Defluoridation of Aqueous Solution by Graphene and Graphene Oxide Nanoparticles: Thermodynamic and Isotherm Studies

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ABSTRACT: *Fluoride, a non-essential element, can enter water resources through several natural processes and human activities. The benefits and risks of fluoride depend on the concentration of this anion on drinking waters. In the present study, the performances of graphene and graphene oxide nanoparticles were investigated for the removal of fluoride from aqueous solution. In the present research, effects of pH, contact time, fluoride initial concentration, adsorbents dosage, as well as temperature in performance of graphene and graphene oxide nanoparticles in removal of fluoride from aqueous solution were examined. Also, isotherms and thermodynamics of the adsorption process were evaluated. For both adsorbents, the maximum adsorption capacities observed during the first 15 minutes at pH=3 and an initial fluoride concentration of 10 mg/L. The results also showed that adsorption of fluoride by graphene and graphene oxide fitted well with Freundlich and Langmuir isotherms, respectively. Furthermore, temperature increase resulted in the adsorption capacity decrease, indicating an exothermic adsorption reaction. According to the results of this research, graphene nanoparticles have higher adsorption capacity of fluoride than graphene oxide nanoparticles.*

KEYWORDS: *Nanoparticles; Graphene; Graphene oxide; Fluoride.*

INTRODUCTION

The chemical nature of the water is one of the most important criteria to determine the usefulness of water for drinking and potable objectives[1]. The type of main ions and their distribution in natural waters is very different

depending on the geological structure and soil type [2]. Fluorine has oxidation degree of -1 is a corrosive gas, pale yellow and has a high toxicity. In nature, due to the high reactivity of fluorine, it not found in elemental form [3].

Fluoride concentration in surface water is low, in comparison toground water where it is higher due to the proximity to minerals such as cryolite, fluorite and fluoride and physico-chemical properties of the water[4]. According to the World Health Organization (WHO), the maximum allowable concentration of fluoride ions in drinking water is 1.5 mg/L. Depending on the concentration and duration of consumption, this anion may cause tooth decay[5]. Long-term consumption of water containing excessive fluoride concentration can lead to fluorosis of the teeth and bones[6].

Fluorosis in its mild form causes mottled teeth and in more severe cases leads to fragile bones and nerve damage [7]. Diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer's syndrome and thyroid disorders can be caused by high concentration of fluorine [8]. In a study conducted by United Nation Children's Fund, the fluorosis has been observed in more than 27 countries [9]. Due to adverse health effects arising from the proliferation of fluorine in the water, removal of excess fluoride from water by appropriate methods is essential. There are several methods to remove excess fluoride from water, including coagulation and sedimentation [10], membrane processes[11], electrochemical treatment [12], ion exchange and its modification [13].

Many of the methods cannot be applied in full scale due to factors such as high costs of installation, operation and maintenance, production of toxic byproducts (pollution), high power consumption and also the need for complex treatment[14]. Among the other methods, the adsorption process is accepted as being economic and effective [15-16]. Adsorption process is widely used due to simple operation as well as availability and existence of broad range of adsorbents [5, 17]
Application of many adsorbents for fluoride removal from aqueous solution was investigated. In a study performed by Bazrafshan et al. efficiency of ZnCl$_2$ treated Eucalyptus leaf as a natural adsorbent for removal of fluoride from water environment was evaluated [18]. In another research, Daifullah and colleagues studied the application of KMnO$_4$-modified activated carbon derived from steam pyrolysis of rice straw for removal of fluoride

from aqueous solution [19]. Zhao and colleagues performed a study entitled "Granulation of Fe–Al–Ce trimetal hydroxide as a fluoride adsorbent using the extrusion method and concluded this adsorbent exhibited a Langmuir maximum adsorption capacity of 51.3 mg/g at pH 7.0 "[20].

Among the adsorbent, graphene (G) and graphene oxide (GO) nanoparticles are relatively new material, which due to their high adsorption capacity and high surface area, are often used to remove contaminants from water [21].Graphene isa two-dimensionalsheetofcarbon atomsin ahexagonalconfiguration(honey comb) in which thecarbon atomsare connectedtogether bySP$_2$ hybrid. Graphene is a carbon porous and has many features material including high surface area and unique structure, suitable for the removal of pollutants. The previous studies showed that graphene nanoparticles had a high potential for the removal of environmental pollutants [22-23].

Graphene oxide is a layer of graphite oxide and usually obtained from graphite oxidation followed by dispersion and delamination in water orsuitable organic solvents. Graphene oxide has hydroxyl and epoxide groups in its structure. The current paper is an attempt to investigate the removal of fluoride from aqueous solution by graphene and graphene oxide nanoparticles. The isotherms and thermodynamics of the adsorption process were also evaluated.

EXPERIMENTAL SECTION

This research was carried out in pilot-scale and batch at 25° C and the effect of various parameters including, pH, and contact time, concentrations off luoride, adsorbent dosage, and temperature were investigated. The experiments took place in a 250 mL flask. Fluoride was measured by spectrophotometer DR5000 (HACH-LANGE Model). For pH measurement, pH meter (765 Model), and for mixing of the samples, shaker (IKA ® KS 260 Model) were used. Also in the process of investigating the effect of temperature on adsorption process, an incubator shaker (SHYSC model) was used. For separation of the adsorbents from solution, a centrifuge (Centurion model) was used.

The adsorption capacity q$_e$ (mg/g) was obtained as follows:

$$q_e = \frac{(C_0 - C_f)V}{M}$$

Table 1: Specifications of Graphene and Graphene oxide nanoparticles in 20 °C.

adsorbents	Specifications							
	Number of layers	Thickness, nm	Purity, %	pH	Diameter, nm	Resistance, ohm.cm	Surface area, m²/g	Density, g/cm³
Graphene (G)	32	2-18	99.5	7-7.7	40-80	4×10^{-4}	150-200	1.9-2.2
Graphene Oxide (GO)	6-10	3.4-7	99	7-7.7	10-50	4×10^{-4}	100 - 300	1

Where C_0 and C_f are the initial and final concentrations (mg/L) of fluoride ions in the aqueous solution, respectively, V is the volume of fluoride solution, and M is the weight of adsorbent.

Preparation and modification of nanoparticles

The nanoparticles used in this study were prepared from Research Institute of Petroleum Industry (RIPI), Tehran, Iran. The specification of Graphene Oxide nanoparticles used in this research presented in Table 1.

For modification of nanoparticles used in this study, adsorbents were rinsed with hydrochloric acid for 30 minutes (on the shaker) at ambient temperature and then washed several times with distilled water until the pH was adjusted to approximately neutral for the solution. Finally, adsorbents were dried in vacuum at 40 °C overnight. To verify the desired structure of the synthesized adsorbents, a Scanning Electron Microscopy (SEM) image was taken with a Camscan MV2300 Microscope. Structural features were investigated by Raman spectroscopy (JobinYvon T-64 000), and X-Ray Diffraction (XRD) (Philips Analytical PC-APD) was used for characterization of the sample.

Preparation of required solutions

High purity water was obtained from an ultra-pure water system. All glassware used in these experiments was acid washed prior to use with nitric acid 5 wt.%, 24 h, and ultra-pure water was used to prevent metal ions adsorption on the flask wall. 100 mg/L stock solution was prepared with dissolving of 0.221 g of sodium fluoride (NaF) in one liter of deionized water. Then, initial fluoride concentrations required in present study (2, 4, 6, 8 and 10 mg/L) were prepared by diluting the prepared sodium fluoride solution. To adjust the pH, 0.1 normal solutions of HCl and NaOH were used.

Study of Point of zero charge

The pH of the zero point of charge (pH$_{zpc}$) is the pH value at which an adsorbent submerged in an electrolyte exhibits zero net electrical charge on the surface. In the present study, for determination of the pH$_{ZPC}$, two series of 30 mL deionized water in conical flasks were prepared with initial pH values in the range of 2–12. These pH values were adjusted by addition of 1 N Hydrochloric acid for the acidic range and 0.1 N Sodium Hydroxide for the basic range, using a pH meter. Then 20 mg of either G or GO was placed in each conical flask of the series and left overnight to reach equilibrium at 25 °C. The final pH was then measured and plotted against the initial pH for each series. The pH$_{ZPC}$ can be readily obtained from the point at which the initial pH versus final pH curve crossed the y=x line on the graph.

Effect of pH

To study the effects of pH on the adsorption of fluoride onto graphene and graphene oxide nanoparticles, 45 mg of adsorbents were dispersed into 100 mL solution containing 4 mg/L of fluoride. The initial pH values were adjusted on 3, 5, 7, 9 and 11 using various amounts of HCl and NaOH and the suspensions were shaken in 250 rpm for 30 minutes at 25± 1 °C. After that, the solutions were filtered through a 0.2 μmfilter and fluoride residue in the solution was determined by a spectrophotometer DR5000.

Effect of contact time and initial concentration of fluoride

After determination of optimum pH, effect of initial concentration of fluoride and contact time at adsorption process was investigated. For this purpose 2, 4, 6, 8 and 10 mg/L initial concentrations of fluoride were prepared from stock solution and each of these solutions mixed with 45 mg adsorbents (G &GO) at 5 to 240 minutes contact times. The mixing speed was 250 rpm. Finally,

like before, residual Fluoride concentration was measured with spectrophotometer and related curves were plotted.

Effect of adsorbent dosage on adsorption process

After determining optimum pH, contact time, fluoride concentration, effect of adsorbents dosage was investigated. For this reason, dosages of 15, 30, 45 and 60 mg of each adsorbent (G&GO) were added to the fluoride solution at optimum conditions.

Adsorption isotherms

In the present study, Freundlich and Langmuir isotherm models were used for mathematical modeling of fluoride adsorption onto graphene and graphene oxide nanoparticles.Langmuir isotherm is based on monolayer and uniform (homogeneous) adsorption of adsorbate with uniform energy on all sites of the adsorbent. Freundlich isotherm is based on adsorption of multi-layered and heterogeneous of adsorbate on adsorbent.

Equations (1) and (2) express the Longmuir and Freundlich isotherm respectively[24]:

$$q_e = \frac{q_{max}K_LC_e}{1+K_LC_e} \tag{1}$$

$$q_e = KC_e^{1/n} \tag{2}$$

Where q_e (mg/g) is the equilibrium fluoride ion concentration in the solid phase; q_{max} (mg/g) is the maximum amount of adsorption; K_L (L/mg) is the Langmuir adsorption equilibrium constant; C_e is the concentration of solute at equilibrium or after adsorption; K_F (mg$^{1-1/n}$L$^{1/n}$/g) is the Freundlich constant representing the sorption capacity, and n is the constant depicting the adsorption intensity. K_F and n must be evaluated for each solute and temperature, and are related to adsorption capacity and energy of adsorption.

Adsorption Thermodynamics:

At this stage, performance of graphene and graphene oxide nanoparticles was evaluated at different temperatures (298, 308 and 318 °K). Furthermore, thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°) and free energy change (ΔG°) that are critical in order to determine the spontaneity of the process were investigated. When by increasing temperature, the ΔG° and ΔH° values decrease, a spontaneous process

occurs. All the thermodynamic parameters were determined from the following equations:

$$K_c = \frac{C_{Ad}}{C_e} \tag{3}$$

$$\Delta G = -RTLnK_C \tag{4}$$

$$LnK_C = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{5}$$

Where K_c is the equilibrium constant, C_{Ad} is the concentrations of fluoride adsorbed on solid at equilibrium (mg/L), C_e is the equilibrium concentration of fluoride in the solution (mg/L), R is the gas constant (8.314 J/(K·mol)) and T is the temperature in Kelvin. The values of ΔH° and ΔS° can be obtained from the slope and intercept of the Van't Hoff plot of ln K_c versus 1/T [25].

RESULTS AND DISCUSSION
Characterization of the adsorbents

Fig. 1 show SEM and TEM images for graphene and graphene oxide nanoparticles. For determination of the accurate diameter of graphene and graphene oxide nanoparticles bundles, the SEM method was used. This technique gives information mainly regarding surface morphology of the graphene and graphene oxide samples. The TEM was used for measurement of graphene and graphene oxide diameter in the bundle [25]. From the TEM image it is possible to determine directly the diameter of one nanoparticle and bundle diameter. Using this information the number of graphene and graphene oxide in the bundle can be found. According to Fig. 1 diameter of grapheme nanoparticles used in thisstudy was 2-18 nm. Also and the number oflayers of this nanoparticles was32layers. Furthermorediameter as well as the number oflayersof graphene oxide nanoparticles was 3.7-4 nmand6-10, respectively.

Fig. 2-a show the XRD patterns for two mentioned adsorbents; graphene and graphene oxide nanoparticles. The broad peak at $2\theta=25.8°$ indicates a random picking of graphene sheets. This peak is corresponding to 002 plane of graphite with interlayer spacing of 0.34 nm which is due to the removal of oxygen atoms that got into the graphite gallery during the intercalation process. In Fig. 2-b, the XRD pattern of sample GO exhibited a strong peak at $2\theta=11.6°$, which corresponded to an interlayer spacing of about 0.76 nm, indicating
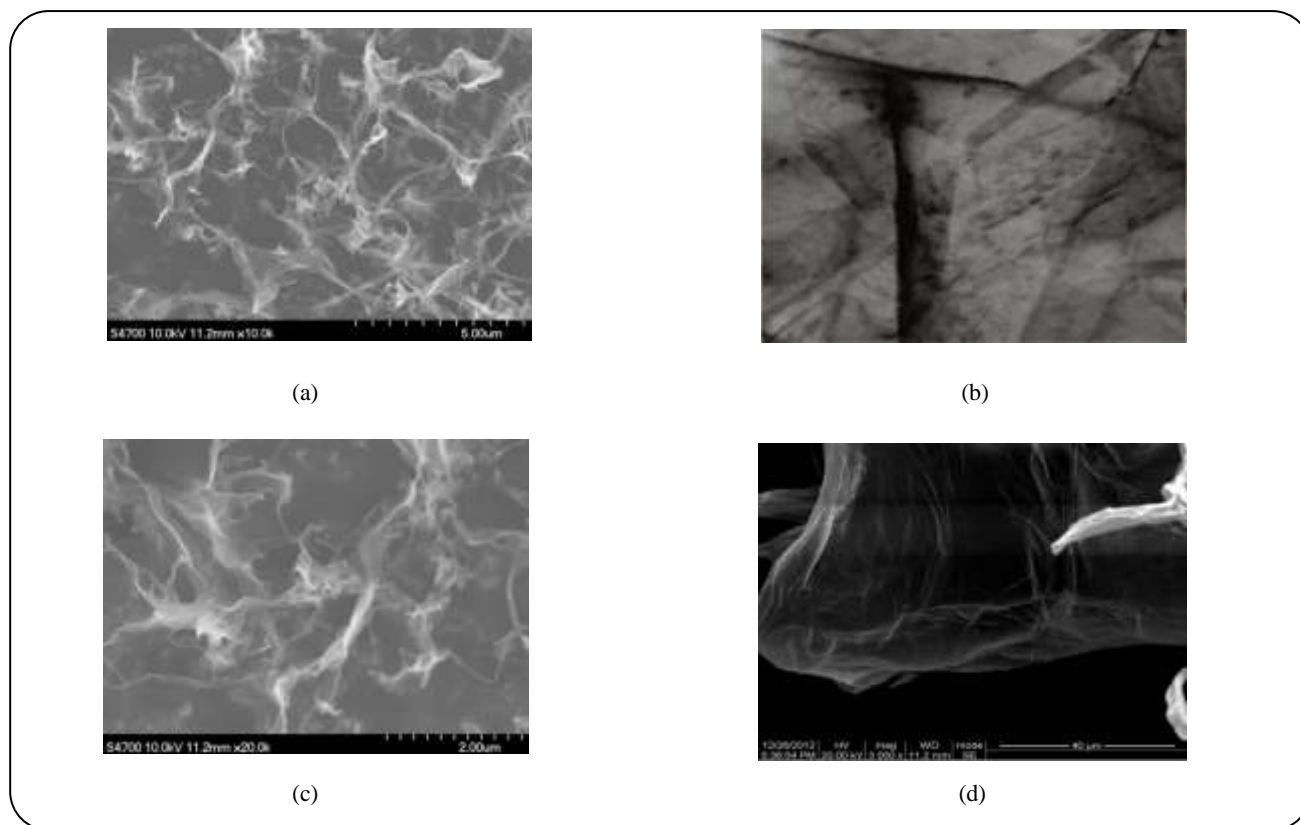
Fig. 1: (a) SEM and (b) TEM images of Graphene nanoparticles (c) SEM and (b) TEM images of Graphene Oxide nanoparticles.
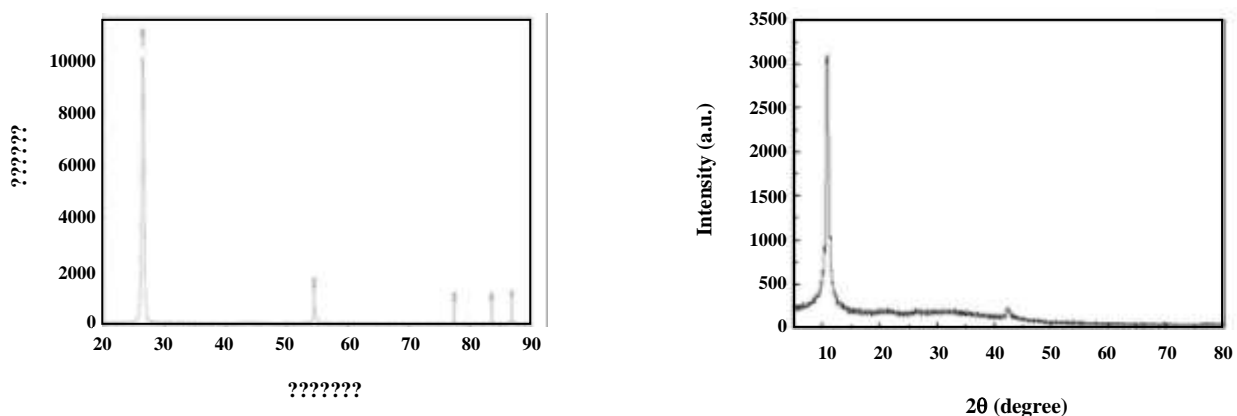

Fig. 2: XRD spectra of (a) Graphene and (b) Graphene oxide nanoparticles.

the presence of oxygen functionalities, which facilitated the hydration and exfoliation of GO sheets in aqueous media.

Determination of pH_{ZPC} and pH

The results of pH_{ZPC} determination for G and GO are shown in Fig. 3. According to this figure, graphene sample exhibited a pH_{zpc} of around 7.87 while the GO sample had its pH_{zpc} about 3.03. These results indicated that graphene samples were negatively charged when exposed to pH> 3.7, while GO sample only becomes negative for pH>7.87. Survey effect of pH on fluoride adsorption onto G and GO are shown in Fig. 4. As can be seen in the figure, the removal efficiencyof fluoride by both studied adsorbents increased with decreasing pH. The maximum adsorption capacity occur in pH=3.
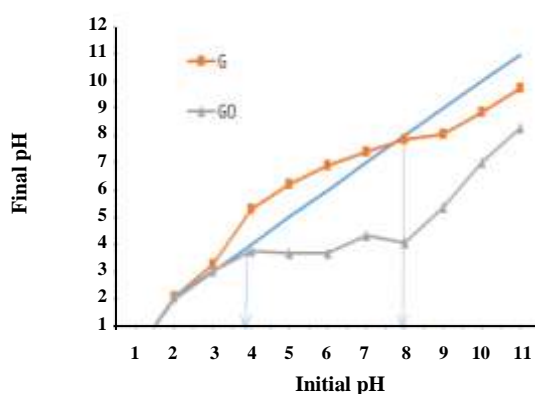
Fig. 3: Determination of pH_{zpc} for G and GO samples.

Fig. 4: pH effect on fluoride adsorption on G and GO (C0=4 mg/L, agitation period= 30 min).

The results from investigation of pH effect on adsorption process show that adsorption capacity decreases with increasing pH. Therefore, all the experiments were conducted at pH=3. Similar findings have been reported in the literature for fluoride removal by iron nano-particle resin[26] and by acid treated spent bleaching earth[5]. In adsorption process, H^+ and OH^- are two ions that determined surface charge [27]. Adsorption properties depend on the number of hydroxyl groups on the surface of the nano particles and the composition of the dissolved ions desorption properties as well as physico chemical properties of the macromolecules [28-29]. This can be explained by the change of surface charge of the adsorbent. It is known that in highly acidic medium, the surface of adsorbent is highly protonated while it is neutralized and tended to have negative charge in alkaline medium. Therefore, high efficiency in acidic medium can be attributed to the gradual increase in attractive forces and low efficiency in alkaline medium can be explained by the repulsion between the negatively charged surface and fluoride [5].

Effect of initial fluoride concentration on adsorption capacity

Adsorption capacities at different initial concentrations of fluoride ions and different contact times are shown in Figs. 5 and 6. The results show that adsorption capacities for both adsorbents increased with increasing the initial fluoride concentrations. Furthermore, during the first minutes of reaction (up to 15 minutes) the amount of adsorption reaches to maximum and then reaches to equilibrium, in a way that increasing contact time to four hours does not increase the adsorption capacities.
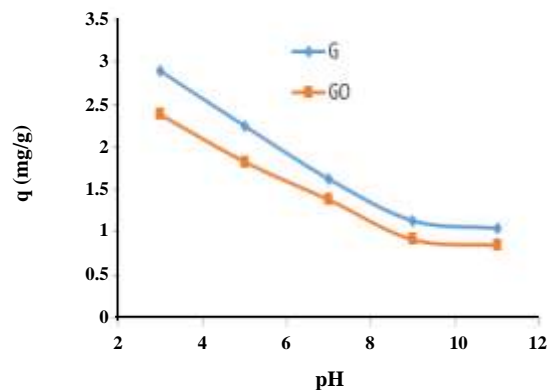
Survey of equilibrium time and initial concentration show that maximum adsorption efficiencies of fluoride for both adsorbents (G&GO) were occurred at 15 minutes and 10mg/L of initial concentration of fluoride.

The reason of high adsorption rate at the first moment of the adsorption reaction is the large numbers of active sites of adsorption. The adsorption rate was higher at higher fluoride concentrations due to aggregation of high concentration of fluoride ions around the adsorbent and increasing the chance of collision. With decreasing fluoride concentrations, the chance of collision between fluoride ions and adsorbent surface decreases and therefore resulting in the decrease of removal efficiency [30]. This finding is in accordance with that *Li et al.* had previously observed on fluoride adsorption [27].

Effect of adsorbent dosage on fluoride removal

Results of effect of different adsorbents dosage (15, 30, 45 and 60 mg) on adsorption capacity at optimum condition (pH=3, initial fluoride concentration=10 mg/L) shown in Fig. 7. As shown in this figure, with increasing the adsorbent dosage removal efficiency increased. The adsorption capacities in 45 and 60 mg of adsorbent dosages were similar; therefore lower dosage (45mg) was selected as optimum dosage.

Based on the results, with increasing the adsorbent dosage from 15 to 60 mg, removal efficiency of fluoride increased due to the greater availability of the exchangeable sites or surface area at higher concentrations of the adsorbent. This led to increasing in collision and also free band on absorbent surfaces [31-32]. These results are in agreement with previous literature such as those reported
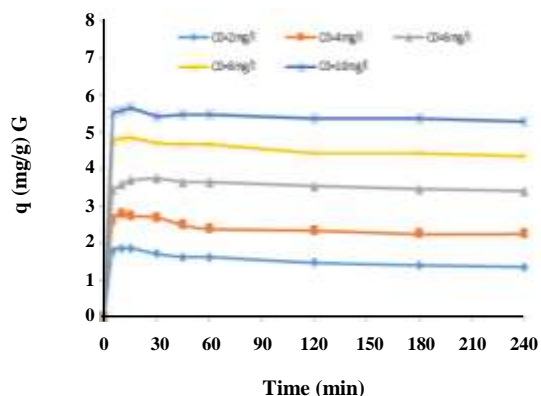
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Fig. 5: Effects of reaction time and initial fluoride concentration on graphene adsorption capacity (pH=3 and adsorbent dosage=45mg).
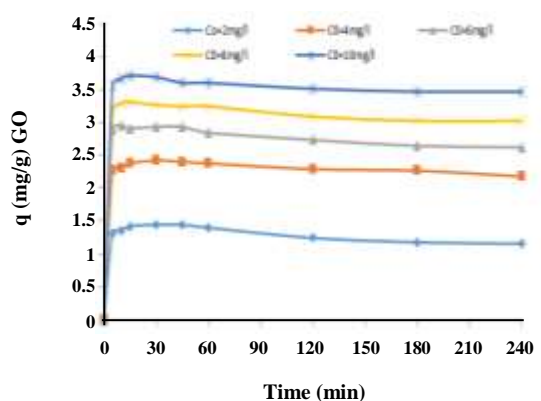

Fig. 6: Effects of reaction time and initial fluoride concentration on graphene oxide adsorption capacity (pH=3 and adsorbent dosage=45mg).
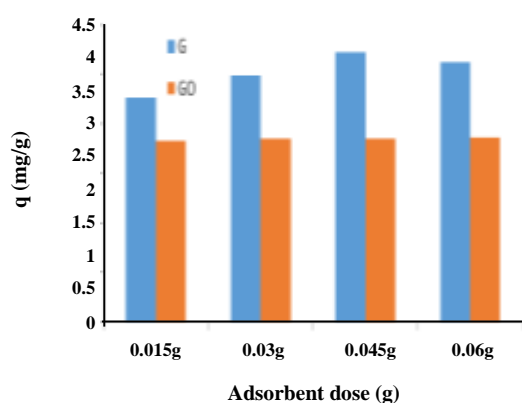

Fig. 7: Effect of adsorbent dosage on fluoride removal by graphene (G) and graphene oxide (GO) (pH=3, initial fluoride concentration=10 mg/L).

by Nan and their colleagues [33]. They studied the adsorption of fluoride from aqueous solution on porous granular ceramic containing dispersed aluminum and iron oxides and reported that with increasing of adsorbent dosage, removal efficiency increased. Moreover the results of present study are in accordance with *Xiaotian et al.* research [34].

Adsorption equilibrium isotherms

Isotherm parameters also presented in Table 2. Regarding to these figures and table, it is obvious that both Freund lich and Langmuir isotherms describe well the adsorption of fluoride by graphene (R^2 equal to 0.98 and 0.96, respectively) and Langmuir isotherm was found to be more suitable for adsorption of fluoride onto GO as evidenced from the value of the regression coefficients (R^2=0.89).

In a study conducted by Dehghani et al regarding fluoride removal by carbon nanotubes from aqueous solution, the researchers found that Freund lich isotherm was more suitable for description of the fluoride adsorption process [35]. In another study performed by Mahvi et al about removal of fluoride by iron nanoparticles, the Langmuir isotherm fitted well the fluoride adsorption process [26].

Effect of temperature on fluoride adsorption and thermodynamic parameters determination

The results of the effect of temperature on efficiency of fluoride ion adsorption by graphene and graphene oxide nanoparticles are shown in Fig. 8. Thermodynamic parameters also presented in Table 3. According to Fig. 8 and Table 3, increasing temperature from 25 to 45°C led to decreasing adsorption capacity by adsorbents. Maximum adsorption capacities occur at ambient temperature (25°C). This is indicative that adsorption reaction of fluoride by G and GO nanoparticles is exothermic.

Temperature is an important parameter affecting the adsorption process[23, 25]. The positive value of free energy change ($\Delta G°$) for both G and GO (2.66 and 3.98 respectively) indicates that the adsorption is not a feasible and spontaneous process, and the value of $\Delta G°$ becomes more positive with the increase of temperature, indicating that the adsorption process is more favorable at lower temperatures.

Table 2: Parameters of Freundlich and Langmuir isotherm models for adsorption of Fluoride onto G and GO.

Adsorbent	Freundlich			Langmuir		
	$K(mg/g)(mg/l)^n$	n	R^2	q_m (mg/g)	B (L/mg)	**R^2**
Graphene	1.61	1.67	0.98	6.98	14.44	**0.96**
Graphene oxide	1.25	2.15	0.79	4.32	6.29	**0.87**

Table 3: Thermodynamic parameters for adsorption of fluoride onto G and GO nanoparticles.

Adsorbent	Thermodynamic parameters	Temperature (k)			R^2
		298	308	318	
Graphene	ΔG (kJ/mol)	2.66	3.36	3.71	0.95
	ΔH (kJ/mol)	1585			
	ΔS(J/mol.K)	-6.4			
Graphene oxide	ΔG (kJ/mol)	3.98	4.42	4.80	0.99
	ΔH (kJ/mol)	987.9			
	ΔS(J/mol.K)	-4.92			
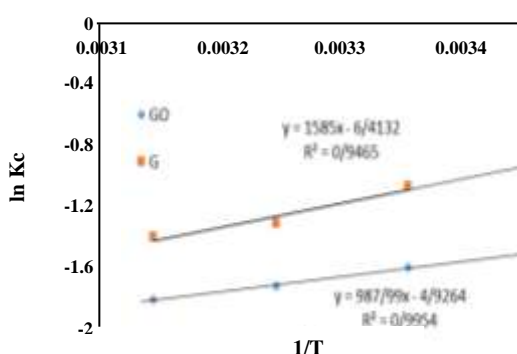
Fig. 8: Linear plot of ln Kc versus 1/T for the adsorption of fluoride onto G and GO nanoparticles.

The negative standard entropy change ($\Delta S°$) indicates the fact that the degree of freedom decreases at the solid–liquid interface during the adsorption of fluoride on to G and GO. Similar results have been previously published by Takaki et al. about adsorption behavior of fluoride ions using a titanium hydroxide-derived adsorbent. They found that rising temperature led to reduction of fluoride removal [31].

Comparison between adsorbents of the present study with other adsorbent

Table 4 shows the comparative evaluation of various adsorbents for removal of fluoride from aqueous solutions. As can be seen in the Table, adsorption capacities of activated carbon derived from *Moringa indica*, Calcium chloride modified natural zeolite, Cellulose@HAP nanocomposites and hydrous bismuth oxides are lower than the adsorbents of the present study. Other adsorbents have higher adsorption capacities.

CONCLUSIONS

In the present study graphene and graphene oxide were used for the adsorption of fluoride from aqueous solution. Maximum adsorption process occurred in pH equal to 3. It was also observed that the increase in the initial concentration of fluoride increases the efficiency of adsorption process. Furthermore most of adsorption was in the first 15 minutes. Increasing of temperature led to reducing the adsorption capacity, indicating an exothermic adsorption reaction. Results of adsorption process show that adsorption of fluoride by graphene obeyed the Freundlich isotherm while adsorption

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Table 4: Comparative evaluation of various adsorbents for fluoride removal.

adsorbent	pH range	Model used to calculate adsorption capacity	Maximum adsorption capacity (mg/g)	References
Graphene oxide	3	Langmuir	3.7	This Study
Graphene	3	Freundlich	5.6	This Study
Activated carbon (rice straw)	2–10	Langmuir	18.9	[36]
Activated carbon (*Moringa indica*)	2–12	Langmuir	0.23	[37]
Biomass	2–11	Langmuir	39.9	[38]
Aluminum (hydr)oxide coated pumice	3–11	Langmuir	7.87	[39]
Apatitictri calcium phosphate	4–11	Langmuir	15.15	[40]
Calcium chloride modified natural zeolite	4–9	Langmuir	1.77	[41]
Cellulose@HAP nanocomposites	4-9	Freundlich	2.76	[42]
Fe-Ti oxide nano-adsorbent	6.9	Langmuir	47.0	[43]
Hydrous bismuth oxides	4–12	Langmuir	1.93	[44]
Sulfate-doped Fe_3O_4/Al_2O_3 nanoparticles	2–12	Langmuir	70.4	[45]

of fluoride by graphene oxide obeyed the Langmuir isotherm

Authors' Contributions

Mahin Mohammadnia carried out the adsorption experiments and participated in the sequence alignment. Elham Derakhshani participated in design of the study and helped to draft the manuscript. Ali Naghizadeh carried out the thermodynamic studies, participated in the sequence alignment and drafted the manuscript.

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