Adsorption performance and response surface optimization of boron in desalinated seawater by UiO-66-NH$_2$

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**ABSTRACT**

Metal-organic framework UiO-66-NH$_2$ was studied as an adsorbent for effective boron removal from desalination seawater for the first time. First, UiO-66-NH$_2$ was synthesized using the solvo-thermal method and then characterized in terms of N$_2$ adsorption/desorption isotherms, zeta potential, scanning electron microscopy, X-ray diffraction, Fourier-transform infrared spectroscopy, and thermogravimetric analysis. Based on the experimental design of response surface methodology, the adsorption of boron on UiO-66-NH$_2$ was optimized using three independent variables: adsorbent dosage (60–80 mg/L), pH (5–7), and temperature (298–318 K). Under the optimized conditions, the maximum adsorption capacity was predicted to reach 24.54 mg/g. Investigation of the kinetics and isotherms revealed that the pseudo-second-order kinetics model and the Langmuir isotherm can well cover the adsorption data of boron. Thermodynamic parameters showed that the adsorption of boron by UiO-66-NH$_2$ is spontaneous and feasible. UiO-66-NH$_2$ also exhibits good reproducibility. It is a highly practical sorbent that can be used to remove boron from desalination seawater.

**Keywords:** UiO-66-NH$_2$; Boron adsorption; Response surface optimization; Kinetics; Thermodynamics; Isotherms

1. Introduction

With the increasingly serious problem of water pollution, the shortage of water resources has become increasingly prominent [1]. Many countries have invested in the study of seawater desalination and the establishment of seawater desalination plants [2]. Boron usually exists in the form of boric acid in seawater at a concentration of approximately 5–6 mg/L [3]. Since boron above a certain concentration will have a negative impact on people and plants, the World Health Organization stipulates that the limit of boron concentration in drinking water is 2.4 mg/L [4]. In irrigation water, the maximum allowable boron concentration ranges from 0.3 to 1 mg/L, according to various national regulations [5,6]. Therefore, the concentration of boron after desalination affects the use of desalinated seawater to a certain extent. Common desalination methods have difficulty removing boron effectively because its amount in untreated seawater is small and uncharged [7]. Among many desalination techniques, reverse osmosis is the preferred method. A single-stage reverse osmosis membrane can reduce the boron concentration in an osmotic solution to approximately 0.9–1.8 mg/L [3,8]. This is not enough to reduce the concentration of boron to a safe level, however, making it necessary to further remove boron from desalinated seawater.
At present, several methods have been developed to remove boron from water bodies, such as reverse osmosis, adsorption, electrocoagulation, ion exchange, and chemical coagulation [9–12]. Although these methods show a positive effect on boron removal, some drawbacks such as the high operating costs and limited absorption of boron at low concentrations limited their practical applications in the desalination of seawater. Among these techniques, adsorption is one of the most promising due to its low cost, good absorption of boron, and easy regeneration [10,13]. There have been many studies of different boron removal adsorbents, including natural minerals [14], chelating resins [15], and nanometer materials [16]. One of the most representative boron adsorbents is amberlite IRA-743, produced by the Rohm and Haas Company (United States). Its adsorption capacity is approximately 10 mg/g, and it is widely used in commercial applications [17]. This amount of boron adsorption capacity is not enough for desalinated seawater, however. In order to improve the efficiency of boron removal and reduce the cost, a new adsorbent with a greater adsorption capacity is urgently needed.

Metal-organic frameworks (MOFs) are porous materials with network structures, which can be formed by organic ligands and metal ions and create complex metal ligands by self-assembly [18]. MOFs materials have unique performance advantages, such as controllable pore size, modified pore surface, low density and high surface area. Therefore, this new type of porous material has been widely used in many fields, including gas purification, gas separation, gas storage, energy storage and photocatalysis [19–23]. In recent years, MOFs have been drawn more attention in water treatment due to their large specific surface area, adjustable channel, and ease of modification [24]. According to the existing research, it has shown good performance in many fields such as the treatment of antibiotics, dyes, heavy metal and radionuclides [25–29]. Among them, UiO-66-NH2, has attracted widespread attention due to its strong heat resistance and chemical stability, various preparation methods, and ease of modification [30]. Currently, UiO-66-NH2, has been investigated for the removal Pb(II) [30], Cr(VI) [31], and methylene blue [32] from water. UiO-66-NH2, also has the potential to remove boron from desalinated seawater, although no related research has yet been reported.

The primary objective of this study was to evaluate the adsorption properties of boron on UiO-66-NH2. This study analyzed the isothermal, kinetic, and thermodynamic characteristics of boron adsorption. The optimization of removal procedures, as well as the determination of the experimental variables (pH, adsorbent dosage, temperature) and their interactions, were investigated using response surface methodology.

2. Materials and methods

2.1. Materials

The primary chemicals utilized in this study were all pure and of analytical grade, and the experimental water was deionized. Zirconium tetrachloride (ZrCl4) and 2-aminothrephthalic acid (H2BDC-NH2) were purchased from the Shanghai Aladdin Shenghua Technology Co., Ltd., (Shanghai, China), N,N-dimethylformamide (DMF), methanol, nitric acid (HNO3), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from the Nanjing Chemical Reagent Co., Ltd., (Nanjing, China).

2.2. Preparation of UiO-66-NH2

UiO-66-NH2 was solvothermal synthesized based on the method of Rui et al. [19]. Zirconium chloride (ZrCl4, 0.772 g) and 2-aminothrephthalic acid (H2BDC-NH2, 0.556 g) were dissolved in DMF (80 mL). The mixture was then transferred to a 100 mL polytetrafluoroethylene-lined stainless steel autoclave and heated for 24 h at 393 K. The mixture was cooled to room temperature, and the yellow powder was obtained by centrifugation at 4,000 rpm. After washing 3 times with DMF and methanol, the powder was immersed in 80 mL of methanol solution and treated in a reactor at 373 K for 12 h. UiO-66-NH2, was obtained by centrifuging the solution with methanol and drying it in a vacuum oven at 373 K for 12 h.

2.3. Characterization methods

The Brunauer–Emmett–Teller (BET) specific surface area, pore size distribution, and pore volume were examined using a fully automatic specific surface area and pore size distribution meter (Micromeritics, ASAP2020 HD88, USA). The sample was measured for the nitrogen adsorption/desorption isotherm at 77 K after degassing at 323 K for 24 h. The specific surface area was estimated using the BET equation. The pore size was estimated using the density functional theory (DFT) method. The high-resolution images of UiO-66-NH2 after gold coating were captured using a field emission scanning electron microscope (JEOL, JSM-7600F, Japan). The accelerating voltage was 20 kV, and the images were taken at 10,000× magnification. The crystalline structure of UiO-66-NH2, was determined by the X-ray diffraction (XRD) pattern on an X’Pert diffractometer (Rigaku, Ultima IV, Japan) with Cu-Kα radiation at a scanning speed of 0.02°/s and a temperature of 27°C, ranging from 5°C to 80°C. The chemical components of UiO-66-NH2, were analyzed using Fourier-transform infrared spectroscopy (FTIR) (Thermo Scientific, Nicolet iS5, USA), by taking 32 scans from 400 to 4,000 cm−1 with a resolution of 2 cm−1 using the potassium bromide pellet technique. Thermogravimetric (TG) analysis was performed using a thermal analyzer (TA, Q500, USA). Experiments were carried out under an N2 atmosphere (30 mL/min flow rate) at a heating rate of 10°C/min from room temperature to 800°C. The particle size and zeta potential of UiO-66-NH2, were analyzed with a laser particle size analyzer (Malvern, ZS90, UK). The zeta potential determination procedure was as follows: 0.1 g of UiO-66-NH2, was placed in 100 mL of pure water and shaken. The pH was adjusted to 4, 5, 6, 7, 8, 9, and 10 with HCl and NaOH. The prepared UiO-66-NH2, suspension was allowed to stand for 5 min, and the zeta potential was then measured.

2.4. Adsorption experiments

Plastic equipment was used throughout the experiment in order to avoid the effects of boron on the glass
equipment. Boric acid was prepared as a stock solution in deionized water, and 50 mL of the desired concentration of boron was mixed with UiO-66-NH2. Afterward, the pH was adjusted with 0.1 M NaOH and HNO3 solution, and the mixture was spun at 160 rpm for a specified time. Next, the mixture was filtered using a 0.22 μm filter, and the supernatant was collected. The remaining boron concentration was determined using inductively coupled plasma mass spectrometry (PE, NeXion 300X, USA).

The effect of pH on the boron adsorption capacity of UiO-66-NH2 was examined for a wide range of pH values (4, 5, 6, 7, 8, 9, and 10). In this experiment, the initial adsorbate concentration, adsorbent dose, contact time, and temperature were controlled at 2 mg/L, 60 mg/L, 420 min, and 27°C, respectively. The effect of adsorbent dose on the boron adsorption capacity of UiO-66-NH2 was studied at adsorption doses of 40, 60, 80, 100, and 120 mg/L. In this experiment, the adsorbate concentration, temperature, contact time, and pH were controlled at 2 mg/L, 27°C, 420 min, and 6, respectively.

The adsorption capacity [Eq. (1)] and the percent removal [Eq. (2)] of boron were determined as follows:

\[
q = \frac{(C_0 - C_t)}{m} \times V
\]

\[
\% \text{Removal of boron} = \frac{C_0 - C_t}{C_0} \times 100
\]

where \(C_0\) is the initial boron concentration (mg/L), \(C_t\) is the boron concentration at equilibrium (mg/L), \(V\) is the volume of solution (L), \(m\) is the mass of UiO-66-NH2 (g), and \(q\) is the adsorption capacity (mg/g).

2.5. Adsorption kinetics

In order to evaluate the adsorption kinetics of boron on UiO-66-NH2, the effect of contact time on the boron adsorption capacity of UiO-66-NH2 was studied at 10, 20, 30, 40, 50, 60, 120, 240, 360, and 420 min. In this experiment, the initial adsorbate concentration, adsorbent dose, temperature, and pH were controlled at 2 mg/L, 60 mg/L, 27°C, and 6, respectively. The pseudo-first-order [Eq. (3)], pseudo-second-order [Eq. (4)], and intraparticle diffusion [Eq. (5)] were applied to fit the experimental data. In addition, the accuracy of these models was evaluated by determining the nonlinear coefficient \(R^2\).

The adsorption time (minutes), \(k_1\) is the rate constant (min\(^{-1}\)), \(k_2\) is the second-order rate constant (g/mg min\(^{1/2}\)), \(k_p\) is the intraparticle diffusion rate constant (mg/g min\(^{1/2}\)), and \(C\) is the boundary layer thickness.

2.6. Adsorption isotherm

In the study of the adsorption isotherm, the initial concentration of boron ranged from 50 to 2,000 mg/L. The contact time, adsorbent dose, temperature, and pH in this experiment were controlled at 420 min, 60 mg/L, 27°C, and 6, respectively. Langmuir [Eq. (6)] and Freundlich [Eq. (7)] models were used to fit the experimental data. In addition, the accuracy of these models was evaluated by determining the nonlinear coefficient \(R^2\). The equations can be expressed as follows:

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}
\]

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

where \(C_e\) is the equilibrium concentration (mg/L), \(q_e\) is the amount adsorbed at equilibrium (mg/g), \(q_m\) is the maximum concentration corresponding to a monolayer (mg/g), \(K_L\) is the Langmuir adsorption constant (L/mg), \(K_f\) is the Freundlich constant (mg/g(L/mg)\(^{1/n}\)), and \(n\) is the heterogeneity factor denoting the adsorption intensity.

2.7. Adsorption thermodynamics

Adsorption experiments were carried out at 27°C, 37°C, and 47°C in order to evaluate temperature effects. The thermodynamic parameters of the adsorption process such as Gibbs free energy change (\(\Delta G\)), enthalpy change (\(\Delta H\)), and entropy change (\(\Delta S\)) can be calculated as follows:

\[
\Delta G = -RT \ln K
\]

\[
\Delta G = \Delta H - T \Delta S
\]

where \(R\) is the ideal gas constant (8.314 J/mol K), \(T\) is the absolute temperature (K), and \(K\) is the adsorption equilibrium constant obtained from the isotherms that have a better fitting parameter. The \(\Delta H\) and \(\Delta S\) values were obtained from the slope and intercept of the plot of \(\Delta G\) vs. \(T\).

2.8. Recycling of UiO-66-NH2

The used UiO-66-NH2 was stirred in 1 M HCl for 6 h at 27°C. Next, the UiO-66-NH2 was washed 3 times with methanol and then dried in a vacuum at 80°C for 12 h. The regenerated UiO-66-NH2 was reused for boron adsorption experiments and characterized using XRD and scanning electron microscopy (SEM). In this recycling experiment, the initial adsorbate concentration, adsorbent dose, contact time, pH, and temperature were controlled at 2 mg/L, 60 mg/L, 420 min, 6, and 27°C, respectively.
2.9. Optimization model with response surface methodology

Response surface methodology (RSM) is a set of mathematical and statistical techniques that are based on the establishment of polynomial equations for experimental data [33]. The equations must describe the behavior of datasets in order to make statistical predictions [34]. There were 3 parameters in this study: adsorbent dosage \((X_1)\), pH \((X_2)\), and temperature \((X_3)\). Their randomized trials were run under the guidance of the Design-Expert version 8 (DX8) program (Table 1). The “response” of the model was the adsorption capacity \((Y)\). Based on the interaction between independent parameters, the mathematical expression of boron adsorption on UiO-66-NH\(_2\) was established and expressed as a second-order polynomial equation, as shown in Eq. (10):

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j
\]

where \(Y\) is the predicted response, and \(X_i\) and \(X_j\) are the independent variables \((i, j = 1, 2, 3, 4, \ldots, k)\). The parameter \(\beta_0\) is the offset coefficient, \(\beta_i\) is the linear coefficient, \(\beta_{ii}\) is the second-order coefficient, and \(\beta_{ij}\) is the interaction coefficient.

3. Results and discussion

3.1. Characteristics of UiO-66-NH\(_2\)

The XRD pattern of the prepared UiO-66-NH\(_2\) (Fig. 1a) exhibited the same diffraction peaks and intensity as...
previously reported [35]. The sharp diffraction peaks demonstrated that it has good crystallinity. The small differences in peak strength were due to changes in sample size and crystal orientation [36,37]. The SEM image of the prepared UiO-66-NH$_2$ at 10,000× magnification (Fig. 1b) revealed that it has a smooth surface and a clear cubic structure. Fig. 1c shows the corresponding curves of the pore size distribution (inset) for UiO-66-NH$_2$. UiO-66-NH$_2$ exhibited strictly type I isotherm with a predominantly microporous structure [38]. This is because the line type of the type I isotherm has a micropore filling feature characterized by a rapid rise in the adsorption volume at low relative pressures, followed by a flat phase before finally reaching a limit [39,40]. The specific surface area, pore-volume, and micropore volume of UiO-66-NH$_2$ are 831 m$^2$/g, 0.239 cm$^3$/g, and 0.217 cm$^3$/g, respectively. As shown in the FTIR spectra (Fig. 1d) of UiO-66-NH$_2$, the synergistic effect of the carboxyl group and Zr$^{4+}$ is shown by the vibration peaks at 1,572 and 1,655 cm$^{-1}$ [41]. The peaks at 1,482 and 1,382 cm$^{-1}$ can be attributed to N-H bending vibration and C–N stretching vibration, respectively [42,43]. The symmetric and asymmetric stretching vibrations of N–H are at 3,351 and 3,459 cm$^{-1}$, respectively [32]. These characteristic peaks prove that the synthesis of UiO-66-NH$_2$ is effective.

3.2. Effect of adsorbent dose on UiO-66-NH$_2$

The relationship between the adsorption capacity of UiO-66-NH$_2$ for boron and the adsorbent dosage is shown in Fig. 3a. As the dosage increased from 40 to 60 mg/L, the amount of boron adsorbed by UiO-66-NH$_2$ increased rapidly to 20.75 mg/g. This was mainly due to the increase of effective adsorption sites with an increase in adsorbent dosage. However, the amount of boron adsorbed by UiO-66-NH$_2$ tended to remain constant as the dosage increased to 120 mg/L. This may be due to the decrease of the concentration gradient between the adsorbate in solution and the adsorbate on the adsorbent surface, which leads to difficulties in aggregation and diffusion of adsorbate sites [46]. Given these results, 60 mg/L was used as the fixed absorbent dose in this study.

3.3. Effect of pH on UiO-66-NH$_2$

The change in the boron adsorption capacity of UiO-66-NH$_2$ at different initial pH values is shown in Fig. 3b. Obviously, the adsorption effect of UiO-66-NH$_2$ on boron is good when the pH is between 4 and 6. UiO-66-NH$_2$ exhibited the best adsorption of boron at pH = 5, when it reached 20.65 mg/g. However, as the pH increased from 7 to 10, the
UiO-66-NH₂ boron adsorption capacity decreased gradually. This is because boron exists in the form of B(OH)₃ or B(OH)₄⁻ when the total concentration of boron is less than 25 mM [47]. When the pH value is between 4 and 6, boron mainly exists in the form of B(OH)₃. Therefore, the surface electrostatic effect of the adsorbent is not obvious. With the increase of pH from 6 to 10, B(OH)₃ gradually transforms into a B(OH)₄⁻ structure. The electrostatic repulsion between B(OH)₄⁻ and the negatively-charged adsorbent then results in the reduction of boron adsorption at high pH.

3.4. Effect of contact time and adsorption kinetics on UiO-66-NH₂

The effect of contact time on the adsorption of boron by UiO-66-NH₂ is shown in Fig. 4a. Since there were enough adsorption sites in UiO-66-NH₂ at the beginning of the adsorption test, the amount of boron adsorbed by UiO-66-NH₂ quickly reached 15.75 mg/g in the first 60 min. Following that, there was a slow adsorption process, which reached equilibrium by 420 min. This was due to the adsorption point saturation during the latter stages of the adsorption test. Under equilibrium conditions, the adsorption capacity of boron by UiO-66-NH₂ was found to be 20.75 mg/g.

In order to study the adsorption mechanism of boron on UiO-66-NH₂, the pseudo-first-order kinetic model (Fig. 4b) and the pseudo-second-order kinetic model (Fig. 4c) were introduced to investigate the adsorption process. The fitting data of the kinetic model are shown in Table 2. The R² value of the pseudo-first-order kinetic model was only 0.9569, indicating that the pseudo-first-order kinetic model is not suitable for the adsorption of boron by UiO-66-NH₂ [48]. In contrast, R² of the pseudo-second-order kinetic model was 0.9989, and the fitted qₑₒₓ was closer to the experimental qₑₒₓ. These results indicate that the adsorption kinetic model of boron on UiO-66-NH₂ conforms to the pseudo-second-order model [49]. The pseudo-second-order model assumes that the adsorption rate is controlled by chemical adsorption [13]. This chemical adsorption involves electron covalence or electron migration between adsorbate and adsorbent [50].

In order to further understand the diffusion mechanism, the intraparticle diffusion model (Fig. 4d) was used to analyze the dynamics. The intraparticle diffusion process consists of 3 steps: mass transfer, adsorption, and diffusion [51]. In this study, the adsorption process (stage 1) and the diffusion process (stage 2) were the main steps of intraparticle diffusion, since the mass transfer process was completed in a short time. The slope and correlation coefficient (R²) of the first and second stages were 2.3706 and 0.4144; 0.9944 and 0.9918, respectively. The adsorption rate of boron on the UiO-66-NH₂ pore was higher than that of the boron intraparticle diffusion in the particle. At the same time, the fitting line did not cross the origin, indicating that intraparticle diffusion was not the only rate control step.

3.5. Effect of initial concentration and adsorption isotherm on UiO-66-NH₂

The effect of initial concentration on the adsorption of boron by UiO-66-NH₂ is shown in Fig. 5a. It can be seen that the adsorption increases with increasing boron solution concentration from 2 to 100 mg/L. This can be explained by the fact that the initial increase of boron concentration provides a driving force for overcoming mass transfer resistance [52,53]. This phenomenon shows that UiO-66-NH₂ still exhibits a good adsorption effect on boron at high concentrations. Thus, UiO-66-NH₂ has potential applications in industrial boron removal.

The study of adsorption isotherms is helpful for understanding the interaction between adsorbates and adsorbents. The fitting curves of the Langmuir and Freundlich models are shown in Figs. 5b and c, respectively. The fitting parameters are listed in Table 3. Based on the correlation
coefficient ($R^2$), the Langmuir model can better describe the adsorption of boron on UiO-66-NH$_2$ than the Freundlich model. This indicates that the adsorption of boron on UiO-66-NH$_2$ is a monolayer [54]. The maximum adsorption capacity of UiO-66-NH$_2$ for boron was found to be 188.67 mg/g, demonstrating a high boron adsorption capacity.

### 3.6. Adsorption thermodynamics

The study of thermodynamics is helpful for understanding the type and mechanism of the adsorption process [55]. The calculated values of $\Delta G$, $\Delta H$, and $\Delta S$ are summarized in Table 4. The value of $\Delta G$ is negative and decreases with increasing temperature. This indicates that the adsorption of boron is spontaneous. The higher the temperature, the better the adsorption of boron by UiO-66-NH$_2$. The positive $\Delta H$ value indicates that the adsorption of boron by UiO-66-NH$_2$ is an endothermic process. The positive $\Delta S$ reveals that UiO-66-NH$_2$ has a good affinity for boron. At the same time, it also shows that the randomness of the solid–liquid interface increases during the adsorption process [56].

### Table 2

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3.7. Reusability of UiO-66-NH₂

In order to explore the reusability of UiO-66-NH₂, 3 successive cycles of adsorption experiments were performed. As can be seen in Fig. 6a, the adsorption amount of boron by UiO-66-NH₂ decreased by 6% after 3 cycles. This indicates that the adsorption of boron by UiO-66-NH₂ was still stable. The SEM and XRD diagrams of UiO-66-NH₂ after 3 regeneration cycles are shown in Figs. 6b and c, respectively. Compared with the original synthesis of UiO-66-NH₂, there was no significant change. This shows that regeneration has no obvious effect on the crystal structure of UiO-66-NH₂.

3.8. Optimization of the boron adsorption capacity of UiO-66-NH₂ by RSM

The Box–Behnken experimental design and results of UiO-66-NH₂ adsorption of boron are shown in Table 5. The experimental data were used to calculate the predictive response of the software. The quadratic polynomial relationship between the experimental response and the independent variable is shown in Eq. (11):

\[
Y = 22.71 + 1.72X_1 + 0.0053X_2 + 0.0655X_3 + 1.41X_1X_2 + 0.04X_1X_3 + 0.16X_2X_3 + 0.032X_1X_4 + 1.27X_1^2 + 0.4X_2^2 + 0.55X_3^2.
\]  

The synergistic efficiency of the analysis of variance data is listed in Table 6, including the sum of squares, degree of freedom, mean square, F-value, and P-value. The variance analysis results demonstrate that the F-value is high and acceptable, while the P-value is low and acceptable. This shows that the proposed quadratic model has statistical significance [57]. Fig. 7a presents the normal...
distribution of the internal research residuals for process response. From this linear profile, it can be seen that the variance did not change greatly, indicating that the prediction model has a high degree of fitting [58]. Fig. 7b shows the abnormal curve of boron adsorption on UiO-66-NH₂. It is not difficult to see that the residuals of the internally studentized data were randomly distributed in all experimental runs. All of the experimental data fell within the range of –2 to +2, and no abnormal values were detected. It can be concluded that the model prediction was accurate [59]. Fig. 8 shows the three-dimensional response surface, which reveals the uniform influence of the 3 factors on the boron adsorption efficiency of UiO-66-NH₂. Generally speaking, the increase of adsorbent dosage, the decrease of solution pH, and the increase of temperature are beneficial to the adsorption process of boron. This is consistent with the previous experimental results. Therefore, the optimum conditions for maximum boron adsorption are dosage > 80 mg/L, pH < 5, and temperature > 318 K. Based on the model, the following optimum conditions were obtained: adsorbent dosage = 75.49 mg/L, pH = 5.3, and temperature = 322.11 K. The predicted maximum adsorption capacity of boron was 24.54 mg/g. In order to verify the accuracy and confidence of the proposed optimization conditions, verification experiments were carried out using the above conditions. The experimental verification revealed that under the optimum conditions, the deviation between the predicted value and the measured value (25.13 mg/g) was 2.4%. This indicates that the optimization model of boron adsorption on UiO-66-NH₂ is highly compatible and can be used to design and optimize experimental conditions. A comparison of different boron adsorption materials is shown in Table 7. Obviously, UiO-66-NH₂ has a more prominent boron adsorption capacity.
Table 5
Results of Box–Behnken design on the adsorption of boron by UiO-66-NH$_2$

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<td>0</td>
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<tr>
<td>8</td>
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<td>–1</td>
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<tr>
<td>9</td>
<td>1</td>
<td>0</td>
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<tr>
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<td>0</td>
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<td>11</td>
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<td>1</td>
</tr>
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<tr>
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<td>0</td>
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<tr>
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<td>0</td>
</tr>
<tr>
<td>15</td>
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<td>–1</td>
</tr>
<tr>
<td>16</td>
<td>–1</td>
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<tr>
<td>17</td>
<td>–1</td>
<td>–1</td>
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Table 6
Analysis of variance data for the boron adsorption model

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Freedom degree</th>
<th>Mean square</th>
<th>F-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>50.99</td>
<td>9</td>
<td>5.67</td>
<td>800.86</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>$X_1$</td>
<td>23.53</td>
<td>1</td>
<td>23.53</td>
<td>3,325.77</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>$X_2$</td>
<td>1.87</td>
<td>1</td>
<td>1.87</td>
<td>264.61</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>$X_3$</td>
<td>15.99</td>
<td>1</td>
<td>15.99</td>
<td>2,260.00</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>$X_1$X$_2$</td>
<td>14.39</td>
<td>1</td>
<td>14.39</td>
<td>0.90</td>
<td>0.3732</td>
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<tr>
<td>$X_1$X$_3$</td>
<td>0.10</td>
<td>1</td>
<td>0.10</td>
<td>14.47</td>
<td>0.0067</td>
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<tr>
<td>$X_2$X$_3$</td>
<td>8.48</td>
<td>1</td>
<td>8.48</td>
<td>0.60</td>
<td>0.4649</td>
</tr>
<tr>
<td>$(X_1)^2$</td>
<td>6.80</td>
<td>1</td>
<td>6.80</td>
<td>961.77</td>
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<tr>
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<td>1</td>
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<tr>
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Table 7
Comparison of boron adsorption for different materials

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>pH</th>
<th>Temperature (K)</th>
<th>Time (h)</th>
<th>$C_0$ (mg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium-chitosan hydrogel bead</td>
<td>24.5</td>
<td>7</td>
<td>298</td>
<td>48</td>
<td>500</td>
<td>[60]</td>
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<tr>
<td>Modified activated carbon</td>
<td>1.5</td>
<td>8.5</td>
<td>298</td>
<td>4</td>
<td>60</td>
<td>[61]</td>
</tr>
<tr>
<td>CA@KH-550@EPH@NMDG</td>
<td>15.62</td>
<td>9.5</td>
<td>298</td>
<td>15</td>
<td>440</td>
<td>[62]</td>
</tr>
<tr>
<td>Few-layer hydrotalcite nanosheet</td>
<td>6.2</td>
<td>7–8</td>
<td>298</td>
<td>15</td>
<td>25</td>
<td>[63]</td>
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<tr>
<td>Pyrocatechol modified resin</td>
<td>4.54</td>
<td>9</td>
<td>298</td>
<td>12</td>
<td>22</td>
<td>[64]</td>
</tr>
<tr>
<td>Calcined magnesite tailing</td>
<td>36.3</td>
<td>6</td>
<td>318</td>
<td>7</td>
<td>67</td>
<td>[65]</td>
</tr>
<tr>
<td>UiO-66-NH$_2$</td>
<td>25.13</td>
<td>5.3</td>
<td>322</td>
<td>14.47</td>
<td>7</td>
<td>This study</td>
</tr>
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</table>
Fig. 7. (a) Internally studentized plot and (b) internally studentized plot vs. run plot.

Fig. 8. (a) Effect of adsorbent dose and pH on boron adsorption (temperature 308 K; adsorbate concentration 2 mg L⁻¹; contact time 480 min), (b) effect of adsorbent dose and temperature on boron adsorption (pH 6; adsorbate concentration 2 mg L⁻¹; contact time 480 min), and (c) effect of pH and temperature on boron adsorption (adsorbent dose 60 mg L⁻¹; adsorbate concentration 2 mg L⁻¹; contact time 480 min).
4. Conclusions

In this study, the adsorption behavior of boron in desalinated seawater by UiO-66-NH$_2$ was investigated. The RSM method was used for optimization. The optimum adsorbent dosage, pH, and temperature were found to be 75.49 mg/L, 5.3, and 322.11 K, respectively. Under these conditions, the model-fitting adsorption capacity of boron (24.54 mg/g) was close to the actual value (25.13 mg/g). The optimization model can thus be used to design and optimize experimental conditions. Kinetic and isotherm models revealed that the adsorption process follows the chemical adsorption and monolayer behavior mechanisms. The thermodynamic parameters demonstrated that the adsorption of boron by UiO-66-NH$_2$ is spontaneous and feasible. UiO-66-NH$_2$ has a higher adsorption capacity than amberlite IRA-743. In addition, it also exhibits good regeneration performance. UiO-66-NH$_2$ shows great potential for use in boron removal after seawater desalination.

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References


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