Adsorption Efficiency of Cement Impregnated Magnesium Oxide on the Removal of Fluoride

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ABSTRACT

Presence of fluoride in drinking water above the prescribed limit may lead to a severe health complication. We present in this paper the fluoride removal capacity of cement impregnated MgO (MgO-cement) from drinking water. MgO-cement was prepared by adding magnesium oxide (MgO) into the cement slurry solution in the ratio of 1:10. Batch experiments were performed as a function of adsorbent dose, contact time, effect of pH and effect of co-ions. The percentage removal decreases with increasing initial fluoride concentration. Co-ions effect revealed that hydroxide ion was found to interfere more with fluoride removal followed by bicarbonate and least effect with sulphate. Reaction mechanism follows Freundlich isotherms. From the kinetic study we observed that uptake of fluoride ion is fast in the first sixty minutes and equilibrium time found to be independent of the initial fluoride concentration. Adsorption kinetics followed the pseudo second order model showing that the sorption of fluoride is a complex process. Surface as well as intraparticle diffusion contribute in the sorption process. No leaching of magnesium in the treated water was detected.

Keywords: Cement; MgO; Fluoride Removal; Adsorption isotherms; Kinetics; Leaching

1. INTRODUCTION

The presence of trace concentration of fluoride in drinking water is beneficial for bones and teeth, but high concentration of fluoride may causes dental and skeletal fluorosis[1,2], endocrine glands damage, neurological damage in some cases effect to liver and thyroid[3,4]. Fluoride in drinking water from more than 3 mg/L to less than 6 mg/L may leads to skeletal fluorosis with irreversible changes in bone structure and when the concentration of more than 10 mg/L crippling of skeletal fluorosis may occur[5]. The Bureau of Indian Standards (BIS) has set a standard guideline value of 1 mg/L as desirable limit and 1.5 mg/L as the permissible level for drinking water[6]. Many approaches for removal of fluoride have been studied, but precipitation[7,8], and adsorption[9-16] methods are still found wide applicable. In recent years, approaches on the removal of fluoride have drawn many researchers to look into some cheaper resources of materials for F removal. For instant, cement paste[17-19], metal oxide coated carbon based adsorbent[20,21], clay materials[22], stone dust and alumina10 and kaolinite, bentonite, charfines, lignite and nirmali seeds[16] were studied.

Removal of fluoride using magnesium oxide (MgO) found to be applicable owing to its high adsorption capacity, less solubility and non toxic[23]. Work on MgO for fluoride removal which relies on precipitation, sedimentation and filtration technique was reported[24], but its wide application is not available. MgO alone is having high removal efficiency but it cannot be applied directly to fluoride removal due to its

fine powder state which increases the turbidity, pH and the suspended particle. Cement powder on the other hand can only reduce the fluoride from high concentration of fluoride to lower concentration but beyond the permissible limit[17]. Hence our approach is to study the fluoride removal using cement impregnated magnesium oxide as an adsorbent based on the fact that, both the materials are known to remove fluoride[18,19,25], secondly, the materials are easily available and thirdly, materials are cost effective. The present work aims to test the efficiency of the prepared materials to remove fluoride from water.

2. MATERIALS AND METHODS
2.1 Materials

Ordinary cement (Topcem brand) was purchased from local commercial source. Magnesium oxide (MgO) and sodium fluoride (NaF) were from E-Merck India Limited. Fluoride solution stock was prepared by taking known weight of NaF in known volume of water and required fluoride solution was done by appropriate dilution from prepared stock solution. Other chemicals used in the study are of AR grade and used without further purification. Water for solution was obtained using Purelab Option Q DV-25 (ELGA) and used throughout for preparing standard and eluent solutions.

2.2 Preparation of Adsorbent

Cement slurry was done by adding 250 ml of water into 500 g of cement. To the slurry, 50 g of MgO was added and the solution (1:10 ratio of MgO-cement) was stirred repeatedly for a few minutes. The pH of the solution mixture was recorded.

It was then kept for one week to set at room temperature. After air drying, the mixture was crushed to small granules of about 0.05 mm in size, soaked overnight in distilled water and thereafter repeatedly washed with water till the run out is clear. The compound is heated to 500 °C in the muffle furnace for 4h. The prepared adsorbent after cooling was kept in airtight container for future use. In similar procedure, adsorbent MgO-cement (in 1:3 ratio of MgO-cement) was also prepared for leaching study purposes.

2.3 Analysis

The ion-meter (Thermo Orion 4 star) with a fluoride-selective electrode (ThermoFisher) used to analyse fluoride. Buffer was used to suppress interfering ions. pH was taken using by Cyberscan pH 510 meter. Functional group detection Alpha T (Bruker) FT-IR was used. All instruments used were calibrated as per recommendation procedure. Ion Chromatography (882 Compact IC Plus, Metrohm) was used to analyse cations for leaching study. IKA KS4000 ic control was used for shaking

2.4 Adsorption Studies

A known volume of spiked solution and a known weight of adsorbent was taken in a 250 ml conical flask and the solution was shaken at room temperature (28±0.2 °C) for three hours in order to attain equilibrium. Same procedure was followed for optimum conditions to study the initial concentration, competitive co-ions, the effect of pH, adsorbent dose. Sorption kinetics experiments were conducted at different concentration of fluoride at 5.1 and 10 mg/L. Uptake of fluoride was obtained using the following equation:

$$q_e = \frac{(C_o - C_e)V}{m}$$

(1)

where q_e (mg/g) is the adsorbed fluoride at time t; V is the volume taken; C_o and C_e (mg/L) are initial and final fluoride concentration at equilibrium at time t respectively; m is the weight of the adsorbent (g).

2.5 Leaching Study

Long term consumption of magnesium rich water might lead to a physiological disorder like bowel obstruction. In this study the matrix of MgO:cement in 1:10 and 1:3 ratios were subjected to leaching experiment. All samples prior to analyses were subjected to pass through 0.22 µm filter paper.

2.6 Regeneration Study

It was carried out by using acid base rinsing procedures with 0.1 M NaOH and HCL respectively. 5 gm of exhausted adsorbent loaded with fluoride was shaken with 50 mL of NaOH solution and HCl solution separately. The filtrate was then analysed for appropriate ions to obtain the fluoride ions released.

3. RESULTS AND DISCUSSION

3.1 Dose Effect

There is an increased fluoride removal efficiency increased from 6.60 % to 90.88 % with increasing adsorbent dose from

0.12 g/L - 30 g/L as shown in Fig. 1. This increased trend is attributed to the increase in the number of active sites available in the MgO-cement for fluoride adsorption.

3.2 Initial Fluoride Concentration Effect

The initial concentration effect on fluoride adsorption by MgO-cement is reflected in Fig. 2(a). With the fixed dose of MgO-cement adsorbent, there is an increased in fluoride removal with increasing initial concentration till uptake value attained the state of equilibrium saturation. With increase in initial concentration the percentage removal is decreasing as shown in Fig. 2(b).

The reason may be due to the lack of free sites for adsorbing fluoride ions on the adsorbent layers thus blocking more adsorption of fluoride and indicating that the fluoride adsorption capacity of MgO-cement was almost over. But at lower concentration, the active sites to total fluoride ratio is more and hence the attraction of fluoride to the adsorbent surface active site was enough for fluoride removal efficiency.
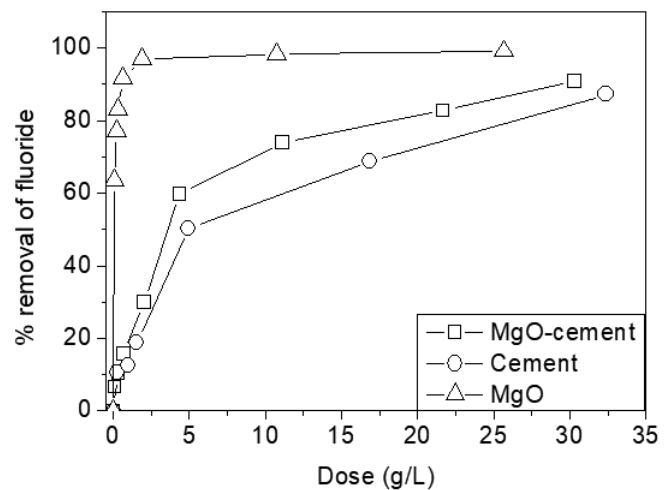

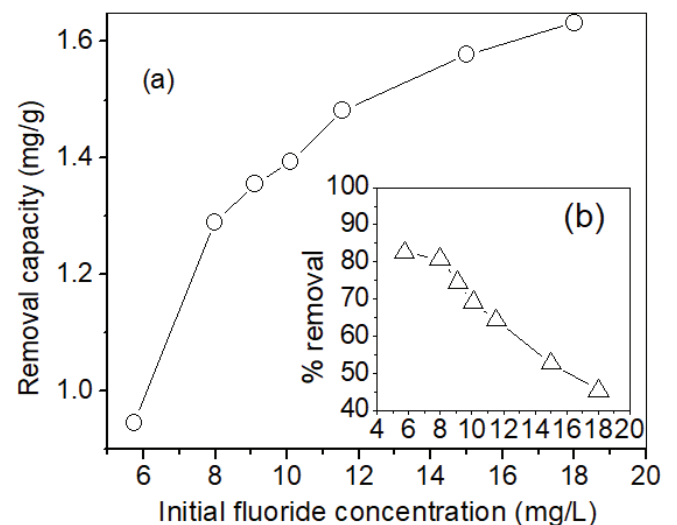Figure 1. Dose effect on fluoride removal.

Figure 2. (a) Fluoride removal at different initial concentration of fluoride and (b) Inset plot is in %removal).

3.3 pH Effect

The removal efficiency of fluoride was found to be pH dependent. The pH effect on removal using MgO-cement over the pH range from 3.0 - 11.5 was investigated and the effect was found to slightly decrease with increasing pH as shown in Fig. 3.

This change on trend with pH increase may be due to more hydroxide ions are present in the adsorbent surface which in turn interferes with the fluoride ion uptake due to similarities in size between the hydroxide and fluoride ions.

3.4 Co-ions Effect

Co-ions effect including hydroxide (OH$^-$), sulphate (SO$_4^{2-}$) and bicarbonate (HCO$_3^-$) on fluoride removal by MgO-cement was investigated at 10 mg/L of fluoride concentration. The concentrations of competing ions were varied from 50 mg/L - 800 mg/L as shown in Fig. 4.

Fluoride adsorption was more influenced by the presence of OH$^-$ followed by HCO$_3^-$ and least by SO$_4^{2-}$ ions. Percentage removal of fluoride found decreased with increasing OH$^-$ concentration. This may be due to the similarity in ionic size between fluoride ions and hydroxide ions. The effect of bicarbonate ions found to be less followed by sulphate ions.

3.5 Adsorption Study

Adsorption study indicates the adsorption capacity mechanism of adsorbent to adsorbate at different aqueous equilibrium concentration. Figures 5, 6 and 7 show adsorption isotherms for fluoride ion onto MgO-cement, at 28 ± 0.2 °C.

3.6 Langmuir Adsorption Model

Langmuir isotherm is expressed as follows[26]:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{2}$$

where q_e is quantity adsorbed at equilibrium (mg/g), q_m is the maximum monomer adsorption (mg/g), C_e the concentration at equilibrium (mg/L), b the sorption constant (L/mg) related to the energy of adsorption. The maximum adsorption capacity, q_m calculated found to be 24.8 mg/g. Langmuir
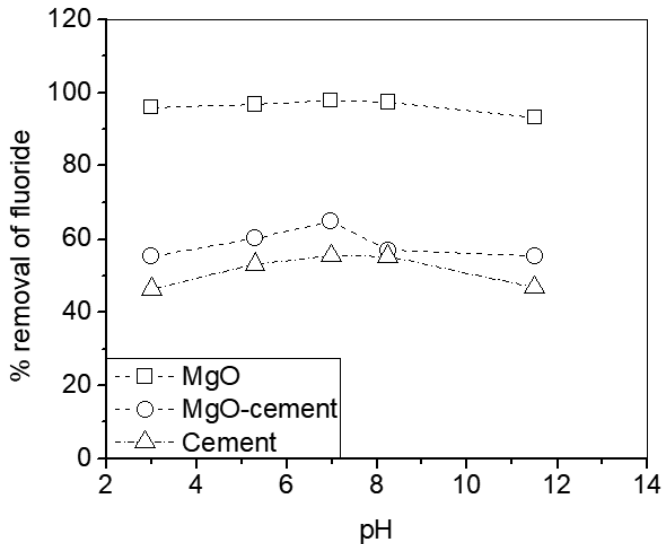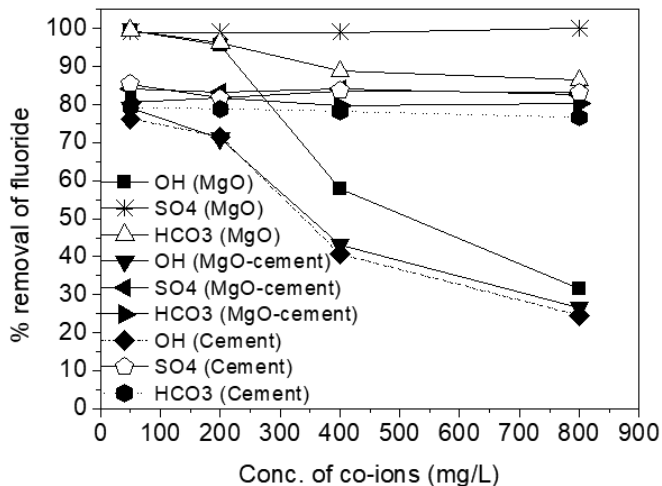
Figure 3. pH effect on fluoride removal.

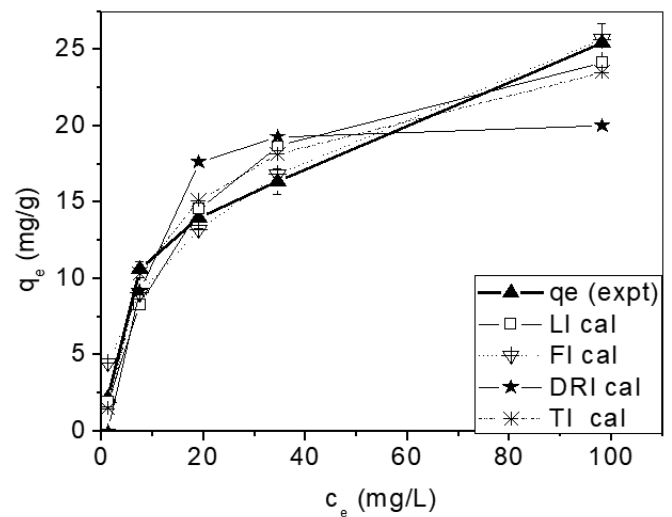Figure 4. Co-ions effect on fluoride removal.

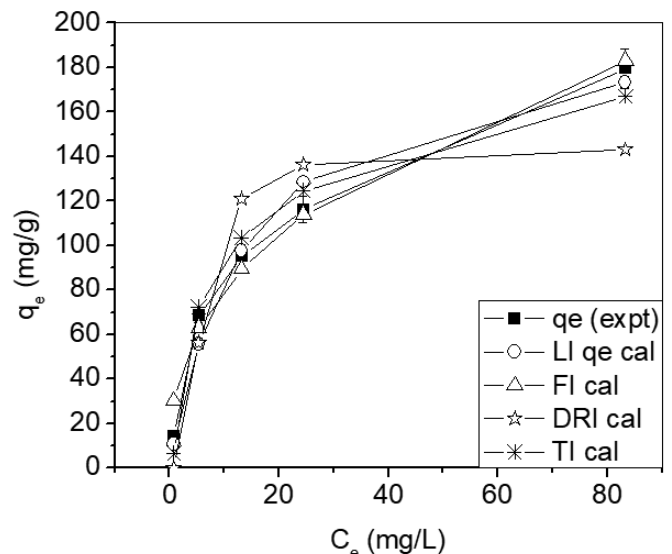Figure 5. The adsorption experimental data modelling using MgO-cement.

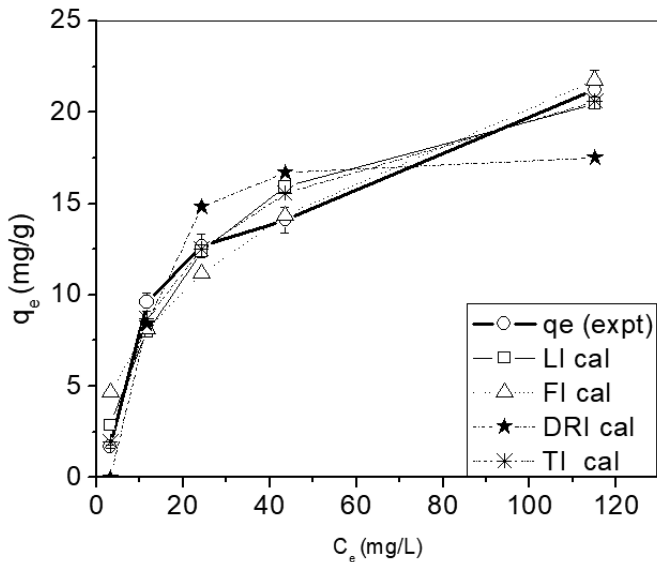Figure 6. The experimental data modelling using MgO.

Figure 7. The adsorption experimental data modelling using cement.

isotherm constant parameter (R_L) can be linked to b using the following Eqn. (3).

$$R_L = \frac{1}{1+bC_o} \tag{3}$$

where C_o is the initial fluoride concentration (mg/L). The R_L value calculated was found lying between 0 and 1 indicating a favourable adsorption for all initial fluoride concentrations.

3.7 Freundlich Adsorption Model

The Freundlich isotherm is given as follows[27]:

$$q_e = K_f C_e^{1/n} \tag{4}$$

where K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1}) is Freundlich constant indicative of the relative adsorption capacity of the MgO-cement adsorbent and n is the empirical parameter representing adsorption intensity of the MgO- cement.

The value of n computed was found to be 2.46 as shown in Table 1, thus showing valid condition for Freundlich isotherms[28]. The adsorption equilibrium data calculated fit well to Freundlich model with a correlation coefficient (R^2) values of 0.9789. in comparison to R^2 values of 0.9603 from Langmuir model. The calculated values of root mean square error (RMSE) of the fitting of Freundlich case were also found to be less than the Langmuir. The same adsorption behaviour of cement and MgO are also reported in the literature[17,23]. This indicated that the characteristic behaviour of the adsorbents under study is heterogeneous in nature.

3.8 Dubinin-Radushkevich Adsorption Model

Dubinin-Radushkevich isotherm (DR isotherm) is expressed as[29,30]:

$$q_e = Q_m Exp(-K\varepsilon^2) \tag{5}$$

where Q_m is the theoretical maximum capacity (mg g^{-1}), ε is the Polanyi potential, K (mol^2 kJ^{-2}) is a constant related to the mean free energy of adsorption and it is defined as Eqn. (6).

Table 1. Summary of studied equilibrium models application to fluoride adsorption onto MgO-cement (also given the present study of MgO and cement adsorbents)

Isotherm models	MgO-cement	MgO	Cement
Langmuir isotherm			
Q_m (mg/g)	28.680	202.70	24.796
b (L/mg)	0.0538	0.0706	0.0410
R_L (10 mg/L)	0.6498	0.5860	0.7090
χ^2	1.0718	5.5264	1.0297
RMSE	2.0808	11.235	1.6163
Freundlich isotherm			
K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	3.9865	32.821	2.8512
n	2.4622	2.5730	2.3362
χ^2	1.5341	6.4317	2.3700
RMSE	1.0506	5.2113	1.2538
Dubinin-Radushkevich isotherm			
Q_m (mg/g)	20.127	143.67	17.657
K (mol^2 kJ^{-2})	8.0444	5.1195	17.299
χ^2	2.9150	20.704	540.57
RMSE	4.4161	30.438	3.1279
Temkin isotherm			
A_T (L mg^{-1}),	0.9940	1.5105	0.4595
b_T (kJ mol^{-1})	0.4829	0.0718	0.4776
χ^2	0.7603	11.084	0.2893
RMSE	1.7197	11.078	1.0722
Redlich-Peterson isotherm			
A (L/g)	4.1319	35.323	1.3634
B (L/mg)	0.5576	0.5678	0.1146
g	0.7205	0.7477	0.8517
χ^2	0.6857	1.8823	1.1615
RMSE	1.2648	4.8512	1.4953

$$\varepsilon = RT \ln(1+\frac{1}{C_e}) \tag{6}$$

where R is Universal Gas constant, T is the absolute temperature. Constants K and Q_m were calculated non-linearly and inserted in Table 1.

The mean free energy of adsorption (E) defined as the free energy change when one mole of ion is transferred to the surface of the solid from infinity in solution can be calculated from the following equation[31]:

$$E = (-2K)^{-0.5} \tag{7}$$

E value calculated was found to be 0.25 kJ/mol. Calculated E value is a useful tool for predicting the type of adsorption. If the value lies between 8 -16 kJ/mol, then adsorption may be due to ion exchange or chemisorptions. The value of E in this study was found to be below 8 kJ/mol suggesting the mechanism was due to physiosorption[32].

3.9 Temkin Adsorption Model

The Temkin isotherm model[33] is given as follow:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{8}$$

where A_T is the equilibrium binding constant, (L/mg), b_T is the Temkin constant related to the variation of the adsorption

energy (kJ/mol)[34]. The adsorption energy calculated shows a positive value (0.48 kJ/mol) thus indicating that the adsorption reaction is exothermic in nature[35]. All other values are reflected in Table 1.

3.10 Redlich–Peterson Adsorption

The Redlich–Peterson isotherm[36] can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \tag{9}$$

where *A* is the Redlich–Peterson constant (L/g), *B* is the affinity coefficient (L/mg), g is the Redlich–Peterson heterogeneity exponent which lies between 0 and 1. The value of *g* calculated was found to be 0.72 showing the heterogeneity of the MgO-cement surface as shown in Table 1.

3.11 Kinetic Studies

It was studied at F concentrations of 5.1 mg/L and 10 mg/L respectively. Three kinetic models were investigated, they are a pseudo first order model (Fig. 8) and a pseudo second order model (Fig. 9) and an intra-particle diffusion.

3.12.1 The Pseudo First Order

The rate expression of the pseudo first order kinetics equation is given by[37]:

$$q_t = q_e[1 - \exp(-k_1 t)] \tag{10}$$

where k_1 (min^{-1}) is the rate constant of pseudo first order adsorption, q_e and q_t (mg/g) the adsorbed amounts at equilibrium and at time *t*. Figure 8 shows the pseudo first order plot.

3.12.2 The Pseudo Second Order

The pseudo second order kinetic is represented by[38]

$$q_t = \frac{q_e^t k_2 t}{1 + q_e k_2 t} \tag{11}$$

where q_e and q_t are the amount of adsorbate at equilibrium and time t (both in mg/g); k_2 is the second order rate constant of sorption (g/mg/min) and *t* is the time (min).

In order to calculate the kinetic parameters to find the best-fitting model, nonlinear method was calculated by using the root mean square error as given by following equation:

$$RMSE = \sqrt{\frac{1}{n-2} \sum_{i=1}^{N} q_{cal_i} - q_{\exp t_i})^2} \tag{12}$$

where, q_{cal} and q_{expt} are the calculated and the observed value of the solid phase fluoride concentrations at equilibrium. Figure 9 shows the pseudo second order plot. The values of the respective rate constants, RMSE are given in Table 2. The data fitted well to the pseudo second order as compared to pseudo first order kinetic indicating the fluoride ions were adsorbed onto the adsorbent surface due to chemical adsorption.

3.13 Intraparticle Diffusion

In order to determine the intraparticle diffusion process, q_t (at any time *t*) was plotted as a function of the square root of time ($t^{1/2}$) as shown in Fig. 10 and calculated from the Eqn. (13).
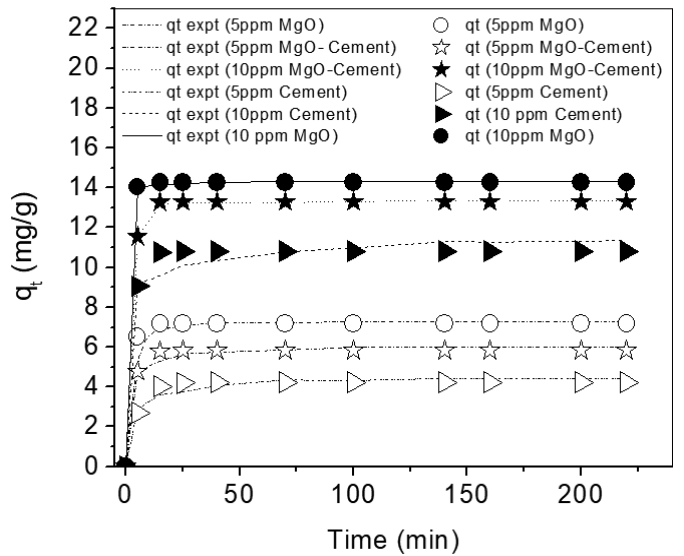

Figure 8. **Comparisons of the Pseudo first order kinetic plots for the sorption of fluoride (qt expt: experimental; qt: calculated).**
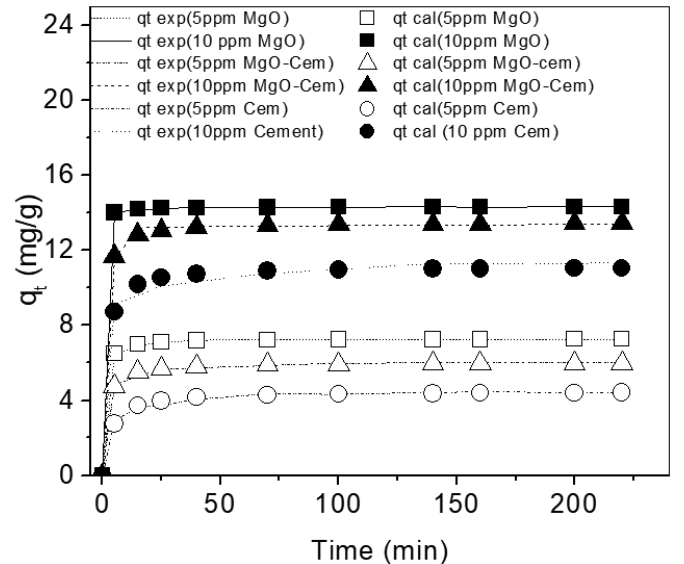

Figure 9. **Comparisons of the Pseudo second order (k_2) kinetic plots for the sorption of fluoride (qt exp: experimental; qt cal: calculated).**

$$q_t = k_i t^{1/2} \tag{13}$$

where k_i (mg/g h[1/2]) is the intraparticle diffusion rate constant. The initial curved portion indicates film or boundary layer diffusion effect while the linear portion that followed attributed to the intraparticle diffusion effect. From the figure, it shows that intraparticle diffusion is slow. The k_i values calculated was found to be 0.5389 and 1.2016 mg/g min[-1/2] for the initial fluoride concentration of 5 mg/L and 10 mg/L, respectively.

It is also observed that linear portion does not pass through the origin, indicating the removal is complex and both surface adsorption and intraparticle diffusion contribute to the rate-limiting step.

Table 2. Adsorption parameters obtained for fluoride sorption onto MgO-cement, MgO and cement

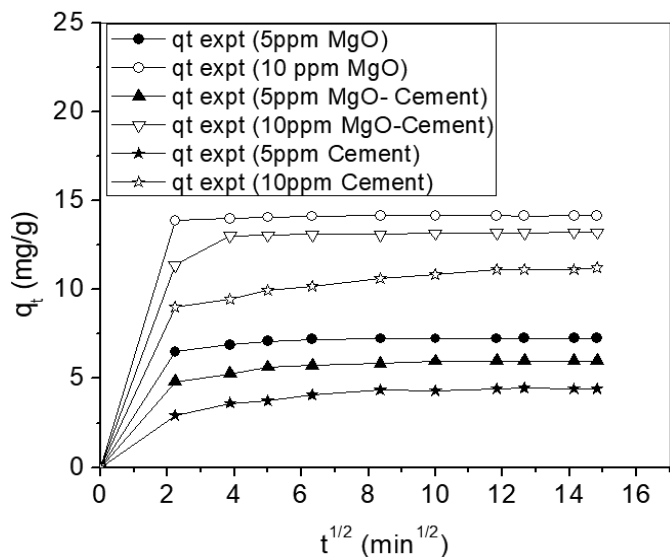| Adsorbent use	Fluoride conc. (mg/L)	Pseudo-first order			Pseudo-second order		
		k_1 (L/min)	q_e (mg/g)	RMSE	K_2 (g/mg/min)	q_e (mg/g)	RMSE
MgO-cement	5	0.3436	5.8253	0.2372	0.1223	6.0025	0.1011
	10	0.4035	13.303	0.0642	0.0976	13.479	0.1557
MgO	5	0.4725	7.1843	0.1244	0.2217	7.2829	0.0433
	10	0.8250	14.274	0.0584	0.6795	14.306	0.0301
Cement	5	0.2056	4.2209	0.2860	0.0729	4.4616	0.1162
	10	0.3659	10.795	0.6229	0.0656	11.115	0.3891

Figure 10. Intraparticle mass transfer curves for fluoride removal.

3.14 FTIR Analysis

The wide band in the region 3423-3436 cm^{-1} [Figs. 11(a), (b)] is due to O-H symmetric and asymmetric stretching of water molecule. The band at 1633-1646 cm^{-1} is due to O-H bending vibration. The band at 3688 cm^{-1} and 1427-1440 cm^{-1} is due to O-H stretching vibration bonded with magnesium and bending mode respectively. There was a slight shifted in the intensity of the % transmittance in fluoride treated MgO-cement adsorbent which may be due to the exchange of O-H from its surface[9].

3.15 Leaching Study

Leaching study was prepared one more adsorbent of the same type but varying only in MgO and cement content in the ratio of 1:3 of MgO-cement. We observed at ratio of MgO-cement (1:10), no leaching of magnesium was detected but when the concentration of cement is decreased in the ratio of 1:3, some quantity of magnesium (0.017 mg/L) was detected in the treated water. Thus 1:10 ratio of MgO-cement found minimum leaching of Magnesium. The overlay chromatograms of the selected determinations viz. standards and samples are presented in Fig. 12. The results of these are summarised in Table 3.
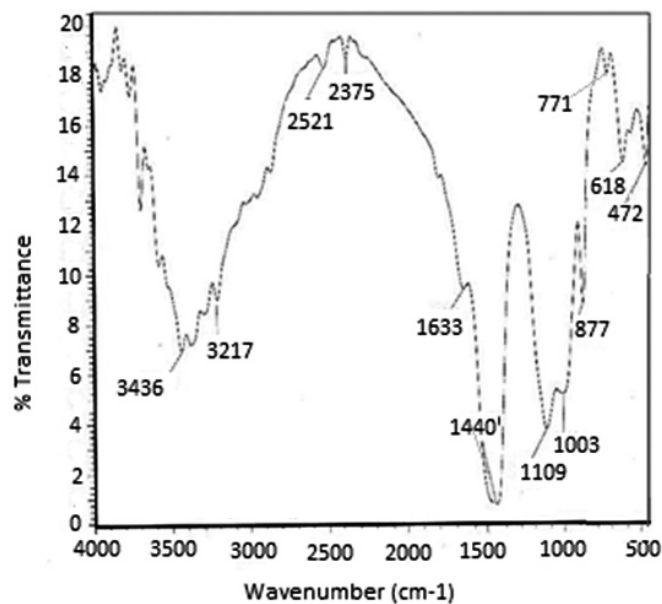
(a)
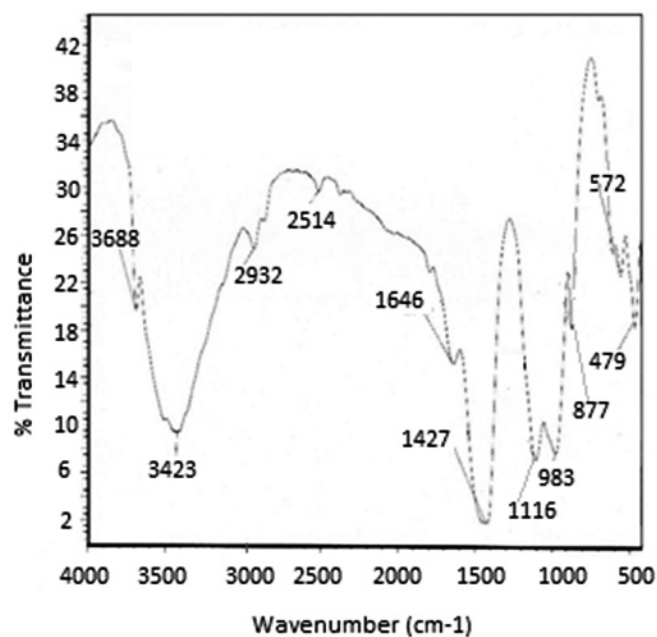
(b)

Figure 11. FTIR of the MgO-cement (a) before and (b) after treatment with fluoride.
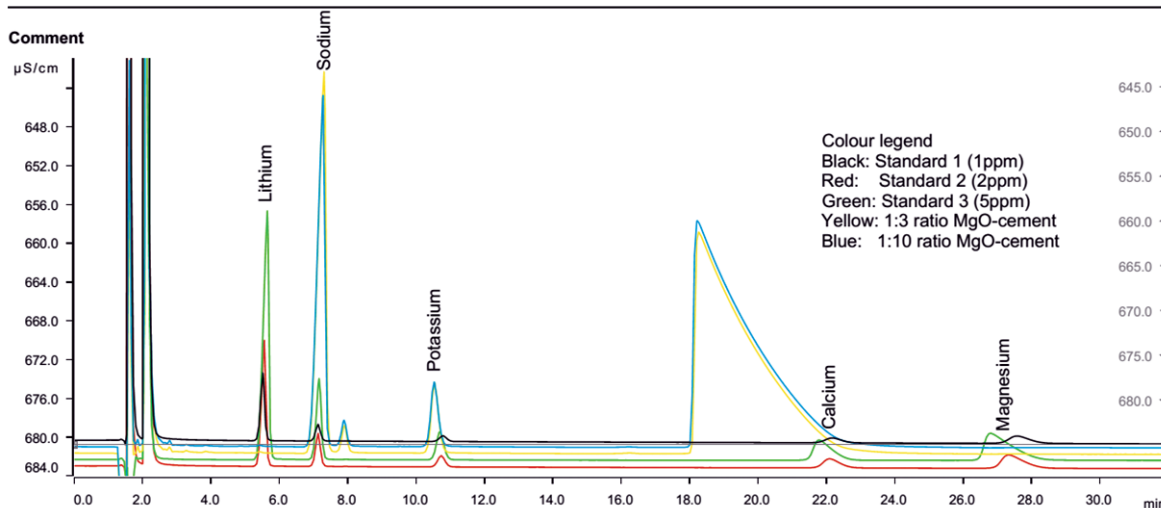
Curves overview

Figure 12. Selected cations content for leaching study (calcium and magnesium) by ion chromatography using a conductivity detector.

Table 3. Order of retention time and concentration of the cations using 1:3 and 1:10 ratio of MgO-cement respectively

Analyte ions	Peak No.	1:3 ratio of MgO-cement		1:10 ratio of MgO-cement	
		Retention time (min)	Concentration (mg/L)	Retention time (min)	Concentration (mg/L)
Li$^+$	1	5.42	0.022	5.43	0.026
Na$^+$	2	7.31	36.503	7.28	31.774
K$^+$	3	10.53	12.481	10.52	11.383
Ca^{2+}	4	22.51	Nil	22.51	Trace
Mg^{2+}	5	27.37	0.017	27.37	Trace

3.17 Regeneration Study

Regeneration study gives an idea how much of the loaded adsorbate be released back from the adsorbent using dilute acid or base. Regeneration of MgO-cement is maximum when 0.1M HCl was used as an eluent as it showed 63 % desorption capacity. But when 0.1M NaOH was used as an eluent, the desorption capacity shows that only 11 % regeneration was obtained.

4. CONCLUSIONS

The maximum adsorption capacity of the adsorbent was found to be 28.68 mg/g at 28 °C. The percentage removal decreases with the increase in initial fluoride concentration and was slightly dependent on pH. Hydroxide ion was found to interfere more with fluoride removal followed by bicarbonate and least with sulphate ion. The sorption data shows better fit to Freundlich model than to Langmuir model indicating that the active sites of the adsorbents appeared to be multilayered. The kinetic study reveals that uptake of fluoride ions was fast in the first 60 minutes and equilibrium time is independent of the initial fluoride concentration. Adsorption kinetics followed the pseudo second order model and the sorption indicate to be a complex process. Surface as well as intraparticle diffusion play an important role in the process of adsorption. Leaching experiments showed that no leaching of magnesium 1:10 ratio MgO-cement in the treated water is detected.

Conflict of Interest: None

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