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Alginate Surface Modification of an Ion Exchange Resin for Fluoride Removal from Aqueous Solutions: Optimization, Kinetics, and Isotherm Studies

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ABSTRACT

Background: Fluoride in drinking water at high concentrations causes dental and skeletal fluorosis. Ion exchange resins are effective for fluoride removal, but require improved efficiency. This study aimed to modify the surface of an anion exchange resin with alginate and evaluate its fluoride removal performance.

Methods: The resin was surface-modified using alginate via calcium crosslinking. X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were used to analyze adsorbent characteristics. Batch experiments were optimized using Box-Behnken design. Kinetics and isotherms were evaluated using pseudo-first/second-order and Langmuir/Freundlich models. Regenerability was tested over five cycles.

Results: Analyses confirmed the successful immobilization of alginate nanoparticles (average size 24.5 nm) onto the resin surface. The optimal conditions were pH 5.0, initial fluoride 7.0 mg/L, and contact time 68 min, resulting in 94.9% removal efficiency and 13.7 mg/g adsorption capacity. Fluoride adsorption followed pseudo-second-order kinetics (R^2 = 0.9997) and the Langmuir isotherm model (R^2 = 0.999), with a theoretical maximum adsorption capacity of 36 mg/g. The modified resin showed an approximately 13% loss in efficiency after five cycles.

Conclusion: Surface modification of the ion exchange resin with alginate is an effective, biocompatible, and cost-efficient method to enhance fluoride removal from water, with suitable stability over consecutive cycles.

1. Introduction

Access to safe drinking water is a key indicator of sustainable development and public health (Nguea, 2024). Water quality is assessed based on various physical, chemical, and microbiological parameters to ensure its safety for human consumption. Among these, fluoride is a common inorganic anion found in natural water resources, particularly groundwater (Al Sabti et al., 2023). Although the presence of fluoride at low concentrations (approximately 0.5 mg/L) prevents dental caries, elevated concentrations pose a serious threat to human health (Habuda-Stanić et al., 2014). The World Health Organization (WHO) has established a guideline value of 1.5 mg/L in drinking water (WHO, 2011). Unfortunately, more than 200 million people worldwide consume groundwater with fluoride concentrations exceeding this guideline value (Raghav et al., 2019). In Iran, numerous studies have reported fluoride concentrations as high as 3.8 mg/L in several arid and semi-arid regions, including Bushehr, West Azerbaijan, and East Azerbaijan (Aghdasi et al., 2014; Dehghani et al., 2019; Hosseinpour Feizi et al., 2012; Taghipour et al., 2016). Long-term exposure to water containing high fluoride levels can lead to serious health complications, including dental and skeletal fluorosis, neurological disorders, renal dysfunction, and diminished quality of life. Consequently, the development of efficient and cost-effective methods for fluoride removal from water is a sanitary and environmental necessity. Several techniques have been proposed for this purpose, including reverse osmosis, nanofiltration, chemical

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coagulation, electrocoagulation, adsorption, and ion exchange (He et al., 2020; Kang et al., 2022). Among these, the ion exchange process is considered a suitable option due to its relatively low cost, operational simplicity, regenerability, and acceptable efficiency (Habuda-Stanić et al., 2014). However, the performance of ion exchange resins for fluoride removal is limited by the small size and high negative charge of the fluoride ion, as well as its weak binding affinity for the resin's functional groups (Samadi et al., 2014). To overcome these limitations, surface modification of resins using bioactive materials has emerged as an innovative strategy (Kumar et al., 2024). In this context, alginate is a natural, biodegradable, and nontoxic polysaccharide extracted from the cell walls of brown algae (Silva et al., 2023). The presence of carboxyl and hydroxyl functional groups in the alginate structure renders it an ideal candidate for enhancing ion exchange capacity and improving selectivity toward fluoride (Kumar et al., 2024). Surface modification of resins with alginate can increase the effective contact area by creating a porous and flexible layer, thereby generating new active sites for fluoride adsorption (Sharma & Bhende, 2024). Despite extensive studies on fluoride removal using various adsorbents, no comprehensive investigation has yet been conducted on the modification of ion exchange resins with alginate, coupled with process optimization using advanced statistical methods. Therefore, this study aimed to investigate the effect of surface modification of an anion exchange resin with alginate and to optimize fluoride removal conditions from aqueous solutions using response surface methodology (RSM), along with kinetic and isotherm modeling.

2. Materials and Methods

2.1 Chemical materials

An anion exchange resin (polystyrene-divinylbenzene with quaternary ammonium groups), sodium alginate, calcium chloride, sodium fluoride, sodium chloride, hydrochloric acid, and sodium hydroxide (all purchased from Merck, Germany) were used in this study.

2.2 Surface modification of adsorbent

Initially, 5 g of raw resin was washed with distilled water, followed by 0.1 M sodium chloride. The complete details of the surface modification procedure are as follows: alginate concentration of 2% (w/v), calcium chloride concentration of 4%, contact time with alginate of 30 min, calcium crosslinking time of 60 min, stirring speed of 300 rpm, room temperature (25 ± 1°C), final washing with distilled water followed by 0.01 M sodium chloride, and drying in an oven at 40°C for 12 hours. The raw resin and pure alginate were also considered as controls (Paudyal et al., 2013).

2.3 Adsorbent characterization

To confirm surface modification and characterize the adsorbents, standard instrumental techniques were employed. X-ray diffraction (XRD) patterns were recorded using a PANalytical diffractometer (X′ Pert Pro, Netherlands) in the 2θ range of 10-80° to determine the crystalline or amorphous structure of the adsorbents. Fourier-transform infrared spectroscopy (FTIR) spectra were obtained using a spectrometer (Spectrum Two, PerkinElmer, USA) over the range of 400-4000 cm^{-1} using the KBr pellet method to identify functional groups. Surface morphology was examined using scanning electron microscopy (SEM, model Sigma VP, ZEISS, Germany) after gold coating of the samples at an accelerating voltage of 15 kV and at various magnifications. Particle size was determined using ImageJ software. The point of zero charge (pHzpc) was determined using the pH-drift method. Briefly, 50 mL of 0.01 M sodium chloride solution was adjusted to initial pH values ranging from 2 to 12, then 0.1 g of adsorbent was added. The samples were shaken at 200 rpm for 24 h, after which the final pH was measured. The pHzpc was determined as the pH at which the ΔpH curve crossed zero. All analyses were performed in triplicate.

2.4 Experimental design and optimization

To optimize the selected independent variables in the experimental design, response surface methodology (RSM) using a Box-Behnken design (15 runs) was applied with Design Expert software (version 11) (Table 1). The adsorbent dosage (0.5 g/L), solution volume (100 mL), and temperature (25 ± 1°C) were kept constant. All experiments were performed in duplicate. The residual fluoride concentration was measured using an ion chromatograph (Metrohm 881). Removal efficiency (%) and adsorption capacity (qe, mg/g) were calculated using Eqs. (1) and (2), respectively.

$$\text{Removal (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

Table 1. Factors and levels of the operational parameters

Factor	Independent variables	Unit	Range and level of actual and coded values		
			-1	0	1
A	fluoride concentration	mg/L	5	10	15
B	pH	-log [H^+]	5	7	9
C	contact time	min	20	50	80

2.5 Kinetics, isotherm, and regenerability studies

Adsorption kinetics studies were conducted under the optimal conditions obtained from the Box-Behnken design (fluoride concentration of 7.0 mg/L, pH 5.0, adsorbent dosage 0.5 g/L, volume 100 mL, and temperature 25 ± 1°C) at time intervals of 5, 15, 30, 45, 60, 75, and 90 min. The resulting data were fitted to pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models (Eqs. 3-5). For adsorption isotherm studies, initial fluoride concentrations ranging from 2 to 30 mg/L were tested under optimal conditions (pH 5.0, contact time 90 min to ensure equilibrium attainment), and the equilibrium data were

analyzed using Langmuir and Freundlich isotherm models (Eqs. 6-7) (Balarak et al., 2018a; Balarak et al., 2018b).

To evaluate the regenerability and reusability of the modified resin, desorption experiments were performed over five consecutive cycles. Accordingly, after each adsorption cycle under optimal conditions, the saturated resin was placed in contact with 100 mL of 0.1 M sodium hydroxide solution for 60 min to release adsorbed fluoride ions from the adsorbent surface. The resin was then washed with distilled water until the pH was neutralized to approximately 7 and subsequently reused in the next cycle. Adsorption and desorption efficiencies were calculated for each cycle and compared with those of the raw resin and pure alginate.

$$\text{Ln}\,(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$q_t = k_{id}\, t^{0.5} + c \quad (5)$$

$$\frac{Ce}{q_e} = \frac{1}{q_m K_L} + \frac{Ce}{q_m} \quad (6)$$

$$\text{Ln}\, q_e = \frac{1}{n} \text{Ln}\, C_e + \text{Ln}\, K_f \quad (7)$$

In above equations, q_e and q_t are the adsorption capacities at equilibrium and at time t (mg/g), respectively; k_1 is the pseudo-first-order rate constant (min^{-1}); k_2 is the pseudo-second-order rate constant (g/mg·min); k_{id} is the intraparticle diffusion rate constant ($mg/g \cdot min^{0.5}$); C is the constant related to the boundary layer thickness; C_e is the equilibrium concentration (mg/L); C_t is the concentration at time t (mg/L); q_m is the maximum adsorption capacity (mg/g); K_L is the Langmuir constant (L/mg); K_F is the Freundlich adsorption capacity (mg/g); *n* is the adsorption intensity; V is the solution volume (L); and *m* is the adsorbent mass (g).

3. Results and Discussion

3.1 Instrumental analysis of the modified adsorbent

The XRD analysis results indicated that the pattern of raw alginate was predominantly amorphous, with broadening in the 2θ range of 13-25°, which is suitable for adsorption applications. In contrast, the raw resin exhibited multiple sharp and narrow peaks corresponding to the semi-crystalline structure of polystyrene-divinylbenzene. In the pattern of the modified resin, a decrease in the intensity of the crystalline peaks of the resin and an increase in the amorphous background were observed, confirming successful coating of the resin surface with the amorphous alginate layer.

FTIR of the modified resin revealed a strong carboxylate peak at 1610 cm^{-1} and hydroxyl broadening at approximately 3400 cm^{-1}, while the peaks corresponding to the aromatic ring and ammonium group of the resin were retained. These findings confirm the successful immobilization of alginate via electrostatic interactions. SEM images showed that alginate was immobilized on the resin surface as nanoparticles with an average size of 24.5 nm and relatively uniform dispersion.

3.2 Optimization and statistical modeling

Table 2 summarizes the ANOVA results for the quadratic model, which was highly significant ($p < 0.0001$), with an R^2 of 0.9959, indicating that 99.6% of the variability in fluoride removal efficiency was explained by the model. The results indicated that fluoride concentration, pH, contact time, and certain interactions among these variables had significant effects on fluoride removal efficiency, indicating nonlinear relationships. The lack-of-fit was not significant ($p > 0.05$), and the coefficient of variation (CV) was 2.64%, confirming the adequacy and reliability of the model for predicting fluoride removal.

In a study conducted by Hashemi et al. (2023), fluoride removal from aqueous solutions was investigated using response surface methodology. The ANOVA results showed that initial fluoride concentration, contact time, and pH had significant effects on fluoride removal efficiency. Additionally, the interaction effects between variables, except for the interaction between fluoride concentration and time, were reported to be significant. The proposed model was quadratic and demonstrated a good fit with the experimental data (Hashemi et al., 2023).

In a study by Sinharoy et al. (2024), fluoride removal from industrial wastewater containing high fluoride concentrations was investigated using a fluidized bed reactor and response surface methodology. The ANOVA results indicated that all independent variables studied had significant effects on fluoride removal efficiency, with *p-values* equal to or less than 0.0001. This finding suggests that the probability of the results arising from random errors or statistical noise is negligible, and the model possesses high statistical validity. The researchers also stated that the quadratic model provided the best fit with the experimental data and was able to predict the behavior of the fluoride removal process with appropriate accuracy. Sinharoy et al. (2024) concluded that pH, hydraulic retention time, and the calcium-to-fluoride ion ratio play decisive roles in the fluoride removal process and that RSM is an effective tool for optimizing this process.

The Box-Behnken design results showed that the removal efficiency ranged from 38% to 94%. The quadratic model adequately described the data. The optimal conditions proposed by the software were a fluoride concentration of 7.0 mg/L, a pH of 5.0, and a contact time of 68 min, under which the predicted removal efficiency was 94.9% and the adsorption capacity was 13.7 mg/g. Table 3 presents the software-predicted optimal conditions and experimental validation results. The predicted removal efficiencies ranged from 94.68% to 96.24%, with corresponding predicted adsorption capacities of 9.84 to 13.70 mg/g. Experimental validation under these conditions yielded removal efficiencies between 93.2% and 95.8%, demonstrating excellent agreement with the model predictions (relative error < 5%).

Table 2. Summary of analysis of variance (ANOVA) results for the quadratic model and the quadratic model fit statistics

Source	Sum of squares	df	Mean square	F-value	*p-value*	
Model	3701.77	9	411.31	135.60	< 0.0001	significant
A-Fluoride Conc.	1250.00	1	1250.00	412.09	< 0.0001	
B-pH	1624.50	1	1624.50	535.55	< 0.0001	
C-Time	420.50	1	420.50	138.63	< 0.0001	
AB	20.25	1	20.25	6.68	0.0492	significant
AC	0.25	1	0.25	0.082	0.7856	not significant
BC	30.25	1	30.25	9.97	0.0252	significant
A^2	210.01	1	210.01	69.23	0.0004	significant
B^2	60.31	1	60.31	19.88	0.0066	significant
C^2	134.78	1	134.78	44.43	0.0011	significant
Lack of Fit	14.50	3	4.83	14.50	0.0652	not significant
R^2 = 0.9959	Adj R^2 = 0.9886	Pred R^2 = 0.9372	Mean = 65.93	CV% = 2.64	Std. Dev. =1.74	

Table 3. Software-predicted optimal conditions and experimental validation

Run	Factor 1 A: Fluoride (mg/L)	Factor 2 B: pH	Factor 3 C: Time (min)	Predicted removal efficiency (%)	Experimental removal efficiency (%)
1	6.21	5.06	71.46	96.24	95.8
2	7.22	5.09	68.38	94.90	94.1
3	5.90	5.19	71.80	95.77	94.7
4	5.38	5.11	61.91	95.28	95.0
5	5.20	5.39	79.29	94.68	93.2

The final equation for the removal response using actual factors is presented as Eqs. 8:

$$\text{Removal} = +54051.40 + 2.04167 \times \text{Fluoride Conc.} + 7.06250 \times \text{pH} + 1.25046 \times \text{Time} + 0.225000 \times (\text{Fluoride Conc.} \times \text{pH}) - 0.001667 \times (\text{Fluoride Conc.} \times \text{Time}) - 0.045833 \times (\text{pH} \times \text{Time}) - 0.301667 \times (\text{Fluoride Conc.}^2) - 1.01042 \times (\text{pH}^2) - 0.006713 \times (\text{Time}^2) \quad (8)$$

This equation is applicable for predicting the response value at different levels of the factors. However, the coefficients cannot be used directly to compare the relative importance of each factor, because the scale and units of each factor differ, and the intersection point is not at the center of the design space. In summary, the model indicates that pH has the greatest positive effect on the response. Furthermore, a positive interaction between fluoride concentration and pH is observed. Nonlinear effects exist, suggesting that excessive increase of any factor may diminish its beneficial effect. This equation serves as a tool for predicting and optimizing fluoride removal conditions (Hashemkhani et al., 2022; Kang et al., 2022). Patil et al. (2025) investigated the fluoride removal process from water using a modified adsorbent and response surface methodology. The analysis of variance results showed that the proposed statistical model for predicting fluoride removal efficiency based on initial fluoride concentration, pH, and contact time was highly significant. The authors reported that all main factors and some interactions between variables had considerable effects on fluoride removal efficiency. Additionally, the presence of significant quadratic terms indicated that the relationship between the operational variables and the process response was nonlinear, and the quadratic model provided the best fit for describing the experimental data. Patil et al. (2025) concluded that to achieve optimal fluoride removal conditions, main effects, interactions between variables, and nonlinear effects must be considered simultaneously in the modeling and optimization process.

3.3 Model validity

In Figure 1 (a), the actual versus predicted plot is presented. As shown in this figure, most data points lie close to the diagonal line, indicating that the model predicts the response relatively well. The model demonstrates good agreement between predicted and actual response values; the points are largely near the diagonal line, and the color spectrum ranging from blue to red indicates acceptable model performance across the range of 38% to 94%. The color mapping reveals that points with high response values (red/orange) exhibit high values for both actual and predicted responses, thus confirming a positive correlation between actual and predicted values. There is no systematic trend toward prediction error at any particular level of the response values (i.e., errors are relatively uniform and do not clearly vary with the response level). Hemanth et al. (2026), in a study on fluoride removal using modified rice straw optimized via response surface methodology, reported an excellent correlation between actual and predicted values. The predicted versus actual plot showed that most points were located near the diagonal line, indicating high model accuracy in predicting fluoride removal efficiency. The authors concluded that the quadratic model possessed high statistical validity and demonstrated suitable capability in describing the fluoride removal process (HS et al., 2026).

Figure 1 (b) shows the perturbation plot, illustrating that the response is sensitive to changes in the three factors: A (fluoride concentration), B (pH), and C (time), and that nonlinear effects are present. Around the reference point (A = 10, B = 7, C = 50), small variations can alter the response, and all three factors contribute to changes in the response. The curvature of the lines indicates a nonlinear relationship. Dzikunu et al. (2024), in a study on the optimization of fluoride extraction and removal using response surface methodology, reported that the perturbation plot revealed a significant influence of operational variables on the process response.

The results showed that pH, contact time, and fluoride concentration all played effective roles in changing the response, and the deviation of each factor's curve from the reference line indicated the magnitude of that variable's effect on process efficiency. Furthermore, the curvature observed in the plots demonstrated that the relationship between the independent variables and the process response was not completely linear. The authors stated that the curvature of the perturbation plots confirmed the presence of quadratic effects and that using a quadratic model was appropriate for describing the system's behavior (Dzikunu et al., 2024).

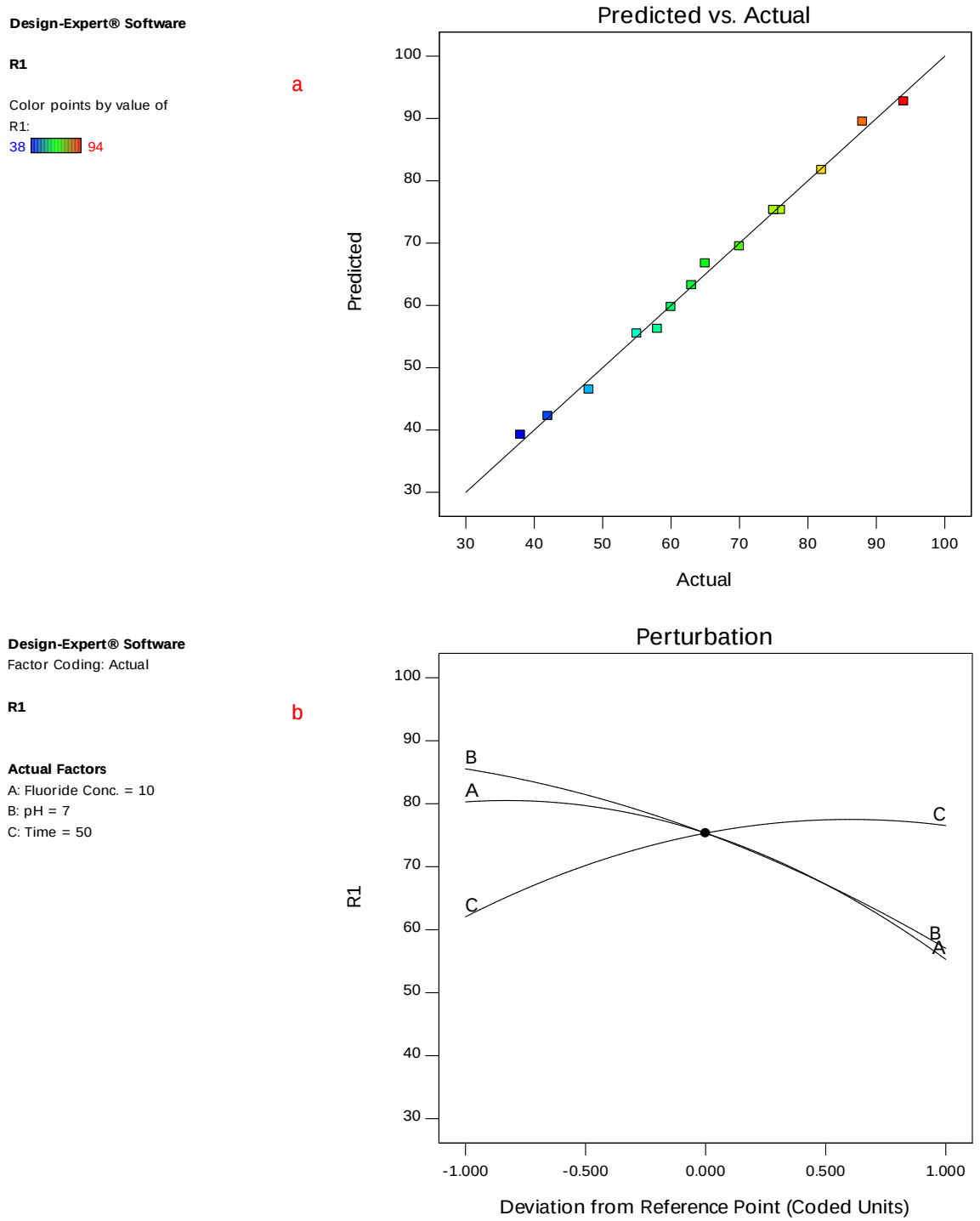


Figure 1. (a) Predicted vs. actual values; (b) Perturbation plot showing the effect of factors A (fluoride concentration, mg/L), B (pH), and C (contact time, min) on fluoride removal efficiency. The reference point is A = 10, B = 7, C = 50

3.4 Investigation of the interaction effects of parameters

3.4.1 Effect of fluoride concentration and pH

As shown in Figure 2, the three-dimensional plot indicates that A and B collectively influence the response, and the relationship changes with different slopes/backgrounds (indicating an interaction). The design points above the predicted surface (dark red) and those below the predicted surface (dark pink) suggest that the model exhibits greater accuracy in some regions and lesser agreement in others; however, the overall coverage of the design space is relatively adequate (Dehghani et al., 2016).

3.4.2 Effect of fluoride concentration and time

As illustrated in Figure 3, the three-dimensional surface for A × C is presented, and this surface confirms that the interaction between A and C is indeed active. The surface is sloped and exhibits curvature rather than being flat. This indicates that the effect of A on the response strongly depends on the value of C, and vice versa. The design points located on the upper surface suggest that the model is more practical in these regions and that the predictions in this area are consistent with the experimental data.

3.4.3 Effect of pH and time

As illustrated in Figure 4, the three-dimensional surface plot for B × C shows that the response reacts nonlinearly to both factors, and the interaction between these two factors is evident. In regions with moderate pH and relatively long contact time, the response reaches its highest value, and the slope of the surface indicates that the sensitivity of the response to changes in C increases with appropriate pH adjustment. The design points located on the upper surface emphasize the predictive accuracy in this region. A ridge or peak near pH 7-7.5 and an appropriate contact time leads to maximization of the response; drastic changes in pH or time outside this range can reduce the response value. Determination of the point of zero charge revealed that the pHzpc values were 8.5 for the raw resin, 6.8 for the modified resin, and 6.5 for pure alginate. The decrease in pHzpc after surface modification is attributed to the presence of acidic functional groups of alginate, which is highly significant for the electrostatic adsorption of fluoride anions in the neutral to slightly acidic pH range. In this study, the optimal pH predicted by the model was 5.0, and the pHzpc of the modified resin was 6.8. It is observed that the optimal pH (5.0) is significantly lower than the pHzpc. This discrepancy is fully consistent with theory and explains why maximum adsorption (over 95%) was achieved at pH 5.0: at this pH, the adsorbent surface possesses a net positive charge, and no electrostatic repulsive force exists. In contrast, at pH 9, which is above the pHzpc of the modified resin, the adsorbent surface becomes negatively charged, and fluoride adsorption decreases sharply. The results of this section clearly demonstrate that the dominant mechanism for fluoride adsorption by the alginate-modified resin is electrostatic interaction, which is controlled by the solution pH and the pHzpc of the adsorbent. Modification of the resin with alginate, while reducing the pHzpc of the adsorbent from 8.5 to 6.8, has provided conditions for achieving maximum adsorption in the neutral to slightly acidic pH range, which is much more desirable from practical and industrial perspectives than highly acidic or alkaline pH conditions. Therefore, controlling the pH at the optimal value of 5.0 (below the pHzpc) is essential for achieving the highest fluoride removal efficiency.

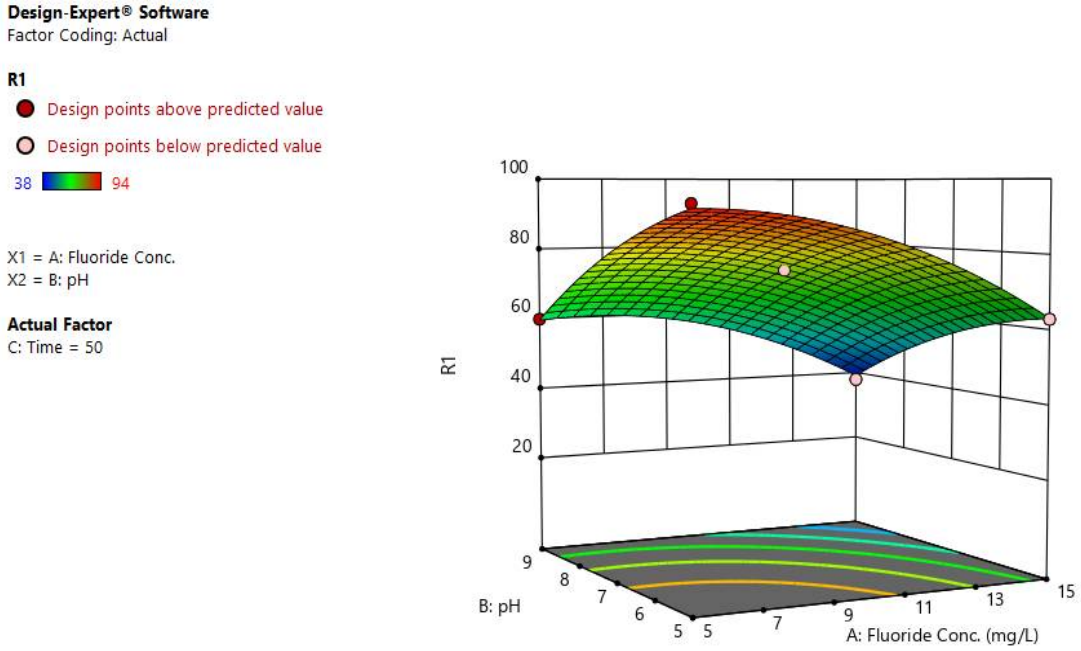


Figure 2. Interaction effects of fluoride concentration (A, mg/L) and pH (B) on fluoride removal efficiency (contact time C = 50 min)

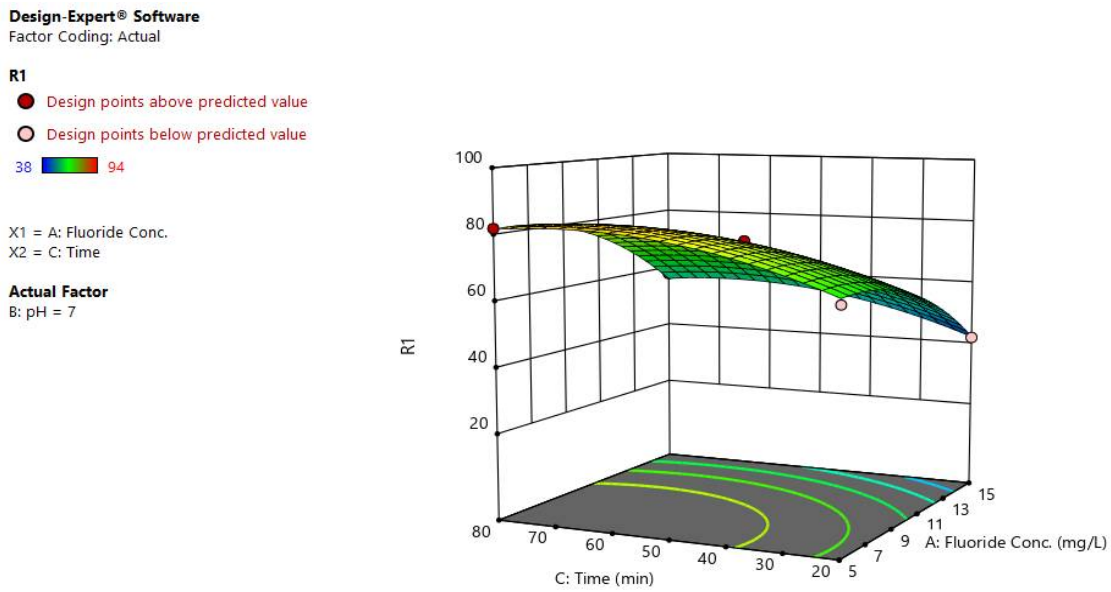


Figure 3. Interaction effects of fluoride concentration (A, mg/L) and contact time (C, min) on fluoride removal efficiency (pH B = 7)

3.5 Adsorption kinetics

The results of the kinetic experiments showed that as the contact time increased from 5 to 90 min, the fluoride adsorption capacity of the alginate-modified resin increased continuously, eventually reaching an equilibrium value of approximately 13.8 mg/g. Notably, within the first 15 min, the adsorption capacity reached 9.39 mg/g (approximately 68% of the final capacity), indicating the presence of abundant and accessible active sites on the external surface of the adsorbent. From 30 to 90 min, the adsorption rate decreased, and the slope of the curve became gentler, reflecting the migration of fluoride ions into the pores and the gradual occupation of internal active sites. Fitting of the kinetic models revealed that the pseudo-second-order model, with a coefficient of determination (R^2) of 0.9997, described the data far better than the pseudo-first-order model. The calculated equilibrium adsorption capacity from the pseudo-second-order model (13.87 mg/g) was in excellent agreement with the experimental value (13.8 mg/g). This result clearly confirms that the rate-limiting step in the adsorption process is chemical interactions between fluoride ions and surface functional groups (such as quaternary ammonium groups on the resin and carboxyl groups on alginate), rather than merely physical transport (Balarak et al., 2018a; Tazerodi et al., 2018). Furthermore, evaluation of the intraparticle diffusion model revealed two distinct stages: the first stage (5-30 min) with a diffusion coefficient (k_{id1} = 1.53) corresponds to boundary layer transport and external surface adsorption; the second stage (30-90 min) with (k_{id2} = 0.27) corresponds to intraparticle diffusion. The fact that the lines do not pass through the origin ($C \neq 0$) in both stages indicates that intraparticle diffusion is not the sole rate-controlling mechanism and that external surface adsorption is simultaneously effective. Therefore, 90 min was selected as the optimal equilibrium time, since no significant increase in adsorption capacity was observed thereafter, and the process remains economically viable.

3.6 Adsorption isotherm

The results of the isotherm experiments showed that as the initial fluoride concentration increased from 2 to 30 mg/L, the equilibrium adsorption capacity (qe) increased continuously, but the percentage removal efficiency decreased. The better fit of the data to the Langmuir model (R^2 = 0.999) compared to the Freundlich model (R^2 = 0.966) indicated that the theoretical maximum adsorption capacity (qm) was 36 mg/g and that adsorption occurred as a monolayer onto homogeneous sites of the resin. The high value of the Langmuir constant (K_L = 1.20 L/mg) further confirmed that the affinity of the modified adsorbent for fluoride is very high, even at low concentrations. Therefore, although increasing the initial concentration raises the adsorption capacity, from an economic and practical perspective, the optimal concentration of 7.0 mg/L (which provides a removal efficiency of 94.9% under optimal conditions) was selected as the balance point between removal efficiency and adsorption capacity (Abedi et al., 2017; Balarak et al., 2018a).

3.7 Regenerability

After five consecutive adsorption-desorption cycles using 0.1 M sodium hydroxide, the adsorption efficiency of the modified resin decreased from 95% to 82%, corresponding to a 13.7% reduction. This demonstrated significantly better stability than that of the raw resin (27.1% reduction) and pure alginate (42.9% reduction). At the optimal conditions, the modified resin exhibited substantially higher adsorption efficiency than the raw resin (48%) and pure alginate (35%) (Table 4).

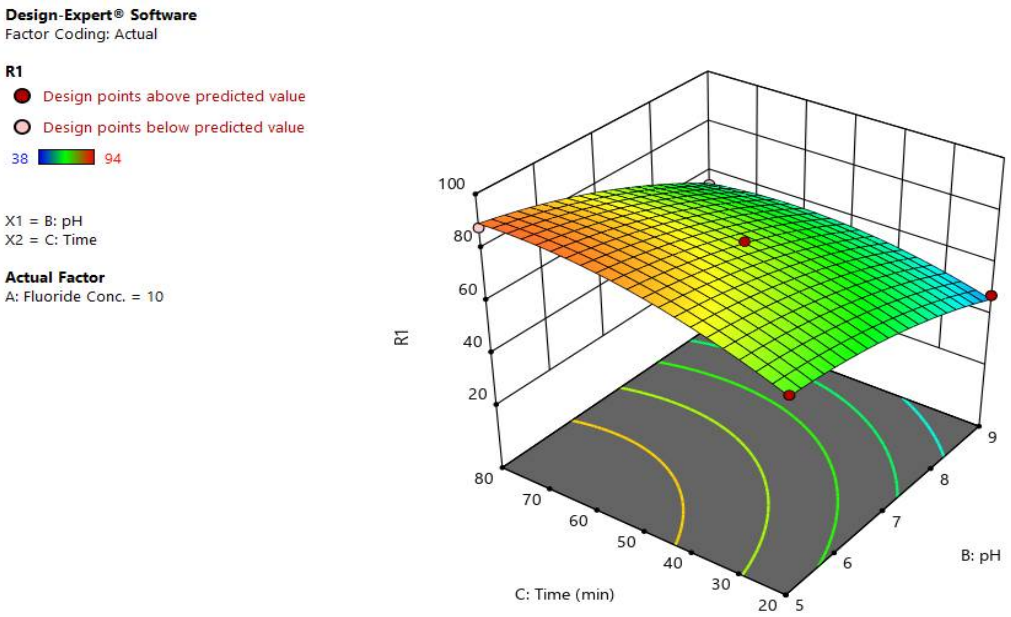


Figure 4. Interaction effects of pH (B) and contact time (C, min) on fluoride removal efficiency (fluoride concentration A = 10 mg/L)

Table 4. Comparison of adsorbent regenerability after 5 cycles

Adsorbent type	Cycle 1 efficiency (%)	Cycle 5 efficiency (%)	Reduction after 5 cycles (%)
Alginate-modified resin	95	82	13.7
Raw resin	48	35	27.1
Pure alginate	35	20	42.9

4. Conclusion

In this study, an anion exchange resin was successfully surface-modified with alginate. XRD and FTIR results demonstrated that alginate was physically immobilized through electrostatic interactions between the COO^- groups of alginate and the quaternary ammonium groups of the resin. SEM images further confirmed the nanoparticle morphology, which provides a large surface area for adsorption. Optimization using the Box-Behnken design revealed that pH was the most influential parameter. Maximum adsorption occurred at pH 5.0, which is below the pHzpc of the adsorbent (6.8). Under these conditions, the adsorbent surface possesses a net positive charge, facilitating the electrostatic adsorption of fluoride anions. The decrease in adsorption under alkaline pH conditions is attributed to competition from OH^- ions with fluoride. The excellent fit of the data to the pseudo-second-order model indicated that the dominant mechanism governing the process is chemisorption. The Langmuir isotherm confirmed monolayer and homogeneous adsorption of fluoride onto the active sites of the adsorbent. The maximum adsorption capacity obtained was 36 mg/g. The favorable regenerability of the modified resin demonstrates its mechanical and chemical stability for practical applications. This research demonstrated that surface modification of an anion exchange resin with alginate is an effective, biocompatible, and economical approach to enhance fluoride removal from water. The modified resin exhibited suitable stability over consecutive cycles and can be proposed as a reliable adsorbent for the treatment of fluoride-contaminated water at an operational scale.

Authors' Contributions

Narges Khalili: Investigation; Data curation; Writing original draft. **Esrafil Asgari:** Supervision; Software; Conceptualization; Funding acquisition; Writing-review & editing. **Mohammad Reza Mehrasbi:** Methodology; Formal Analysis. **Ali Assadi:** Investigation; Visualization.

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Conflicts of Interest

The authors have declared no competing interests.

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Ethical Considerations

The article is extracted from the project with the ethics code of IR.ZUMS.BLC.1404.083.

Using Artificial Intelligence

No type of artificial intelligence was used.

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