



Adsorption Isotherm, Kinetic and Thermodynamic Studies for Removal of Fluoride Ions from Drinking Water Using Modified Natural Pumice

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ABSTRACT

This study aimed to modify pumice using aluminum chloride as an adsorbent for defluoridation. Batch and column experiments were carried out to evaluate the effects of pH, initial fluoride concentration, contact time, dose, and temperature. The modified pumice adsorbent showed good fluoride removal in both batch and column studies. Fluoride up-take was observed to be effective >7%, at pH 6.5-7.5, and adsorption equilibrium time was observed at 60 min. The adsorption results were modelled using kinetic and isotherm models. Experimental data indicated that fluoride adsorption follows the second-pseudo-order kinetics model ($R^2 > 0.99$) and fits well with both the Freundlich and Langmuir isotherm models, which showed favorability for the adsorption of fluoride with a maximum capacity of 0.083 mg/g. The negative values of ΔH° and ΔG° indicate that the adsorption process was feasible, exothermic, and spontaneous. The column performance showed the best fluoride uptake efficiency, with a breakthrough capacity of 0.48 mg/g. The %R was approximately %100 using 0.1M NaOH. Fluoride levels in real wells water decreased dramatically (e.g. 4.1-0.88, 7.1-1.54, and 6.2-1.46 mg/L). The results revealed that modified pumice has the potential for fluoride removal from drinking water.

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1. INTRODUCTION

Groundwater is the primary and preferred drinking water supply in many regions of the world, including many rural and urban towns. The types of rocks in the area are the primary determinants of naturally occurring fluoride in the groundwater. For instance, sedimentary rocks, sandstone, and limestone are primary sources of fluoride [1]. In drinking water, fluoride is one of the many essential trace elements that must be present within the allowed limits (<1.5 mg/L) for the normal growth of human and animal bones [2]. However, consumption of more than the permitted concentration limit, is harmful to bone formation [3]. Excess fluoride can have detrimental effects on human health by interacting with calcium in the bones. As a result, it results in skeletal fluorosis

(bone cancer) and/or dental fluorosis [4]. Other negative effects of excessive fluoride in drinking water include thyroid issues, arthritis, and Alzheimer's disease [5]. Fluoride ion removal from solutions is important in various industries, such as water treatment, pharmaceuticals, and food production. There are several methods available for removing fluoride ions from solutions, such as ultrafiltration [6], osmosis [7], ion exchange [8], coagulation [9], electrodialysis [10], adsorption [11, 12] were studied. Adsorbents are generally regarded as low-cost adsorbents because they are widely available and need little processing [13–15]. The main characteristics that affect the permeability, stability, and longevity of granular filters, are their size, shape, distribution, porosity and texture of the employed particles [16]. In addition, modi-

fied natural adsorbents with high capacity can be used for fluoride removal from drinking water, such as zeolite [17], kaolin [18], bentonite [19], gypsum [20], and pumice [21], which are important natural adsorbent resources that can be used for demineralization. Pumice is a high volcanic rock that is primarily composed of silica and aluminum oxide, with large surface area and skeleton structure, porosity and mechanical strength, low cost, and non-toxic are the major benefits over the other synthetic or natural adsorbents materials. This method has been widely applied to remove pollutants from aquatic environments [22]. Yemen is one of the most water-scarce people in the world, with 18 million people unable to obtain safe and clean water or sanitation with acceptable quality, and some of them who can't provide drinking water are among the biggest problems they will face the people of Yemen in the next generation [23]. In recent years, the regional war in Yemen has led to the poor maintenance of water treatment plants, which has led to poor quality of water, which constitutes a threat to consumers' health. To the best of our knowledge, there are no reported data related to the use of Yamani pumice stone as an adsorbent for water. Therefore, the present work aimed to study the possibility of modifying natural pumice for defluoridation from wells water and to investigate the parameters affecting the adsorption efficiency and selectivity for fluoride ions.

2. MATERIALS AND METHODS

2.1. CHEMICAL AND REAGENTS

All chemicals were used without further purification, and all reagents were of analytical grade. Extra pure sodium fluoride was purchased from Merck, aluminum chloride hexa hydrate (97%), sodium hydroxide (97%), and sulfuric acid (95-98% w/v) were purchased from BDH, Hydrochloric acid (37% w/v) was purchased from SIGMA.

2.2. PREPARATION OF SOLUTIONS

- A stock solution (100 mg/L) of fluoride ions was prepared by dissolving an accurate weight (0.02210 g) of NaF in a 100 ml volumetric flask with deionized water.
- (0.5M) solution of aluminum chloride was prepared with an accurate weight (12.4454 g) of $AlCl_3 \cdot 6H_2O$ and dissolved in 100.0 mL of deionized water.
- (0.1M) solution of sodium hydroxide was prepared by accurately weighing (0.4124 g) of NaOH and dissolving in 100.0 mL of deionized water.
- (0.1M) H_2SO_4 and HCl were prepared individually by diluting the appropriate volume of acid in the required volume with deionized water.

2.3. INSTRUMENTS

All spectrophotometric measurements were performed using (DR-3900 HACH) according to method No. 8029.

- pH measurements were performed using a pH meter (Palintest PT 1330 Micro 800 pH meter, United Kingdom) connected to a combined glass electrode.
- A mechanical shaker (Gallenkamp flask shaker device, UK) was used. The water was purified using a Direct-Q3 water purification system (Millipore, Bedford, MA, USA).

2.4. MODIFICATION OF PUMICE (M.P)

The pumice stone was collected from the Isbil area of the Dhamar Governorate. First, the coarse Pumice stone was washed with deionized water to remove dust and impurities, then crushed using a mortar, and sieved to produce the desired particle size fractions. Next, to modify the adsorbents, the desired pumice particle size was soaked in an aluminum chloride solution for 24h at room temperature, and the solid material was separated and soaked again in sodium hydroxide for 5h. After that washed with deionized water until the pH of the solution was neutral. The modified adsorbent was oven-dried for 5h at 300 °C and stored in a closed bottle until use.

2.5. BATCH EXPERIMENTS

In separate 50mL stopper flasks, an accurate weight (0.5 ± 0.001 g) of M.P was added to 15mL of an aqueous solution containing many fluoride ions, and the solution pH was adjusted to the desired values using (0.1M) sodium hydroxide or hydrochloric acid solutions. The solution was shaken for the optimum time, the solid phase was separated, and the concentration of fluoride ions was determined spectrophotometrically [24]. The amount of fluoride ions removed was calculated from the difference. The adsorption percentage (%E) was calculated using the following equations [25]:

$$\%E = \frac{C_0 - C}{C_0} \quad (1)$$

where C_0 and C are the fluoride ion concentrations before and after adsorption, respectively. The influence of shaking time, fluoride ion concentration, and foreign ions, etc. was investigated in the same manner under specific conditions, as shown in Table 1.

2.6. COLUMN EXPERIMENTS

To study the breakthrough capacity, the standard solution of fluoride ions was adjusted to the optimum separation condition and percolated through the M.P packed column at 2ml/min. flow rate. Fluoride ion content before and after percolation was measured. Then the column was washed with a suitable eluting agent to strip the trapped



Table 1. Experimental conditions at 25 ° C.

Run	parameters	pH	F ⁻¹ conc mg L ⁻¹	adsorbent dose g /15mL	time min.
1	Effect of pH	4-9	4	0.5	120
2	Effect of contact time and adsorption kinetic	7	3	0.5	3-120
3	Effect of (M.P) dose	7	4	0.1-1.5	60
4	Effect of foreign ions	7	4	0.5	60
5	Effect of initial concentration	7	0.1-15	1	60
6	Effect of temperature (298, 308, 318 K)	7	3	0.5	3-120

fluoride ions for use in subsequent cycles.

3. RESULTS AND DISCUSSION

3.1. pH EFFECT

One crucial factor affecting fluoride adsorption processes is pH. In a range of 4 to 9, and under the conditions in Table 1, the effect of solution pH on the removal of fluoride was investigated. As shown in Figure 1, the maximum adsorption percentage was attained at pH 7 with an adsorption efficiency of 80%, which could be attributed to the ability of the modified adsorbent to form strong electrostatic interactions with fluoride species. On the other hand, the unmodified pumice did not adsorb fluoride ions, with E% equal to zero, which indicates the successful treatment of pumice for the removal of fluoride ions from solutions. In addition, from Figure 1, we can see that at higher pH values, the presence of hydroxide ions could potentially interfere with the adsorption process, hindering the adsorbent's ability to effectively bind fluoride ions, which led to a decreased removal efficiency of fluoride ions.

3.2. EFFECT OF SHAKING TIME AND ADSORPTION KINETIC STUDY

Using batch tests, the effect of the shaking time was investigated under the conditions illustrated in Table 1. After the equilibrium, the adsorbent was separated and the amount of fluoride ions remaining in the solution was measured. The adsorption efficiency and the amount of fluoride ions were calculated as usual. The obtained results are plotted in Figure 2. Showed that the optimum time required for maximum fluoride adsorption was approximately 60 min. And the static capacity was 0.083 mg/g.

- Adsorption kinetics:

Two simplified kinetic models, pseudo-first-order and

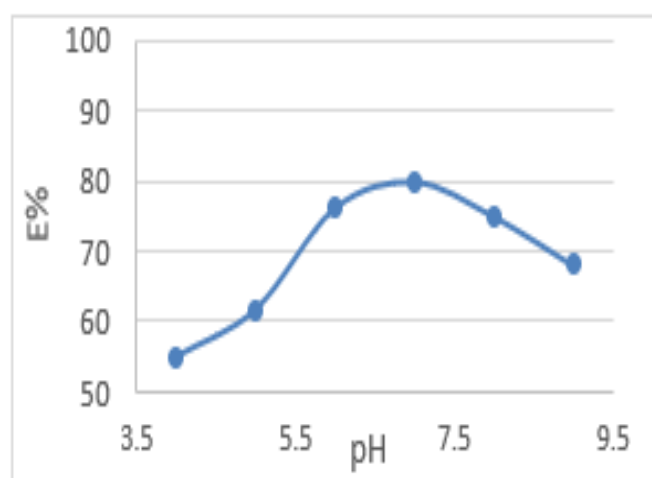


Figure 1. Effect of pH on the adsorption efficiency.

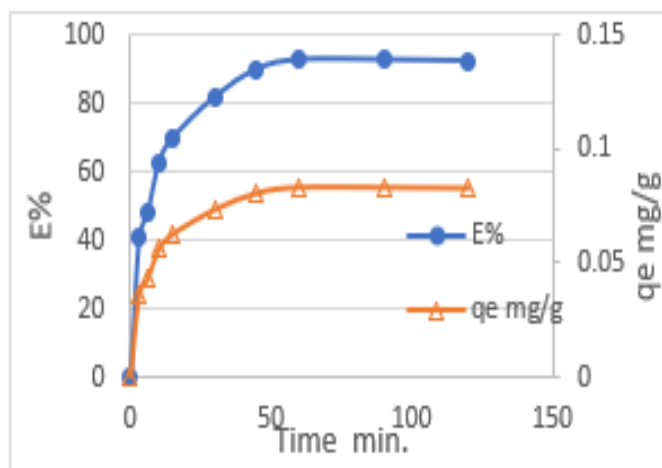


Figure 2. Effect of time on the adsorption efficiency.

pseudo-second-order, were applied to investigate the adsorption kinetics of M.P. [25].

- Pseudo-first-order kinetics model:

The linear pseudo-first order equation was given by

equation 2:

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303} \quad (2)$$

where q_e and q_t (mg/g) represent the adsorption capacities at equilibrium and time t (min), respectively, and k_1 (min^{-1}) is the adsorption rate constant obtained from the slope of the plot of $\log(q_e - q_t)$ against time (t), as shown in Figure 3. The experimental results are presented in Table 2.

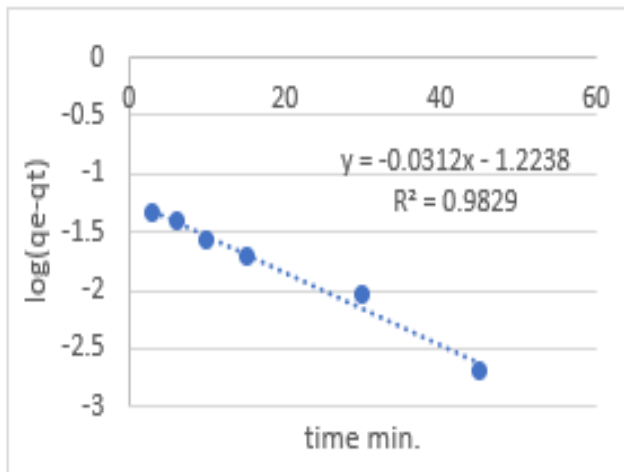


Figure 3. pseudo first order kinetic model for adsorption.

- Pseudo-second-order kinetics model:

The linear equation of the pseudo-second-order model is given by equation 3.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e and q_t as described previously, k_2 (g/mg·min) is the adsorption rate constant obtained from the intercept of plotting (t/q_t) against time (t). The calculated parameters are summarized in Table 2, and demonstrated in Figure 4 was indicated that the R_2 values obtained from both models are close to unity, but R_2 for pseudo-second-order kinetic model (0.9991) was the best fit. The adsorption behavior of fluoride ions by the adsorbent indicated that adsorption was the rate-controlling step. In addition, the calculated q_e value (0.087 mg/g) agrees well with the experimental q_e value (0.083 mg/g).

- **Kinetic Validation Study:** The most suitable model for describing the kinetic studies of fluoride ion adsorption onto the adsorbents was identified using standard deviation (%S.D.) [26], which was calculated using equation 4:

$$\%S.D. = 100 \sqrt{\frac{\sum [(q_{e,exp} - q_{e,cal}) / q_{e,exp}]^2}{N - 1}} \quad (4)$$

where N is the number of data points, and $q_{e,exp}$ and

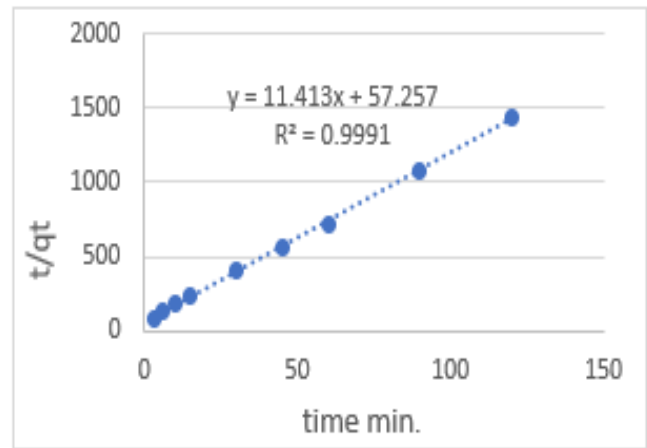


Figure 4. pseudo second order kinetic model for adsorption.

$q_{e,cal}$ (mg/g) are the experimental and calculated equilibrium adsorption capacities, respectively. As shown in Table 2, the lowest value of % S.D. of the pseudo-second-order kinetic model (1.9679) suggests that the pseudo-second-order model is the most appropriate equation for describing the adsorption kinetics.

3.3. EFFECT OF ADSORBENT DOSE

Different adsorbent doses were introduced into the solution and adjusted to the optimal conditions for adsorption, as shown in Table 1. The obtained results are shown in Figure 5. The results show that the adsorption percentage is directly proportional to the amount of M.P. dose required to reach a maximum adsorption efficiency of 80% at 0.5g. At a higher dose of more than 0.5g of M.P., the adsorption percentage remained constant [27].

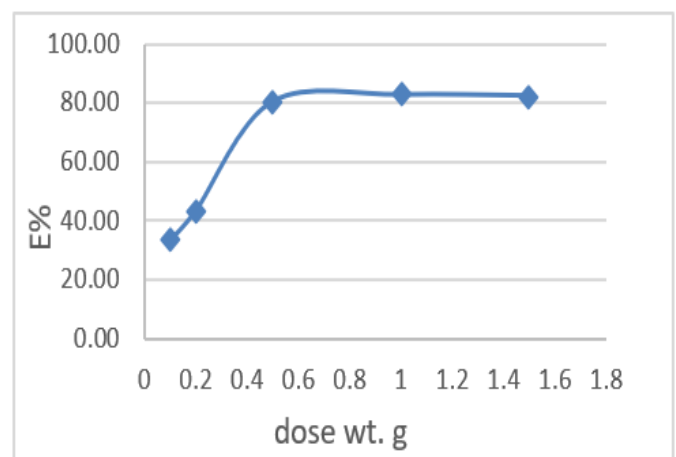


Figure 5. Effect of adsorbent dose.

3.4. EFFECT OF FOREIGN ANIONS

The effects of foreign anions such as chloride, bicarbonate, sulfate, nitrate, and phosphate were investigated.

Table 2. Parameters of adsorption kinetics study for pseudo-first and second-order kinetics

Kinetic mode	pseudo first order					pseudo-second order				
	Parameter	q_e exp mg/g	q_e calc mg/g	K_1 min ⁻¹	R ²	%S.D	q_e (calc) mg/g	K_2 (g/mg).min	R ²	%S.D
Fluoride		0.083	0.059	0.072	0.982	9.912	0.087	2.275	0.999	1.968

Under the conditions described in Table 1, the choice of anions and their concentrations were based on their availability in groundwater. The results are shown in Figure 6. The results in Figure 6 show that the defluoridation efficiency was unaffected by the presence of up to 50mg/L of nitrate ions, sulfate, chloride ions up to 200mg/L, phosphate ions 0.5mg/L and bicarbonate ions up to 10mg/L. but at higher concentrations ex: 5mg/g phosphate ions and 200mg/g bicarbonate ions the defluoridation efficiency decreases to 62% and 55%, respectively. These results demonstrate the selectivity of M.P for defluoridation under the investigated conditions.

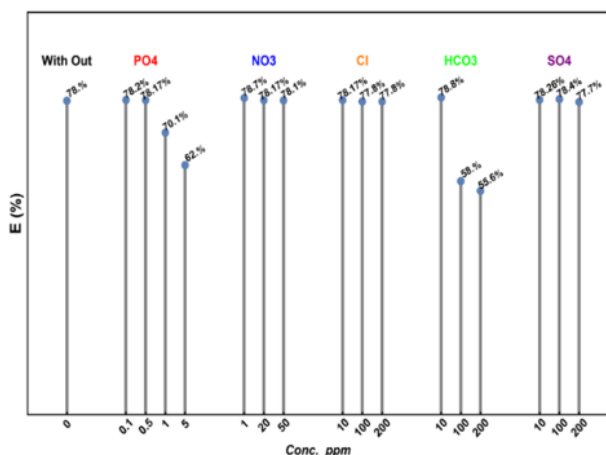


Figure 6. Effect of foreign anions.

3.5. THERMODYNAMIC INVESTIGATIONS

To clarify and validate the mechanism of fluoride adsorption onto M.P., the thermodynamic parameters ΔG° , ΔH° , and ΔS° of adsorption under the conditions indicated in Table 1 were evaluated using equations (5-7), [28].

$$\Delta G^\circ = RT \ln K_c \quad (5)$$

$$K_c = \frac{C_{Ad}}{C_e} \quad (6)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

The values of ΔH° and ΔS° can be obtained from the slope and intercept of the plot of $\ln K_c$ against $1/T$. The obtained data are presented in Table 3. From these

data, we can see that at each tested temperature, the calculated values of ΔG° were negative, indicating that fluoride ion adsorption onto M.P. occurred spontaneously and that M.P. has a high affinity for fluoride ion adsorption from solution under experimental conditions. The calculated values of ΔH° and ΔS° are $-47.4222 \text{ kJ mol}^{-1}$ and $-0.1385 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively. A negative value of ΔH° indicates an exothermic adsorption process. A negative ΔS° value indicates a decrease in randomness at the solid/solution interface during the fluoride adsorption process [29, 30]. The hypothesis of fluoride ion chemisorption onto M.P. was validated by the thermodynamic investigation results.

Table 3. Thermodynamic parameters at different temperatures.

T.°C	$\ln K_c$	ΔG° kJ mol ⁻¹	ΔH° kJ mol ⁻¹	ΔS° kJ mol ⁻¹ K ⁻¹	R ²
25	2.488	-6.165	-47.422	-0.138	0.999
35	1.843	-4.720			
45	1.285	-3.398			

3.6. ADSORPTION ISOTHERM

The adsorption of different initial concentrations of fluoride ions was investigated using batch experiments. Isotherms describe the precise relationship between the amount of fluoride adsorbed onto M.P. under the experimental conditions in Table 1. Consequently, using four of the most widely used isotherm models, an analysis of isotherm data for the maximum capacity q_m and other parameters was performed [31, 32].

- Langmuir adsorption model:

The Langmuir isotherm assumes that a single adsorbate binds to a single site on the adsorbent, and all surface sites on the adsorbents have the same affinity for the adsorbate, which implies a homogenous surface energy distribution. The saturation monolayer can be represented by equation 8.

$$\frac{1}{q_e} = \frac{1}{(C_e K_L q_m)} + \frac{1}{q_m} \quad (8)$$

where C_e is the equilibrium concentration of the sor-

bent (mg/L), q_m is the maximum sorption capacity of the adsorbent (mg/g), K_L is the Langmuir constant, and q_e is the equilibrium sorption capacity of the adsorbent in mg/g sorbent. From the slope and intercept of the plot of $1/q_e$ versus $1/C_e$ as shown in Figure 7 the values of q_m and k_L were determined and the calculated parameters are summarized in Table 4. On this basis, the monolayer maximum adsorption capacity, q_m was found to be 0.0399 mg/g fluoride ions. From an analysis of a distinctive feature known as the dimensionless equilibrium (R_L), as given in equation 9.

$$R_L = \frac{1}{1 + K_L C_o} \quad (9)$$

where C_o is the highest initial concentration (15 mg/L) and the Langmuir constant K_L and the Langmuir adsorption isotherm are confirmed by the value of R_L , where $R_L > 1$ is unfavorable, $R_L = 1$ is linear, $0 < R_L < 1$ is favorable, and $R_L \leq 0$ is irreversible. In the present study, the R_L value was (0.01884), indicating that the sorption intensity for fluoride ions was the most favorable.

- Freundlich adsorption model:

The Freundlich model is an empirical method for adsorbents with heterogeneous adsorbing surfaces, assuming that multilayer adsorption occurs on heterogeneous surfaces. The Freundlich adsorption isotherm is given by equation 10:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

where q_e and C_e are the amount adsorbed (mg/g) and the adsorbate concentration at equilibrium, respectively. The Freundlich isotherm constant K_F and the intensity of adsorption (n) are Freundlich constants that affect the adsorption process. K_F and n can be determined from a plot of $\log q_e$ vs. $\log C_e$, as shown in Figure 8. The isotherm evaluation results are presented in Table 4. As shown in this Table, the n value (1.5418) was greater than 1; therefore, it can be concluded that M.P. is a suitable adsorbent and beneficial for the adsorption process. The R_2 values obtained from the Langmuir and Freundlich adsorption models were close to unity (0.9941 and 0.9835, respectively), but the Langmuir adsorption model best fitted the fluoride ion adsorption behavior of the adsorbent.

- Temkin adsorption model:

Temkin and Pyzhev (1940) explained the heat of adsorption of all molecules on the adsorbent surface by assuming indirect adsorbate/adsorbent interactions in adsorption isotherms. The Temkin isotherm model in equation 11 can be represented as follows:

$$q_e = B_T \ln K_T + K_T \ln C_e \quad (11)$$

where q_e is the amount of fluoride ions adsorbed per gram of adsorbent (mg/g), C_e is the equilibrium con-

centration in the solution (mg/L), and K_T ($L \text{ mg}^{-1}$) is the binding constant that represents the maximum binding energy. B_T is the adsorption heat linked to the Temkin isotherm constant, b_T as shown in equation 12:

$$B_T = \frac{RT}{b_T} \quad (12)$$

where R is the gas constant (8.31 J/mol K) and T is absolute temperature (298 K). The isotherm constants k_T and B_T can be obtained from the slope and intercept of the plot of q_e versus $\ln C_e$ as shown in Figure 9. The experimental results showed low correlation with the Temkin isotherm ($R^2 = 0.8556$). The value of b_T was more than 8KJ/mole indicating a very strong connection between the fluoride ions and the surface of the adsorbent.

- Dubinin–Radushkevich (D-R) adsorption model:

The adsorption mechanism and the energy required for the process should be ascertained using other isotherms, as the Langmuir and Freundlich isotherm models do not provide information on the mechanisms or the energy needed for adsorption. These data can be acquired by applying the (D-R) isotherm formula 13:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (13)$$

where q_e is the equilibrium adsorbed amount of the adsorbed substance ($\text{mg} \cdot \text{g}^{-1}$), q_m is the theoretical saturation capacity ($\text{mg} \cdot \text{g}^{-1}$), β is the D–R model constant ($\text{mol}^2 \text{ kJ}^{-2}$), ε is the Polanyi potential (kJ mol^{-1}), and is given by equation 14.

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (14)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (298 K), and C_e is the equilibrium concentration of the adsorbate (mg L^{-1}). The values of β and q_m can be calculated from the slope and intercept of the plot of $\ln q_e$ vs. ε^2 as shown in Figure 10. The mean free energy of adsorption (E , kJ mol^{-1}) can be calculated using equation 15 based on the β value.

$$E = \frac{1}{\sqrt{2\beta}} \quad (15)$$

From the D-R isotherm parameters in Table 4, the calculated value of E is $11.9522 \text{ kJ mol}^{-1}$. The range of values of E between 8 and 16 kJ mol^{-1} indicates that, under the operating conditions, chemical adsorption plays a significant role.

3.7. BREAKTHROUGH CAPACITY

A solution of 3mg/L of fluoride ions adjusted to the optimum conditions for adsorption was passed through the column packed with 1 g of M.P. at a flow rate of $2 \text{ mL} \cdot \text{min}^{-1}$ until the effluent concentration reached that of



Table 4. Physicochemical adsorption parameters of fluoride ions by M.P.

Isotherm models	Symbol	Parameters	Values
Langmuir	q_m	Maximum adsorption capacity (mg/g)	0.03994
	K_L	Langmuir constant(L/mg)	3.4721
	R_L	Dimensionless equilibrium	0.01884
	R^2	Correlation coefficient	0.9941
Freundlich	n	Intensity of adsorption g/mg	1.5418
	K_f	Freundlich isotherm constant (L/mg)	0.03294
	R^2	Correlation coefficient	0.9835
Temkin	K_T	Temkin equilibrium binding constant (L/g)	30.7739
	b_T	Temkin isotherm constant (kJmol ⁻¹)	165.1714
	B_T	Temkin isotherm constant related to heat of sorption (J/mol)	0.015
	R^2	Correlation coefficient	0.8556
D-R	q_m	adsorption capacity (mol g ⁻¹)	1.9146 * e ⁻⁶
	β	D-R constant (mol ² kJ ⁻²)	0.0035
	E_D	Free energy (kJmol ⁻¹)	11.9522
	R^2	Correlation coefficient	0.9951

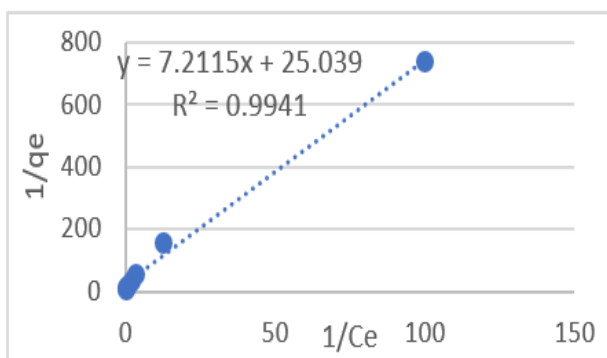


Figure 7. Langmuir isotherm

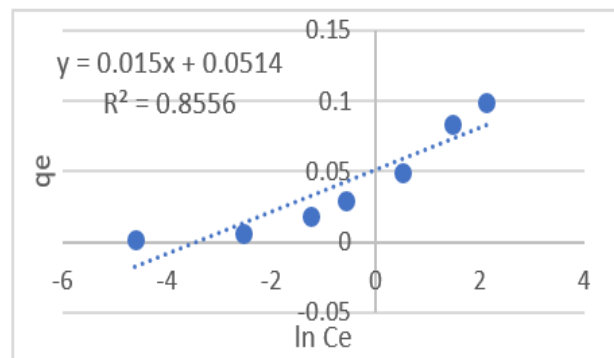


Figure 9. Temkin isotherm

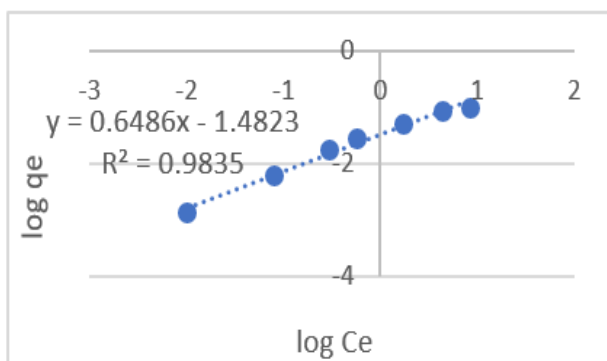


Figure 8. Freundlich isotherm

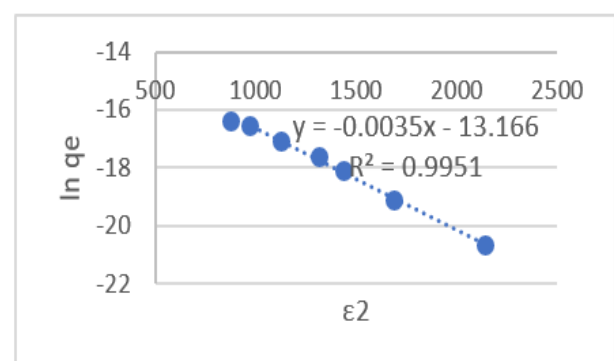


Figure 10. D-R isotherm

the feed solution. The breakthrough capacity per gram ($\text{mg}\cdot\text{g}^{-1}$) of adsorbent was calculated according to the following equation:

$$\text{Dynamic Capacity} = \frac{V_{50\%} \times C_o}{m} \quad (16)$$

where $V_{50\%}$ is the effluent volume (mL) at 50% breakthrough curve, C_o is the concentration of the feed solution (mg/L), and m is the mass of the adsorbent (g). The breakthrough curves are shown in Figure 11. Saturation of the column was reached after passing 350mL of 3 mg/L fluoride ions. The capacity of the M.P. column for fluoride ions was estimated to be 0.48 mg g^{-1} .

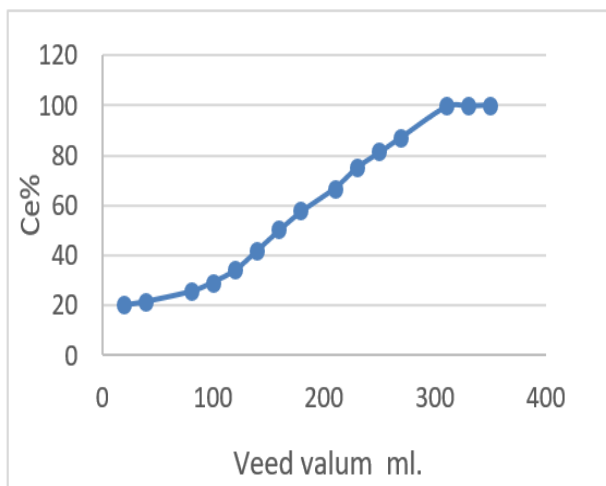


Figure 11. Breakthrough curve for fluoride ions using M.P adsorbent

3.8. EFFECTED OF ELUTING AGENTS ON THE RECOVERY OF FLUORIDE IONS

After the percolation of fluoride ions through a column packed with M.P., the trapped ions on the column can be stripped out using different eluting agents such as (0.1M HCl, H_2SO_4 or NaOH). The obtained data are summarized in Figure 12. Sodium hydroxide exhibited a higher recovery percentage ($R\%=100\%$) of loaded fluoride ions on M.P., while HCl or H_2SO_4 exhibited a lower recovery percentage ($R\%=40\%$ and 65% , respectively).

3.9. REGENERATION AND REUSED STUDY

The regeneration and reuse of the adsorbent were evaluated by passing 100 mL of a 3 mg/L fluoride solution through the column at a flow rate of 2 mL/min. Then, the untrapped fluoride ions in the effluent were determined, and the amount of fluoride ions adsorbed was calculated using equation no. 17.

$$q_e = [(C_o - C_e) * V] / m \quad (17)$$

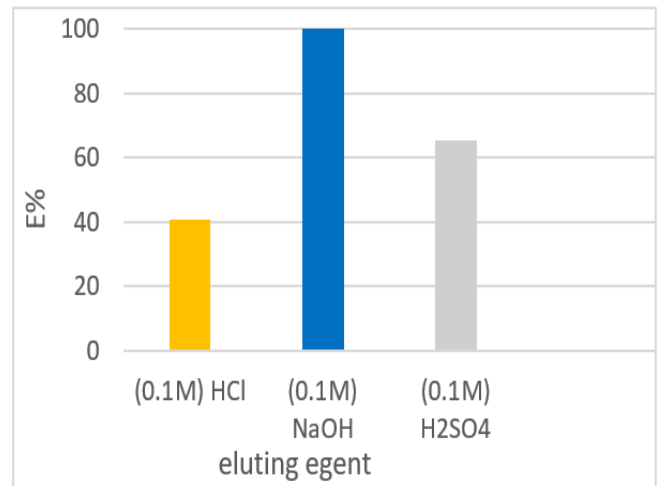


Figure 12. Effect of deferent eluting agent on the stripping of fluoride ions

where q_e is the amount of adsorbed fluoride ($\text{mg}\cdot\text{g}^{-1}$), C_o is the initial concentration of fluoride ($\text{mg}\cdot\text{L}^{-1}$), and C_e is the equilibrium fluoride concentration in the solution ($\text{mg}\cdot\text{L}^{-1}$), m is the mass of the adsorbent (g), and V is the volume of the ions solution (L). Also, the adsorption efficiency calculated by using the equation no. 1. After that pass 20mL of 0.1M NaOH to elute the loaded fluoride ions on the column. The eluted fluoride ions in the effluent were then determined and the recovery % R was calculate. In the last step, the column was washed with deionized water until the effluent solution became neutral. Subsequently, the previous procedures were repeated several times. The obtained data are summarized in Table 5, which shows the successful regeneration of the column four times with recovery per cent ranging from 100% to 68%; however, the adsorption efficiency in the subsequent cycles dropped from 79% to 40% in the third cycle; so, we can use the column for defluoridation with satisfactory efficiency for three cycles. On the other hand, the decreasing adsorption efficiency with subsequent cycles may be due to the weak loading between the modifier and adsorbent surface or may be due to a high concentration of the letting agent 0.1M NaOH, which requires a fourth study to show the nature of binding between the modifier and adsorbent surface.

Table 5. Regeneration and reused efficiency of M.P for defluoridation.

No. of Cycle	$Q_e \mu\text{g}$	E%	$Q_R \mu\text{g}$	R%
1	240	79	240	100.0
2	240	70	180	85.7
3	240	40	84	70.0
4	240	29	60	68.9



3.10. APPLICATION FOR DRINKING WATER

Water samples were collected from different wells (w) and treatment plants (s) in Sana'a City according to the standard method [24]. 100mL of water samples was passed through a column packed with M.P. under lap experimental conditions. The fluoride ion concentration was measured before and after the treatment (feed and effluent), and the results are summarized in Table 6. The results showed that the fluoride ion concentration in the wells water was higher than that in the treatment plant, where in wells water ranged from to 2.6-7.1 mg/L while the fluoride ion concentration in the treatment plant was 1.55, 2.1 mg/L. After passing the wells water samples through the column packed with M.P. ranged from 0.53 to 1.54 mg/L and these values are within the acceptable value permitted according to WHO and YSMO (≤ 1.5 mg/L). Also, in the water samples of the treatment plant after percolating through the column the fluoride ions concentration was 0.3, 0.4 mg/L these values are lower than the permitted value. From these results, we can conclude that the M.P. is able to remove fluoride ions under the study conditions with high efficiency. This has improved the quality of drinking water and reduced its consumer health.

Table 6. Characteristics of actual drinking water quality before and after adsorption.

Sample code	Conc. Before mg/L	Conc. After mg/L	E%
w1	4.1	0.88	78.5
w2	2.6	0.53	79.6
w3	4	0.87	78.2
w5	5.9	1.33	77.4
w6	6.2	1.46	76.4
w7	3.5	0.71	79.7
w8	7.1	1.54	78.3
S1	1.55	0.3	80.6
S2	2.1	0.43	79.5

4. CONCLUSION

This study focused on the desorption and regeneration of Yemeni local natural pumice for fluoride removal from aqueous solutions and its application to wells water defluoridation. The results indicate that modified pumice is a good choice because it is a low-cost, easily prepared, and effective sorbent with a relatively high adsorption capacity for fluoride. The sorption capacity of the modified pumice as a sorbent was significantly affected by the

contact time and initial concentration of fluoride ions in the solution. Co-existing anions were significantly unaffected by the adsorption efficiency of fluoride ions, even at high concentrations. Further investigations are needed for field studies, such as optimization of application in drinking water treatment plants.

5. AUTHOR CONTRIBUTIONS

M. A., A. A and Gh. A. performed and designed the experiment and methodology, M. A., A. A., analyzed the data, Gh. A. and M. A.; writing-original draft preparation: M. A., A. A., and Gh. A. writing-review and editing, M. A. and A. A. supervised M. A. and all authors have read and agreed to the published version of the manuscript

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