

Article

Multivariate optimization of high removal of lead(II) using an efficient synthesized Ni-based metal–organic framework adsorbent

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ABSTRACT

A new metal–organic framework (MOF) with the chemical formula of $[\text{Ni}_2\text{F}_2(4,4'\text{-Bipy})_2(\text{H}_2\text{O})_2](\text{VO}_3)_2 \cdot 8\text{H}_2\text{O}$ was introduced to adsorb Pb(II) with the highest capacity. The sorbent was characterized by thermogravimetric analysis (TGA), infrared spectroscopy (FT-IR), field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray (EDX), and elemental analysis. The optimum conditions were obtained by a face-centered central composite design (FCCD) as follows: adsorbent dosage (m) = 1.2 mg, initial concentration of Pb(II) (C) = 390 $\text{mg} \cdot \text{L}^{-1}$, and pH = 5. According to the Langmuir model ($R^2 = 0.9999$), the maximum monolayer uptake capacity of lead(II) is 2400.7 $\text{mg} \cdot \text{g}^{-1}$, which is the highest observed amount for lead(II) adsorption. Neither of the old adsorbents for lead(II) has the uptake capacity over 2000 $\text{mg} \cdot \text{g}^{-1}$. The model of pseudo-second-order describes well the process kinetics. The adsorption process of lead (II) is independent of temperature changes. This compound can adsorb lead (II) from tap water. In addition to introducing a new MOF with the highest uptake capacity for removal of Pb(II) that is the outright novelty of this study, the concurrent modeling of both the removal percent (R) and the uptake capacity (q) is another important advantage. Because it achieves the more economical and favorable optimum conditions in comparison with the single optimization of each response.

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1. Introduction

The heavy metals include the harmful ions like cadmium(II), nickel(II), mercury(II), copper(II), arsenic(V), chromium(III), manganese(II), zinc(II), and lead(II) [1–6]. Since large amount of these ions are released to the natural water sources by industries and mining activities annually, the clean and fresh water sources are decreasing [2,7]. Lead is a toxic and carcinogenic heavy metal, which gets released to the environment via mining and industries activities such as batteries, steel, and explosive products. Since lead can cause severe damages to the health of humans and other livings, its removal from water is a critical environmental challenge [5,8,9]. Among the decontamination methods of Pb(II), the adsorption method is a simple and low cost way which needs an economical and suitable adsorbent [2,10–13]. According to the studies performed, some compounds can adsorb lead, such as MOF-800 [7], sodium carboxymethyl cellulose-based adsorbent (CMC-PAMA) [14], COF-TE [15], MOF-2(Cd) [16], mesoporous conjugated adsorbent (MpCA) [17], UiO-66-RSA [18], water-soluble Fe_3O_4 nanoparticles [19], BAC@SiO₂-EDTA [20], and Ni-Fe-CO₃ LDH-NGO [21]. However, neither of them has the uptake capacity over 2000 $\text{mg} \cdot \text{g}^{-1}$.

MOFs, abbreviated of metal–organic frameworks, are a new group of crystalline porous compounds composed of metal ions and bridging organic ligands, which are excellent adsorbents to remove heavy metal ions, including lead [22–26]. The sonochemical method, a fast and facial technique, employs ultrasonic waves for the synthesis of MOFs, which have a smaller size in comparison with the solvo/hydrothermal methods [27–30]. MOFs are usually utilized for the adsorption-based separation and determination applications due to their valuable properties, such as diverse structures, tunable topologies, and porosity in the nanoscale [24,31]. For the first time, synthesis of $[\text{Ni}_2\text{F}_2(4,4'\text{-Bipy})_2(\text{H}_2\text{O})_2](\text{VO}_3)_2 \cdot 8\text{H}_2\text{O}$ as a new MOF was reported [32]. According to the proposed structure (Fig. 1), each fluoride connects between two Ni ions. The coordinative positions of the Jahn–Teller active nickel(II) ions are occupied by two bridging fluorides and four 4,4'-Bipy ligands. Two anionic VO_3^- balance the charge of the Ni^{2+} ions. Furthermore, there are two coordinated H_2O . So far, this MOF only was employed for the Congo red dye adsorption with a high capacity of 242.1 $\text{mg} \cdot \text{g}^{-1}$ [32]. In this study, it was used as an excellent adsorbent for the removal of lead(II) that is the outright novelty of this study.

Multivariate optimization is a statistical and economical approach for attaining optimum conditions for removal of lead [33]. It finds the relationship between response and effective factors with consideration of the interactions among the variables [33–36]. Therefore, the removal

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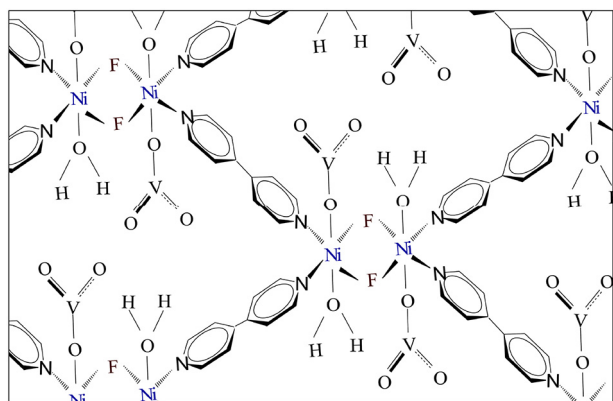


Fig. 1. Propounded chemical structure for $[\text{Ni}_2\text{F}_2(4,4'\text{-Bipy})_2(\text{H}_2\text{O})_2](\text{VO}_3)_2 \cdot 8\text{H}_2\text{O}$ [32].

conditions were optimized using a face-centered central composite design (FCCD). Equilibrium and kinetic behavior of introduced sorbent with lead(II) were also taken into consideration in details.

2. Materials and Methods

2.1. Materials

Merck company's nickel(II) acetate tetrahydrate ($\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$), sodium fluoride (NaF), ammonium monovanadate (NH_4VO_3), 4,4'-bipyridine ($\text{C}_{10}\text{H}_8\text{N}_2$), sodium hydroxide (NaOH), nitric acid (HNO_3), and lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$) were used without further purification (Merck group; Darmstadt, Germany). Double distilled water is employed as the solvent for the preparation of all solutions. Costech instrument ECS 4010 elemental analyzer, Alpha Bruker spectrometer, MIRA3 XM microscope, and Perkin Elmer instrument technology SII are employed for elemental analysis, FT-IR, FESEM and EDX, and TGA, respectively.

2.2. Synthesis and characterization

The MOF of $[\text{Ni}_2\text{F}_2(4,4'\text{-Bipy})_2(\text{H}_2\text{O})_2](\text{VO}_3)_2 \cdot 8\text{H}_2\text{O}$ was synthesized according to the previous experience (yield of 60%) [32]. 26 ml of the 4,4'-bipyridine (1 mmol) and NaF (1 mmol) aqueous solution was slowly added to 52.5 ml of the nickel(II) acetate (1 mmol) and NH_4VO_3 (1 mmol) aqueous solution with adding speed of a drop per second in the ultrasonic bath (Metason HT200; frequency = 50 Hz and output power = 140 W). The pale green precipitate was produced, which was dried in ambient temperature after the washing with double distilled water. The synthesis procedure was repeated over 30 times, and the resulting precipitates were mixed for the adsorption applications. The FT-IR spectra were obtained using the KBr pellets. To calculate the free H_2O molecules of the sample before TGA, a little MOF was heated in an oven at about 95°C for 1 h. The TGA was done from 30 to 900°C at a $15^\circ\text{C} \cdot \text{min}^{-1}$ heating speed of under an atmosphere of N_2 .

2.3. Removal of lead

In a generic experiment (Fig. 2), $m(\text{g})$ of the adsorbent was mixed with a $V(\text{L})$ volume of lead(II) solution, possessed of $C(\text{mg} \cdot \text{L}^{-1})$ concentration and a specific pH by a reciprocating shaker (OS 2 basic-Yellow line) at 300 min^{-1} for 20 min. After separation of the adsorbent by a centrifuge, the Pb(II) concentration (C_e) was measured by flame atomic absorption spectrophotometer (PG990 Instruments) in the separated solution. The percent of removal (R) and Pb(II) equilibrium uptake capacity (q or $q_e (\text{mg} \cdot \text{g}^{-1})$) were calculated using the equations

of $R = 100 \times [(C - C_e)/C]$ and $q = (C - C_e)V/m$. The uptake capacity at a specific time (q_t) are calculated using the second equation.

2.4. Optimization using FCCD

The preliminary experiments (Fig. S1) detected that sorbent dosage (m), initial concentration of Pb(II) (C), and pH are three effective factors to remove lead. The FCCD was performed using Minitab 17.0 and Design Expert 7 software. The FCCD is a type of central composite design (CCD), which its star points stay at center of the cubic faces ($\alpha = \pm 1$). This design considers low (-1), middle (0), and high ($+1$) levels for each factor [34]. In this study, the number of experiment (N) needed to perform FCCD is 16. It is calculated from $N = 2^k + 2k + C_p$ equation, where C_p and k are the replicate number at the center point and the efficient factors number, respectively [34]. The k and C_p values are equal to three and two, respectively.

2.5. Adsorption process studies

Both isotherm and kinetics of the Pb(II) adsorption process were studied under the optimal conditions. The determination coefficient (R^2), the nonlinear chi-square (χ^2), and the normalized standard deviation (Δq) data showed the most compatible models (kinetics and isotherm) with experimental data [37–41]:

Their equation follows as:

$$R^2 = \frac{\sum (q_{e,\text{meas}} - \bar{q}_{e,\text{cal}})^2}{\sum ((q_{e,\text{meas}} - \bar{q}_{e,\text{cal}})^2 + (q_{e,\text{meas}} - q_{e,\text{cal}})^2)} \quad (1)$$

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e,\text{meas}} - q_{e,\text{cal}})^2}{q_{e,\text{cal}}} \quad (2)$$

$$\Delta q = \sqrt{\frac{\sum [(q_{e,\text{meas}} - q_{e,\text{cal}})/q_{e,\text{meas}}]^2}{n-1}} \quad (3)$$

$$\bar{q}_{e,\text{cal}} = \sum q_{e,\text{cal}} / n \quad (4)$$

where n , $q_{e,\text{meas}}$, $q_{e,\text{cal}}$ are the data number, the measured and calculated q_e , respectively. Both χ^2 and Δq values close to zero and the R^2 value close to 1.0 are indicators to detect the more agreeable model.

3. Results and Discussion

In the current study, the novel $[\text{Ni}_2\text{F}_2(4,4'\text{-Bipy})_2(\text{H}_2\text{O})_2](\text{VO}_3)_2 \cdot 8\text{H}_2\text{O}$ metal–organic framework was synthesized via an organic solvent-free method. It was employed for Pb(II) adsorption.

3.1. Characterization analyses

As demonstrated in Fig. 3, the following results confirm the adsorbent structure in a good agreement with reported results elsewhere [32].

The illustration of FESEM (Fig. 3(a)) shows the morphology of the adsorbent particles. The data of elemental analysis, N: 6.60, C: 29.14, and H: 4.68%, are close to their theoretical amounts (N: 6.62, C: 28.40, and H: 4.29%). The EDX analysis also confirms the elements of Ni, F, V, N, C, and O in the adsorbent structure (Fig. 3(b)). As shown TGA curve (Fig. 3(c)), three steps of weight loss were observed: First, 5.11% within 201°C (loss of coordinated H_2O molecules), second, 16.62% within $201\text{--}439^\circ\text{C}$ (elimination of C_6H_4 and 2F^-), and third, 32.84% within $439\text{--}990^\circ\text{C}$ (removal of $\text{C}_{14}\text{H}_{12}\text{N}_4$). The TGA data is consistent with the reported MOF [32]. The FT-IR spectra of adsorbent and Pb(II)-loaded adsorbent are illustrated

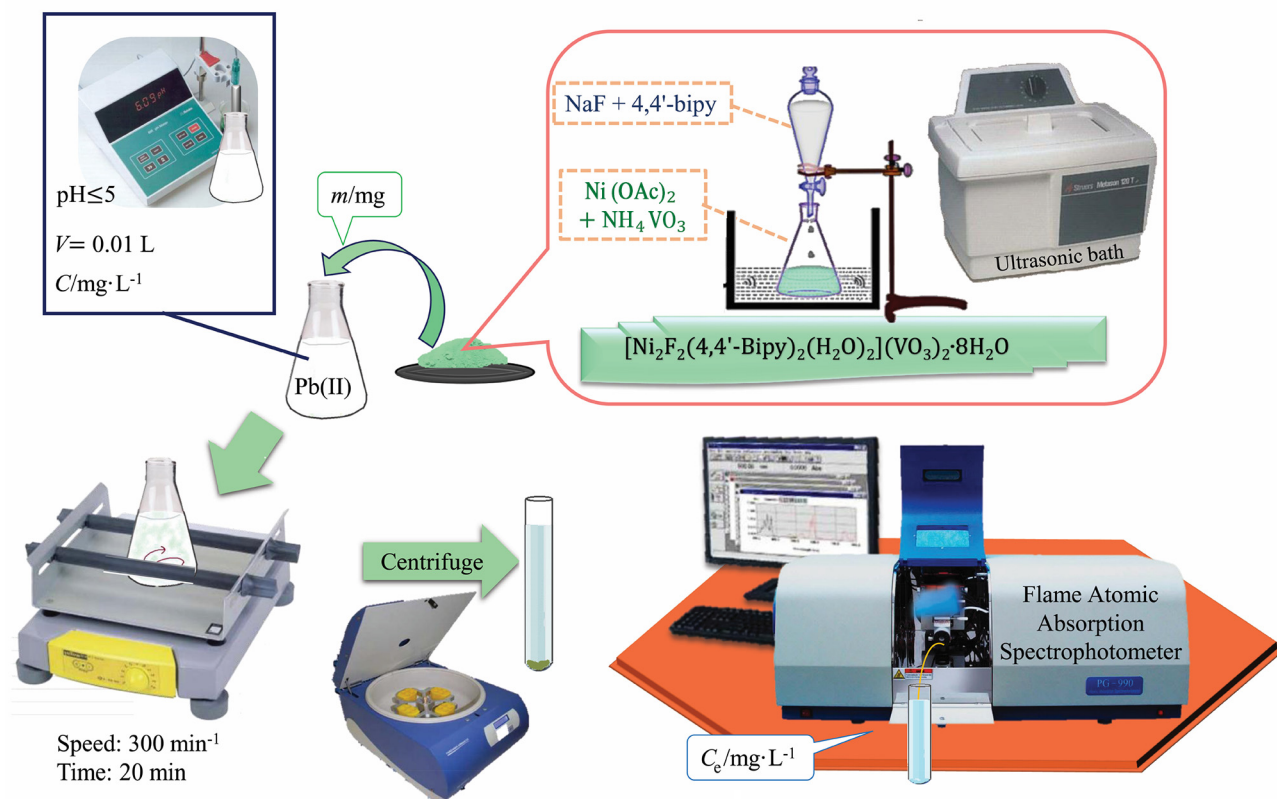


Fig. 2. Procedure of Pb(II) adsorption process.

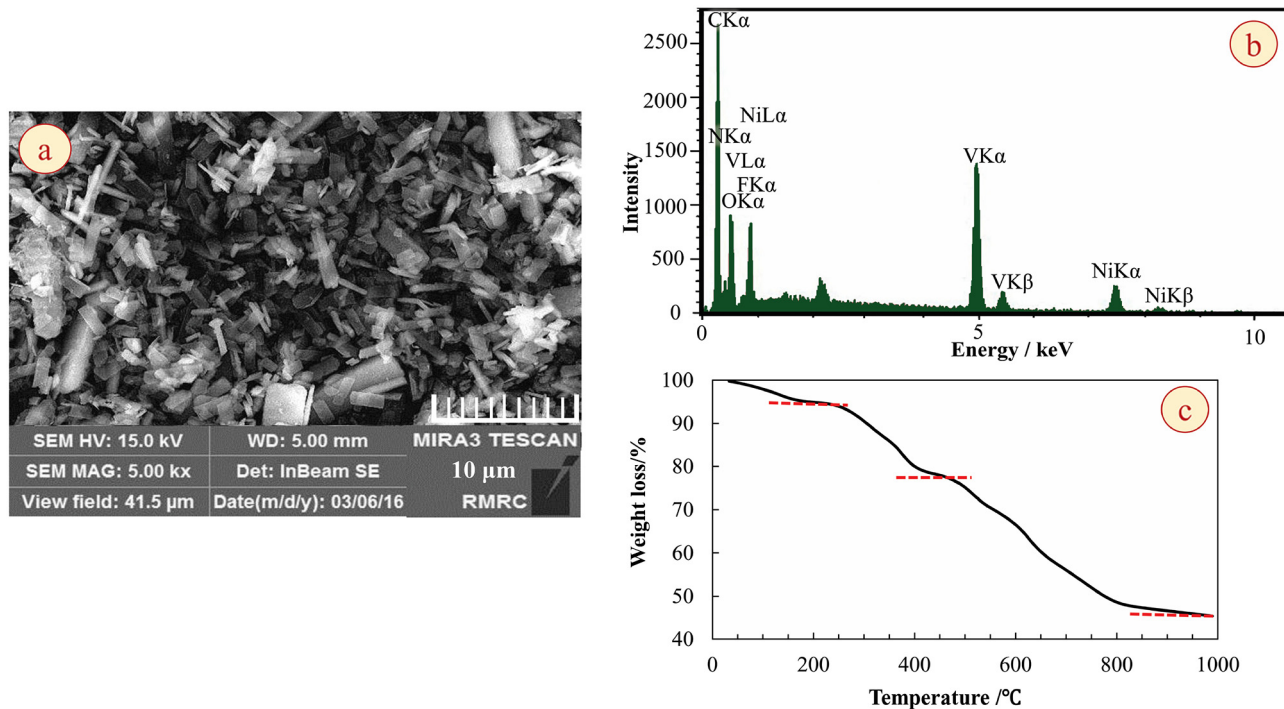


Fig. 3. FE-SEM image (a), EDX spectrum (b), and TGA plot of the as-prepared adsorbent(c).

in Fig. 4. The peaks assignment of the adsorbent FT-IR spectrum (Fig. 4(a)) are listed in Table 1 [32,42–44].

The FT-IR spectrum of the adsorbent loaded with Pb(II) was used to determine the nature of interaction between functional groups of the

adsorbent and Pb(II). In Fig. 4(b), the peak of 581 cm⁻¹ is related to Pb-O stretching vibrations. Furthermore, the intensity of Ni-O peak has decreased. Therefore, it can result in an interaction between the electron pairs of oxygens of the ligand with unoccupied orbitals of Pb(II) ions.

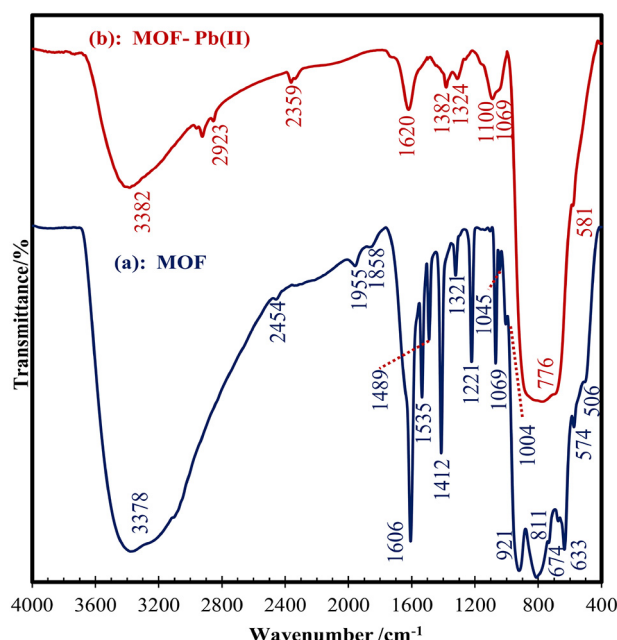


Fig. 4. The FT-IR spectra of the pristine adsorbent (a) and loaded Pb(II) onto adsorbent (b).

Table 1
Assignment of peaks in the adsorbent FT-IR spectrum^①

Peak/cm ⁻¹	Related to	Result
3000–3500	Stretching vibration of hydrogen-bonded H-O groups	Coordinated and crystallized H ₂ O molecules
811	Bending vibration (out-of-plane (oop)) of H-C bondings in aromatic rings of para substitution	4,4'-Bipyridine ligand has been connected to a metal of Ni by its side nitrogen
1858 and 1955	Aromatic rings of para substitution	
574	Ni-N vibration	
1606, 1412, 1535, and 1221	Stretching vibration of C=C, C=N, and C-N bondings in bipyridine	
1321 and 1069	Bending vibration of C-H of aromatic rings	
633, 674, and 921	V-O and V=O stretching vibration	VO ₃ ⁻ and water molecules have been connected to a metal of Ni by its oxygen
506	Ni-O vibration	

^① (Fig. 4(a)).

3.2. Optimization of the removal conditions

According to previous performed experiences (Fig. S1), adsorbent dosage ($m/0.5$ – 2.5 mg or 0.0005 – 0.0025 g), initial concentration of Pb(II) ($C/200$ – 800 mg·L⁻¹), and pH/3–5 were selected as factors that affect the R and q of Pb(II). Fig. S1(a) shows that lead adsorption process is independent of temperature changes. The pH and m factors have positive effect on R , while the C factor negatively affects R [40]. These effects play inverse role for q . The Pb(II) ions precipitate when pH increases above 6 [26]. As shown in Fig. S1(c), both R and q values increase when the solution pH raises. This is due to the increase of negatively charged sites on the MOF surface, which leads to enhancement of Pb(II) adsorption caused by electrostatic attraction [45].

According to the FCCD design (Table 2), 16 experiments were performed in a random order. Either R or q was fitted to a model with an appropriate regression analysis.

These models were obtained by optimal Box-Cox approach via natural log-transformation [39,40]. According to Table 3, the m , C , and pH factors

Table 2
The face-centered central composite design (FCCD) for R and q

Standard order	Run order	Uncoded (coded) value			$R/\%$	$q/\text{mg} \cdot \text{g}^{-1}$
		m/mg	$C/\text{mg} \cdot \text{L}^{-1}$	pH		
1	5	0.5 (−1)	200 (−1)	3 (−1)	26.425	1057.00
2	8	2.5 (+1)	200 (−1)	3 (−1)	64.150	513.20
3	12	0.5 (−1)	800 (+1)	3 (−1)	11.900	1904.00
4	2	2.5 (+1)	800 (+1)	3 (−1)	21.025	672.80
5	16	0.5 (−1)	200 (−1)	5 (+1)	38.762	1550.50
6	4	2.5 (+1)	200 (−1)	5 (+1)	84.825	678.60
7	3	0.5 (−1)	800 (+1)	5 (+1)	18.525	2964.00
8	11	2.5 (+1)	800 (+1)	5 (+1)	35.319	1130.20
9	15	0.5 (−1)	500 (0)	4 (0)	22.819	2281.87
10	6	2.5 (+1)	500 (0)	4 (0)	44.938	898.75
11	10	1.5 (0)	200 (−1)	4 (0)	62.769	836.92
12	13	1.5 (0)	800 (+1)	4 (0)	23.862	1272.67
13	14	1.5 (0)	500 (0)	3 (−1)	31.025	1034.17
14	1	1.5 (0)	500 (0)	5 (+1)	41.512	1383.75
15	7	1.5 (0)	500 (0)	4 (0)	36.825	1227.50
16	9	1.5 (0)	500 (0)	4 (0)	37.581	1252.71

and the $m \times m$, $m \times C$, and $C \times C$ (just for q) interactions significantly affected on the R (%) and q values because of the P -value falls lower than 0.05. After refusing insignificant interaction terms from each suggested models, the resulting models are given as following based on uncoded factors:

$$\ln R = 2.541 + 0.9621 m - 0.001214 C + 0.1915 \text{ pH} - 0.1703 m^2 - 0.000190 m \times C \quad (5)$$

$$\ln q = 6.159 - 0.706 m - 0.003431 C + 0.1915 \text{ pH} + 0.1175 m^2 - 0.000002 C^2 - 0.000190 m \times C \quad (6)$$

For $\ln R$: $R^2 = 0.9919$, $R_{\text{adj}}^2 = 0.9878$, and $R_{\text{pred}}^2 = 0.9734$.

For $\ln q$: $R^2 = 0.9919$, $R_{\text{adj}}^2 = 0.9839$, and $R_{\text{pred}}^2 = 0.9636$

Since the lacks of fit of both models are not significant (0.188 for $\ln R$ model and 0.179 for $\ln q$ model), the Analysis of Variance (ANOVA) confirms the validity of both models (Table 3). For each model, the coefficients of determination (R^2) are close to 1 and also the normal distribution of residuals confirms the adequacy of the models [33,39,46]. To be sure from the validation of the models, the actual and predicted responses were compared [35,36]. It shows $r = 0.99$ correlations coefficient between both values (Table S1). Furthermore, the t -test of pair data confirms the prediction ability of the models. Because the difference between experimental and model values of both responses is not statistically significant (critical t -value > calculated t -value). This test was performed by the Data Analysis section of Excel software. Therefore, both models can satisfactorily predict the R and q . Hence, the required adsorbent amount can be determined for a certain concentration of lead to reach the desired result.

The response surface graphs were displayed in Fig. 5 for both responses of R and q versus m , C , and pH factors. They are obtained from varying two factors, while the third factor is kept constant at middle level [39,40,47]. These plots clearly show the interaction between effective factors.

Simultaneous optimization of both adsorption responses (R and q) is an advantageous strategy from economical and environmental viewpoint [39,40]. This can be done by using Derringer's desirability function (D). According to this, the geometric mean of the individual desirability value (d_i) which corresponds to each response should reach to 1.0000 and as a result the overall desirability (D) raises up to 1.0. This criterion is to optimize concurrent of R and q [35,36,48]. Therefore, the optimum conditions obtained from simultaneous optimization of

Table 3
ANOVA test for checking the adequacy of the models

Source	For $\ln R$					For $\ln q$				
	DF ^①	SS ^②	MS ^③	F-value	P-value	DF ^①	SS ^②	MS ^③	F-value	P-value
Model	5	3.79083	0.75817	244.13	0.000	6	3.12873	0.52146	153.59	0.000
Linear	3	3.65610	1.21870	392.42	0.000	3	2.97189	0.99063	291.78	0.000
m	1	1.26893	1.26893	408.60	0.000	1	2.01151	2.01151	592.46	0.000
C	1	2.02045	2.02045	650.59	0.000	1	0.59367	0.59367	174.86	0.000
pH	1	0.36672	0.36672	118.08	0.000	1	0.36672	0.36672	108.01	0.000
Square	1	0.10878	0.10878	35.03	0.000	2	0.13089	0.06545	19.28	0.001
$m \times m$	1	0.10878	0.10878	35.03	0.000	1	0.04049	0.04049	11.93	0.007
$C \times C$	1	0.12948	0.12948	38.14	0.000	1	0.12948	0.12948	38.14	0.000
Interaction	1	0.02594	0.02594	8.35	0.016	1	0.02594	0.02594	7.64	0.022
$m \times C$	1	0.02594	0.02594	8.35	0.016	1	0.02594	0.02594	7.64	0.022
Error	10	0.03106	0.00311			9	0.03056	0.00340		
Lack of fit	9	0.03085	0.00343	16.59	0.188 ^④	8	0.03035	0.00379	18.36	0.179 ^④
Pure Error	1	0.00021	0.00021			1	0.00021	0.00021		
Total	15	3.82189				15	3.15929			

^① Degree of freedom.

^② Sum of squares.

^③ Mean square.

^④ The lack of fit (LOF) of the model is not statistically significant (P -value > 0.05).

both adsorption responses (R and q) are $m = 1.2$ mg, $C = 390$ mg·L⁻¹, and pH = 5.

3.3. Adsorption process study: kinetics and isotherm

According to Table 4, three adsorption kinetic models were studied for the rate-controlling step determination. k_{id} , k_1 , and k_2 as the rate constants of the models were calculated from the slope of their relevant linear plots (Fig. S2(a–b)) [38,49]. In between first and second-order pseudo models, the experimental data obey the model that has the R^2 value close to one and q_e close to the experimental q_e . The data of Table 4 demonstrate the adequacy of the pseudo-second order model

to describe the experimental data. The chemisorption is probably the rate-controlling step if experimental data fit well with pseudo-second-order model [45,50]. Therefore, the removal process of lead(II) is more likely to be chemisorption. The kinetic of adsorption process is composed of three following steps:

1. External diffusion: The lead ions diffusion takes place across the liquid film surrounding the MOF particles.
2. Diffusion of intra-particle or internal diffusion (the first section of the plot of q_t against $t^{1/2}$ in Fig. S2(b)): Diffusion in the active sites or pores of the MOF.
3. The second section of the plot of q_t against $t^{1/2}$ in Fig. S2(b): The MOF adsorbs Pb(II) by its active sites.

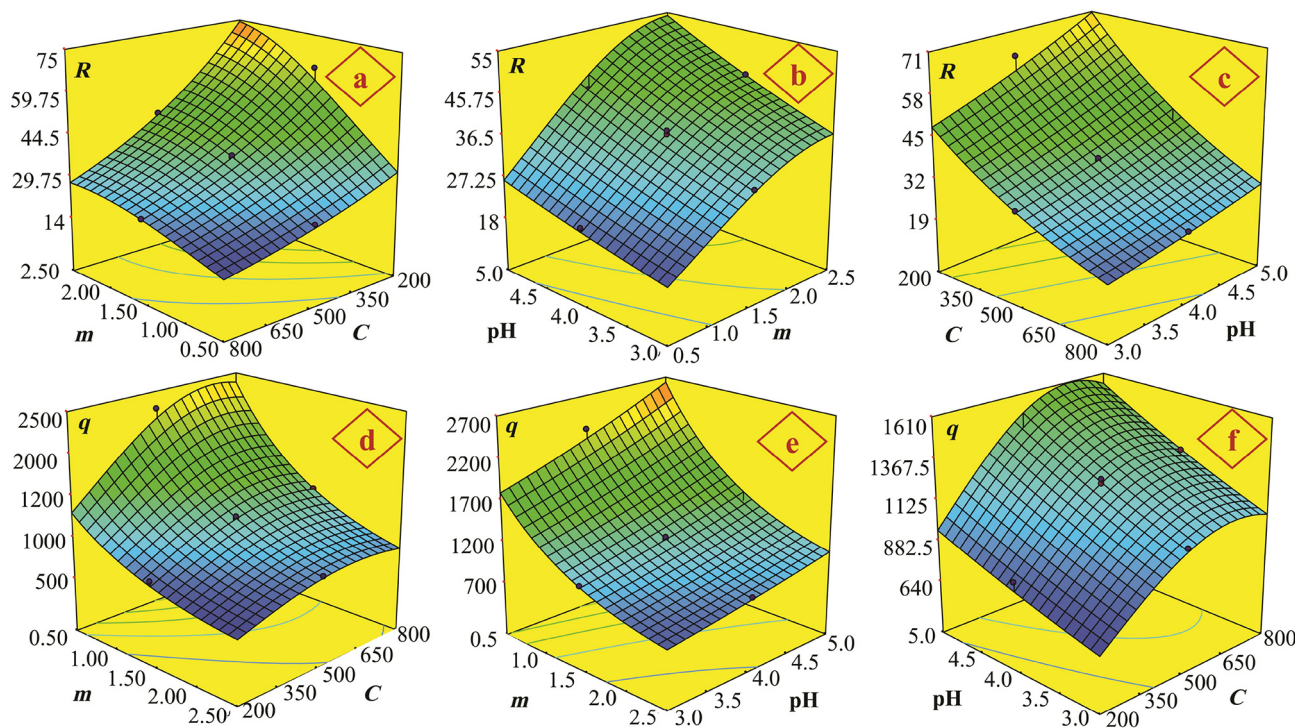


Fig. 5. Response surface plots showing effective factors and their mutual effects on removal percent (R) and uptake capacity (q) of Pb(II) removal while the other variables are kept constant at middle level; (a,d) the effect of adsorbent amount (m) and initial concentration of Pb(II) (C); (b,e) the effect of pH and amount of adsorbent (m); the effect of pH and initial concentration of Pb(II) (C); (c,f).

Table 4

The equations and parameters of kinetic models of pseudo-first-order, pseudo-second-order, and intra-particle diffusion

Kinetic model	Linear equation/plot	Parameters			R^2
		Rate constants	Calculated $q_e/\text{mg}\cdot\text{g}^{-1}$	Experimental $q_e/\text{mg}\cdot\text{g}^{-1}$	
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$ $\ln(q_e - q_t)$ versus t	k_1/min^{-1} 0.238	8869.7	1873	0.9066
Pseudo-second order	$t/q_t = t/(k_2 q_e^2) + t/q_e$ t/q_t versus t	$k_2/\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ 0.000119	2000	1873	0.9995
Intraparticle diffusion	$q_t = k_{id} t^{1/2} + Q$ q_t versus $t^{1/2}$	$k_{id}/\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$ 225.6	$Q/\text{mg}\cdot\text{g}^{-1}$ 743.1		0.9997

Table 5

Parameters of models of Langmuir, Freundlich, and Dubinin-Raduskovich isotherms

Isotherms	Equation	Parameters			R^2	χ^2	Δq
		$q_{\max}/\text{mg}\cdot\text{g}^{-1}$	$K_L/\text{L}\cdot\text{mg}^{-1}$				
Langmuir	Linear: $C_e/q_e = 1/(K_L q_{\max}) + C_e/q_{\max}$	2500.0	0.015	0.9981			
	Non-linear: $q_e = (q_{\max} K_L C_e)/(1 + K_L C_e)$	2400.712	0.014	0.9999	6.1163	0.0197	
Freundlich	Linear: $\ln q_e = \ln K_F + (1/n) \ln C_e$	$K_F/\text{mg}^{(1-1/n)}\cdot\text{L}^{1/n}\cdot\text{g}^{-1}$ 246.411	n 2.812	0.9392			
	Non-linear: $q_e = K_F C_e^{1/n}$	326.807	3.288	0.9311	112.2644	0.1145	
DR	Linear: $q_e = q_s \exp(-\beta \varepsilon^2)$	$q_s/\text{mg}\cdot\text{g}^{-1}$ 5424.6	$\beta/\text{mol}^2\cdot\text{kJ}^{-2}$ 4.00E-09	$E/\text{kJ}\cdot\text{mol}^{-1}$ 11.180	0.9627		
	Non-linear: $\ln q_e = \ln q_s - \beta \varepsilon^2$	4743.8	3.52E-09	11.898	0.9528	73.3640	0.0943

Note: $\varepsilon = RT \ln[1 + 1/C_e]$; $C_e/\text{mol}\cdot\text{L}^{-1}$; $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; $T = 298 \text{ K}$.

According to the above observation, internal diffusion is not only rate-controlling step because neither of linear segments of the plot passes through the origin (Fig. S2(b)) [39,51,52].

Three adsorption isotherms were investigated to determinate the adsorption equilibrium characteristics (Table 5). The linear and non-linear values of parameters were reported in Table 5 [37,38,53]. K_L , K_F , and β are the isotherms constant, $q_{\max}$ and q_s are the maximum uptake capacity ($\text{mg}\cdot\text{g}^{-1}$), and n and ε are the data number and Polanyi adsorption potential ($\text{J}\cdot\text{mol}^{-1}$), respectively [37,38]. These parameters were calculated by their relevant linear plots (Fig. S3) and the Solver of Excel software [47], where $q_{\max}$ and K_L are found from the linear plot between C_e/q_e and C_e (Fig. S3(a)); n and K_F from the linear plot between $\ln q_e$ and $\ln C_e$ (Fig. S3(b)); and β and q_s from the linear plot between $\ln q_e$ and ε^2 (Fig. S3(b)). The non-linear plots of these isotherms are also shown in Fig. S3(a).

Freundlich isotherm represents a multilayer, reversible, and non-desired adsorption, while Langmuir isotherm is formulated for single layer chemisorption of lead(II) on equal positions of the MOF [37,54]. Dubinin-Radushkevich (DR) isotherm is a useful model to recognize the type of adsorption mechanism [33,37]. The average adsorption free energy ($E/\text{kJ}\cdot\text{mol}^{-1}$) less than eight calculated from the $E = 1/\sqrt{2\beta}$ is representative of the physisorption. The free energy is found to be $E = 11.898 \text{ kJ}\cdot\text{mol}^{-1}$, therefore the mechanism is more likely to be chemisorption [33].

Consideration of R^2 , χ^2 , and Δq values (Fig. S3(a)) illustrates that the Langmuir isotherm is more in agreement with the empirical data (Table 5). According to all obtained results from adsorption isotherms studies, the Pb(II) adsorption is a monolayer, favorable, and reversible chemisorption process with a $q_{\max}$ of $2400.7 \text{ mg}\cdot\text{g}^{-1}$.

The uptake capacity ($q_{\max}$) values of the reported adsorbents for Pb(II) are listed in Table 6. It shows that this compound has a very higher $q_{\max}$ than the others reported elsewhere [7,14–21,55–66] and the utilization of synthesized MOF for lead(II) removal is promising and economical.

3.4. Real sample

To investigate efficiency of adsorbent at real sample, a Pb(II) solution of $390 \text{ mg}\cdot\text{L}^{-1}$ concentration at $\text{pH} = 5$ was prepared by tap

water. The solution was contacted by 1.2 mg of the adsorbent. The R for the lead(II) solution by tap water was obtained around 55%. It shows that this adsorbent has the good potential to remove lead from tap water as well.

Table 6

Comparison of the maximum monolayer uptake capacity of lead (II) onto various adsorbents

Adsorbents	$q_{\max}/\text{mg}\cdot\text{g}^{-1}$	Ref.
$[\text{Ni}_2\text{F}_2(4,4'\text{-Bipy})_2(\text{H}_2\text{O})_2](\text{VO}_3)_2\cdot 8\text{H}_2\text{O}$	2400.7^b	This work
MOF 800	170.74	[7]
PA808	119.9	[7]
PV808	85.95	[7]
F300	148.133	[7]
PA300	150.95	[7]
CMC-PAMA	840.11	[14]
COF-TE	185.7	[15]
MOF-2 (Cd)	769.23	[16]
Mesoporous conjugated adsorbent (MpCA)	192.2	[17]
UiO-66-RSA	191.6	[18]
Water-soluble Fe_3O_4 nanoparticles	96.8	[19]
BAC@SiO ₂ -EDTA	123.45	[20]
Ni-Fe-CO ₃ LDH-NGO	1945.3	[21]
MnO ₂ /CNTs	78.74	[55]
Treated granular activated carbon (AC-S)	29.44	[56]
Coconut-shell carbon (CSC)	26.50	[57]
Modified alkaline lignin (MAL)	79.9	[58]
Torrefied poplar-biomass	30	[59]
Mercaptoamine-functionalised silica-coated magnetic nanoparticles (MAF-SCMNPs)	292	[60]
NH ₂ -mag MCM-41	1665.295	[61]
Rape straw biochars oxidized with KMnO_4 (BC-Mn)	278.26	[62]
GO/SiO ₂ /Fe ₃ O ₄	333.3	[63]
Go-MnFe ₂ O ₄	673	[63]
Reduced GO/COFe ₂ O ₄	299.4	[63]
GO-EDTA	479	[63]
SiO ₂ -GNSs	113.6	[63]
Coir pith waste	263	[64]
ZnOmp-CSD matrix	70.42	[65]
Thiol-functionalized Fe_3O_4 @Cu ₃ (btc) ₂ microspheres	215.05	[66]

^b The value of $2400.7 \text{ mg}\cdot\text{g}^{-1}$ is the highest adsorption capacity for lead(II).

4. Conclusions

The results showed that the new MOF of $[\text{Ni}_2\text{F}_2(4,4'\text{-Bipy})_2(\text{H}_2\text{O})_2](\text{VO}_3)_2 \cdot 8\text{H}_2\text{O}$ acts as a very suitable adsorbent for lead(II). The adsorbent amount, initial concentration of Pb(II), and pH as the significant variables on the Pb(II) removal were optimized using FCCD. Their optimum conditions are $m = 1.2 \text{ mg}$, $C = 390 \text{ mg} \cdot \text{L}^{-1}$, and $\text{pH} = 5$. Based on all experimental evidences discussed in the current study, the introduced synthesized MOF has a great potential to be used as a sorbent to remove Pb(II) from water.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2020.08.011>.

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