved surfaces in the 3D diagrams indicated a strong interaction between the factors, and the nearly parallel x-shaped lines and curved surface showed weak interaction between them. According to the results of Fig. 5, the simultaneous effect of pH and contact time in a certain dose of nickel-based metal-organic frameworks show that cadmium removal rate increased with increasing solution pH and contact time under certain adsorbent dosage. Moreover, with increasing contact time, the nickel-based metal-organic framework shows higher removal efficiency in an aqueous medium. As it is evident, the removal rate is stronger, and therefore, contact time has a significant effect on cadmium removal on nickel metal-organic framework (Fig. 5a).

3.4.2. Effect of pH and adsorbent dose

According to the findings of the present study, the final concentration of cadmium decreased very rapidly with increasing pH, but it decreased very slowly with further increasing pH up to 5. Adsorption efficiency decreased at pH above 5. In fact, the competition between hydroxide ion present in the solution and adsorbent sites for cadmium metal ion deposition actually creates metal-organic framework bonds, which resulted in a steady-state in the metal present in the solution and it, in turn, reduces metal transfer to the adsorbent and reduces adsorption efficiency [45]. Therefore, it can be said that the binding of metal ions by the functional group is strongly affected by pH; thus, the pH of the aqueous solution is a very important parameter in the adsorption process. Determination of optimum pH for adsorption of metal ions is dependent on the type of ion and adsorbent used. The effect of this parameter is directly dependent on the ability of the hydrogen ions to compete with the adsorbent ion on the active sites of the adsorbent surface. Fig. 5b shows the effect of pH and adsorbent dose in constant time for a nickel-based metal-organic framework adsorbent. With an increase in pH and adsorbent does during a specific time of adsorption, cadmium removal is decreased. However, the increase is more significant for contact time, and the variation curve will be subsequently in saddle form. Additionally, the increase in adsorption dose to some extent will result in increasing cadmium removal efficiency. It has been also observed that increasing the adsorbent dose in the aqueous solution increased the concentration gradient between the liquid and solid mass, which results in an increase in the rate of mass transfer and cadmium removal in an aqueous medium (Fig. 5b).

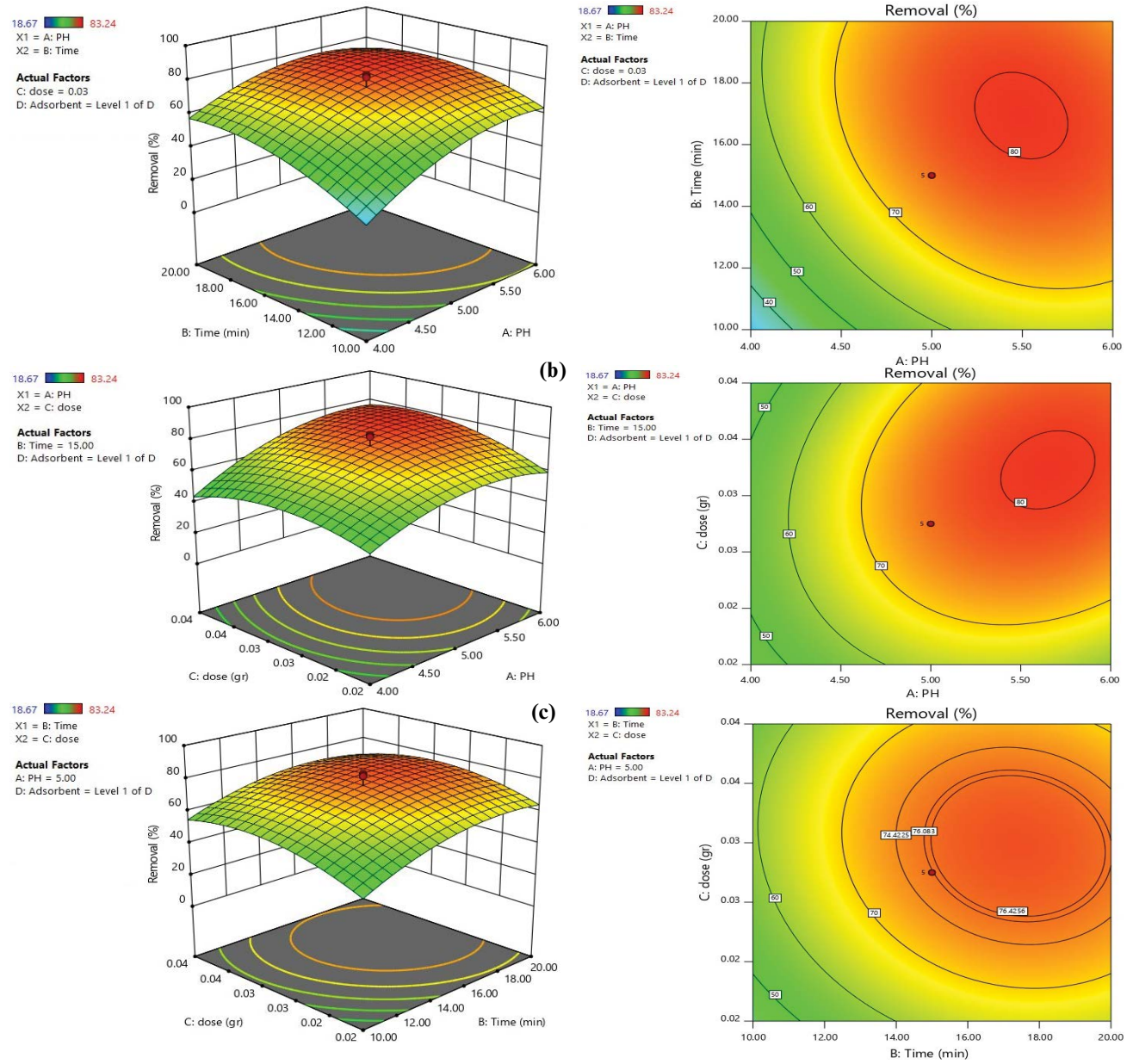

Fig. 5. 3D plots and counterplots for Cd removal using adsorption process: effects of (a) pH and time, (b) adsorbent dose and pH, and (c) adsorbent dose and time.

3.4.3. Effect of contact time and adsorbent dose

The adsorbent dose has been viewed as an important parameter in adsorption, and the determination of optimal adsorbent amount will reduce wastewater treatment cost and pollution, and sludge [45]. In cadmium ion adsorption by nickel metal-organic framework, the gradual increase in adsorbent reduces the secondary concentration of cadmium ion, and subsequently, adsorption efficiency is increased. Of course, a further increase in adsorbent is accompanied by cadmium removal rate increase but this increase takes place with less asleep and speed, and the further adsorbent increase will not result in more efficiency. It can be said that the reason for increased efficiency with increasing adsorbent dose is that more sites are available for adsorbent [45]. However, more adsorbent causes active sites of adsorbent to experience a small degree of overlap. Subsequently, it reduces the number of active sites. An increase in adsorbent concentration results in an increase in the number of unsaturated sites. Another reason for the decrease in adsorption capacity or decrease in percentages of cadmium removal from the aqueous medium is a reduction in the contingency of adsorbent collision with an adsorbate. The contingency was due to the aggregation of adsorbent which eventually reduces the surface area and increases the energy distribution path length [46]. As shown in Fig. 4c, with the increase in adsorbent dose and contact time at a constant pH, the cadmium removal rate of

the nickel-based metal-organic framework is constantly increased. However, the increase is more noticeable for time changes at a specific pH. Meanwhile, the removal efficiency is increased with the adsorbent dose. According to this figure, at a particular pH, cadmium removal variation range is changed with contact time changes, and as the contact time increases, it increases steadily, which indicates the contact time factor is more significant than the adsorbent dose (Fig. 5c).

3.5. Isotherm studies

According to the results, the cadmium ion adsorption process on the adsorbent surface is divided into slow and fast categories, where the first phase is slowly carried out for metal ion internal penetration. In the second stage, which occurs more rapidly, the active bonding groups are located in the cell wall of the adsorbent particles. Thus, the high initial adsorption speed is due to surface bonds established between these active groups and metal ions, and over time, reducing the frequency of active sites slows down the rate of metal adsorption. Furthermore, the quick phase of metal ion adsorption by desired adsorbents is the result of a lot of pores and cavities and the structure of pores existing in adsorbent, which allows rapid penetration for metal adsorption on binding sites [47]. Therefore, in heavy metals adsorption, the efficiency is decreased with an increase in contact time. In the next stage, the goal was to find the model which describes experimental data behaviors, and to this end, Freundlich and Langmuir isotherm models were used to explain adsorbent–adsorbate behavior. According to Fig. 6, the equilibrium experimental data under the conditions including pH of 5, a contact time of 15 min, adsorbent dose of 0.03 g, and temperature of 25°C showed great consistency with a relatively high correlation coefficient on the linear form of Langmuir plot, and it can be argued that Langmuir isotherm is a suitable model to describe cadmium adsorption mechanism on the adsorbent. On the other hand, it indicates that Langmuir isotherm governs the homogenous distribution of active sites on nickel metal-organic framework and monolayer coverage of cadmium ion on the surface.

In addition, according to Fig. 7, equilibrium experimental data in laboratory conditions, for example, pH of 5, a contact time of 15 min, adsorbent dose of 0.03 g, and temperature of 25°C showed acceptable agreement with a good correlation coefficient on Freundlich linear plot. Therefore, it can be concluded that the Freundlich isotherm is a suitable model to describe the cadmium adsorption mechanism on the nickel-based metal-organic framework. Table 5 shows the data for the Freundlich and Langmuir isotherms for the modified adsorbent. The results showed that the isotherms data for the modified adsorbent follows the Langmuir isotherm. R^2 values for the adsorption of cadmium ion by modified sorbent for Freundlich and Langmuir isotherm were 0.8379 and 0.9182, respectively.

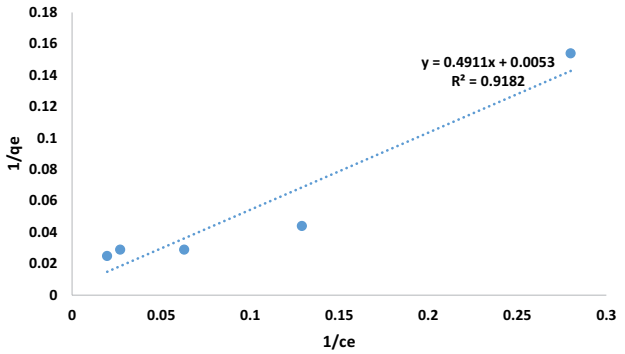

Fig. 6. Langmuir isotherm model with experimental data for cadmium ion adsorption on the nickel-based metal-organic framework.

3.6. Kinetic studies

To kinetically study the metal ions adsorption on the different adsorbents, 25 mL of cadmium solution with 5 mg/L concentration and pH = 5 was dissolved with 0.03 g of different adsorbents, and the mixture was stirred for 1–25 min. Then, the sample suspension was centrifuged, and the amount of cadmium ion adsorbed on the adsorbent was calibrated. The speed of metal ions adsorption was measured based on kinetic equations of pseudo-first-order (Eq. (6)) and pseudo-second-order (Eq. (7)) [48–50].

$$\ln\left(q_e - q_t\right) = \ln\left(q_e\right) - k_1 t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e t} \tag{7}$$

One of the most important factors to design an adsorption system is the prediction of the adsorption speed process controlled by system kinetics. Adsorption kinetics

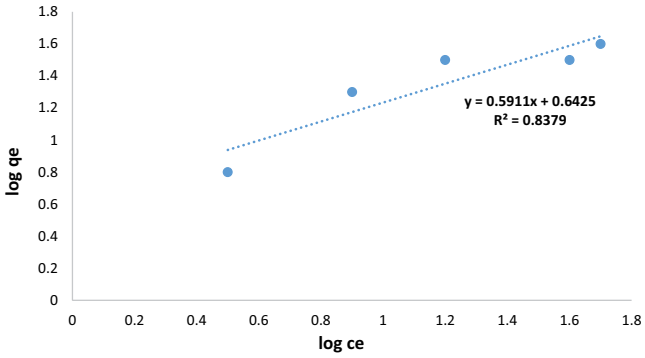

Fig. 7. Freundlich isotherm model with experimental data of cadmium adsorption on the nickel-based metal-organic framework.

Table 5
Isotherm models parameters for cadmium ion adsorption onto nickel-based metal-organic framework

Langmuir isotherm				Freundlich isotherm		
R^2	q_e	K_L	R_L	R^2	K_f	n
0.9182	39.33	0.088	0.5	0.8379	5.67	1.94

Table 6
Data used for kinetic analysis of pseudo-first-order and second-order to adsorb cadmium on nickel-based metal-organic framework

Kinetics	Time (min)	1	3	5	6	10	15	20	25
Pseudo-first-order	$\log(q_e - q_t)$	0.19	0.71	0.65	0.61	0.38	0.35	0.19	0.003
Pseudo-second-order	t/q_t	0.19	0.32	0.63	0.82	1.04	1.54	1.86	2.31

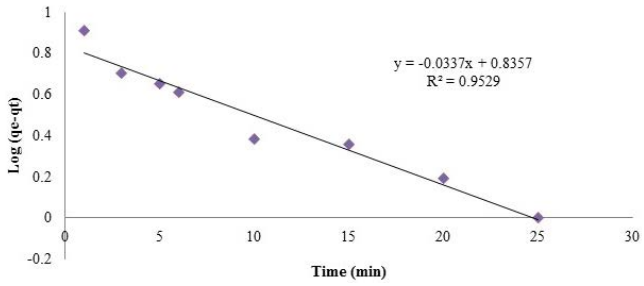

Fig. 8. Pseudo-first-order kinetic model with experimental data using the nickel-based metal-organic framework in 25°C, pH = 5 for cadmium ion.

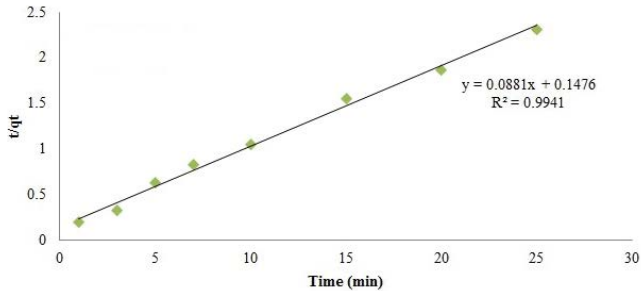

Fig. 9. Pseudo-second-order kinetic model with experimental data using the nickel-based metal-organic framework in 25°C, pH = 5 for cadmium ion.

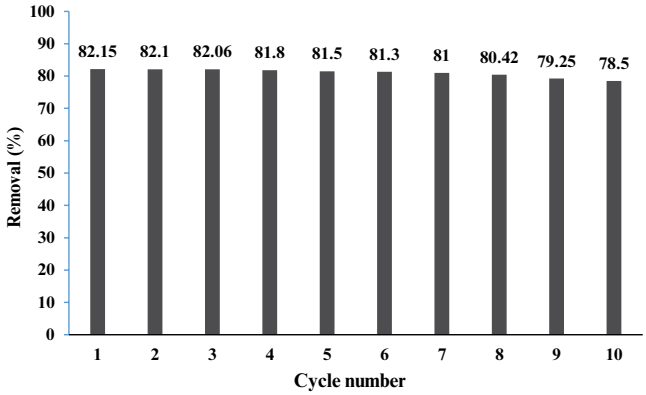

Fig. 10. Recyclability performance of the nickel-based metal-organic framework for removal of cadmium ion (pH = 5.0, time = 15.0, and adsorbent dose = 0.03 g).

depends on the physical and chemical properties of adsorbent substance and adsorbent which affect the adsorption mechanism. Given the results of pseudo-first-order kinetics based on the Langmuir equation, it has been indicated that experimental data with pseudo-first-order kinetics are not completely overlapped. On the same line, therefore, they have a lower correlation coefficient (Figs. 8 and 9). As it is shown in Fig. 9, pseudo-second-order kinetics, given the equation, displays better performance for cadmium ion adsorption on different adsorbents. Additionally, experimental data are aligned on one line and show a higher correlation coefficient. Thus, it can be concluded that the adsorption is carried out chemically, and it follows pseudo-second-order kinetics. Actually, pseudo-second-order kinetics is able to explain different factors including liquid components penetration, adsorption, and internal penetration of particles. Therefore, it improves our understanding of the cadmium absorption mechanism by the adsorbent. The data needed to investigate the pseudo-first-order and second-order kinetics for the adsorption of cadmium metal ions on the nickel metal-organic framework are presented in Table 6.

3.7. Recyclability performance of the adsorbent for the adsorption of cadmium ion

The recyclability performance of an adsorbent is an important parameter to evaluate the application of the adsorbent. The re-use of the nickel metal-organic framework adsorbent in the adsorption of cadmium ion was tested by continuous adsorption experiments under the determined optimum operating parameters by using RSM-CCD. The process mentioned above was repeated 10 times under the same conditions to determine the recyclability performance of the adsorbent. The removal efficiency of cadmium ion was investigated consecutively to determine the reusability of the adsorbent (Fig. 10). As shown in Fig. 10, after 10 times reuses of adsorbent, the removal efficiency of cadmium ion was reduced by only about 3.0%. As a result, the nickel metal-organic framework adsorbent exhibited excellent reproducibility for cadmium ion adsorption, indicating its potential for practical application.

4. Conclusion

In this study, the nickel metal-organic framework was employed to investigate the removal of cadmium heavy metals in aqueous solutions. The results demonstrated that the application of metal-organic frameworks can be a useful method for the adsorption of these heavy metals from wastewater and contaminated water. A direct relationship was observed between the factors including pH, adsorbent dose, and type of adsorbent and with adsorption efficiency. The better adsorption efficiency is obtained at higher solution pH. The optimum values for the studied variables were pH of 5, adsorbent dose of 0.03 g/L, and contact time

of 15 min. The studied adsorbent could provide a removal efficiency of 76.5%. The ANOVA of the results obtained from different models revealed that a quadratic model was chosen to estimate the removal of cadmium by the adsorption process using the nickel metal-organic framework adsorbent. The linear regression coefficient (R^2) between experiments and different response values in the model was 0.91 for cadmium. The studied adsorbent for the removal of cadmium followed the Langmuir isotherm and the pseudo-second-kinetics. According to the results, the adsorption process can be an effective process for the removal of metal ions, for example, cadmium.

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