



Defluoridation of water using magnesia/chitosan composite

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ABSTRACT

Magnesia (MgO) is a well-known adsorbent showing extremely high defluoridation capacity (DC). In order to overcome the limitations of MgO for field applications, an attempt has been made to modify magnesia with abundant biomaterial chitosan to form magnesia/chitosan (MgOC) composite in a usable form and its merits over conventional magnesia and raw chitosan is established. Removal of fluoride from aqueous solution with MgO and MgOC composite was studied with batch equilibrium experiments. At equilibrium, MgOC composite has a DC of 4440 mg F⁻/kg while for magnesia it is only 2175 mg F⁻/kg. The physicochemical properties of the synthesised MgOC composite were analyzed with FTIR and SEM with EDAX studies. The equilibrium data were fitted with isotherm and kinetic models. Thermodynamic parameters viz, ΔG° , ΔH° and ΔS° were calculated to understand the nature of sorption. Field studies were carried out to find the suitability of these sorbents at field conditions.

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1. Introduction

Fluoride related health hazards are major environmental problems in many parts of the world. Excess of fluoride in drinking water is harmful to human health. Various reports and studies established both the risks of high fluoride dosing and benefits of minimal exposure [1]. The permissible limit of fluoride concentration in drinking water is 1.5 mg/L as per WHO [2]. Various defluoridation technologies based on the principle of precipitation [3], ion exchange [4], adsorption [5] and electrochemical methods [6] have been proposed to remove excess fluoride in drinking water and industrial effluents. Among the methods, adsorption is considered as most suitable technique for fluoride removal. Some adsorbents have been successfully used for the removal of fluoride, including activated alumina [7], magnesia (MgO) [8], activated carbon [9], clay [10,11], rare earths [12], etc. However the most widely used and accepted sorbents are activated alumina and activated carbons in terms of field applicability. Though MgO showed extremely high defluoridation capacity (DC), it is not suitable for field applications in view of its powder form as it would cause pressure drop and may affect filtration during field applications. Moreover, it needs one hour as the minimum contact time for maximum DC and pH of the treated water was found to be alkaline irrespective of the initial pH [13].

In the present study, in order to explore the possibility of utilizing the higher DC of MgO and to overcome its limitations, a biocomposite adsorbent which could be shaped into any desired form was prepared using MgO with chitosan, a biocompatible, non-toxic and biodegradable biopolymeric material. Chitosan has been recognised to remove cations and only a few reports are available about its capacity to remove anions [14–16]. Chitosan despite being abundant in nature, its adsorption ability has not been at satisfying level because chitosan flakes/powder swells and crumbles and also has a tendency to form a gel in aqueous media. Although the amine and hydroxyl groups are responsible for adsorption, these active-binding sites are not readily available in gel or natural form. The adsorption capacity of the chitosan can be increased by spreading chitosan on physical supports that can increase the accessibility of the adsorbate-binding sites [17]. Hence chitosan has been selected for the preparation of composites with magnesia. The studies have been conducted on the optimisation of various experimental conditions like pH, dosage, different initial fluoride concentrations, influence of competitor anions and the effect of temperatures on fluoride sorption. The DC of MgOC composite was compared with that of MgO and chitosan. The advantages of using MgOC composite over MgO and chitosan as a defluoridation agent have been established. The mechanism of fluoride removal is reasonably explained by adsorption isotherms. The nature and morphology of the sorbents are discussed on the basis of SEM with EDAX and FTIR studies. Various kinetic models including pseudo-first-order, pseudo-second-order, particle diffusion and intraparticle diffusion models were used to describe the adsorption process. The sorbents were tested with a field sample collected in

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a nearby fluoride-endemic village for their suitability under field conditions.

2. Experimental

2.1. Synthesis of MgOC composite

Chitosan was purchased from Pelican Biotech and Chemicals Labs, Kerala (India). Its degree of deacetylation is 85%. MgO and all other chemicals used were of analytical reagent grade and used without further purification. The synthesis of MgOC composite was carried out by mixing magnesium oxide and chitosan in the ratio 3:2 and the aqueous mixture was kept for 24 h and filtered. Then the mixture was dried at 80 °C in an oven and calcined at 400 °C to get MgOC composite [18].

2.2. Adsorption studies

Batch technique was selected to obtain the equilibrium and kinetic data. Stock fluoride solution (100 mg/L) was prepared by dissolving 0.221 g of anhydrous sodium fluoride in 1 L distilled water and was further diluted to get the desired concentration. About 0.1 g of sorbent was added to 50 ml of solution containing 10 mg/L as initial fluoride concentration. The mixture was shaken in a thermostated shaker at a speed of 200 rpm at room temperature. The effect of different initial fluoride concentrations at three different temperatures viz., 303, 313 and 323 K on sorption rate was studied by keeping the mass of sorbent as 0.1 g and volume of solution as 50 ml in neutral pH. The fluoride concentration was measured using expandable ion analyzer EA 940 and the fluoride ion selective electrode BN 9609 (Orion, USA). The pH measurements were carried out with the same instrument with pH electrode. All other water quality parameters were analyzed by using standard methods [19]. The pH at zero point charge (pH_{zpc}) of sorbents was measured using the pH drift method [20].

2.3. Instrumental studies

The surface morphological studies of treated and raw samples were characterised using SEM with EDAX HITACHI-S-3400H model. FTIR spectra of both treated and raw samples were characterised using JASCO-460 plus model FTIR spectrophotometer to detect the functional groups. The specific surface area of the composite was analyzed using BET isotherm method with NOVA 1000 model.

Computations were made using Microcal Origin (Version 6.0) software. The goodness of fit was discussed using regression correlation coefficient (r) and χ^2 -analysis.

3. Results and discussion

3.1. Characterisation of the composite

The specific surface area of MgOC composite was found to be 45.5143 m²/g. FTIR spectrum is a useful tool to identify functional groups in a molecule, as each specific chemical bond often has a unique energy absorption band and can obtain structure, bond information, study of strength and fraction of hydrogen bonding. FTIR spectra of MgOC composite before and after treated with fluoride were given in Fig. 1 a and b. The band at 3700 cm⁻¹ corresponds to –OH stretching vibration. Although there is a possibility of overlapping between –NH₂ and –OH stretching vibrations, the band 3437 cm⁻¹ corresponds to –OH and –NH₂ stretching vibrations. The band at 1660 cm⁻¹ corresponds to amide stretching vibration [21].

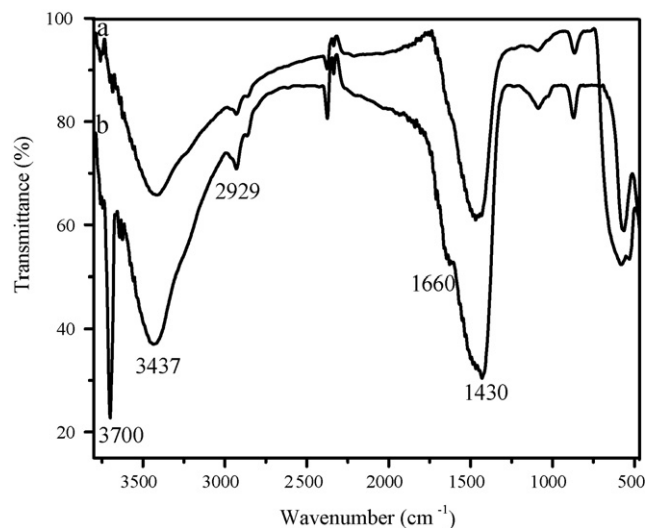


Fig. 1. FTIR spectra of (a) MgOC composite and (b) fluoride-sorbed MgOC composite.

The bands at 2929 and 1430 cm⁻¹ corresponds to aliphatic stretching vibrations of –CH and –NH bending vibrations of chitosan, respectively. The slight broadening of –OH stretching vibration band at 3437 cm⁻¹ in the fluoride-sorbed MgOC composite when compared with MgOC composite corresponds to the formation of O–H...F bond [21] which confirms the existence of hydrogen bonding.

The changes in the surface of the MgOC composite before and after sorbed with fluoride was identified by SEM micrographs and are presented in Fig. 2a and b, respectively. The presence of relevant elements in MgOC composite was confirmed by their respective peaks (cf. Fig. 2c). The presence of fluoride peak in the EDAX spectra of fluoride treated MgOC composite confirms the fluoride sorption which is shown in Fig. 2d.

The surface morphological changes of magnesia and MgOC composite were also confirmed by the shifting of pH_{zpc} values [22]. The pH_{zpc} of MgO is 10.0 where as for MgOC composite this value shifted to 10.6 which clearly indicate the occurrence of structural changes in the composite (cf. Fig. 3).

3.2. Effect of contact time

Fig. 4 shows the effect of contact time on the removal of fluoride by chitosan, MgO and MgOC composite for an initial fluoride concentration of 10 mg/L. The rate of fluoride removal was rapid initially and gradually it attained equilibrium. It is quite interesting to note that the MgOC composite reached saturation at 30 min whereas for MgO it was rather slow and attained equilibrium only after 60 min. The DC of MgOC composite (4440 mgF⁻/kg) is also very high which is just double than that of MgO (2175 mgF⁻/kg). As raw chitosan experienced a minimum DC (52 mgF⁻/kg), further studies were carried out with MgOC composite and MgO for comparison. Based on these observations, for subsequent experiments the shaking time was fixed as 30 min for MgOC composite and 60 min for MgO.

3.3. Effect of sorbent dosage on fluoride sorption

The effect of the adsorbent dosage of both MgO and its chitosan composite MgOC is carried out with an initial fluoride concentration of 10 mg/L and shown in Fig. 5. It is observed that the percentage fluoride removal increased with the increase in the dosage of the sorbent in both cases and it is obvious due to the

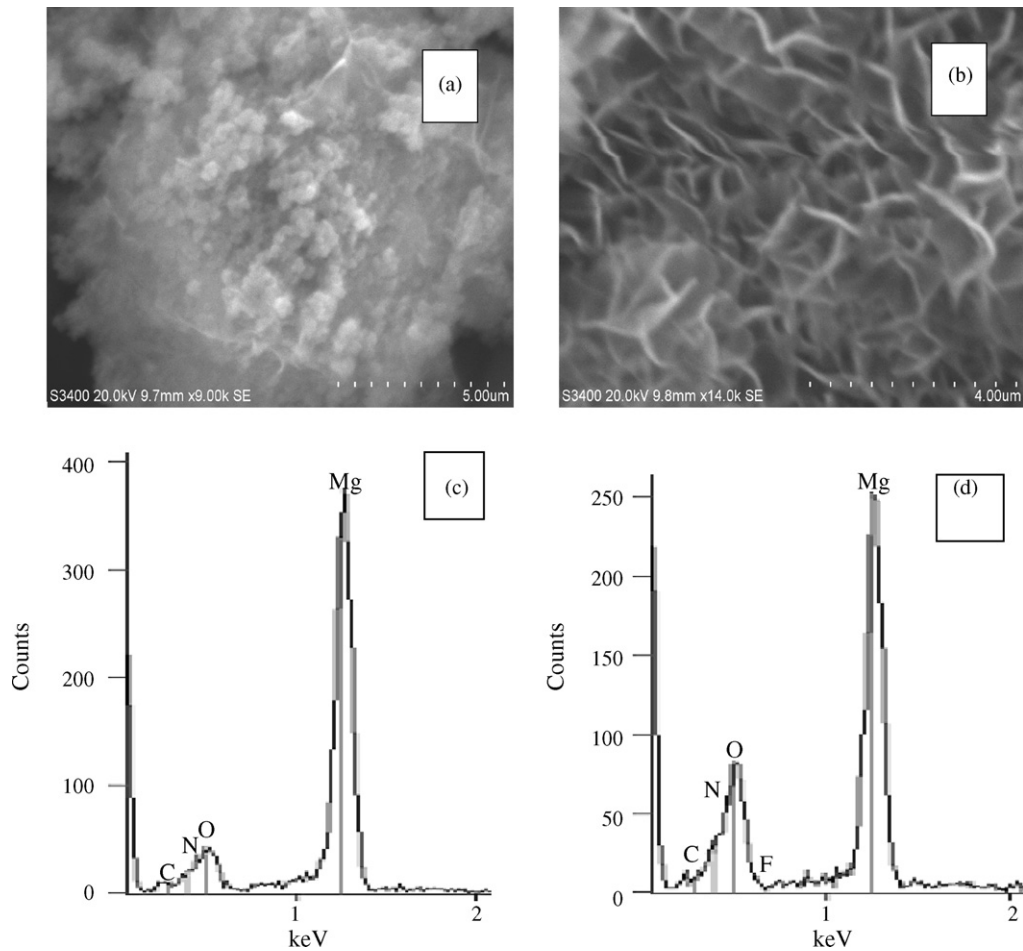


Fig. 2. SEM images of (a) MgOC composite and (b) fluoride-sorbed MgOC composite, EDAX spectra of (c) MgOC composite and (d) fluoride-sorbed MgOC composite.

enhanced active sites with an increase in the amount of sorbent [23]. The percent removal of fluoride by MgOC composite is higher when compared to MgO. For 0.1 g of MgOC composite, the percent removal is 91% and for MgO it is 40%. However to make a comparative study, 0.1 g was fixed as optimum dosage for both MgO and MgOC composite.

3.4. Influence of pH

The sorption of fluoride from aqueous solution was highly dependent on the solution pH, as it altered the surface charge on the sorbent. Fig. 6 shows sorption of fluoride using MgO and MgOC composite as a function of pH with an initial fluoride concentration of 10 mg/L at 303 K. It was observed that there is no marked

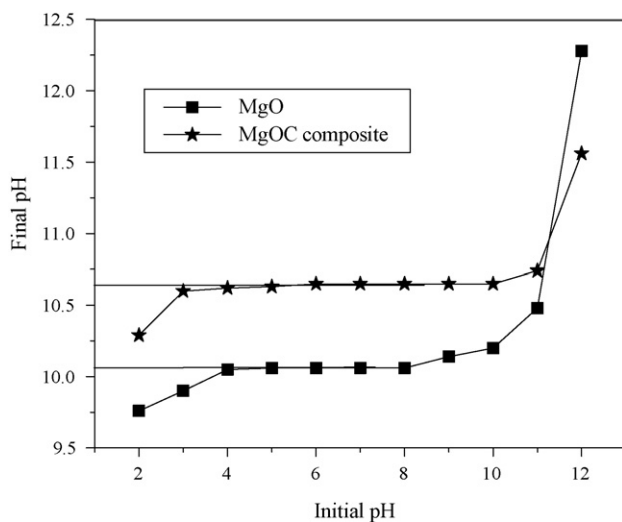


Fig. 3. pH_{zpc} of the sorbents.

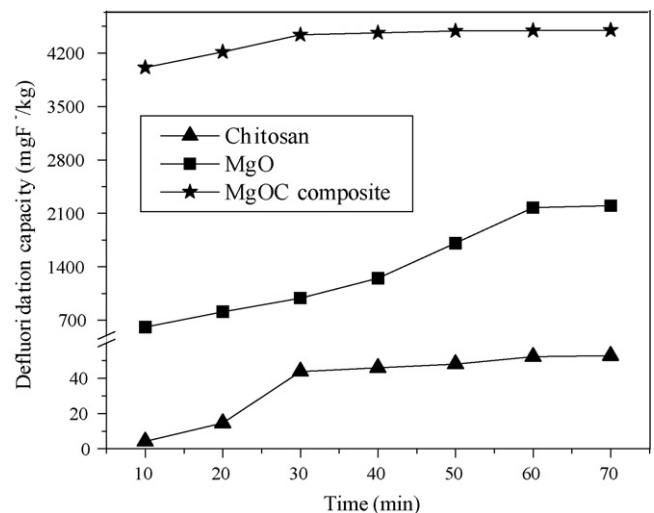


Fig. 4. Effect of DC of sorbents with contact time.

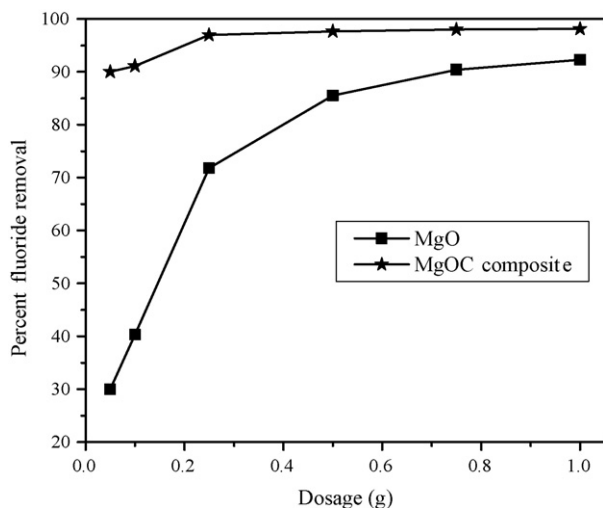


Fig. 5. Effect of dosage of sorbents in the percent removal.

difference in DC of both sorbents at different pH environment and concluded that the DC was not influenced by the pH of the medium. However the pH of the treated water was found to be alkaline irrespective of the initial pH and it is obvious as the material itself is basic in nature. The pH of the treated water samples in both cases falls in between 10.1 and 10.4.

3.5. Effect of initial fluoride concentration

The adsorption of fluoride onto MgO and MgOC composite with various initial fluoride concentrations ranging from 10 to 23 mg/L were carried out and presented in Fig. 7. It is observed that the DC of both the sorbents increases with increase in initial fluoride concentration. Similar results were reported by Lv et al. [24] while studying fluoride sorption on layered double hydroxides. It can also be inferred that the fluoride removal is significant at higher concentrations in both cases. However the DC of MgOC composite is higher when compared to MgO. As the MgOC composite has higher DC than that of MgO, further studies were limited to with MgOC composite.

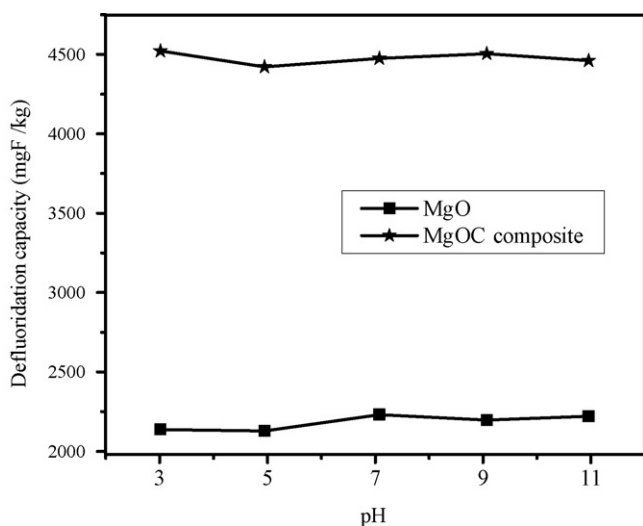


Fig. 6. Influence of pH.

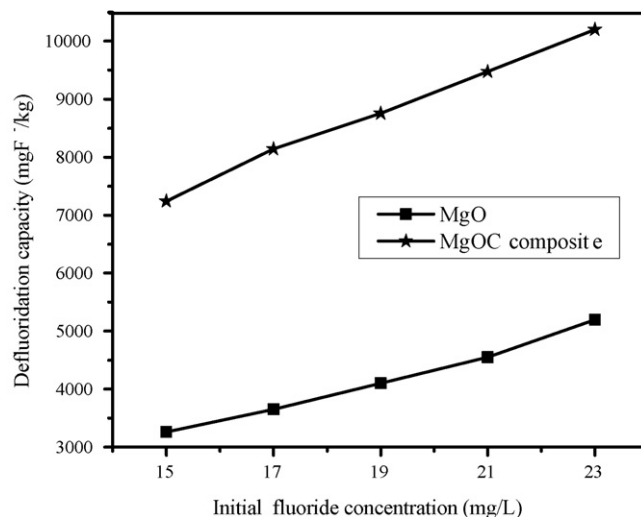


Fig. 7. Effect of DC with different initial fluoride concentrations.

3.6. Effect of other anions

The fluoride-contaminated drinking water may contain several other anions which may compete with the sorption of fluoride. The DC of MgOC composite was experimentally verified in the presence of other common anions like Cl^- , SO_4^{2-} , NO_3^- and HCO_3^- was investigated with varying initial concentrations of these ions ranging from 100 to 500 mg/L by keeping 10 mg/L as initial fluoride concentration at 303 K. Fig. 8 shows the influence of other anions in the DC of MgOC composite. There is a slight increase in the DC of MgOC composite in the presence of Cl^- , SO_4^{2-} and NO_3^- ions, but the DC decreases in presence of HCO_3^- ions. This is due to the competition of bicarbonate ions with fluoride ions in the sorption process. Parallel interference of bicarbonate ions on the DC has been cited earlier by Karthikeyan et al. [10] while using montmorillonite adsorbent for fluoride removal.

3.7. Sorption isotherms

To quantify the sorption capacity of the MgOC composite for the removal of fluoride, two isotherms namely Freundlich and Langmuir have been adopted.

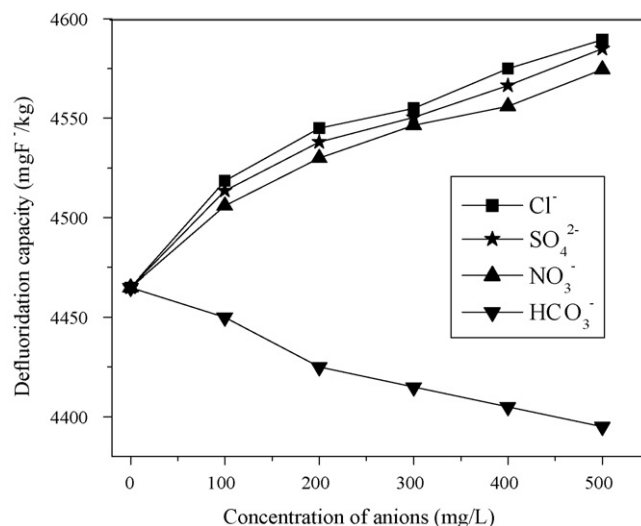


Fig. 8. Effect of other anions in the DC of MgOC composite.

Table 1
Isotherms and their linear forms

Isotherms	Linear form	Plot
Freundlich $q_e = k_F C_e^{1/n}$	$\log q_e = \log k_F + \frac{1}{n} \log C_e$	$\log q_e$ vs. $\log C_e$
Langmuir $q_e = \frac{Q_0 b C_e}{1 + b C_e}$	$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$	$\frac{C_e}{q_e}$ vs. C_e

3.7.1. Freundlich isotherm

The linear form of Freundlich isotherm [25] is given in Table 1. The linear plot of $\log q_e$ vs. $\log C_e$ indicates the applicability of Freundlich isotherm. The constants k_F and $1/n$ relates to the measure of adsorption capacity and adsorption intensity, respectively. These constants of Freundlich isotherm of MgOC composite is given in Table 2. Values of $1/n$ are lying between 0 and 1 and the n -value lying in the range of 1–10 confirms the favorable conditions for adsorption [7]. The adsorption capacity k_F increases with increase in temperature suggesting that the fluoride uptake by MgOC composite is an endothermic process.

3.7.2. Langmuir isotherm

The linear form of Langmuir isotherm [26] is represented in Table 1. The Langmuir constants Q_0 and b are related to sorption capacity and sorption energy, respectively. Maximum sorption capacity (Q_0) represents monolayer coverage of sorbent with sorbate and b represents the energy of sorption and should vary with temperature. The linear plot of C_e/q_e vs. C_e indicates the applicability of Langmuir isotherm. The values of Langmuir constants are given in Table 2.

In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L [27]

$$R_L = \frac{1}{1 + b C_0} \quad (1)$$

where b is the Langmuir isotherm constant and C_0 is the initial concentration of fluoride (mg/L). The R_L -values between 0 and 1 indicate favorable adsorption for all the temperatures studied (cf. Table 2).

3.7.3. χ^2 -analysis

To identify a suitable isotherm model for the sorption of fluoride on MgOC composite, this analysis has been carried out. The equivalent mathematical statement is

$$\chi^2 = \sum \left(\frac{(q_e - q_{e,m})^2}{q_{e,m}} \right) \quad (2)$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is experimental data of the equilibrium capacity (mg/g). If data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ, χ^2 will be a bigger number. Therefore, it is also necessary to analyze the data set using the non-linear χ^2 -test to confirm the best-fit isotherm for the sorption system [5]. The results of χ^2 -analysis are presented in Table 2. The lower χ^2 -values of Freundlich isotherm indicate the better applicability for the fluoride sorption on MgOC composite.

Table 2
Freundlich and Langmuir isotherm parameters of fluoride sorption on MgOC composite with r - and χ^2 -values

Temperature (K)	Freundlich isotherm					Langmuir isotherm					
	$1/n$	n	k_F (mg/g) (L/mg)	$1/n$	r	χ^2	Q_0 (mg/g)	b (L/g)	R_L	r	χ^2
303	0.169	5.917	8.472		0.970	0.003	11.236	2.967	0.019	0.996	0.012
313	0.161	6.211	8.810		0.960	0.005	11.364	3.520	0.016	0.995	0.018
323	0.145	6.897	9.141		0.952	0.006	11.494	4.350	0.013	0.995	0.025

Table 3
Thermodynamic parameters

Thermodynamic parameters	Equations	Plot
Standard free energy	$\Delta G^\circ = -RT \ln K_0$	$\ln(q_e/C_e)$ vs. C_e
Standard enthalpy change	$\ln K_0 = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$	$\ln K_0$ vs. $1/T$
Standard entropy change		

Table 4
Thermodynamic parameters of fluoride sorption on MgOC composite

Thermodynamic parameters	MgOC composite
ΔG° (kJ mol ⁻¹)	
303 K	-1456.15
313 K	-1057.74
323 K	-629.62
ΔH° (kJ mol ⁻¹)	14.28
ΔS° (kJ mol ⁻¹ K ⁻¹)	42.32

3.8. Thermodynamic treatment of the sorption process

Thermodynamic parameters associated with the adsorption, viz., standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated [5,28] using the equations given in Table 3. The values of thermodynamic parameters are shown in Table 4. The negative values of ΔG° confirm the feasibility and the spontaneous nature of fluoride sorption. The value of ΔH° is positive indicating that the sorption reaction is endothermic. The positive value of ΔS° which is a measure of randomness at the solid/liquid interface during fluoride sorption indicates the sorption process is irreversible and stable.

3.9. Sorption kinetic models

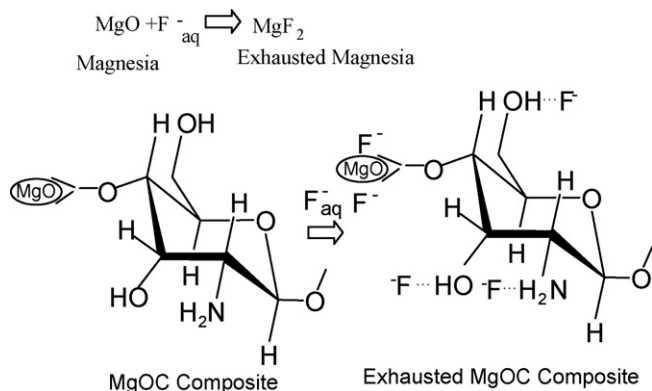
The two main types of sorption kinetic models namely reaction-based and diffusion-based models were adopted to fit the experimental data [29]. The study of sorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid/solution interface. A relatively higher r -value indicates that the model successfully describes the kinetics of sorption of fluoride on the sorbent.

3.9.1. Reaction-based models

The most commonly used pseudo-first-order and pseudo-second-order models were employed to explain the solid/liquid adsorption. A simple pseudo-first-order kinetic model [30] is represented in Table 5. The slope of the straight-line plot of $\log(q_e - q_t)$ against t for different experimental conditions will give the value of the rate constants (k_{ad}) and are given in Table 6. There are four types of linear pseudo-second-order kinetic models [31], the most popular linear form is given in Table 5. The fitness of the data and the values of q_e , k , and h were obtained from the plots of t/q_t vs. t for fluoride sorption at different temperatures viz., 303, 313 and 323 K of MgOC composite is presented in Table 6. The plot of t/q_t vs. t gives a straight-line with higher correlation coefficient r -values which is higher than that observed with pseudo-first-order model indicating the applicability of pseudo-second-order model.

Table 5
Kinetic models and their linear forms

Kinetic models	Linear form	Plot
Reaction-based		
Pseudo-first-order	$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t$	$\log(q_e - q_t)$ vs. t
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$	$\frac{t}{q_t}$ vs. t
Diffusion-based		
Particle diffusion	$\ln\left(1 - \frac{C_t}{C_e}\right) = -k_p t$	$\ln\left(1 - \frac{C_t}{C_e}\right)$ vs. t
Intraparticle diffusion	$q_t = k_i t^{1/2}$	q_t vs. $t^{1/2}$

**Fig. 9.** Mechanism of fluoride sorption on MgO and MgOC composite.

3.9.2. Diffusion-based models

For a solid–liquid sorption process, the solute transfer is usually characterised either by particle diffusion or intraparticle diffusion control. A simple equation for the particle diffusion controlled sorption process [5,32] is given in Table 5. The intraparticle diffusion model used here refers to the theory proposed by Weber and Morris [33]. The intraparticle diffusion equation is given in Table 5. The straight-line plots of $\ln(1 - C_t/C_e)$ vs. t and q_t vs. $t^{0.5}$ indicates the applicability of both particle and intraparticle diffusion models. The k_p , k_i and r -values of particle and intraparticle diffusion models are illustrated in Table 6. The higher r -values obtained for both particle and intraparticle diffusion models suggest that MgOC composite follow both the models on fluoride sorption.

3.10. Mechanism of fluoride removal

The mechanism of fluoride removal of both MgO and MgOC composite was mainly governed by adsorption and is illustrated in Fig. 9. Interestingly, both the sorbents has little or no effect with the change in the pH of the environment. The pH_{zpc} values of MgO and MgOC composite happened to be at 10 and 10.6, respectively,

Table 6
The parameters of various kinetic models with r -values

Kinetic models	Parameters	303 K				313 K				323 K			
		17 mg/L	19 mg/L	21 mg/L	23 mg/L	17 mg/L	19 mg/L	21 mg/L	23 mg/L	17 mg/L	19 mg/L	21 mg/L	23 mg/L
Pseudo-first-order	k_{ad} (min^{-1})	0.128	0.148	0.154	0.148	0.137	0.127	0.145	0.199	0.157	0.133	0.132	0.163
	r	0.980	0.979	0.871	0.890	0.988	0.991	0.979	0.949	0.952	0.971	0.961	0.969
Pseudo-second-order	q_e (mg/g)	0.804	0.961	1.098	1.068	0.881	1.034	1.101	1.115	0.915	1.046	1.162	1.252
	k (g/mg min)	0.412	0.670	0.452	0.479	0.613	0.652	0.735	0.460	1.034	1.125	0.441	0.315
Particle diffusion	h (mg/g min)	0.266	0.618	0.545	0.546	0.475	0.698	0.891	0.572	0.865	1.230	0.596	0.494
	r	0.996	0.999	0.999	0.999	0.999	0.999	0.999	0.999	1.00	0.999	0.998	0.998
Intraparticle diffusion	k_p (min^{-1})	0.167	0.194	0.223	0.211	0.102	0.103	0.078	0.077	0.057	0.065	0.044	0.046
	r	0.980	0.979	0.871	0.890	0.976	0.984	0.957	0.968	0.967	0.828	0.902	0.840
Intraparticle diffusion	k_i (mg/g min ^{0.5})	1.409	1.549	1.702	1.872	1.389	1.565	1.677	1.836	1.371	1.592	1.650	1.787
	r	0.891	0.931	0.969	0.983	0.864	0.921	0.903	0.930	0.841	0.907	0.866	0.872

Table 7
Field trial results of the sorbents

Water quality parameters	Before treatment	After treatment	
		MgO	MgOC composite
F ⁻ (mg/L)	4.13	3.44	0.66
pH	9.60	10.12	10.10
Cl ⁻ (mg/L)	85.20	85.20	81.60
Total hardness (mg/L)	240.00	220.00	210.00
Total dissolved solids (mg/L)	2400.00	2270.00	2190.00
Na ⁺ (mg/L)	173.00	173.00	172.00
K ⁺ (mg/L)	23.00	22.00	21.00

which indicates that both the materials have their zero point charge at this pH levels, which in turn suggesting that the sorbents possesses positive charge upto this pH values and hence the positively charged surface of the sorbents removes fluoride by means of electrostatic attraction for a wide pH range. The higher DC of MgOC composite may be attributed to the fact that chitosan also contribute in the enhancement of DC by removing fluoride through hydrogen bonding [17,21,34].

3.11. Field trial

The sorbents used in our study are also tested with field sample taken in a nearby fluoride-endemic village. About 1.0 g of sorbent was added to 50 ml of fluoride water sample and the contents were shaken with constant time at room temperature. These results are presented in Table 7. The field trial results suggest that these sorbents can be effectively used as defluoridating agents at the field level. There is a significant reduction in the levels of other water quality parameters also in addition to fluoride.

4. Conclusions

In the present study, a novel adsorbent namely MgOC composite was prepared to remove fluoride from drinking water which possesses an appreciable higher DC than magnesia. The DC of both the sorbents is not influenced by pH of the medium. The DC of MgOC composite was not affected in the presence of co-anions except bicarbonate ion. The sorption process follows Freundlich isotherm. The thermodynamic parameter values indicate that the fluoride removal process is spontaneous and endothermic in nature. The kinetics of MgOC composite follows pseudo-second-order, particle and intraparticle diffusion models. The results of field trial indicate that both the sorbents can be effectively used to remove fluoride from water. However the treated water found to be alkaline in nature when both the sorbents were used as the defluoridating medium. Among the two adsorbents, MgOC composite being biocompatible, biodegradable, cost effective, shaped into

any desired form which possesses higher DC with minimum contact time and can be used as a promising sorbent for fluoride removal.

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