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Removal of fluoride from aqueous solution by natural and acid-activated diatomite and ignimbrite materials

Esengül Kır[a,*], Hatice Oruc[a], Ismail Kır[b], Tugba Sardohan-Koseoglu[a]

[a]*Faculty of Arts and Science, Department of Chemistry, Suleyman Demirel University, 32260 Isparta, Turkey, Tel. +90 246 2114336, +90 246 2114261; Fax: +90 246 2371106; emails: esengulkir@sdu.edu.tr (E. Kır), haticegunduz1985@hotmail.com (H. Oruc), tugbasardohan@sdu.edu.tr (T. Sardohan-Koseoglu)*
[b]*Faculty of Arts and Science, Department of Biology, Suleyman Demirel University, 32260 Isparta, Turkey, Tel. +90 246 2114064; Fax: +90 246 2371106; email: ismailkir@sdu.edu.tr*

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ABSTRACT

The aim of this study was to investigate the adsorption capabilities of some natural adsorbents for the removal of fluoride from aqueous solution. The adsorption of fluoride onto diatomite and ignimbrite in aqueous solutions was studied in a batch system. Batch adsorption experiments were conducted to examine the influence of various parameters such as pH, adsorbent amount, contact time, initial fluoride concentration, and temperature. In order to increase adsorption capacity, diatomite and ignimbrite were activated by H_2SO_4. The fluoride adsorption capacity of acid-activated form was found to be higher than that of the natural form of adsorbents. Characterization of the acid-activated adsorbents was confirmed through scanning electron microscopy, Brunauer–Emmett–Teller, and Fourier transform infrared spectroscopy. All adsorption experimental data fitted with the Freundlich and Dubinin–Radushkevich isotherms. The maximum fluoride removal was obtained within 2 h at an optimum adsorbent amount of 0.3 g/mL. Mechanism of fluoride adsorption was found to follow a pseudo-second-order rate equation for both adsorbents. Thermodynamic parameters were calculated to explain the nature of adsorption process. Fluoride removal properties for drinking water were evaluated by acid-activated adsorbents. Overall results showed that acid-activated diatomite material shows better fluoride removal capacity than ignimbrite in drinking water. The presence of other ions in drinking water did not affect fluoride removal efficiency.

Keywords: Acid activation; Adsorption; Diatomite; Fluoride; Ignimbrite

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1. Introduction

Fluoride is one of the important anionic chemicals found on earth. Fluoride has significant effects on humans depending on its concentration [1]. Fluoride affects mainly on teeth and skeleton. Small amounts of fluoride are beneficial for strengthening our teeth and bone tissue (less than 1.5 mg/L), whereas intake of excess fluoride may cause mottled teeth and bone damage, neurological disorder, and fluorosis (around 5 mg/L) [2,3]. According to World Health Organization, the fluoride concentration in drinking water must not exceed 1.5 mg/L [1].

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*Corresponding author.

The concentration of fluoride in groundwater is found at levels higher than 1.5 mg/L in some regions of the world. Excessive amounts of fluoride have been reported in various countries including Iraq, Iran, Syria, India, The United States, Argentina, China, and Turkey [4–7]. The amount of fluoride in surface and groundwater in some parts of Anatolia is above 1.5 mg/L [8]. In groundwaters, high fluoride concentrations occur in large and extensive geographical belts associated with volcanic and granitic rocks and fluoride minerals [1]. These fluoride minerals are fluorspar (CaF_2), sellaite (MgF_2), Villianmite (NaF), cryolite (Na_3AlF_6), apatite ($Ca_{10}(PO_4)_6F_2$), mica, and others, with low solubility in water. The various factors that govern the release of fluoride into groundwater are pH, temperature, the nature of geological sources interacted by water, and slow dissolution of fluorine-containing rocks [9,10].

Fluoride compounds are widely used in various branches of industry such as metal refining, aluminum smelters, and high-tech semiconductor factories [5,11–14]. Hence, fluorides can also be present in groundwater because of these industries and contribute to fluoride pollution to a great extent. Many technologies have been developed to remove excessive fluoride from drinking water such as chemical precipitation [15], ion exchange resins [16], electrocoagulation [17], reverse osmosis [18], Donnan dialysis [19,20], electrodialysis [21,22], and adsorption [23–27]. Adsorption technique is widely used for fluoride removal from water because of its simplicity, effectiveness, and low costs.

In recent years, many researchers have extensively investigated for the development of low-cost and effective adsorbents for defluoridation. Among these, alumina, activated carbon, red mud, and mixed rare earth oxides are the most widely used adsorbents [28–31]. Diatomite and ignimbrite, which are low cost and natural materials, were selected as adsorbents in this study. These materials were activated by an acidic medium in order to increase the percentage of fluoride removal. It is generally known that adsorption capacity of the adsorbents can be improved with increased acidity [32]. Thus, acid-activated diatomite and ignimbrite materials were used as an adsorbent for the first time for fluoride removal in this study.

The main goal of this study is to investigate the effects of H_2SO_4 activation of diatomite and ignimbrite surfaces on fluoride removal from the drinking water. The most commonly used acids for acid activation include HCl, H_2SO_4, H_3PO_4, and HNO_3. Therefore, H_2SO_4 as a strong acid was chosen for acid activation in this study [33–35].

Both natural and acid-activated diatomite and ignimbrite materials were used for fluoride removal by adsorption. The effects of adsorption parameters including pH, adsorbent amount, contact time, and temperature on fluoride adsorption were evaluated and adsorption capacity was determined by equilibrium isotherms. The batch adsorption results were then verified for practical application on a natural drinking water source with a high fluoride concentration in Isparta, Turkey.

2. Materials and methods

2.1. Materials

All chemicals (H_2SO_4, HCl, NaOH) were reagent grade and purchased from the Merck Co and Aldrich. The deionized water was used for the preparation of aqueous solutions. Adsorption materials (diatomite and ignimbrite) were supplied from Ankara and Kütahya regions of Anatolia (Turkey). Adsorbents were obtained from SDU Pumice Research Center (SDU-PRC). Details of used adsorbents were also provided by SDU-PRC and given in Tables 1 and 2. The chemical composition of the adsorbents (before and after acid activation) showed that they were mainly composed of silica as SiO_2 (Table 1). The main characteristics of the adsorption materials are also listed in Table 2.

2.2. Preparation and characterization of the materials

The acid-activated materials (diatomite and ignimbrite) were prepared according to the following procedure: 15 g of each material was refluxed with 250 mL of 2-mol/L H_2SO_4 for 2 h at 373 K. After reflux, the materials were suction filtered, washed with de-ionized water several times until it was free of SO_4^{2-} and oven-dried at 373 K overnight [34,35]. The changes in the acid-activated and natural material surface morphology were assessed with a scanning electron microscopy (SEM) (Vega Tescan, Czech Republic). The infrared spectrum was obtained using Perkin Elmer Spectrum BX FTIR spectrophotometer (USA) in the range of 400–4,000 cm^{-1} (KBr pellets). The chemical composition of the adsorbents (natural and acid-activated) was determined by ICP-OES (Perkin Elmer DV Optima 2100, USA). The specific surface area was determined by multipoint method (BET–Surface Area Micromeritics Gemini 2360, USA).

2.3. The batch adsorption experiments

The fluoride solutions with different concentrations were prepared by dilution of 100 mg/L stock solution

Table 1
The chemical composition of adsorption materials

Chemical composition (wt%)	Diatomite (before acid-activated)	Ignimbrite (before acid-activated)	Diatomite (after acid-activated)	Ignimbrite (after acid-activated)
SiO_2	80.64	68.52	80.47	68.60
Al_2O_3	2.57	12.28	2.51	12.34
Fe_2O_3	0.96	1.53	0.94	1.51
CaO	5.85	0.91	5.72	0.87
MgO	0.98	0.55	0.40	0.50
Na_2O	0.84	3.05	0.82	3.03
K_2O	0.68	4.80	0.51	4.34
TiO_2	0.10	0.05	0.10	0.05
Loss	6.53	6.71	6.93	7.31

Table 2
Properties of adsorption materials

Properties	Diatomite	Ignimbrite
Particle size (μm)	250	125
Density (g/cm^3)	2.1	2.27
Unit mass (g/cm^3)	0.35	0.94
Porosity ratio (%)	79–87	54–61
Pore size range (μm)	3−18	3−18

prepared from standard solution of 1,000 mg/L (analytical grade). In batch adsorption experiments, pre-defined amounts of materials (0.5 g) and fluoride solution (10 mL) were taken in 50-mL volumetric flasks. The suspension was shaken at a constant speed (500 rpm) with magnetic stirrer at 25 ± 2˚C for 120 min and filtered. Then, the filtrate was analyzed for fluoride concentration by a specific ion electrode (Mettler Toledo Perfect Ion Combination Fluoride Electrode, USA). TISAB II (Merck) was used as a buffer for maintaining the ionic strength, constant pH, and eliminating the interference effect of complexing ions. The pH optimization was assessed by varying the pH of sodium fluoride solution from 5 to 7. A digital pH meter (Mettler Toledo Seven Multi pH/Ion meter, USA) was used for pH measurement. All measurements were performed at 298 K. The experimental parameters studied were adsorbent amount (0.1–1 g), contact time (0.5–48 h), initial fluoride concentration (1–20 mg/L), and pH (5–7). Freundlich, Langmuir, and Dubinin–Radushkevich isotherms were used to model the adsorption process.

3. Results and discussion

3.1. Chemical composition and surface area of adsorbents

The chemical analysis showed that the main structures of adsorbents are SiO_2 and Al_2O_3 compounds (Table 1). After acid activation, chemical composition was not changed significantly due to the low solubility of these oxides in acid solutions. Small reductions in weight percent of some oxide compounds were observed. Percentage of both the exchangeable ions and the octahedral cations were decreased, while silica virtually remains same due to its lower solubility in acid solutions (Table 1). Similar results were also reported [35,36].

The results of Brunauer–Emmett–Teller (BET) analysis are given for both natural and acid-activated diatomite and ignimbrite materials in Table 3. Specific surface area of adsorbents has been slightly increased with acid treatment compared to the natural adsorbents and fluoride removal was enhanced as well.

3.2. The characterization of the materials

The changes in the surface morphology of acid-activated diatomite and ignimbrite were investigated by SEM. Figs. 1–4 show natural and acid-activated surfaces of diatomite and ignimbrite, respectively. The SEM images indicate that the surfaces of acid-activated materials are different. Acid activation causes surface erosion, collapse, and a decrease in the particle size on the natural materials because of some acid-soluble salts coalescence. Similar results were also

Table 3
BET surface area of the natural and acid-activated diatomite and ignimbrite

Sample	S_{BET} (m^2/g)
Natural diatomite	100.05
Acid-activated diatomite	106.50
Natural ignimbrite	34.65
Acid-activated ignimbrite	40.34

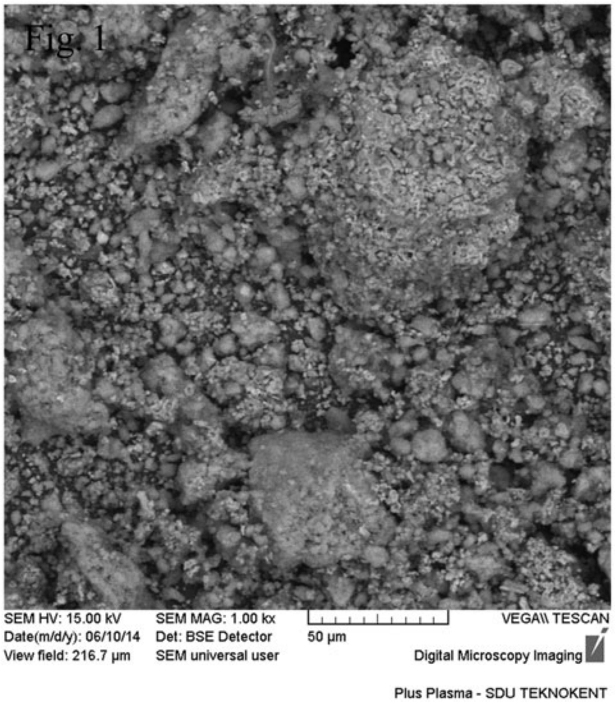

Fig. 1. SEM image of the surface of natural diatomite.

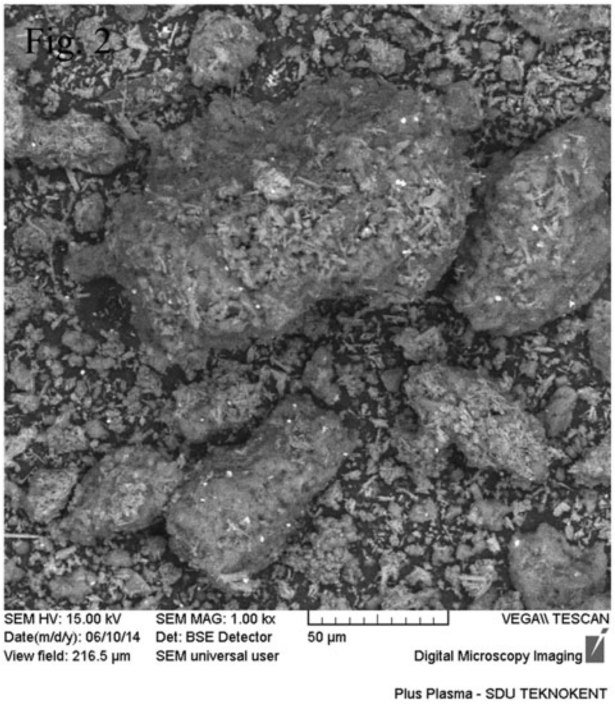

Fig. 2. SEM image of the surface of acid-activated diatomite.

Fig. 3. SEM image of the surface of natural ignimbrite.

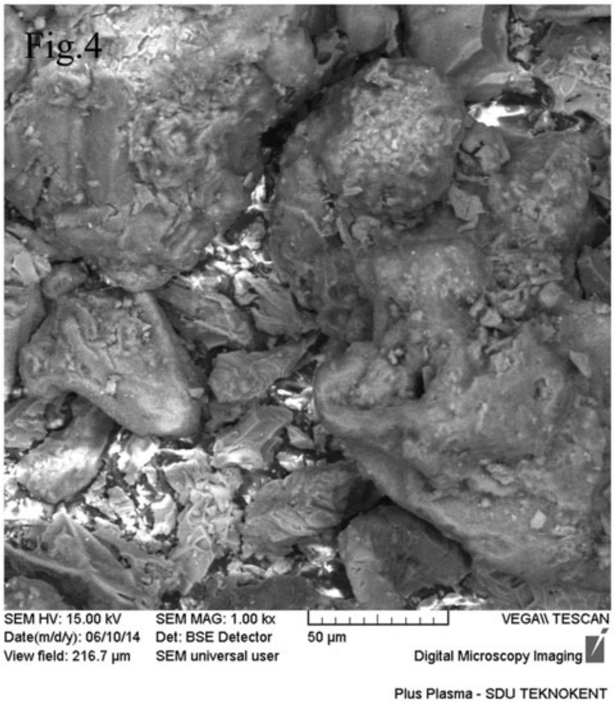

Fig. 4. SEM image of the surface of acid-activated ignimbrite.

reported for the adsorption of phosphate onto raw and activated red mud and fly ash [32] and the recovery of Mg content from natural smectite clay [37]. Fourier transform infrared (FTIR) spectroscopy is one of the oldest and most sensitive methods for the analysis of material structures. The FTIR spectra of the natural and acid-activated diatomite and ignimbrite adsorbents are given together in Figs. 5 and 6. For all adsorbents, an absorption band in the region of 464.31–466.5 cm^{-1} which can be assigned to the deformational vibration of the Si–O band was observed. The broad and very intense band with a maximum at 1,037–1,151 cm^{-1} can be related by the asymmetric stretching modes of Si–O–Si bonds. For acid-activated adsorbents, the Si–O–Si band frequencies showed maximum shifts due to the interaction between H^+ ions and the adsorbent surface (both diatomite and ignimbrite). The other bands were not significantly affected by the acid treatment. In addition, these bands at 1,151 and 1,080 cm^{-1} showed increased intensity for the acid-activated diatomite and ignimbrite adsorbents.

The broad bands at 3,444 cm^{-1} in Fig. 5 and at 3,464 cm^{-1} in Fig. 6 can be attributed to the OH deformation vibrational mode of the hydroxyl molecule for acid-activated diatomite and ignimbrite adsorbents, respectively. This deformation band is not observed for natural diatomite and ignimbrite adsorbents. The peaks at 1,627–1,638 cm^{-1} can also be caused by the stretching vibrations of adsorbed water. Although the chemical structure of the diatomite and ignimbrite adsorbents was not affected by the acid treatment, the sign of structural deformation can be seen after acid treatment. Obtained results are in very good agreement with those in the literature [38–40]. Generally, the intensity of all specific peaks belongs to adsorbents which increased after acid treatment.

3.3. The effect of pH

pH is one of the important factors which significantly affects the adsorption capacity of the adsorbent. The effect of aqueous solution pH on fluoride adsorption was investigated at different pH values ranging from 5 to 7 with both adsorbents. At a pH above 7, fluoride adsorption decreases because of the stronger competition with OH^- ions on adsorbent surface. Besides, at a pH below 5, adsorption is also not favored because of the complexation of F^- by H^+ [41]. Therefore, in this study, a pH range of 5–7 was selected. Fig. 7 shows the effect of pH on adsorption of fluoride onto activated adsorbents. It can be observed from the results that the maximum adsorption of fluoride was obtained at pH 6 and then

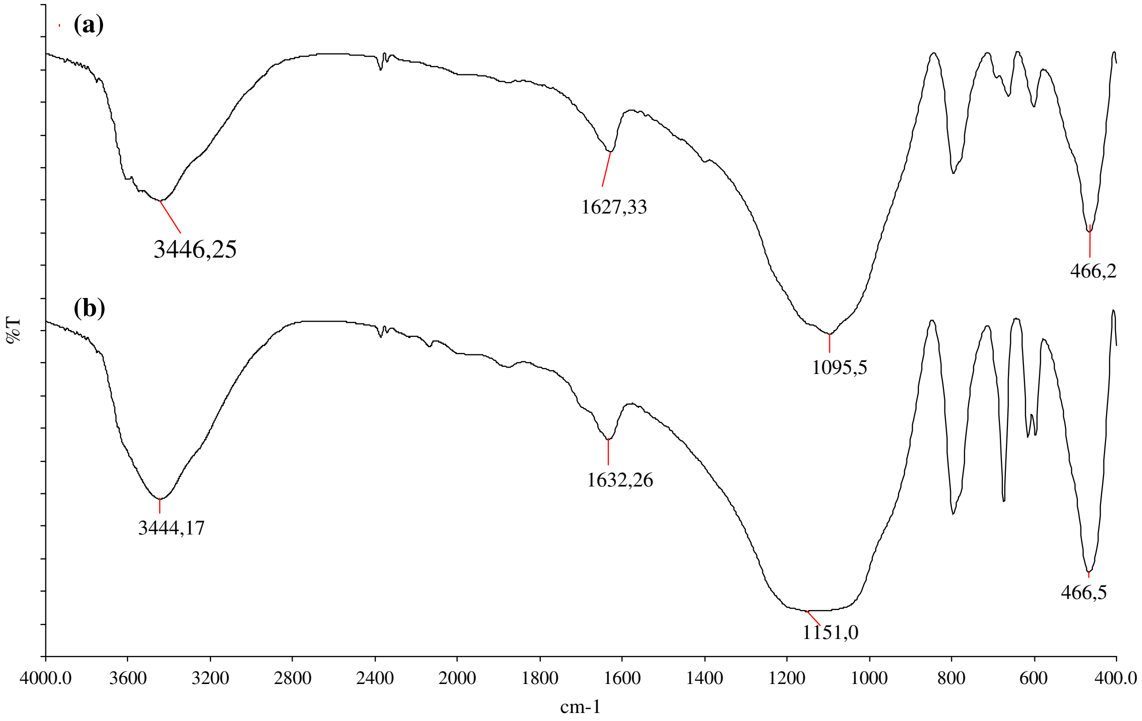

Fig. 5. FTIR spectra of adsorbents: natural (a) and acid-activated diatomite (b).

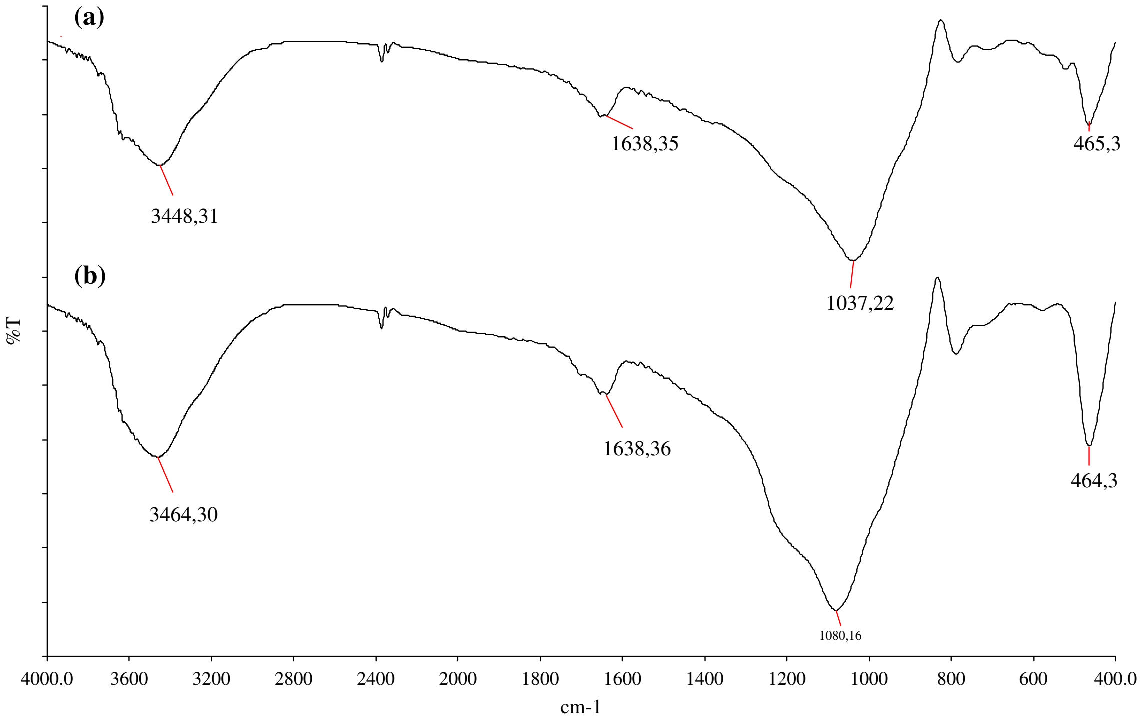

Fig. 6. FTIR spectra of adsorbents: natural (a) and acid-activated ignimbrite (b).

decreased with increasing pH. Results were concordant with other fluoride removal studies [24,42,43]. The oxygen atoms present on the adsorbent surface interact with water in an acidic medium, forming positive charge formation, which result in favor of the uptake of fluoride [38]. At a pH above 6, a decrease in fluoride adsorption is observed as a result of strong competition of hydroxide ions on the active sites of adsorbent.

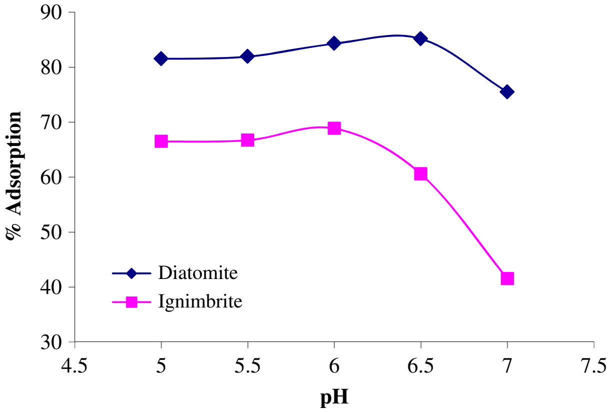

Fig. 7. The effect of pH on the adsorption of fluoride (F: 10 mg/L, *t*: 120 min, amount of adsorbent: 0.5 g, temperature: 298 K).

3.4. The effect of contact time and adsorption kinetics

The removal of fluoride as a function of time was determined at pH 6. Fig. 8 illustrates the adsorption of fluoride by adsorbents. Experiments were performed with both of the acid-activated adsorbents by varying the contact time from 30 to 2,880 min. It was observed that the adsorption capacity of fluoride increased with an increase in contact time. The adsorption equilibrium is obtained within 120 min for both adsorbents. The initial rapid adsorption may be due to the unsaturated active sites on the surface of adsorbents. With a

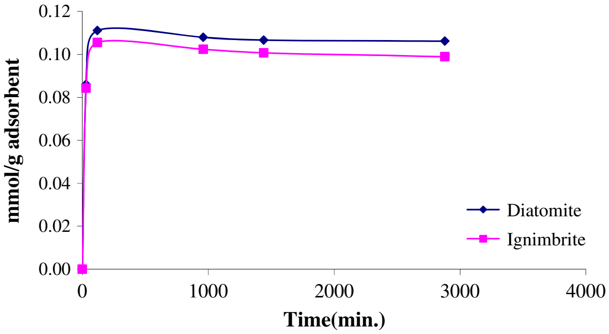

Fig. 8. The effect of contact time on the adsorption of fluoride (pH 6, F: 10 mg/L, amount of adsorbent: 0.5 g, temperature: 298 K).

further increase in contact time, adsorption brings to a level off due to the saturated active sites. Similar results were reported in the literature [25,44]. In order to determine the kinetics of adsorption process, the experimental data were studied using pseudo-first-order model and pseudo-second-order model. Figs. 9 and 10 show the pseudo-second-order kinetic model for diatomite and ignimbrite adsorbents, respectively. The kinetic parameters were calculated from curves and are listed in Table 4. As shown in Table 4, the kinetic data fit with the pseudo-second-order model better than pseudo-first-order model for adsorbents. As indicated in Table 4, the R^2 values of pseudo-second-order kinetic model (>0.9988) were much higher than that of pseudo-first-order kinetic model (<0.907) and experimental qe values are also concordant with the calculated qe values. The rate constants of pseudo-second-order kinetic model are in good agreement with the values in previous studies [42].

Pseudo-second-order kinetic model suggests that chemisorption or chemical adsorption may be responsible for the fluoride adsorption [45,46]. Results overall suggested that adsorption mechanism is concordant with the chemisorption mechanism.

3.5. The effect of adsorbent amount on adsorption

The effect of adsorbent amount on adsorption of fluoride at pH 6 and contact time of 120 min. for the acid-activated adsorbents were performed. Adsorbent amount varied from 0.1 to 1 g and equilibrated at an initial fluoride concentration of 10 mg/L. The results are presented as fluoride removal amount vs. function of adsorbent amount in Fig. 11. From the results, it is observed that the amount removal of fluoride increased with an increase in the amount of adsorbent up to a certain level, and then leveled off. The removal of fluoride with activated ignimbrite was 0.1366 mmoL/g, whereas the corresponding value with activated diatomite material was 0.1671 mmoL/g for 0.3 g adsorbent. As it can be seen from Table 2, porosity ratio of diatomite (79–87%) is higher than ignimbrite (54–61%). Thus, surface area of both natural and activated diatomites is higher than ignimbrite (Table 3). Therefore, the adsorption capacity of diatomite is higher than ignimbrite. However, the adsorption capacity decreases with the increase in adsorbent dosage. Since all F⁻ binding sites entirely reached saturation, the amount of fluoride adsorbed on the adsorbent surface was decreased [47].

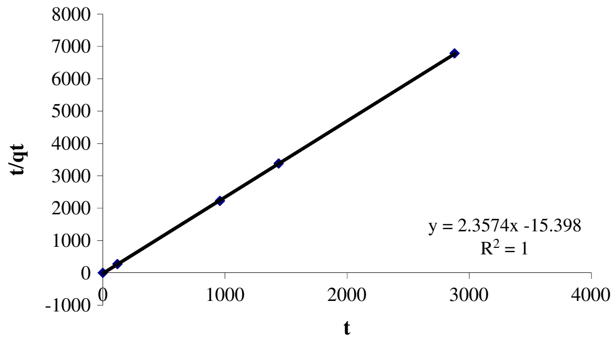

Fig. 9. The pseudo-second-order model for fluoride on diatomite (pH 6, F⁻: 10 mg/L, amount of adsorbent: 0.5 g, temperature: 298 K).

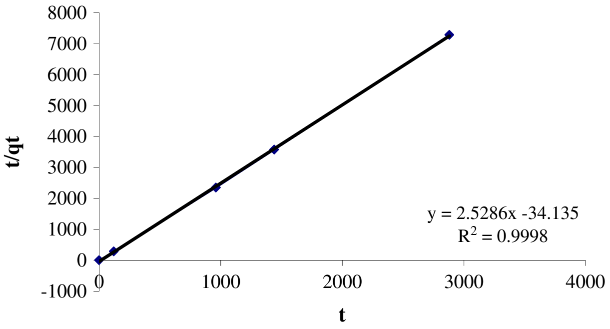

Fig. 10. The pseudo-second-order model for fluoride on ignimbrite (pH 6, F: 10 mg/L, amount of adsorbent: 0.5 g, temperature: 298 K).

3.6. The effect of initial concentration and adsorption isotherms

The effect of initial concentration on fluoride adsorption was studied at different initial fluoride concentrations under optimum conditions. The effect of initial fluoride concentration is illustrated in Figs. 12 and 13 for natural and acid-activated adsorbents. The results showed that fluoride adsorption efficiency was increased by increasing the initial fluoride concentration on both natural and activated adsorbents. It is also clearly seen from these figures that the amount of adsorbed fluoride on activated diatomite and ignimbrite was higher than that of natural diatomite and ignimbrite materials. The obtained results in this study were concordant with the literature [30,48], which reported that the amount of adsorbed ions increased by acid-activated materials. Acid treatment improves the adsorption capacity by increasing surface area [49]. Both surface area and net positive charge are increased after acid treatment which leads to enhanced adsorption of anionic fluoride ion [50].

Table 4
The rate constants of adsorption kinetic model for fluoride on adsorbents

		Pseudo-first-order			Pseudo-second-order		
Adsorbent	q_t (experimental)	k_1	q_e (calculated)	R^2	k_2	q_e (calculated)	R^2
Diatomite	0.4318	2.3×10^{-5}	4.6377	0.757	0.3609	0.4241	1.000
Ignimbrite	0.4074	4.6×10^{-5}	4.3366	0.907	0.1873	0.3954	0.9988

Notes: q_t = mg/g, k_1 = min^{-1}, q_e = mg/g, k_2 = g/mg min, R^2 = correlation coefficient.

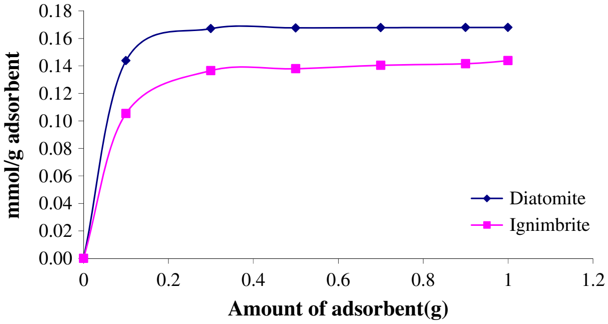

Fig. 11. The effect of adsorbent amount on the adsorption of fluoride (pH 6, F: 10 mg/L, temperature: 298 K, t: 120 min).

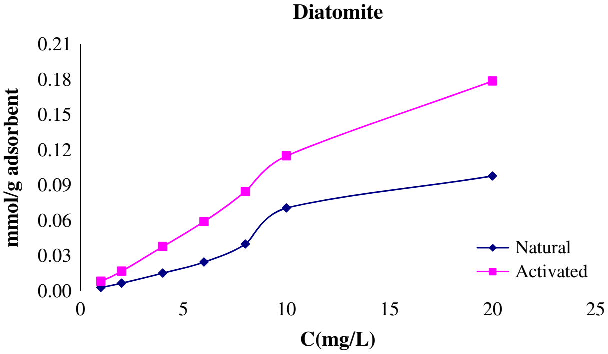

Fig. 12. The effect of initial concentration for the adsorption of fluoride on natural and acid-activated diatomite (pH 6, t: 120 min, amount of adsorbent: 0.5 g, temperature: 298 K).

The experimental data were applied to Freundlich, Langmuir, and Dubinin–Radushkevich adsorption isotherms. The Freundlich isotherm deals with physicochemical adsorption on heterogeneous surfaces with non-uniform distribution of energy levels [51]. The Langmuir isotherm is based on homogenous surface with a finite number of identical sites [52]. Dubinin–Radushkevich adsorption isotherm is generally applied to explain the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous adsorbent surface [53]. The parameters of these isotherms were calculated for fluoride adsorption by natural and acid-activated adsorbents and these are presented in Table 5. On the comparison of the R^2 values, Freundlich and Dubinin–Radushkevich isotherms represent an excellent fit to the experimental data compared to the Langmuir isotherm for all adsorbents. This result is also concordant with the SEM images, which proved the heterogeneous structure of adsorbents. From the linear plot of Dubinin–Radushkevich adsorption isotherm, E, the mean free energy was determined as 4.08247 kJ/mol for both activated diatomite and ignimbrite adsorbents. In this study, the obtained value of E is less than 8 kJ/mol, suggesting that the adsorption process is of a physical nature [54].

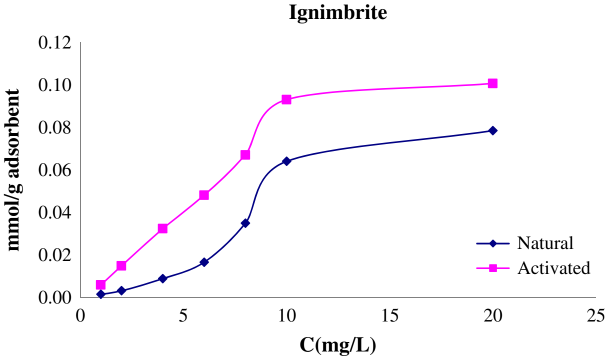

Fig. 13. The effect of initial concentration for the adsorption of fluoride on natural and acid-activated ignimbrite (pH 6, t: 120 min, amount of adsorbent: 0.5 g, temperature: 298 K).

3.7. Comparison of fluoride adsorption with other adsorbents

The maximum fluoride adsorption capacities of acid-activated diatomite and ignimbrite adsorbents at pH 6 were calculated as 12.0337 and 8.8267 mmol/g of adsorbents, respectively. Comparison of the

Table 5
Parameters of adsorption isotherms

Model	Adsorbent	Parameters							
		Natural			Acid-activated				
		K_b	A_s	R^2	K_b	A_s	R^2		
Langmuir	Diatomite	0.9737	0.0574	0.5507	1.5175	0.0605	0.1526		
	Ignimbrite	1.4410	0.0319	0.5574	3.6125	0.0661	0.6386		
		K_F	$1/n$	R^2	K_F	$1/n$	R^2		
Freundlich	Diatomite	8.1677	1.2695	0.9825	12.0337	0.9904	0.9335		
	Ignimbrite	4.3551	1.5812	0.9568	8.8267	0.8335	0.8471		
		Natural				Acid-activated			
		q_s	K_{ad}	R^2	E	q_s	K_{ad}	R^2	E
Dubinin–Radushkevich	Diatomite	19.628	5.0×10^{-8}	0.9459	3.1623	39.960	3.0×10^{-8}	0.9810	4.0824
	Ignimbrite	11.240	7.0×10^{-8}	0.9205	2.6726	15.533	3.0×10^{-8}	0.9599	4.0824

Notes: K_F = adsorption capacity (mmol/g adsorbent), n = experimental constant, R^2 = correlation coefficient, A_s = adsorption capacity (mmol/g), K_b = adsorption energy constant (L/mmol), q_s = theoretical isotherm saturation capacity (mmol/g), K_{ad} = Dubinin–Radushkevich isotherm constant (mol^2/kJ^2), E = mean free energy (kJ/mol).

maximum fluoride adsorption capacities of acid-activated diatomite and ignimbrite adsorbents in the present study with those reported for various adsorbents in the literature is given in Table 6. The data show that the adsorption capacities of these adsorbents which were investigated in this study are higher than those reported in the relevant literature. The fluoride adsorption capacities obtained in this work may be attributed to high affinity between Si/Al/ Ca oxides and fluoride ions on the surface. Besides, the used diatomite and ignimbrite adsorbents can be obtained cheaply and used safely for the practical applications of fluoride removal from water.

3.8. Effect of temperature and thermodynamic parameters

The influence of temperature on fluoride removal by acid-activated diatomite and ignimbrite materials was studied at pH 6 for four different temperatures (298, 308, 323, and 333 K). Fig. 14 shows the change in the fluoride removal efficiency as a function of temperature. It can be seen that the removal of fluoride was decreased with an increase in temperature for both adsorbents. This is due to the exothermic adsorption reactions of fluoride with adsorbents. The maximum fluoride removal was obtained at 298 K.

Table 6
Comparison of adsorption capacity of acid-activated diatomite and ignimbrite for fluoride with various adsorbents

Adsorbent	pH	q_m (mmol/g)	Refs.
Saponified orange juice residue loaded Sm(III)(Sm-SOJR)	5	1.22	[2]
Saponified orange juice residue loaded Ho(III)(Ho-SOJR)	5	0.92	[2]
Amberlite resin	7	3.286	[16]
Granular red mud	4.7	0.470	[55]
Activated red mud	5.5	3.082	[30]
Orissa mining corporation (OMC)	5–6	0.798	[56]
Fe(III) loaded carboxylated chitosan beads	7	0.810	[57]
Cerium impregnating fibrous protein (CeFP)	3	5.59	[58]
Ca-pretreated macrophyte biomass	6	0.110	[59]
Zirconium(IV)-impregnated collagen fiber	5.5	2.29	[60]
Acid-activated diatomite	6	12.0337	In current study
Acid-activated ignimbrite	6	8.8267	In current study

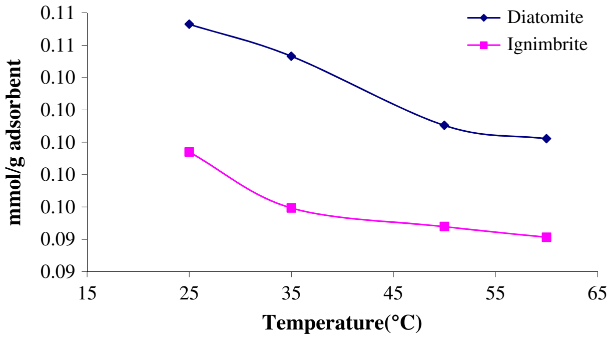

Fig. 14. The effect of temperature on the adsorption of fluoride (pH 6, F: 10 mg/L, amount of adsorbent: 0.5 g, *t*: 120 min).

Thermodynamic parameters such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) were determined by following equations:

$$\Delta G^\circ = -RT \ln K \tag{1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^0 \tag{2}$$

$$\log K = (\Delta S^0/2.303\,R) - \left(\Delta H^0/2.303\,RT\right) \tag{3}$$

where ΔG° is the change in free energy (kJ/mol), ΔH° is the change in enthalpy (kJ/mol), ΔS° is the change in entropy (kJ.mol/K), T is the absolute temperature (K), R is the gas constant (8.314×10^{-3}), and K is the equilibrium constant. By considering Eq. (3), the enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of fluoride adsorption were estimated from the slope and intercept of the plot of $\ln K_D$ vs. $1/T$ yields, respectively (Fig. 14). The obtained parameters of the adsorption process were shown in Table 7. As it can be seen from Table 7, negative ΔG° values confirm the feasibility of the process and spontaneous reaction for adsorbents. The decrease in ΔG° values with an increase in temperature shows a decrease in feasibility of fluoride adsorption at higher temperatures. The negative values of ΔH° indicate the exothermic nature of the adsorption and also its values give information on the type of adsorption, which can be either physical or chemical.

It is generally known that the enthalpy value of physical adsorption is between 0.5 and 5 kcal/mol (2.1–20.9 kJ/mol), where chemical adsorption is between 20.9 and 418.4 kJ/mol [61]. ΔH values of activated diatomite and ignimbrite were −4.5290 and −2.8649 kJ/mol, respectively. Thus, it can be concluded that the adsorption mechanism is physical. Results are also concordant with the results of Dubinin–Radushkevich adsorption isotherm model. The negative values of ΔS° suggest a decrease in the degree of freedom of the adsorbed species [62]. Similar results were obtained for both of the adsorbents.

3.9. Sorption mechanism

The mechanism of fluoride removal by acid-activated adsorbents can be considered as a combination of chemical and physical adsorption mechanisms. Since the SiO_2 content of both adsorbents is high, expected reaction of the fluoride on adsorbent surface can be given as:

$$\text{Si–OH}_2^+ + \text{F}^- \leftrightarrow \text{Si–OH}_2^+\,\text{F}^-$$

Results overall suggested that adsorption has a physical mechanism due to the R^2 of Freundlich and Dubinin–Radushkevich adsorption isotherm models and ΔH values. However, pseudo results pointed out a chemical adsorption. Results overall are concordant with the literature findings [63,64].

Table 7
Thermodynamic parameters for the adsorption of fluoride on adsorbents

	T (K)	1/*T*	ln K (kJ/mol)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
Diatomite	298	0.0033	0.5236	−1.2985		
	308	0.0032	0.4726	−1.1901	−4.5290	−0.0108
	323	0.0031	0.3639	−1.0275		
	333	0.0030	0.3433	−0.9191		
Ignimbrite	298	0.0033	0.3227	−0.7493		
	308	0.0032	0.2371	−0.6783	−2.8649	−0.0070
	323	0.0031	0.2087	−0.5718		
	333	0.0030	0.1925	−0.5008		

Table 8
Fluoride removal values of natural drinking water samples

	Milas fountain water			Andık River		
Adsorbent	C_{initial}	C_{residual}	R (%)	C_{initial}	C_{residual}	R (%)
Acid-activated diatomite	1.722	0.34	80.25	2.638	0.458	82
Acid-activated ignimbrite	1.722	0.646	62.48	2.638	0.834	68

Table 9
The physicochemical properties of natural drinking water samples

Sample	pH	Conductivity (μS/cm)	Turbidity (NTU)	Total hardness (mg/L $CaCO_3$)	TDS (mg/L)	Alkalinity	Ca^{2+} (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)
Andık River	8.15	543	4.16	284.80	272.00	274.50	63.05	4.28	62.54	1.66
Milas fountain water	7.64	360	0.06	160.20	180.00	183.00	52.95	2.79	23.92	7.97

3.10. Performance of adsorbents on drinking waters

The removal amounts of fluoride from two natural drinking water sources (Andık River and Milas fountain water), which were collected from Isparta, Turkey, are given in Table 8. Adsorption experiments were carried out using activated diatomite and ignimbrite adsorbents under pre-determined optimum conditions (298 K, pH 6, 2 h, 0.5 g). In Table 8, the results of the activated diatomite and ignimbrite showed that the percentage removal of fluoride for diatomite is higher as compared to ignimbrite in drinking water samples. The physicochemical properties of drinking water samples before the adsorption are also presented in Table 9. As it can be seen from Table 9, natural waters include various different ions. Fluoride removal was improved in the natural waters with activated adsorbents due to the presence of different ions. The presence of different anions and cations in natural waters has a positive effect on fluoride removal [65]. This phenomenon should be investigated in future studies.

4. Conclusions

Overall results showed that diatomite and ignimbrite adsorbents were effective toward fluoride removal from drinking water. The main conclusions of this study are given below:

(1) The acid-activated diatomite shows higher fluoride adsorption capacity for defluoridation of drinking water as compared to acid-activated ignimbrite.
(2) The characterization of acid-activation process was confirmed by SEM, FTIR, and BET analysis.
(3) The removal of fluoride with activated ignimbrite was 0.1366 mmol/g, whereas the corresponding value with activated diatomite material was 0.1671 mmol/g for 0.3 g adsorbent.
(4) The maximum adsorption of fluoride was obtained at pH 6, with the contact period of 120 min and 10 mg/L fluoride concentration.
(5) Adsorption of fluoride on adsorbents from aqueous solution followed pseudo-second-order reaction, and the adsorption characteristics of fluoride removal on adsorbents fitted with the Freundlich and Dubinin–Radushkevich adsorption isotherms.
(6) The presence of other ions in natural drinking water did not significantly affect fluoride removal.

In general, the results in this work have demonstrated that diatomite and ignimbrite adsorbents could be used for removal of fluoride from water as low-cost materials.

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