HIGHLY EFFICIENT ADSORPTION OF FLUORIDE FROM AQUEOUS SOLUTIONS BY METAL ORGANIC FRAMEWORKS: MODELING, ISOTHERMS, AND KINETICS

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ABSTRACT: High concentrations of fluoride in drinking water have adverse health effects for consumers. So, the aim of this study was to study the effectiveness of metal organic frameworks for fluoride adsorption. The adsorption process of fluoride using one of these novel adsorbents, known an Uio-66, was optimized using a central composite design. As-synthesized Uio-66 was characterized by XRD, FT-IR spectra, FE-SEM, EDX, and BET surface area. Furthermore, the variables of fluoride concentration, pH, adsorbent dose, and contact time were investigated. The findings showed that the maximum capacity of Uio-66 for fluoride adsorption was 31.09 mg g^{-1}. The experimental data of Uio-66 fitted well with the pseudo-second order model and the Langmuir I model. The findings also showed that Uio-66 adsorbent has a high capacity for fluoride adsorption and can be functionalized to enhance the adsorption capacity.

Keywords: Adsorption; Fluoride; Groundwater; Metal organic framework; Uio-66.

INTRODUCTION

One of the ions in drinking water is fluoride and by this route fluoride can be taken into the body.[1] A high concentration of fluoride in drinking water has become a critical health hazard for consumers. Ground water and food are the main sources of fluoride intake to the consumer's body.[2,3] A high fluoride intake may result in fluorosis with adverse effects including reduced IQ in humans,[4] abnormal behavior in animals, and long-term damage to the brain, liver, thyroid, and kidney.[5,6] So far, various adsorbents have been used for fluoride adsorption from potable water. Adsorbents such as modified zeolite,[7] activated alumina,[8] red mud,[9] bio-sorbents,[10] granular ceramic,[11] ferric poly-mineral,[12] acid activated kaolinite clay,[13] bentonite/ chitosan beads,[14] modified *Azolla* facilities,[15] and bone char[16] have been used in different places. Often, conventional adsorbents have a low capacity for fluoride adsorption. Recently, new adsorbents have been developed as metal organic frameworks (MOFs).[17] MOFs are classified as porous substances that are composed of a metal core and a ligand.[18,19] Thus, in this research, we investigated the effectiveness of Uio-66 for removing fluoride from ground waters and reviewed the underlying adsorption mechanism.

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MATERIALS AND METHODS

Materials: Zirconium chloride and terephthalic acid were obtained from Merck Company. N, N-dimethylformamide, and methanol were prepared by Sigma-Alderich. Whole reagents and solvents were used as received from the commercial suppliers without further purification.

Synthesis and preparation of Uio-66: First, UiO-66 was prepared via a modification of a reported procedure.[19,20] In a typical synthesis, $ZrCl_4$ $[Zr_6O_4(OH)_4(BDC)_6]$[21] (0.2332 g) and terephthalic acid (0.161 g) were dissolved in DMF solution (50 mL). Then, the solutions was transferred to a 100 mL Teflon autoclave. The autoclave was sealed and heated in an oven at 120ºC for 48 hours (two days) under constant pressure. After cooling, the final sample (a white powder) was washed three times with methanol. After washing, the white powder was dried in vacuum at 100ºC for 12 hours. After drying, the end product was obtained.

General characterization: The prepared UiO-66 was determined by x-ray diffraction, Fourier transform infrared spectroscopy spectra, field emission scanning electron microscopy, energy dispersive x-ray spectroscopy, and the Brunauer-Emmett-Teller surface area. The total pore volumes of the samples were revealed from nitrogen adsorption isotherms at 77 K.

Adsorption studies: In the study, all the tests were performed in batch conditions. The effect of variables such as pH, fluoride concentration, reaction time, adsorbent dose, and co-existing anions were investigated. At first, a stock solution of fluoride was made and stored under standard conditions (in a refrigerator). An absorbent dose was added to 50 mL of fluoride solution. At the end, the remaining adsorbent was separated from the solution by centrifugation (3000 rpm, 20 min). Then, the fluoride concentration was determined by a spectrophotometer (UV-UVIS)(SPAND method).[22] The experiments were done at room temperature (25±1ºC).[23]

Experimental design and statistical analysis: The response surface methodology (RSM) is a useful method to study the relationship between the response and the independent variables.[24,25] In the RSM class, a central composite design (CCD) model that is appropriate for fitting second order polynomial equations has been frequently discussed for optimizing several research problems.[26] Generally, the 30 runs (16 factorial points, 8 axial points, and 6 center points) as used as per the experimental design obtained from design expert software (Table 1). After accomplishing the experiments, the coefficients of the polynomial model were computed by equation 1:[27]

$$Y(\%) = a_0 + \sum_{i=1}^{n} a_{ii} X_i^2 + \sum_{i-1}^{n-1} \sum_{j=2}^{n} a_{ij} X_i X_j + e \qquad \text{Equation 1}$$

where: i = linear coefficient
j = quadratic coefficient
a_0 = constant coefficient
a_i = linear coefficient
a_n = interaction coefficient
a_{ij} = quadratic coefficient

Table 1. The experimental runs for fluoride adsorption by the central composite design (CCD) model

Run	F conc. (mg L^{-1})	pH	Dose (g L^{-1})	Time (min)	Residual conc. (mg L^{-1})	Removal efficiency (%)	Predicted value (%)
1	15	7	0.1	30	8.64	40	42.92
2	10	5	0.2	42.5	3.54	60	58.76
3	20	5	0.2	42.5	11.28	35	37.36
4	15	7	0.3	30	2.82	70	71.84
5	20	9	0.2	42.5	10.68	40	35.08
6	15	3	0.3	30	5.88	50	47.44
7	10	5	0.4	42.5	1.26	80	81.73
8	15	7	0.3	30	2.82	71	71.84
9	15	11	0.3	30	11.4	11	12.08
10	20	9	0.4	42.5	8.82	48	52.05
11	15	7	0.3	30	2.82	74	71.84
12	15	7	0.5	30	1.92	80	75.35
13	15	7	0.3	5	6.48	53	53.34
14	25	7	0.3	30	14.88	34	36.84
15	10	9	0.2	42.5	4.8	44	45.68
16	20	9	0.4	17.5	12.18	34	34.05
17	10	5	0.2	17.5	3.72	60	62.26
18	10	5	0.4	17.5	1.92	75	77.73
19	15	7	0.3	30	2.82	70	71.84
20	20	5	0.4	42.5	5.94	60	60.33
21	20	5	0.2	17.5	9.42	45	40.86
22	15	7	0.3	30	2.82	74	71.84
23	10	9	0.4	17.5	4.26	45	44.65
24	10	9	0.4	42.5	3.24	64	62.65
25	15	7	0.3	55	2.46	70	67.84
26	10	9	0.2	17.5	5.94	33	35.18
27	20	5	0.4	17.5	6.6	55	56.33
28	20	9	0.2	17.5	14.88	28	24.58
29	5	7	0.3	30	0.3	73	68.84
30	15	7	0.3	30	2.82	73	71.84

Equilibrium adsorption modeling: The isotherm models (Langmuir, Freundlich, and Tempkin) were used to specify the relationship between equilibrium capacity (q_e) and equilibrium concentration (C_e).[28-30] Adsorption kinetic models were applied to predict the adsorption mechanism of fluoride onto the Uio-66 adsorbent. To describe the fluoride adsorption, the pseudo first order, pseudo second order, Elovich, and intraparticle diffusion kinetic models were used.[23,31,32]

RESULTS AND DISCUSSION

Characterization of Uio-66: The as-synthesized Uio-66 was in the form of a white powder. The crystallographic structure of the synthesized Uio-66 was investigated by x-ray diffraction (XRD). Figure 1 shows the XRD pattern of the as-synthesized Uio-66. The XRD pattern of the Uio-66 adsorbent had two clear peaks at 7º and 8.45º [19]. The XRD pattern for the synthesized Uio-66 was identical to the reported XRD patterns.[20,33-35]

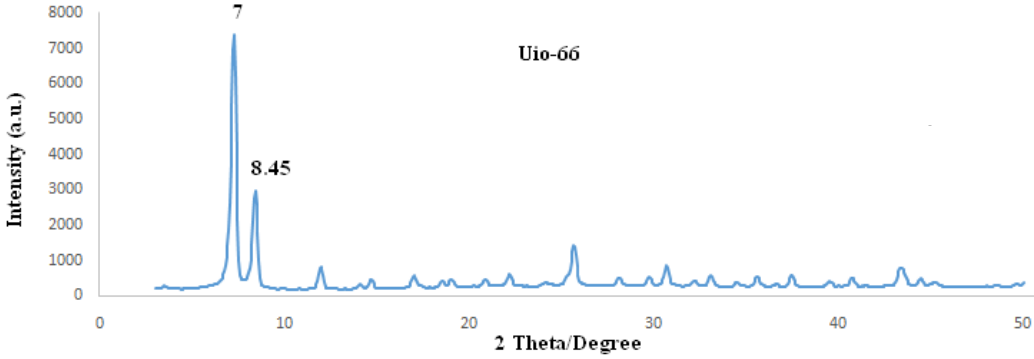

Figure 1. X-ray diffraction spectra of the as-synthesized Uio-66

The morphology of the synthesis Uio-66 is shown in Figure 2.

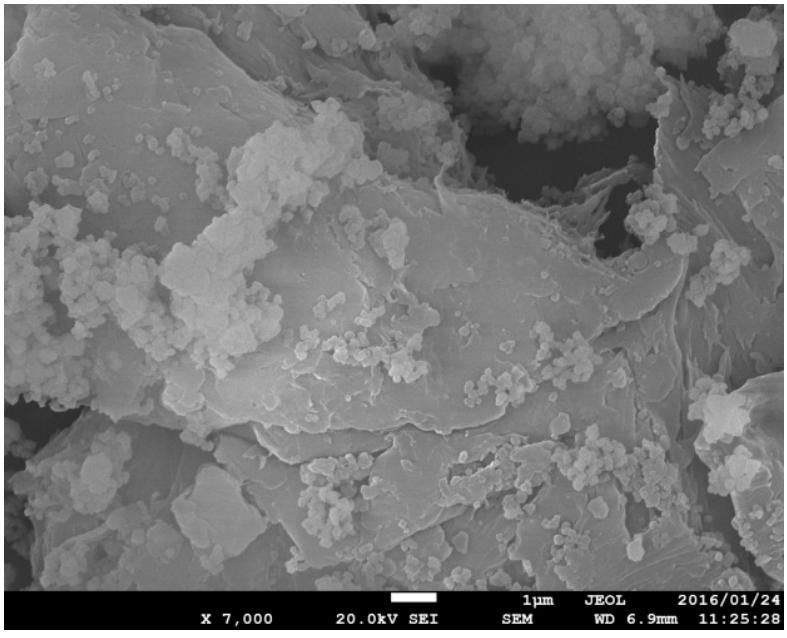

Figure 2. Field emission scanning electron microscopy (FE-SEM) image of as-synthesized Uio-66.

The FE-SEM analysis graph showed that the size of Uio-66 crystals was between 153 and 213 nm. A study by Lin found a Uio-66 size of 20–500 nm.[36] The results of the EDX analysis showed that the percentages of C, O, Zr, and Cl compounds were 46.84%, 23.65%, 26.64%, and 2.87%, respectively

Statistical analysis and the model fitting: The response variables and the test variables were related by the following equation: final equation (in terms of coded factors):

$$\text{Removal efficiency} = 72 - (8.08 \times A) - (8.83 \times B) + (8.17 \times C) + (3.75 \times D) + (2.75 \times A \times B) - (1.5 \times B \times C) + (3.5 \times B \times D) + (1.88 \times C \times D) - (4.79 \times A^2) - (10.54 \times B^2) - (3.17 \times C^2) - (2.79 \times D^2)$$

Table 2 shows the results of the variance analysis for the CCD model. According to the Table 2, the model F_{value} was 69.19 which implies the quadratic model was significant. There was only a 0.01% chance that a model F_{value} this large could occur due to noise. The P_{value} greater than 0.1 indicated the model terms were not significant. The lack of fit F value of 3.94 implied there was a 7.01% chance that a lack of fit F_{value} this large could occur due to noise. Thus, the model F_{value} was 73.35 with $P_{value}<0.0001$ and the model sum of square was 10590.77. The results indicated that the model for fluoride adsorption was significant and could appropriately describe the relationship between the response and the independent variables. The findings indicated that cubic model was found to be aliased. Also, it was found that the quadratic model had a maximum adjusted and predicted R^2. The predicted R^2 of 0.92 was in acceptable agreement with the adjusted R^2 of 0.966. The quadratic model ratio of 31.948 indicated an adequate signal. This model can be used to navigate the design space. The optimum conditions were pH:7, fluoride ion concentration:14.6 mg L^{-1}, Uio-66 dosage: 0.4 g l^{-1}, contact time: 41.5 minute, removal efficiency of 80.21 percent, and a desirability of 1.

Table 2. Variance analysis of experimental data by the central composite design (CCD) model

Source	Sum of Squares	Degrees of freedom	F Value	Probability > F	
Model	9198.63	12	69.19	< 0.0001	Significant
Residual	188.33	17			
Lack of fit	170.33	12	3.94	0.0701	Not significant
Pure error	18	5			
Corrected total	9386.97	29			
R^2= 0.98	Adjusted R^2= 0.966		Predicted R^2= 0.92		

Effect of pH: The interaction between pH and contact time on fluoride adsorption is shown in Figure 3. The findings showed that the fluoride adsorption increases with pH, reaches a maximum of 80% at pH=7, and then decreases with a further increase in the pH to pH=9. For a pH between 6 and 9, the adsorption capacity of fluoride was approximately unchanged with the increase of pH.[37] The slight reduction in fluoride adsorption with an acidic pH may be due to the formation of weak HF bonds or the combined influence of both the chemical and the electrostatic interaction between the adsorbent and the fluoride ions.[38,39] In the present study, the optimum pH for fluoride adsorption was 7. At the optimum pH, the removal efficiency of fluoride was 81.11%.

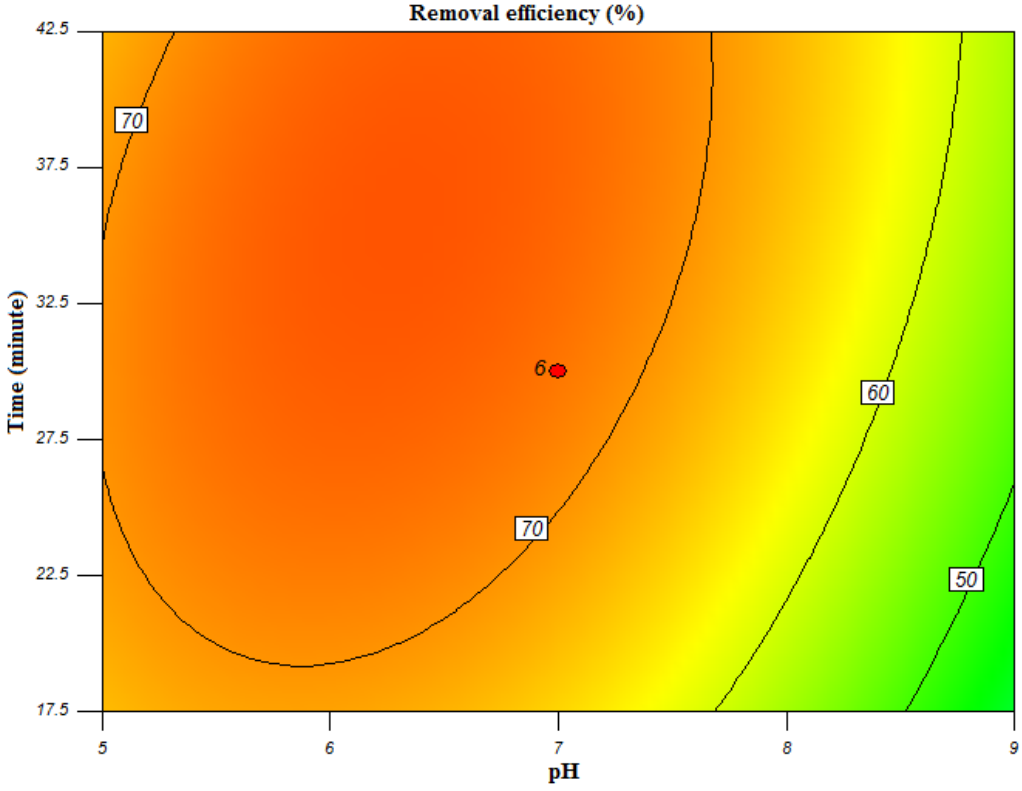

Figure 3. Contour plot of the pH vs. the contact time on the removal efficiency of fluoride with Uio-66.

Effects of fluoride concentration: Figure 4 shows the interaction between the various concentrations of fluoride and the pH. The removal efficiency of fluoride was reduced with increasing the fluoride concentration. In the present study, the optimum concentration of fluoride was 11.52 mg L^{-1}. In the optimum dose, the removal efficiency of fluoride was 80.61%. As a result, the dose of 0.4 g of Uio-66 was used as the optimal dose in all the following experiments.

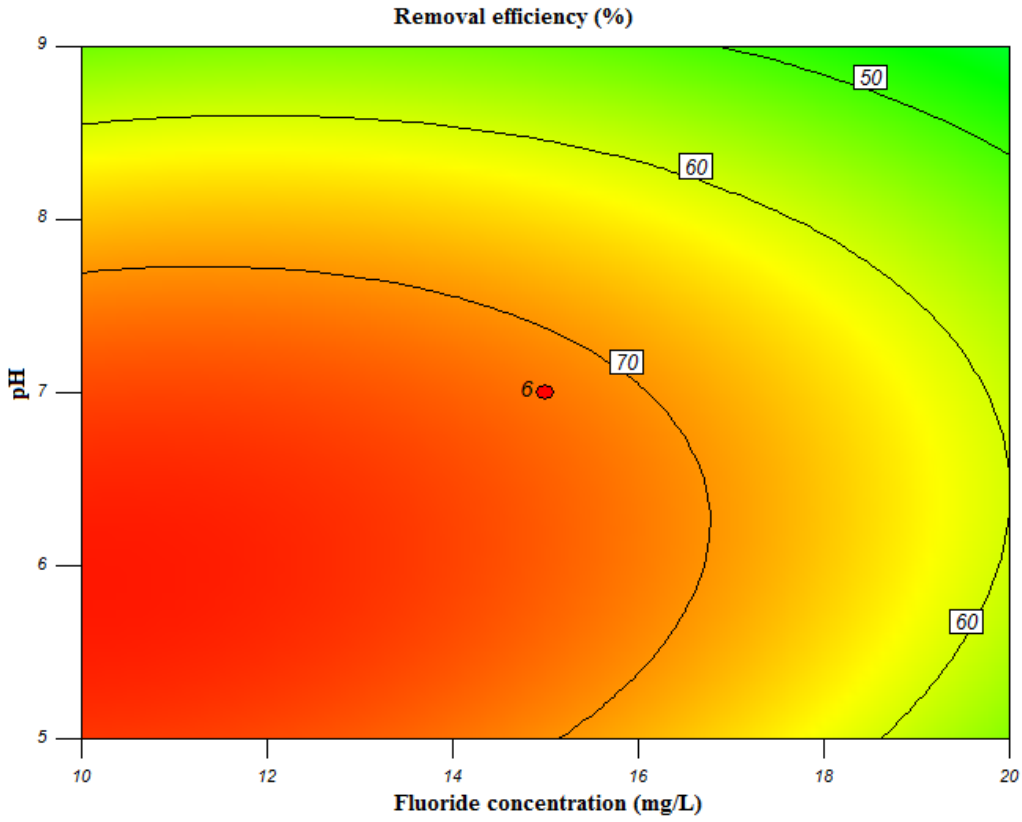

Figure 4. Contour plot of the fluoride concentration vs. the pH on the removal efficiency of fluoride by Uio-66.

Effect of adsorbent dose: Figure 5 shows the effect on fluoride adsorption of the interaction between the Uio-66 dose and the pH. To assess the optimal Uio-66 dosage for reducing the fluoride concentration in aqueous solutions, dosages between 0.1 to 0.5 g L^{-1} were studied. The findings showed that the fluoride adsorption increased with an increase in dosage and attained a maximum adsorption capacity at 0.4 g L^{-1}. The optimum dosage of the Uio-66 adsorbent was 0.4 g L^{-1}.

Effect of co-existing anions: In real conditions, fluoride must be removed along with other ions such as HCO_3^{-1}, SO_4^{-2}, Cl, NO_3^{-}, PO_4^{-3}, and As. So, fluoride adsorption onto Uio-66 in the presence of other anions was investigated. The findings showed that these anions did not have a significant effect on the fluoride adsorption (there was a maximum of a 10% decrease in the removal efficiency). Previous studies have also shown that co-existing anions have no significant effect, or only a minor effect, on the ability of Uio-66 to remove fluoride.[32,37] A study by Zhang et al, revealed no significant effect on fluoride adsorption with a metal organic framework of NO_3^{-}, HCO_3^{-1}, and PO_4^{-3}.[14] In the study by Zhao et al., Cl, NO_3^{-}, and SO_4^{-2} were found to have no significant effect on fluoride adsorption.[37] They also reported that HCO_3^{-1} ions decreased the adsorption capacity of Uio-66 with an increasing fluoride concentration.[37]

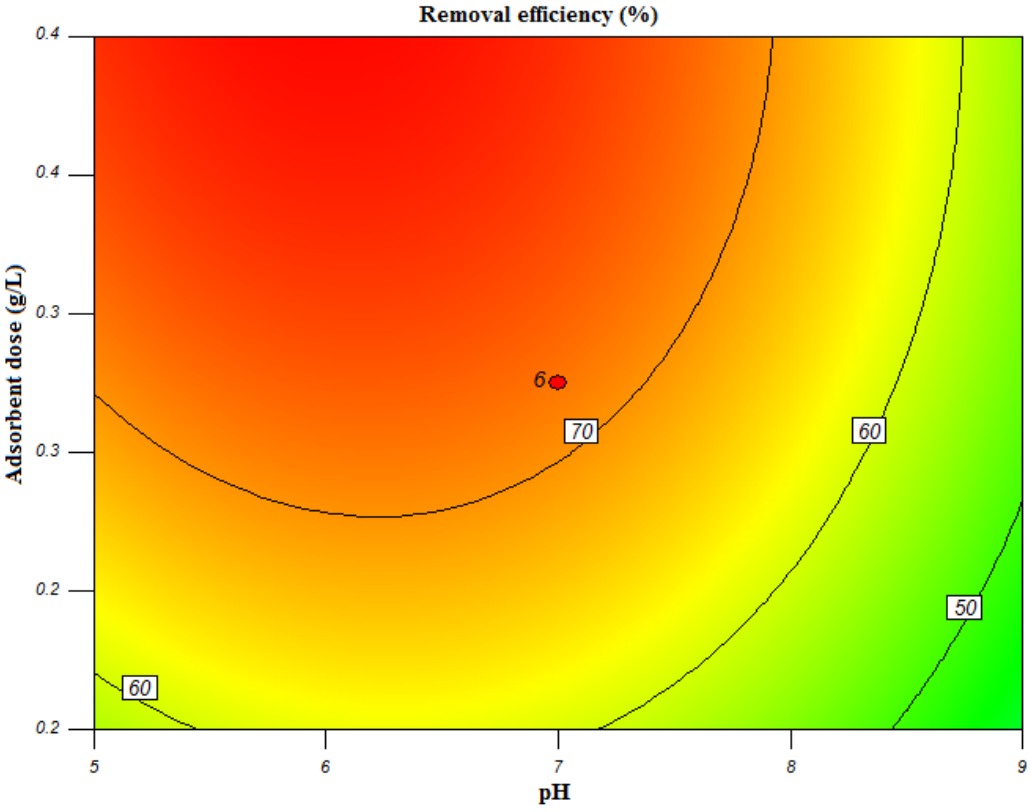

Figure 5. Contour plot of the adsorbent dose vs. the pH on the fluoride removal efficiency with Uio-66.

Adsorption kinetics and adsorption isotherms: The kinetic of adsorption commonly describes the rate of adsorption of the pollutant (e.g., fluoride) onto the adsorbent.[42] As shown in Figure 6, the initial fluoride adsorption was very fast. Almost 85% of the fluoride adsorption occurred in the first 60 min. Then, the adsorption process of fluoride slowed down and the adsorption reached an equilibrium status after 120 min of contact time. To better understand the mechanism of fluoride adsorption onto Uio-66, the kinetics models were further analyzed. The correlation coefficient for the pseudo-second-order model was more than 0.99 and the q_e was calculated from the experimental data. Accordingly, the fluoride adsorption onto Uio-66 was found to follow the pseudo-second-order model.[42] Isotherm models are used to determine the adsorption capacity of adsorbents and to investigate the mechanisms of adsorption. The findings showed that the Langmuir I model had the highest correlation coefficient (R^2=0.9885) and, as a result, fluoride adsorption with Uio-66 conforms to this model. According this model, the maximum of the fluoride adsorption capacity was 31.1 mg g^{-1}. In the study by Zhao et al., the maximal adsorption capacities of Uio-66 (Hf) and Uio-66 (Zr) for fluoride adsorption were 33.35 and 40.09 mg g^{-1}, respectively.[37]

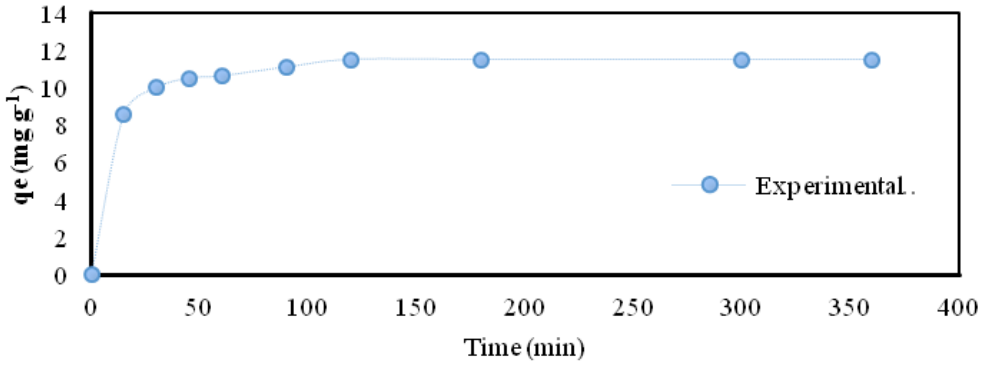

Figure 6. Kinetics of fluoride adsorption by Uio-66 (C_0=5 mg g^{-1}, Uio-66 dose=0.4 g L^{-1}, pH=7)

Reuse studies: The reuse of saturated adsorbent in an adsorption process is an important factor. To reduce the cost of adsorbent synthesis, the used or saturated adsorbent should be regenerated. In this work, the used Uio-66 was regenerated with methanol solution. Reuse was performed for up to 5 cycles. Figure 7 shows the removal efficiency of adsorbent that has been regenerated. The findings show that, after five cycles the adsorption capacity of the reused adsorbent for fluoride was not significantly reduced (an almost 7% reduction in removal efficiency).

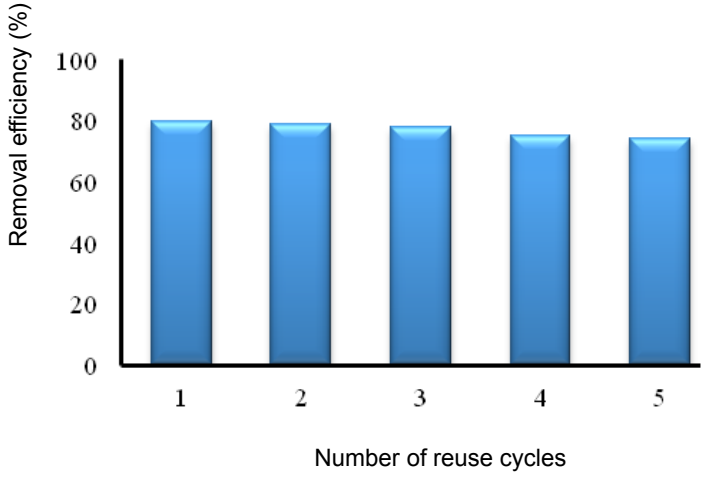

Figure 7. Effect of the number of reuse cycles on the fluoride adsorption efficiency of Uio-66

CONCLUSION

In this research, Uio-66 was synthesized and used to remove fluoride from water. The results showed that a second-order-polynomial regression model gave a good representation of the experimental data of fluoride adsorption by Uio-66. The experimental results showed that Uio-66 had a good adsorption for fluoride. The maximum adsorption capacity of fluoride onto Uio-66 was 31.09 mg L^{-1}. The kinetic data showed that the fluoride adsorption onto Uio-66 followed the kinetic mode of the pseudo-second-order model. The isotherm data show that the Langmuir I

isotherm model had the highest correlation coefficient and, as a result, the fluoride adsorption with Uio-66 was considered to conform to this model.

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