

Original Article

Investigation of fluoride adsorption from aqueous solutions by modified eucalyptus leaves: isotherm and kinetic and thermodynamic studiesMaryam Faraji¹ Edris Bazrafshan² Mohammad Almasian³ Nahid Khoshnamvand^{2,4*}

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Abstract

Background and purpose: The World Health Organization (WHO) has specified the tolerance limit of fluoride content of drinking water to be 1.5 mg/L, since excessive intake of fluoride leads to various detrimental diseases. The present study assessed the adsorption effectiveness of HCl-modified eucalyptus leaves in fluoride removal from synthetic solutions.

Materials and Methods: In this experimental study, pseudo-first and pseudo-second order kinetics, Langmuir and Freundlich isotherm models, as well as pH (2-12), initial concentration (5-30 mg/L), adsorbent dose (0.1-1 g/L), and temperature (25-45 °C) were investigated on defluoridation.

Results: The results with the maximum removal efficiency of 90% was obtained in pH = 10, initial concentration = 5 mg/L, and adsorbent dose = 0.1 g/L. In the investigation of the effect of temperature on removal rates, the maximum removal of fluoride was observed to be in 45 °C. The removal efficiency also decreased while the adsorbent dose increased, the initial concentration of fluoride increased, and the temperature in the studied ranges decreased. It was also found that the adsorption equilibrium and kinetic data were in good agreement with Langmuir Model (R²=0.994) with q_{max}= 61.35 mg/g and pseudo-second order reaction (R²=0.999).

Conclusion: On the basis of the obtained results, HCl-modified eucalyptus leaves were found to be able to remove fluoride from aqueous environments with good removal efficiency and adsorption capacity.

Keywords: Adsorption; Fluoride Removal; Eucalyptus

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1. Introduction

Fluoride is the first halogen element in the periodic table that cannot be found as elemental form mainly due to high reactivity (1). Because of the presence of fluoride in the inorganic compounds of the earth's crust, such as fluorspar, cryolite, and fluorapatite, fluoride compounds can usually be found in low concentrations in groundwater (2). The World Health Organization (WHO) has specified the tolerance limit of fluoride in drinking water to be 1.5 mg/L. This concentration of fluoride in drinking water has positive effects on bones and teeth, especially in children under 8 years of age (3). Depending on the concentration and duration of continuous absorption, the absorption of high amounts of fluoride could lead to osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer's disease, stained teeth, impaired DNA synthesis, and impaired metabolism of carbohydrates, lipids, proteins, vitamins and minerals (4). Contact with mineral deposits and the discharge of industrial wastewater containing fluoride are considered as important factors in the contamination of surface and ground water with high fluoride concentrations (5). In areas rich in minerals containing fluoride, its concentrations in groundwater can be as high as 10 mg/l and more. The maximum concentration of fluoride in water in the world has been reported to be 2800 mg/l (3).

Coagulation and precipitation with 3-valent iron and aluminum, activated alumina, ion exchange, reverse osmosis, electrodialysis, adsorption, and electrocoagulation are among the methods of removing fluoride from drinking water (6-11). Among these methods, adsorption is one of the most widely used techniques of removing fluoride. Around 100 different types of adsorbent have so far been

used to absorb fluoride, such as alumina and alumina-based adsorbents, adsorbents based on iron and calcium, oxides and metal hydroxides, impregnated metal oxides, carbon-based adsorbents, natural materials used as adsorbents, bioadsorbents, agricultural and industrial waste, apatite and hydroxyapatite, building materials, and nanoadsorbents (11, 12).

In recent years, the use of inexpensive natural adsorbents in natural or modified form in the removal of water contaminants has received attention (13-16). Natural pumice (NP), and FeCl₃·6H₂O modified pumice (FEMP), and hexadecyl trimethyl ammonium bromide (HDTM.Br) modified pumice (HMP) have been used for fluoride removal in maximum removal efficiency of 9.39, 76.45, and 95.09% for NP, FEMP, and HMP, respectively (11). The findings of another study showed that the use of pumice stone modified with MgCl₂, and a maximum efficiency of fluoride removal of 68.4% from an aqueous solution was obtained at the optimal pH of 6 (17). Using pumice stone modified with HDTMA, and the concentration of 10 mg/L of fluoride was removed at the optimum pH of 6 with an efficiency of 96% (18). Using an inorganic phosphate mineral called brushite, the removal efficiency was also obtained 88.78% at a pH of 5.36 with the maximum adsorption capacity of 29.21 mg/g (19). In one other research, fluoride was removed using hydroxyapatite at a pH of 4.16 with a removal efficiency of 86.34% and with the maximum adsorption capacity of 3.12 mg/g (20).

Eucalyptus (*eucalyptus camadulensis* Dehnh) is among the plants that grow in the southwestern and south-eastern parts of Iran. The present study was an attempt for the first time to investigate the efficiency of eucalyptus

leaves modified with HCl in the removal of fluoride.

2. Materials and Methods

This study was experimentally conducted on a laboratory scale in the Water and Wastewater Chemistry Laboratory of the Zahedan University of Medical Sciences, Iran, in which eucalyptus leaves modified with HCl were used as adsorbents to remove fluoride from synthetic aqueous solutions.

2.1. Preparation of the Adsorbent

The preparation and modification of adsorbent was initially done based on the method presented by Khavidaki et al. and Fazlzadeh et al., respectively, with some modification (21, 22). First, eucalyptus leaves were collected from the trees growing in the region. Next, the leaves were washed with distilled water and dried in an oven for 2 hours. Then, the dried leaves were ground and the resulting powder was graded into 60 to 200 mesh sizes using standard ASTM sieves. To modify the adsorbent, 250 grams of eucalyptus leaf powders prepared in the previous step were then mixed with 8% HCl and left at normal room temperature for 3 hours. After that, the samples were filtered, washed with distilled water, and dried in an oven for 24 hours. Thus, the desired adsorbent was prepared and used in the subsequent stages of the study. For determine the pH of zero point of charge (pHZPC), 0.01 M NaCl was prepared and the suspension pH was adjusted within the range 2.0–12.0 using 0.1 M NaOH and HCl. Then 50 mL different pH of 0.01 M NaCl solution was taken into a conical flask containing 0.5 g Adsorbents. The mixtures were shaken for 24 h and then the final pH was measured (23).

2.2. Batch Experimental

In the current study, in order to determine the optimal, batch fluoride adsorption, certain experiments were conducted. Hence, the effect of the variables of time (15-150 min), temperature (25-45 °C), pH (2-12), adsorbent dosage (0.1-1 g/L), and the initial concentrations of fluoride (5-30 mg/L) were all examined. It should be noted that each experiment in the present research was repeated three times. For the purpose of this study, a stock solution of fluoride was made by dissolving NaF (2.21 g) in distilled water (1,000 mL). Then, 100 mL of fluoride solution was mixed with various doses of the adsorbent at different pH and fluoride concentrations at equilibrium time in a reciprocating shaker at 200 rpm.

After determining the optimal points, an investigation of the effects of various temperatures (25-45 °C) on various concentrations of fluoride was conducted. To adjust pH, one normal NaOH and H₂SO₄ solutions were used. After that, the solutions were filtered (0.45 μm, Whatman filter paper), and then the residual fluoride concentration was analyzed at a maximum wavelength of 570 nm using UV/VIS spectrophotometer (PerkinElmer, Lambda 25) according to the standard methods for the examination of water and wastewater (24).

The amount of adsorbed fluoride at equilibrium (q_e) (mg/g) was calculated using equation 1, and fluoride removal efficiency (%) was calculated using equation 2:

$$q_e = \frac{V}{M} \times (C_o - C_e) \quad (1)$$

$$Y(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where,

q_e : Adsorption capacity (mg/g)

C_o : Initial concentration of fluoride in the solution (mg/l)

C_e: Equilibrium concentration of fluoride after the establishment of equilibrium

V: Solution volume (L)

M: Adsorbent mass (g)

2.3. Determining adsorption kinetics:

To determine the adsorption equilibrium time, the fluoride solution with various concentrations containing 2 g/L adsorbent was mixed at a speed of 200 rpm at a pH of 7, and at fixed intervals. The sampling was then performed between the times of 15 min and 150 min. The samples were filtered, and the final concentrations of fluoride were recorded. To determine the adsorption levels at various times, pseudo first order and pseudo second order kinetic models, the equations of which are presented in Table 2, were used, where q_t (mg/g) is the adsorption capacity at time t , k_1 is the pseudo first order reaction speed constant ($\text{min}^{-1} \text{g mg}^{-1}$), k_2 is the pseudo second order speed constant ($\text{min}^{-1} \text{g mg}^{-1}$), and q_e (mg/g) is the equilibrium adsorption capacity.

2.4. Determining adsorption isotherm:

After conducting batch adsorption experiments and determining the optimal values for time, pH, initial fluoride

concentration, and adsorbent dosage, the isotherm of fluoride adsorption onto the adsorbent was determined at 25 °C. The agreement of the experimental data with the Freundlich and Langmuir Isotherm Models was also investigated. Hence, the best model was selected using the R^2 coefficient.

3. Results

In this study, after preparing and modifying the adsorbent, the adsorption equilibrium time was determined, and then the effects of various variables on the adsorption efficiency and capacity were studied by conducting batch experiments.

3.1. The effect of contact time

The results of determining the equilibrium time are presented in Figure 1. The highest rates of fluoride removal by modified eucalyptus leaves were obtained at 60 min, and it was observed that the removal efficiency had a descending trend after 60 min. Thus, a contact time of 60 min was considered as the equilibrium time in other parts of the study.

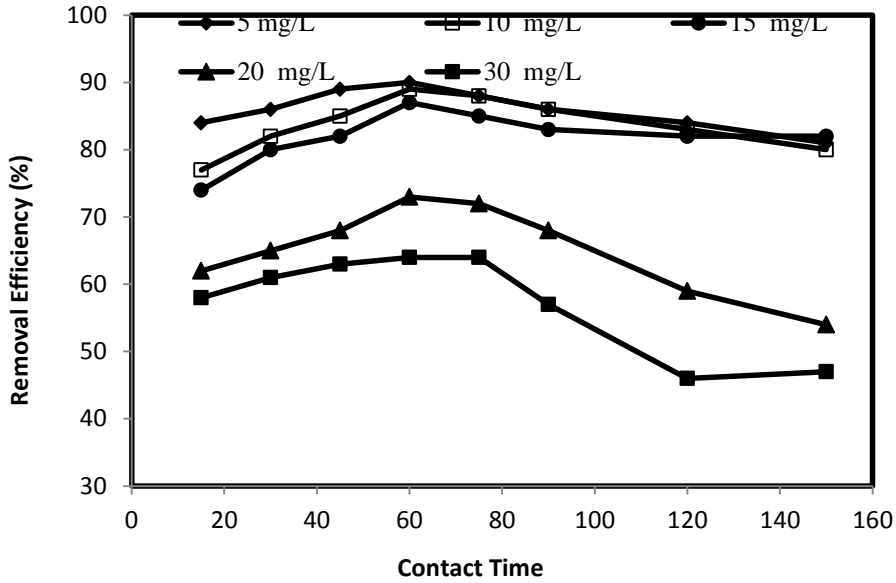


Figure 1. The effect of time on fluoride adsorption by modified eucalyptus leaves.

3.2. The Effect of pH

Investigating the effect of pH in the range of 2-12 showed that the highest fluoride removal efficiency (86%) at a contact time of 60 min

can be achieved at a pH level of 10. Also, the pH_{pzc} values for adsorbents were 11.2. Figure 2 presents the effect of pH on fluoride removal efficiency.

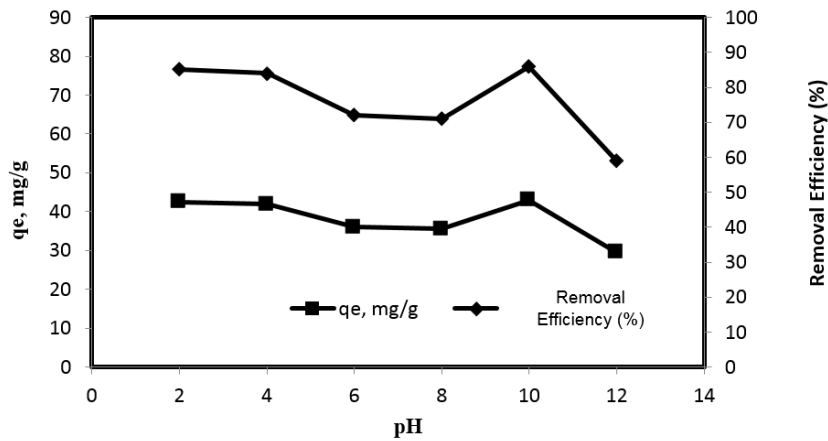


Figure 2. The effect of pH on the adsorption of fluoride onto modified eucalyptus leaves.

3.3. The Effect of Adsorbent Dosage

The results of the investigation of the adsorbent dosage and the optimal pH and equilibrium time are presented in Figure 3. As the adsorbent dosage increases from 0.1 to 1 g/L, the removal efficiency and adsorption

capacity decreases. The highest fluoride removal efficiency (83%) was achieved at the adsorbent dosage of 0.1 g/L at the optimal pH and the equilibrium time. Thus, the adsorbent dosage of 0.1 g/L was used in the following stages as the optimal adsorbent dosage.

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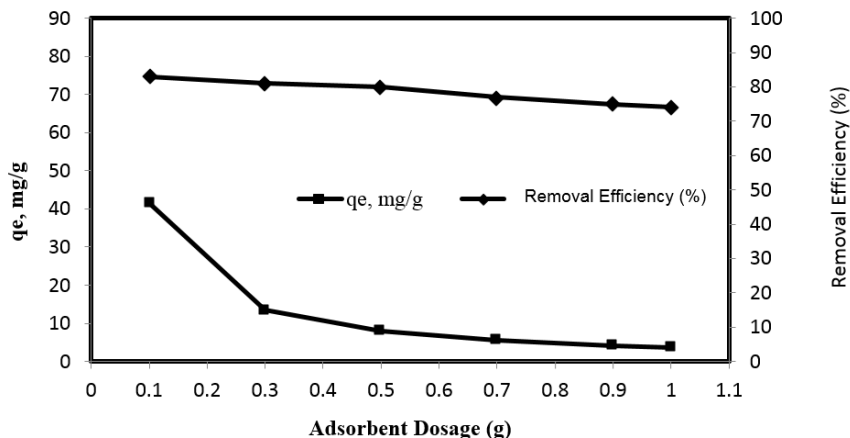


Figure 3. The effect of adsorbent dosage on the adsorption of fluoride onto modified eucalyptus leaves.

3.4. The Effect of the Initial Concentration

The results of fluoride removal efficiency at the optimal pH and adsorbent dosage levels with various initial concentrations of fluoride are presented in Figure 4. The highest and lowest removal efficiencies were achieved at

the initial fluoride concentrations of 5 and 30 mg/L, respectively. As can be seen in Figure 4, the adsorption capacity of fluoride by the utilized adsorbent increases as the initial concentration of fluoride increases.

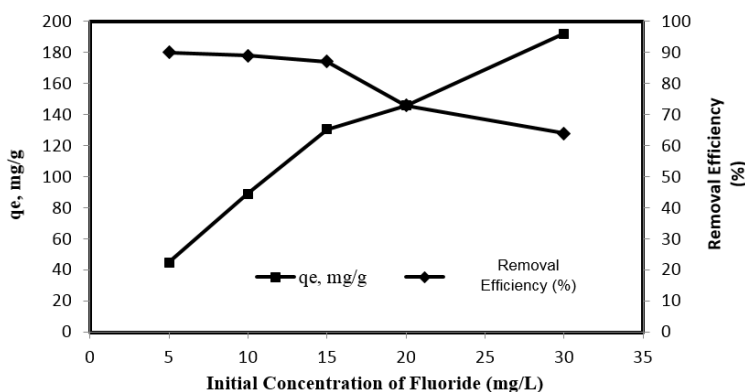


Figure 4. The effect of the initial concentration of fluoride on fluoride adsorption by modified eucalyptus leaves.

3.5. The Effect of Temperature

Figure 5 presents the results of the investigation of temperature on fluoride removal efficiency at optimal pH and

adsorbent dosage at various initial concentrations of fluoride. The thermodynamic parameters are also exhibited in Table 1.

Table1. Thermodynamic parameters

E_a (kJ/mol)	ΔG					ΔS°	ΔH°
3.26	25°C	30°C	35 °C	40 °C	45 °C	0.16	34.97
	-6.49	-6.79	-7.38	-7.81	-9.54		

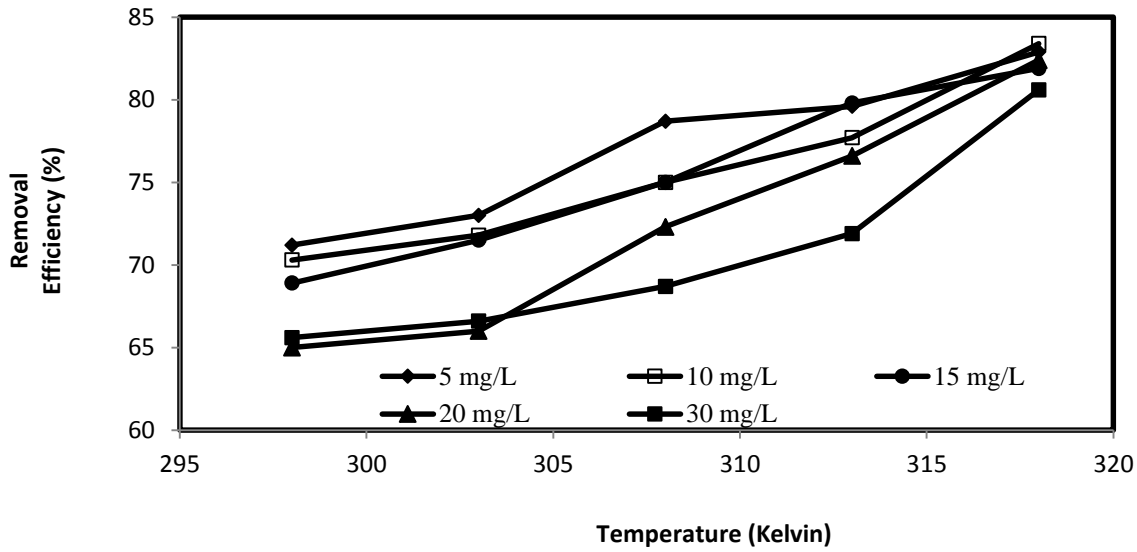


Figure 5. The effect of temperature on the adsorption of fluoride onto modified eucalyptus leaves

Thermodynamic parameters were evaluated by using the standard free energy (ΔG), standard enthalpy change (ΔH°), standard entropy change (ΔS°), and sticking probability (SP), given by equation 3-7 and reported between 25 and 45 $^\circ\text{C}$.

$$Sp = (1-\beta) \exp - (E_a/RT) \quad (3)$$

$$\beta = 1 - C_e/C_0 \quad (4)$$

3.6. Investigating Adsorption Kinetics

Adsorption amounts at various times were investigated using pseudo first-order and pseudo second-order kinetic models. The results of the matching of fluoride adsorption kinetic parameters with pseudo first-order and

$$\ln K = \Delta S/RT \quad (5)$$

$$K = q_e / C_e \quad (6)$$

$$\ln K = \Delta S / R - \Delta H^\circ / RT \quad (7)$$

Here, β is surface coverage, E_a is activation energy (kj/mol), R is gas law constant (8.314 J/mol. $^\circ\text{k}$), T is absolute temperature ($^\circ\text{k}$), and K is sorption equilibrium constant (11).

pseudo second-order kinetic models are presented in Table 2. The obtained results indicated that fluoride adsorption onto modified eucalyptus complied with the pseudo second-order kinetic model with R^2 equal to 0.999.

Table2. Kinetic parameters

Kinetic models	Kinetic parameters	Kinetic parameter values
Pseudo first-order kinetic model $\frac{dq_t}{dt} = k_1(q_e - q_t)$	q_e (exp) (mg/g)	15
	q_e (cal) (mg/g)	2.35
	K	-0.015
	R^2	0.9679
Pseudo second-order kinetic model $\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	q_e (exp) (mg/g)	15
	q_e (cal) (mg/g)	15.15
	K	0.08
	R^2	0.999

3.7. Investigating Adsorption Isotherm

The Freundlich isotherm is an empirical formula based on adsorption onto a heterogeneous surface. The value of *n* indicates how favorable the isotherm is. Thus, an *n* value of 2 to 10 indicates favorability. A value between 1 and 2 shows relative favorability. And a value of less than 1 indicates poor adsorption characteristics (18). One of the features of Langmuir’s equations is the dimensionless separation factor parameter *R_L*, which is calculated by equation

$$8; \frac{1}{1+bC_0} \quad (8)$$

where *C₀* is the initial concentration of fluoride. Using this parameter, the type of the adsorption process can be determined. The values of this parameter follow (Table 3) (25).

Table 3. Parameters and correlation coefficients

Isotherm type	<i>R_L</i>
Unfavorable	<i>R_L</i> > 1
Linear	<i>R_L</i> = 1
Irreversible	<i>R_L</i> = 0
Favorable	0 < <i>R_L</i> < 1

Table 4 shows the parameters and correlation coefficients of the three isotherms at a temperature of 25 °C. Examining the

adsorption isotherm showed that fluoride adsorption onto modified eucalyptus leaves complied with the Langmuir isotherm.

Table 4. Adsorption isotherm parameters

Adsorption isotherms	Isotherm constants	Isotherm constant values	<i>R²</i>
Langmuir $q_e = \frac{q_m b c_e}{1 + b c_e}$	b (L/mg)	0.74	0.9944
	<i>q_{max}</i> (mg/g)	61.35	
	<i>R_L</i>	0.06-0.21	
Freundlich $q_e = k_f c_e^{1/n}$	<i>K_f</i>	25.11	0.856
	<i>n</i>	2.03	

The results of fluoride adsorption studies using different adsorbents are also presented in Table 5 (17-20, 26).

Table 5. The studies of fluoride adsorption using different adsorbents.

Adsorbent	Optimum pH	Suitable kinetic model	Suitable isotherm model	Maximum adsorption capacity (q _m) (mg/g)	References
Pumice modified with MgCl ₂	6	Pseudo second order	Freundlich	5.5	(17)
Pumice modified with H ₂ O ₂	6	Pseudo second order	Freundlich	11.76	(17)
Natural pumice	6	Pseudo second order	Freundlich	4.5	(17)
Pumice modified with HDTMA	6	Pseudo second order	Langmuir	41	(18)
Brushite	5.36	Pseudo second order	Langmuir	29.2	(19)
Hydroxyapatite	4.16	Pseudo second order	Langmuir and Freundlich	3.12	(20)
Eucalyptus leaves modified with ZnCl ₂	6	-	Langmuir	3.5	(26)
Eucalyptus leaves modified with HCl	10	Pseudo second order	Langmuir	61.35	The present study

4. Discussion

In this study, the efficacy of eucalyptus leaves modified with HCl in the removal of fluoride from aqueous solutions was examined taking into account variables affecting the adsorption process. As the pH of the solution increased from 2 to 10, the fluoride removal efficiency increased, such that the maximum removal efficiency (86%) and the adsorption capacity (43 mg/g) were achieved at the time of 60 min, and at a pH of 10. After that, the increase in the pH from 10 to 12 led to a decrease in the removal efficiency down to 59%. The reason for this phenomenon was the anionic structure of fluoride and the dispersion of the positive and negative charges on the surface of the adsorbent as a function of the solution pH and the adsorbent p_{H_{pzc}}, such that if the pH was equal to p_{H_{pzc}}, the electric charges present on the surface of adsorbent would be balanced. However, if solution pH was less than adsorbent p_{H_{pzc}}, due to the fact that adsorbent surface was surrounded by

carboxylic agents containing protons and the increased positive charge on the adsorbent surface, the electrostatic attraction between the anions of fluoride and the adsorbent increased. At the same time, at pH levels higher than adsorbent p_{H_{pzc}}, the electrostatic attraction decreased due to the negative charge of the adsorbent. Since this study was the first attempt to investigate the characteristics of surface adsorption onto modified eucalyptus leaves, it was not possible to compare the results with similar studies. However, similar results have been reported about phenol removal by bentonites, in which increasing the pH from 4 to 12 resulted in an increase in removal efficiency (27). In the studies conducted on the adsorption of fluoride by various adsorbents, the optimal pH has been determined to be at the acidic and neutral range (11, 17, 19, 28). In the current study, investigating the effect of adsorbent dosage on the adsorption process made it clear that, as the adsorbent dosage

increased from 0.1 to 1 g/L, the adsorption efficiency and capacity decreased, so that the maximum efficiency (83%) and adsorption capacity (41.5 mg/g) were achieved at the concentration of 0.1 g/L. In fact, at the initial stage, there were found many empty spaces available to the adsorbate for adsorption. However, increasing the mass of the adsorbent more than 0.1 g/L led to overlaps in the adsorbent surface and the aggregation of the adsorbent, so that the available useful surface reduced. On the other hand, due to the competition that is created among the contaminant molecules in occupying adsorbent empty spaces, the adsorbent surfaces were not fully used, and all of its capacity was not used optimally, resulting in reduced contaminant removal levels (29).

Additionally, investigating the initial concentration of fluoride on the adsorption process showed that as the concentration of fluoride increased, the removal efficiency decreased, in a way that the highest efficiency (90%) was achieved at a concentration of 5 mg/L. The reason for this was the saturation of available adsorption spaces and their ineffectiveness at higher concentrations (30, 31). The results obtained at this stage were found to be consistent with the findings of certain other studies (12, 28). As the initial concentration of fluoride increased, the adsorption capacity increased, too, and the highest adsorption (192 mg/g) occurred at a fluoride concentration of 30 mg/L, which was due to the increased removal of fluoride at higher concentrations.

On the other hand, studying the effect of time on fluoride removal efficiency showed that temperature increase can lead to increased removal efficiency. The trend of increases in the removal efficiency occurred slowly in the temperature range of 25-45 °C. Afterwards,

this trend accelerated and reached its maximum level at 45 °C. Thus, the process of fluoride adsorption was facilitated as the temperature rose, which was a result in line with certain other studies conducted on fluoride adsorption (17, 18).

Generally, the values of activation energy specified the type of adsorption to be either physical (5-40 kJ/mol) or chemical (40-800 kJ/mol). The values of E_a suggested physical adsorption with weak interactions (i.e., hydrogen bonding) between the fluoride ion and the adsorbent. As seen in Table 1, the negative ΔG in all temperatures suggested spontaneous adsorption. This finding indicated that adsorbent had a high affinity for the fluoride adsorption from the solution under experimental conditions. Furthermore, the positive values of ΔH° and ΔS° verified that the adsorption phenomenon was endothermic and random (at solid/ solution interface) during fluoride adsorption. Due to the endothermic nature of adsorption, the adsorption of fluoride was higher in high temperatures. Randomness is a motive force in the thermodynamic process. These results were found to be in agreement with certain previous studies (11). The parameters obtained from kinetic equations and presented in Table 2 indicated that fluoride adsorption complied with the pseudo second order kinetic model with a high correlation coefficient ($R^2 = 0.999$). The calculated values for adsorption capacity (q_e (cal) (mg/g)) were documented to be very close to the experimental adsorption capacity values (q_e (exp) (mg/g)). The gained information confirmed the compliance of fluoride removal by any adsorbent with the pseudo second order kinetic model, too. Based on the findings of the current research, the isotherm equations represented a relationship between

the concentration of adsorbate onto the surface of adsorbent at experimental conditions and its equilibrium concentration in the liquid phase. Thus, investigating the adsorption isotherm made it possible for the researchers to determine the maximum adsorption capacity and define an equation in order to design an adsorption column (11). As illustrated in Table 3, examining the correlation coefficient of the curves of the adsorption models of Langmuir and Freundlich showed that fluoride adsorption onto the utilized adsorbent complied with the Langmuir adsorption isotherm. The Langmuir isotherm model proposes that adsorption occurs on a homogeneous adsorbent surface via monolayer adsorption without the occurrence of any reactions among adsorbent molecules at a constant adsorption energy (32-34). The reduction in removal efficiency, which occurs as a result of increased initial fluoride concentration, can be accounted for successfully by the fact that adsorption behavior complies with the Langmuir isotherm model with monolayer contaminant adsorption. The theoretical values for b and q_{\max} were obtained to be 0.74 L/mg and 61.35 mg/g, respectively. In this study, the R_L value was calculated and found to be in the range of 0.06 to 0.21 for various concentrations of fluoride, which is indicative of the favorable adsorption of fluoride onto the adsorbent, based on Table 3. Also, comparing the data in Table 4 showed that HCl-modified eucalyptus leaves as adsorbent in this study had the highest q_{\max} equal to 61.35 mg/g. At the same time, comparing the values of q_{\max} in Table 4 indicated that the adsorbent used in this study, each gram of which can remove 61.35 mg of fluoride, had the highest adsorption capacity in comparison with the other adsorbents. By comparing eucalyptus leaves modified with

ZnCl₂ and HCl in Table 4, it can be concluded that any modification with HCl could lead to a several-fold increase in the maximum adsorption capacity in comparison with ZnCl₂, and as a result, it can be said that HCl had better applicability for the modification of eucalyptus leaves as a natural adsorbent which is used in the removal of fluoride from aqueous media. In the Freundlich isotherm model, n is a measure of the intensity of adsorption, and if this value is between 1 and 10, the isotherm model is mathematically favorable (30). In this study, the obtained value for n in fluoride adsorption onto the utilized adsorbent was found to be 2.03 indicating the favorability of adsorption under the experimental conditions.

5. Conclusion

The general results of this study showed that any modification of eucalyptus leaves with HCl could lead to surface adsorption of fluoride from aqueous solutions with a maximum adsorption capacity of 61.35 mg/g under the optimal adsorption conditions of a pH of 10, initial concentration of 5 mg/L, and the adsorbent dosage of 0.1 g/L, giving a maximum removal efficiency of 90%. It was also documented that the pseudo-second order kinetic model and the Langmuir isotherm model had the best fit with the experimental data, and fluoride adsorption process was facilitated, as the temperature increased from 25-45 °C. Based on the results of the current study, and given the easy availability and abundance of the eucalyptus plant in various areas of Iran and the ease with which it can be modified, it can be very well used to remove fluoride from aqueous solutions with favorable adsorption capacity under optimal conditions. It is finally recommended that larger studies to be conducted on this

substance as an option to be used as adsorbent in the treatment of water and wastewater.

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Conflicts of interest

The Authors have no conflict of interest.

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