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Original Research

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Defluoridation of groundwater using gypsiferous limestone

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ABSTRACT

Background: Fluorosis is a chronic environmental health problem caused by intake of excess fluoride, mainly in the drinking groundwater. Therefore, adsorptive removal of fluoride by locally available low-cost materials is very important for the provision of safe drinking water in the fluorosis endemic regions where there are no water treatment facilities. **Aim:** The purpose of the study was to investigate fluoride sorption capacity of gypsiferous limestone (GLS) using natural groundwater samples containing different fluoride concentrations. **Materials and Methods:** Sets of batch adsorption setup along with blank and control experiments were conducted at room temperature to examine the pattern of fluoride removal with varying contact time, solution pH, adsorbent dose and initial concentration using contaminated natural groundwater. **Results:** Equilibrium was achieved within 24 h of agitation time. Kinetics data of fluoride adsorption followed well the nonlinear pseudo-first order rate equation (R^2 ~0.99). Fluoride adsorption was greatly dependent on the pH of the groundwater. High fluoride removal efficiency (~89%) was observed over acidic medium at pH 3 and 5. The Langmuir isotherm model well described the equilibrium fluoride adsorption, giving an adsorption capacity of 1.07 mg/g. The removal of fluoride enhanced when the adsorbent was calcined at 200°C for 4 h. The fluoride-loaded adsorbent was successfully regenerated using NaOH solution. **Conclusion:** The results of the study have provided fundamental information for further investigation of GLS in the defluoridation of drinking water.

KEY WORDS: Adsorption isotherm, groundwater, gypsiferous limestone, thermal activation, sorption kinetics

INTRODUCTION

Health problems, such as dental fluorosis, skeletal fluorosis and crippling fluorosis, associated with the consumption of excess fluoride are growing, and millions of people across the globe are exposed to high fluoride concentrations, mainly from drinking groundwater [1]. The problem is severe in China, India, Sri Lanka and Ethiopia [2]. Water sources in the main Ethiopian Rift contain high fluoride levels [3,4]. WHO sets a guideline value for fluoride concentration in drinking water to 1.5 mg/L [1]. Various defluoridation technologies, such as membrane techniques, application of different chemicals and adsorption methods have been used to remove fluoride. Membrane methods effectively reduce fluoride concentration to acceptable levels [5]; however, these methods are complex, require skilled labor, and demand high initial and maintenance costs [6]. Similarly, defluoridation using various chemicals is complex, uneconomical, and requires skilled labor and chemical handling [7]. These drawbacks limit the implementation of both membrane and chemical defluoridation techniques in the fluorosis endemic regions, especially in the developing countries like Ethiopia. Researchers have been working to come up with simple, low-cost, and effective removal techniques using locally available materials. Thus, different materials, such as soils [8], bauxite [9], iron (III)-loaded ligand cotton [10], granular red mud [11], granular ceramic [12], allophane [13], bone char [14], cellulose fibers [15], and many others have been investigated. Almost all of the previous investigations of the effect of different parameters affecting the adsorptive removal of fluoride had been carried out using synthetic fluoride solution. The main purpose of the present study was to investigate the adsorptive removal efficiency of gypsiferous limestone (GLS) using fluoride contaminated natural groundwater samples collected from the main Ethiopia Rift region. Therefore, the aim of the study were (1) to characterize samples of groundwater, (2) to evaluate fluoride sorption capacity of GLS under batch adsorption setup, (3) to assess fluoride adsorption efficiency with respect to varying contact time, solution pH, adsorbent dose, thermal activation and initial fluoride concentration using contaminated natural groundwater and (4) to investigate the regenerative property of fluoride-loaded GLS.

MATERIALS AND METHODS

Adsorbent

GLS is limestone containing gypsum. Fresh unweathered GLS sample was collected in April 2013 from Roge locality, Kuyu

District, North Shawa Zone, Oromia Regional National State, Ethiopia. Sample of the adsorbent was washed with distilled water to remove dusts and afterwards dried at room temperature in the laboratory. The air-dried sample was crushed and sieved with 0.075 mm diameter opening mesh to obtain particle size <0.075 mm. Specific gravity of the adsorbent was determined using pycnometer method and was found to be 4.73. The chemical composition of GLS given in Table 1 was analyzed on X-ray fluorescence.

Groundwater

Six groundwater samples of different fluoride concentrations were collected in October 2013 in decontaminated 2 L polyethylene bottles from different locations in the Ethiopian Rift Valley region. The physicochemical properties of the samples were determined before batch studies according to the standard methods [16] and given in Table 2. Fluoride levels of the samples were analyzed by alizarin photometric method using double beam spectrophotometer (Hitachi High-Technologies Corporations Tokyo, Japan U-2000) and the absorbance was read at 550 nm. Calcium was directly determined by ethylenediaminetetraacetic acid titrimetric method. Magnesium was determined using gravimetric method after calcium content determination using washings from the calcium determination. Phosphate concentration of each sample was determined on double beam spectrophotometer. Argentometric method was applied to determine chloride concentration of the samples. Total dissolved solid (TDS) was measured using TDS Meter (4076 ELE International Bibby Scientific Limited, Beacon Road, Stone, Staffordshire, ST15 OSA, UK) and turbidity was measured using Microprocessor Turbidity Meter (Hanna Instruments 93703 Italia Srl, Via E.Fermi, 10, 35030 Sarmeola di Rubano-PD, Italy).

Batch Adsorption Experiment

Batch adsorption experiments were conducted from October 2013 to December 2013 to examine fluoride adsorption behavior on GLS as a function of contact time, pH, initial fluoride concentration, adsorbent dose and activation temperature. In all sets of the experiments, 500 mL groundwater containing known concentration of fluoride and desired amount of GLS were mixed in acid-washed polyethylene bottles and agitated for 24 h at 300 rpm on a horizontal shaker. All the experiments were in duplicate at room temperature (24.5-26.5°C), and average results were reported. Blank (only with GLS) and control (only with fluoride) experiments were conducted at every set of experiments.

Throughout the study, particle size of <0.075 mm GLS, groundwater sample containing 11.28 mg/L fluoride (except in the study of the effect of initial fluoride concentration and thermal activation), and 15 g/L of GLS (except in the investigation of the effect of adsorbent dose) were used. 100 ml supernatant solution was drawn at a desired time intervals (0-24 h). The supernatant solution was then filtered with 0.45 μm acetate filter paper (Sartorius Stedim Biotech GmbH, Germany) for the analysis of residual fluoride. The effect of contact time was investigated using Kentiri groundwater sample containing 11.28 mg/L fluoride. The influence of solution pH was investigated by adjusting the initial pH of Kentiri groundwater sample from 3 to 11. The effect of the adsorbent dose was examined by varying the amount of the adsorbent from 1 to 20 g/L under the initial fluoride concentration of 11.28 mg/L. The influence of initial concentration of fluoride was examined using six different groundwater samples containing fluoride level ranging from 2.24 to 29.58 mg/L. The percentage of fluoride removed, A%, and the amount of fluoride adsorbed per unit mass of the adsorbent, q_t (mg/g), at any time t (h) are computed respectively using Eqs. 1 and 2.

$$A\% = (C_0 - C_t) \times 100/C_0 \tag{1}$$

$$q_t = (C_0 - C_t) \times V/M \tag{2}$$

where, q_t (mg/g) is the amount of fluoride adsorbed at any time, t (h); A (%) is the percentage of fluoride adsorbed; C_0 (mg/L) is initial fluoride concentration; C_t (mg/L) is concentration of fluoride in the aqueous phase at any time, t; V (L) is volume of the groundwater used; and M (g) is mass of GLS used in the experiment.

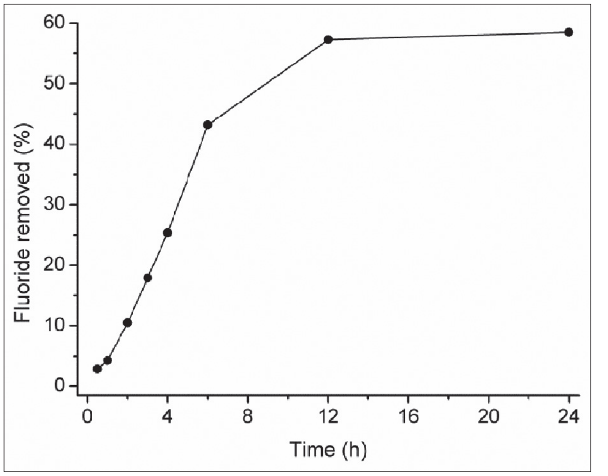

Figure 1: Effect of contact time on the removal of fluoride from natural groundwater sample

Table 1: Chemical compositions of GLS

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	MnO	TiO_2	P_2O_5	SO_3	Cl	H_2O
Weight%	0.94	<0.01	0.56	46.25	0.28	<0.01	0.02	<0.01	0.07	13.71	<0.01	4.07

GLS: Gypsiferous limestone

RESULTS AND DISCUSSIONS

Effect of Contact Time

Figure 1 shows fluoride removal percentage versus contact time. The plot has two portions: The steep portion, for contact time from 0.5 to 12 h within which steady increase in the percentage of adsorption was observed and the last flat part for contact time from 12 to 24 h within which fluoride adsorption percentage significantly approached constant. It was assumed that the equilibrium time is that at which curves appear nearly asymptotic to the time axis [17]. Thus, the equilibrium time was achieved within 24 h at which about 59% of 11.28 mg/L fluoride of the Kentiri groundwater was removed without adjusting the pH of the water.

Kinetics of Fluoride Adsorption

Nonlinear forms of pseudo-first order and pseudo-second order rate equations [18] respectively given in Eqs. 3 and 4 were applied to analyze the kinetics of fluoride adsorption onto GLS.

$$q_t = q_e(1 - \exp^{-K_1 t}) \tag{3}$$

$$q_t = (K_2 q_e^2 t) / (1 + K_2 q_e t) \tag{4}$$

where, q_t (mg/g) is the amount of fluoride adsorbed per unit mass of the adsorbent at time t (h), q_e (mg/g) is the modeled amount of fluoride adsorbed per unit mass of GLS at equilibrium, K_1 (h^{-1}) is pseudo-first order rate constant, and K_2 (g/mg/h) is pseudo-second order rate constant.

The nonlinear plot of kinetics of fluoride adsorption is given in Figure 2. The rate constants of the adsorption kinetics summarized in Table 3 were obtained from their respective nonlinear plots of the models using OriginPro® 8 (OriginLab Corporation, Northampton, MA, USA) scientific graphing and data analysis software. The suitability of a model to describe the kinetics data was evaluated comparing values of the coefficient of determination, R^2. The R^2 value of pseudo-first order rate equation was higher, and this rate equation satisfactorily predicted the experimental equilibrium adsorption capacity of GLS [Table 3]. Therefore, pseudo-first order rate equation well-described the kinetics of fluoride adsorption onto the adsorbent.

Table 2: Physicochemical properties of groundwater samples

Characteristics	Groundwater well					
	Dado	BSS	Jirme	Dakko	Dado	Kentiri
Depth, m	46	22.00	250	142	46	7.50
(F^-), mg/L	3.42	29.58	4.78	2.24	3.42	11.28
pH	7.70	8.73	8.78	7.70	7.62	7.87
Conductivity, μS/cm	0.88	2.79	0.80	0.88	1.20	3.15
TDS, mg/L	592	1852	462	543	741	1.00
Turbidity, NTU	0.10	8.70	0.21	0.20	0.45	5.61
Alkalinity as $CaCO_3$, mg/L	592	1240	392	604	592	480
(Ca^{+2}), mg/L	22.8	31.40	12.16	22.8	26.8	40
(Mg^{+2}), mg/L	0.46	0.34	0.28	0.34	0.46	4.56
(PO_4^{3-}), mg/L	0.26	0.22	0.24	0.26	0.26	2.20
(Cl^-), mg/L	184.94	279.91	134.96	164.95	184.94	185.35

TDS: Total dissolved solid; NTU: Nephlometric turbidity unit; BSS: Bulbula shell station

Table 3: Pseudo-first order and pseudo-second order rate constants for the sorption of fluoride onto GLS

$q_{e,\,exp}$ (mg/g)	Pseudo-first order			Pseudo-second order		
	K_1 (h^{-1})	q_e (mg/g)	R^2	K_2 (g/mg/h)	q_e (mg/g)	R^2
0.44	0.14	0.48	0.959	0.66	0.17	0.930

GLS: Gypsiferous limestone

Effect of Adsorbent Dose

The effect of adsorbent dose on the removal of fluoride was investigated by varying the amount of GLS from 1 to 20 g/L while keeping the other experimental conditions constant. The percentage of fluoride adsorbed and fluoride adsorption capacity at different GLS doses are given in Figure 3. According

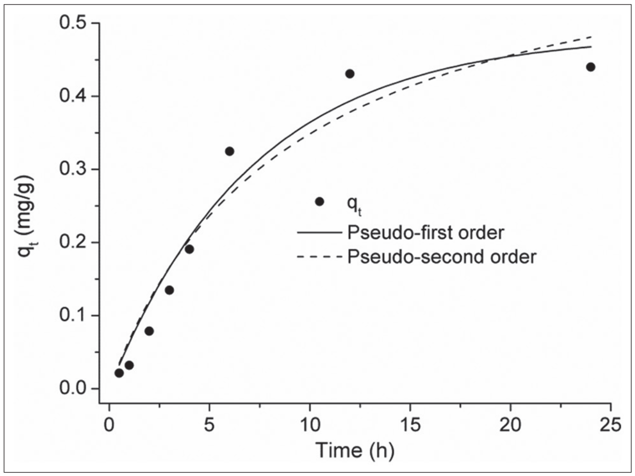

Figure 2: Pseudo-first order and pseudo-second order kinetics by nonlinear method and experimental kinetics for the sorption of fluoride onto gypsiferous limestone

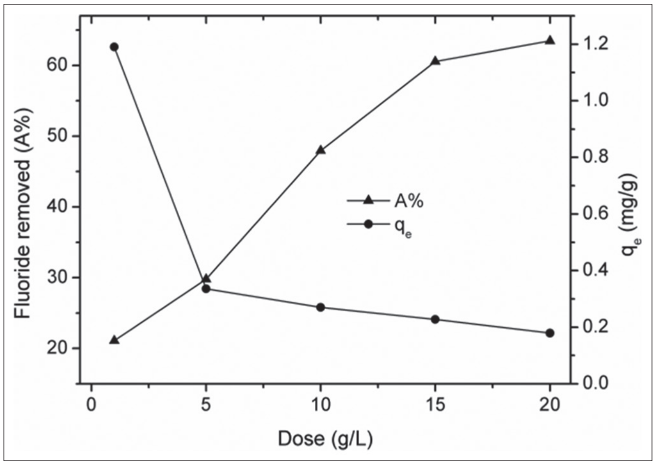

Figure 3: Effect of adsorbent dose on the removal of fluoride by gypsiferous limestone

to the results obtained, the percentage of fluoride adsorbed increased with the increase in the adsorbent dose. The increase in the percent of adsorption with the adsorbent dosage can be attributed to the availability of more adsorption sites at a higher adsorbent mass [19]. On the other hand, the amount of fluoride adsorbed decreased with the increase in the adsorbent dose. The decrease in the adsorption capacity was possibly due to the lower ratio of fluoride ions to the available active binding sites with an increase in the mass of the adsorbent [20]. Fluoride removal increased significantly up to the adsorbent dose of 15 g/L, which adsorbed ~60 % of 11.28 mg/L fluoride in the Kentiri natural groundwater. However, no significant increase in the percentage of fluoride removal was observed beyond 15 g/L GLS.

Effect of pH

The effect of pH on the removal of fluoride was examined by adjusting the pH of Kentiri groundwater sample from 3 to 11. The plot in Figure 4 indicates that fluoride adsorption onto GLS was dependent on pH. It was observed that fluoride adsorption was high (~89%, ~0.67 mg/g) in the acidic range at pH 3 and 5. According to Kang *et al.*, [21] in acidic medium Ca^{2+} is leached out from $CaCO_3$ forming CaF_2 or adsorbing F^- ions. The higher fluoride adsorption at lower pH might be, therefore, due to GLS solubility in the acidic medium generating Ca^{2+} that form CaF_2 or adsorbs F^- ions. However, fluoride adsorption decreased in the basic medium, which could be due to competition of hydroxyl ion with fluoride ion for active adsorption site.

Effect of Initial Concentration and Adsorption Isotherm

The effect of initial concentration of fluoride was assessed using six natural groundwater samples containing fluoride level ranging from 2.24 to 29.58 mg/L without adjusting the pH of each of the samples (Table 2). Fluoride adsorption at various initial concentrations of fluoride was presented in Figure 5a. The results indicated that fluoride adsorption capacity increased with the increase in the initial fluoride concentration, whereas the percentage of fluoride removal decreased. The increase in the adsorption capacity could be due to the availability of more fluoride ions at higher fluoride concentration for adsorption on poorly reachable sites with weak sorption energy [22,23]. However, the percentage of fluoride removal decreased with the increase in the initial concentration. This can be explained in that at a higher concentration level the number of available adsorption sites became fewer, thus resulting in a relatively lower percentage of fluoride removal.

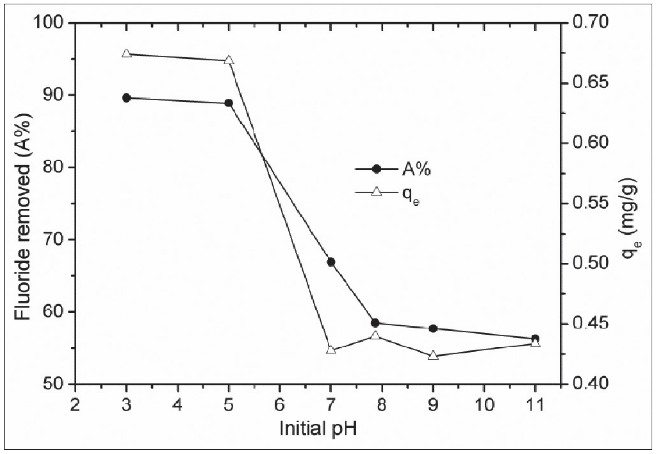

Figure 4: Effect of pH on the removal of fluoride by gypsiferous limestone

The nonlinear forms of two widely used isotherms [9,22], namely the Freundlich (Eq. 5) and the Langmuir (Eq. 6) equations, were used to estimate the fluoride adsorption capacity of the adsorbent.

$$q_e = K_F C_e^{1/n} \tag{5}$$

$$q_e = \frac{Q_{\max} b C_e}{(1 + bC_e)} \tag{6}$$

where C_e (mg/L) is fluoride concentration in the aqueous phase at equilibrium, q_e (mg/g) is the amount adsorbed at equilibrium per unit mass of GLS, $Q_{\max}$ (mg/g) is the saturation capacity based on the Langmuir equation, and b (L/mg) is the Langmuir constant, KF ($[mg^{1-1/n}L^{1/n}]/g$) is the Freundlich adsorption coefficient, and $1/n$ is the adsorption intensity based on the Freundlich equation. The plot of the equilibrium adsorption isotherm is graphically presented in Figure 5b, and the values of the equilibrium constants computed from the isotherm models are given in Table 4. The isotherm model that best describes the fluoride-GLS adsorption system was determined by evaluating the values of the coefficient of determination, R^2, and Chi-squared test given by $\chi^2 = \Sigma\,(q_e - q_{e,\,cal})^2/q_e$, where $q_{e,\,cal}$ (mg/g) is the equilibrium capacity obtained by calculating from the model; and q_e (mg/g) is the experimental equilibrium capacity. Accordingly, the Langmuir isotherm had higher R^2 and smaller χ^2 values (Table 4), indicating that the model satisfactorily described the adsorption isotherm of fluoride on the adsorbent [24]. The fitting of the equilibrium data to the Langmuir isotherm indicated the monolayer adsorption of fluoride on the homogeneous surface sites of the adsorbent. The nature of adsorption isotherm can be predicted by evaluating the essential characteristic of the Langmuir isotherm expressed in terms of a dimensionless constant separation factor, R_L, computed by $R_L = 1/(1 + bC_0)$ [24], where C_0 (mg/L) is initial fluoride concentration; and b (L/mg) is the Langmuir constant. The adsorption process is irreversible if $R_L = 0$, favorable if $0 < R_L < 1$, linear if $R_L = 1$ and unfavorable if $R_L > 1$. The values of R_L computed for fluoride adsorption on GLS were from 0.03 to 0.30 with decreasing in value at a high level of initial concentration. The obtained values of R_L are within the range 0

Table 4: Isotherm parameters of the equilibrium adsorption of fluoride on GLS

Freundlich isotherm		Langmuir isotherm	
Parameter	Value	Parameter	Value
K_F ($[mg^{1-1/n}L^{1/n}]/g$)	0.41	$Q_{\max}$ (mg/g)	1.07
$1/n$	0.34	b (L/g)	1.03
R^2	0.886	R^2	0.987
χ^2	0.017	χ^2	0.002

GLS: Gypsiferous limestone

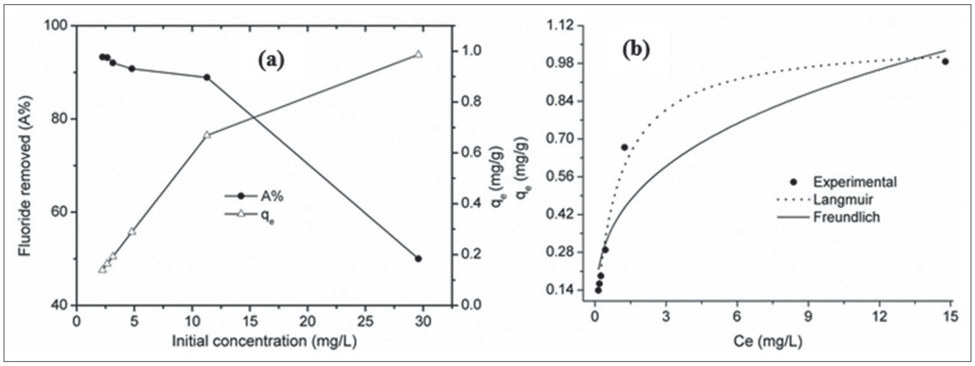

Figure 5: (a) Effect of initial concentration and (b) equilibrium isotherms of adsorption of fluoride on gypsiferous limestone

to 1, signifying the favorable equilibrium adsorption of fluoride on GLS [24]. The magnitude of the adsorption intensity, 1/*n*, computed from the Freundlich equation can suggest the type of isotherm. In that, the adsorption is favorable when $0 < 1/n < 1$, irreversible when $1/n = 1$ and unfavorable when $1/n > 1$ [22]. The value of 1/*n* obtained for the equilibrium adsorption of fluoride was 0.34. Therefore, fluoride was adsorbed favorably on GLS, as the numerical value of 1/*n* is in the range 0 to 1.

Effect of Thermal Activation

Fluoride uptake by calcined GLS steadily increased for the initial fluoride concentration from 2.24 to 11.28 mg/L, but the amount adsorbed did not significantly differ for the initial fluoride concentration from 11.28 to 29.58 mg/L [Figure 6]. Thermal treatment of GLS at 200°C could lead to surface modifications, structural transformation, and loss of structural water molecules and CO_2 molecules, which ultimately enhanced the adsorption of fluoride ions [25]. Therefore, the adsorption capacity of calcined GLS was found to be higher than raw GLS. It was observed that 15 g/L dose of the calcined GLS was capable to reduce initial fluoride concentration ranging between 2.24 and 11.28 mg/L to below the WHO guideline value 1.5 mg/L fluoride in the drinking water [1].

Desorption

The effect of pH on fluoride adsorption (Figure 4) shows that adsorption efficiency was significantly reduced in the basic medium, suggesting the possibility of desorbing fluoride from the fluoride-loaded GLS using alkaline solution. Based on this, the batch desorption experiment was conducted using 500 mL solution of 0.2 M NaOH, which had a pH >12, under identical experimental conditions of the equilibrium batch adsorption. According to the obtained results, it was observed that ~81 and ~86% fluoride were respectively desorbed from raw and calcined GLS. Thus, it could be concluded that exhausted GLS would be satisfactorily recycled using NaOH solution.

CONCLUSION

From the present study, it can be concluded that fluoride removal from natural groundwater by GLS is dependent on contact time, dose, pH, initial fluoride concentration and thermal activation. Kinetics study showed that fluoride adsorption kinetics followed the pseudo-first order rate equation, signifying that the adsorption process was not mainly controlled by chemical adsorption mechanism. The Langmuir isotherm equation satisfactorily described the adsorption isotherm of fluoride, assuming the occurrence of monolayer adsorption of fluoride on the homogenous surface of the adsorbent. Thermal activation at 200°C enhanced groundwater defluoridation capacity of GLS, and thus further investigation need to be focused to assess the effect of various parameters on the fluoride adsorption efficiency of calcined GLS. In general, the results of the present study have provided basic information for further investigation of GLS in the defluoridation of natural groundwater.

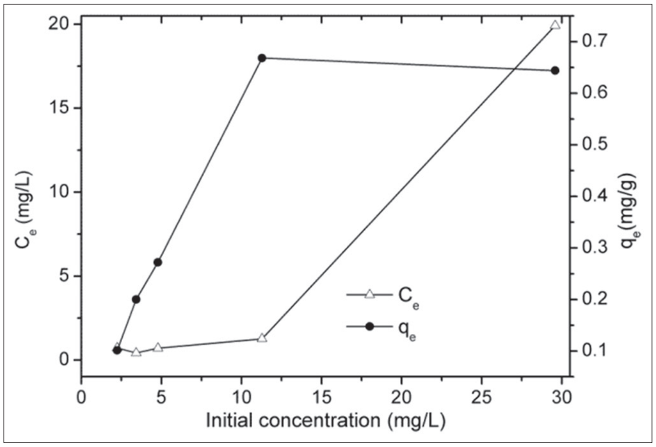

Figure 6: Effect of thermal activation on the adsorption of fluoride

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