



Magnesium incorporated bentonite clay for defluoridation of drinking water

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ABSTRACT

Low cost bentonite clay was chemically modified using magnesium chloride in order to enhance its fluoride removal capacity. The magnesium incorporated bentonite (MB) was characterized by using XRD and SEM techniques. Batch adsorption experiments were conducted to study and optimize various operational parameters such as adsorbent dose, contact time, pH, effect of co-ions and initial fluoride concentration. It was observed that the MB works effectively over wide range of pH and showed a maximum fluoride removal capacity of 2.26 mg g^{-1} at an initial fluoride concentration of 5 mg L^{-1} , which is much better than the unmodified bentonite. The experimental data fitted well into Langmuir adsorption isotherm and follows pseudo-first-order kinetics. Thermodynamic study suggests that fluoride adsorption on MB is reasonably spontaneous and an endothermic process. MB showed significantly high fluoride removal in synthetic water as compared to field water. Desorption study of MB suggest that almost all the loaded fluoride was desorbed ($\sim 97\%$) using 1 M NaOH solution however maximum fluoride removal decreases from 95.47 to 73 (%) after regeneration. From the experimental results, it may be inferred that chemical modification enhances the fluoride removal efficiency of bentonite and it works as an effective adsorbent for defluoridation of water.

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1. Introduction

Presence of fluoride above 1.5 mg L^{-1} in drinking water can result in multidimensional health problems, such as dental and skeletal fluorosis [1]. However, fluoride is beneficial when present within the permissible limit of $1.0\text{--}1.5 \text{ mg L}^{-1}$ for calcification of dental enamels [2]. World Health Organization and Bureau of Indian Standard have recommended a tolerance limit of 1.5 and 1.0 mg L^{-1} , respectively for fluoride in drinking water [3,4]. The contamination of ground water with fluoride may occur due to natural and anthropogenic sources. Fluoride is frequently encountered in naturally occurring minerals and geo-chemical deposits and can enter ground water by natural processes such as natural weathering and leaching. On the other hand, several fluoride containing compounds are widely used in many industries like aluminium manufacturing industry, fertilizer, semiconductor manufacturing industry, etc. for leaching and cleaning process, generating high concentration of fluoride in their wastewater and thus contribute to fluoride pollution [5–7]. Fluorosis is endemic in at least 25 countries across the globe and affected millions of people. In India

alone, more than 62 million people are affected with fluorosis and it is a major problem in 19 states, especially Rajasthan, Madhya Pradesh, Andhra Pradesh, Tamil Nadu, Gujarat and Uttar Pradesh [8]. Therefore, mitigation of fluorosis is a very important area of research and needs continued attention. A number of treatment methods have been reported in literature for defluoridation of water namely precipitation [9,10], membrane processes [11], electrolytic treatment [12], ion-exchange [13], Nalgonda technique [14] and adsorption [15]. Among these methods, adsorption is the most promising method for defluoridation of water due to ease of operation, lower cost and being relatively more environment friendly process. Most of the above methods are effective and can remove the fluoride to permissible level, however they are expensive and require frequent regeneration of resin beads or membrane. In recent years, researchers have devoted much attention to study the various low cost materials for cost effective defluoridation of water. Many low cost adsorbents have been tried for fluoride removal from water namely fly ash [5], brick powder [9], activated alumina [16], mechanochemically activated kaolinites [17], china clay [18], bentonite and montmorillonite [19], bone char [20], zeolite [21], laterite [22], spent bleach earth [23], bleaching powder [24], plaster of paris [25], agriculture waste [26], oxides ores [27] and hydrated cement [28], etc.

Bentonite clay belongs to the class of aluminosilicate clay group, which comprises of layers of aluminosilicate sheets. It exhibits a low cation exchange capacity and low permeability. Bentonite clay

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Nomenclature

C_0	initial concentration of fluoride (mg L^{-1})
C_e	equilibrium concentration of fluoride (mg L^{-1})
h	initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$)
k_F	Freundlich constants related to adsorption capacity (mg g^{-1})
k_p	intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$)
K	second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$)
K_{ad}	equilibrium rate constant of pseudo-first-order adsorption (min^{-1})
K_L	Langmuir constant (L mg^{-1})
K_0	sorption equilibrium constant
n	adsorption intensity (heterogeneity factor)
q_e	equilibrium adsorbate capacity (mg g^{-1})
q_{max}	amount of adsorbate at complete monolayer coverage (mg g^{-1})
q_t	amount of fluoride adsorbed per unit mass of adsorbent at time t (mg g^{-1})
r	dimensionless quantity
V	volume of the aqueous solution (mL)
W	mass of adsorbent (g)

Greek letters

ΔG°	standard free energy change (kJ mol^{-1})
ΔH°	standard enthalpy change (kJ mol^{-1})
ΔS°	standard entropy change ($\text{kJ mol}^{-1} \text{K}^{-1}$)

typically contains SiO_2 , Al_2O_3 and oxides of Mg, Ca and K, which might contribute towards the fluoride adsorption. Srimurali et al. have reported the low cost bentonite clay for fluoride removal from drinking water, which showed a maximum of 46% fluoride removal at an initial fluoride concentration of 5 mg L^{-1} and pH of 2.8 [29]. In our earlier communication, we have also studied defluoridation properties of bentonite clay modified with different metal oxides [30]. Although, lanthanum oxide incorporated clay shows higher fluoride uptake, however, considering the lower cost of MgO and possible toxicity with lanthana incorporated clay, the MgO incorporated bentonite clay has been further studied in the present work [30]. In this way, the present study deals with the detailed investigations on MgO modified bentonite clay for its fluoride removal properties on simulated as well as field waters containing fluoride.

2. Experimental

2.1. Materials and methods

All chemicals used in the present study were of analytical reagent grade. Bentonite clay was procured from LOBA Chemie. Sodium fluoride, sodium chloride, sodium sulfate, sodium nitrate, sodium bicarbonate and magnesium chloride were obtained from E-Merck India Ltd., Mumbai, India. A stock solution of fluoride was prepared by dissolving 2.21 g sodium fluoride in 1 L of deionized water and test fluoride solution of 5 mg L^{-1} was prepared from fresh stock fluoride solution by appropriate dilution. Concentration of magnesium chloride solution as well as calcination temperature was optimized to achieve best fluoride uptake.

2.2. Synthesis of adsorbent

10 g of bentonite clay was mixed with 100 mL of 1.25 M magnesium chloride solution and the mixture was agitated for 6 h. After

shaking, the above solution was transferred into glass Petri dish and dried at 150°C in oven. Dried mass was then ground to fine powder and calcined at 450°C for 4 h in muffle furnace. The calcined powder was cooled to room temperature and washed twice with distilled water in 1:20 ratio. The material was finally dried at 70°C for 6 h and the yield was recorded.

2.3. Adsorption experiments

50 mL of the test fluoride solution was taken into a 250 mL of PVC conical flask and known weight of adsorbent was added to it and then shaken at 150 rpm on a horizontal rotary shaker (Model No.CIS-24, Remi Instruments, Mumbai, India) in order to attain equilibrium. The flask was removed from the shaker and then allowed to stand for 5 min for settling the adsorbent. The solution was then filtered using Whatman filter paper no. 42 and the filtrate was analyzed for residual fluoride concentration using ion selective electrode. The total ionic strength adjusting buffer (TISAB-III) was added in 1:10 (mL) ratio to the sample and standard solutions in order to regulate the ionic strength. The addition of TISAB also resulted in pH adjustment and elimination of polyvalent cations such as Al(III), Fe(III) and Si(IV). These polyvalent cations have the ability to form the complex or precipitate with the fluoride ions and reduce the free fluoride concentration in the solution. Similarly, all the fluoride removal experiments were studied for different operational conditions including effect of adsorbent dose, initial fluoride concentration, solution pH and effect of co-ion on fluoride removal. Also, the fluoride removal ability of modified bentonite was tested in field water collected from Dhar district of Madhya Pradesh, India. All the experiments were carried out at room temperature ($25 \pm 2^\circ\text{C}$). The effect of pH on fluoride removal was studied by adjusting the pH of the solution using 0.1 M HCl and 0.1 M NaOH solutions.

2.4. Desorption study

Desorption of adsorbed fluoride from MB was carried out by using different concentrations of sodium hydroxide solution. 0.5 g of fluoride loaded MB was shaken with 50 mL of different concentrations of NaOH solution (0.1–1.0 M) for 1 h on a horizontal rotary shaker. Adsorbent was separated by filtration and the filtrate was diluted to 100 mL. The filtrate was analyzed using ion selective electrode to quantify the desorbed fluoride from adsorbent. The residue on filter paper was washed with deionized water and dried at 70°C for 4 h. Regenerated adsorbent was subjected to fluoride adsorption experiment to determine the fluoride removal efficiency after regeneration.

2.5. Method of analysis

The fluoride concentration in the treated water sample was measured using ion selective electrode 9609 BNWP Orion (USA make) attached with Orion 920A + ISE/pH/mV/ORP meter. Similar ion meter coupled with pH electrode was used for measuring pH of the treated samples. Magnesium contents in MB as well as leaching of metals if any from the adsorbent was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Model OPTIMA 4100DV). Experiments were repeated twice for better accuracy and blank experiments were also performed throughout the studies. Similar experimental procedure was followed to study the effect of co-existing ions, pH and initial concentration of fluoride, etc. Water quality parameters of the treated and untreated water samples were analyzed using standard methods [31].

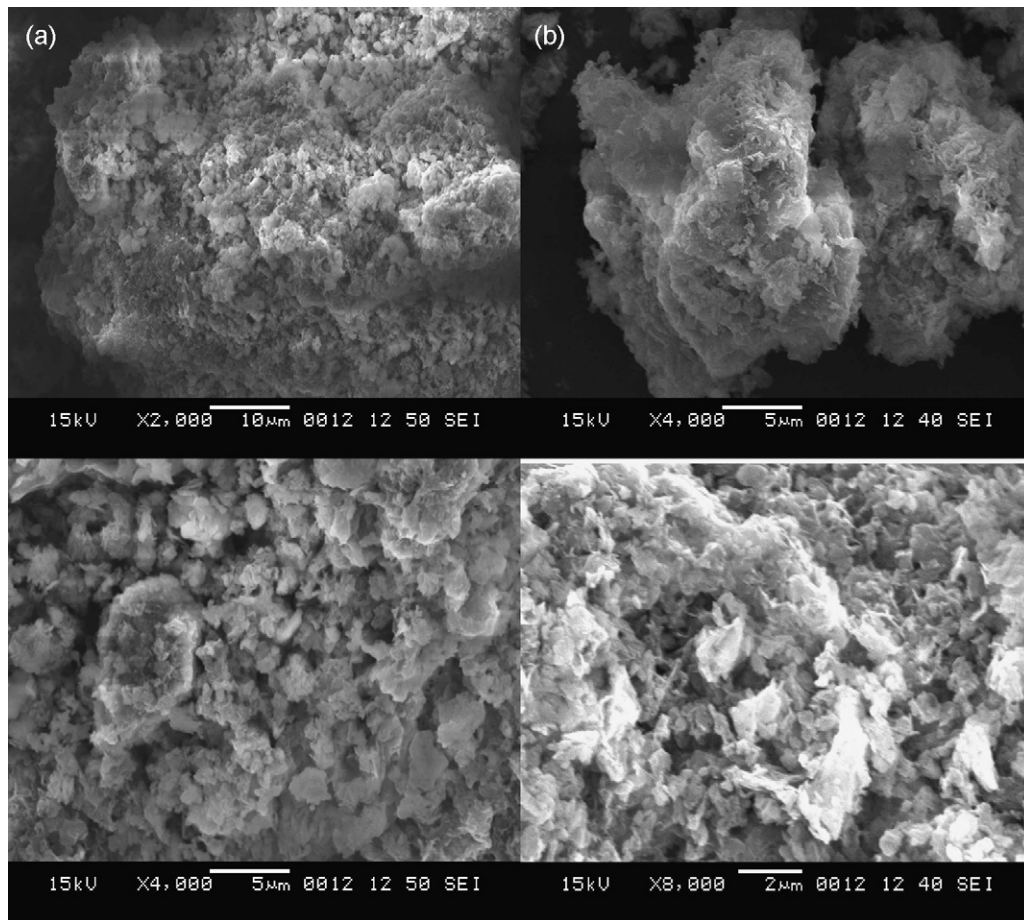


Fig. 1. SEM image of modified bentonite (MB) (a) as such and (b) after fluoride treatment.

2.6. Physical characterization

XRD patterns of MB as such and samples after fluoride adsorption with fluoride were recorded on Rigaku Miniflex II, Desktop X-ray diffractometer with $\text{CuK}\alpha$ radiation (λ 0.5405), in order to study the effect on structure if any. The samples were scanned for 2θ range from 10° to 80° . The surface morphology of the MB as such and fluoride loaded sample was determined by using scanning electron microscope (Jeol, JXA-840 A) coupled with electron probe microanalyser.

3. Results and discussion

3.1. Characterization of adsorbent

3.1.1. SEM

SEM images of MB powder (Fig. 1a) reveal spongy appearance with irregular structure in the surface morphology. Also, MB powder appears to be highly porous in nature and shows large agglomerates of very fine particles of MgO. The pores and voids generated could be due to the swelling of bentonite clay during treatment with magnesium salt, which on drying and calcination lead to the formation of MgO clusters between the interlayer spaces of bentonite clay. These MgO clusters formed between the interlayers are rigid enough not only to prevent the interlayer spacing from collapsing, but also to generate pores larger than those of conventional zeolites [32]. SEM image of the used MB powder (Fig. 2b) also reveals porous structure with open voids.

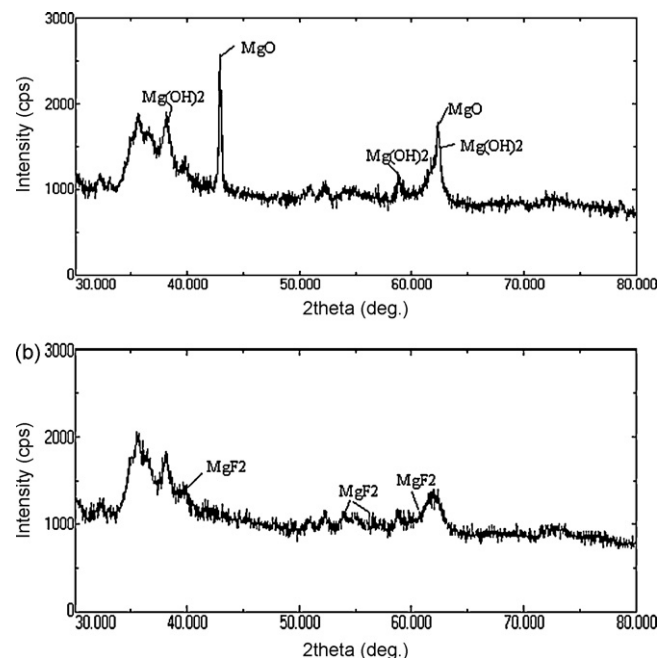


Fig. 2. XRD pattern of MB (a) as such and (b) after fluoride treatment.

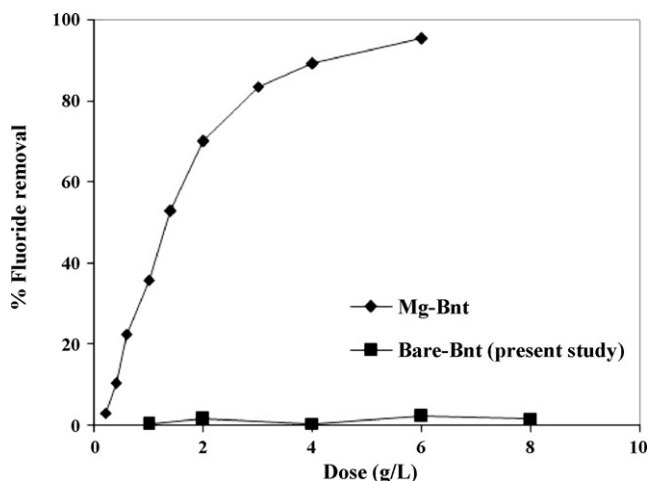


Fig. 3. Effect of adsorbent dose on fluoride removal by MB and bare bentonite (present study).

3.1.2. XRD

XRD patterns of MB as such and after fluoride adsorption are shown in Fig. 2a and b. XRD pattern of MB before fluoride adsorption shows presence of MgO in crystalline cubic phase. The peaks at 2θ diffraction angle of 42.96° and 62.32° (JCPDS: 75-0447) can be assigned to formation of pure phase of periclase MgO and the peaks at 2θ diffraction angle of 38.40° , 58.96° and 62.52° can be attributed to $\text{Mg}(\text{OH})_2$, which might have formed due to the reaction of MgO with water. XRD pattern of the used MB shows the presence of magnesium fluoride at 2θ diffraction angle of 40.24° , 53.9° , 56.6° and 60.8° (JCPDS: 70-2269) and is in accordance with that reported by Nagappa and Chandrappa [33].

3.2. Batch adsorption studies

3.2.1. Effect of contact time

The effect of contact time on fluoride removal efficiency of the MB was studied. It was observed that the fluoride removal gradually increases with time and reaches equilibrium in 10–12 h after which, no significant increase in the fluoride removal was observed. Therefore, 12 h duration was considered as the optimum equilibrium contact time for further adsorption studies.

3.2.2. Effect of adsorbent dose

The minimum amount of adsorbent required to bring down the fluoride concentration below 1.5 mg L^{-1} (WHO prescribed limit) was determined by studying the effect of variation in adsorbent dose ($0.2\text{--}6 \text{ g L}^{-1}$) on fluoride removal efficiency (Fig. 3). It was observed that, fluoride removal efficiency increased from 2.9% to 95.47% with increase in adsorbent dose of $0.2\text{--}6 \text{ g L}^{-1}$ of MB, while it was almost negligible in case of bare bentonite. This increase in the fluoride removal efficiency of MB with increase in adsorbent dose was obviously due to the enhancement in the number of active sites available for adsorption of fluoride ions. Srimurali et al. have reported maximum of 46% fluoride removal for bentonite clay at an initial fluoride concentration of 5 mg L^{-1} and pH of 2.8 [29]. This pH is very low and cannot be maintained during drinking water defluoridation. The pH of MB was therefore maintained at 6–7. In the present study, the fluoride concentration below 1.5 mg L^{-1} was achieved at an adsorbent dose of 3 g L^{-1} and hence considered as the optimum adsorbent dose for further adsorption studies.

3.2.3. Effect of initial fluoride concentration

The effect of initial fluoride concentration on the percent removal of fluoride of MB was studied and is shown in Fig. 4.

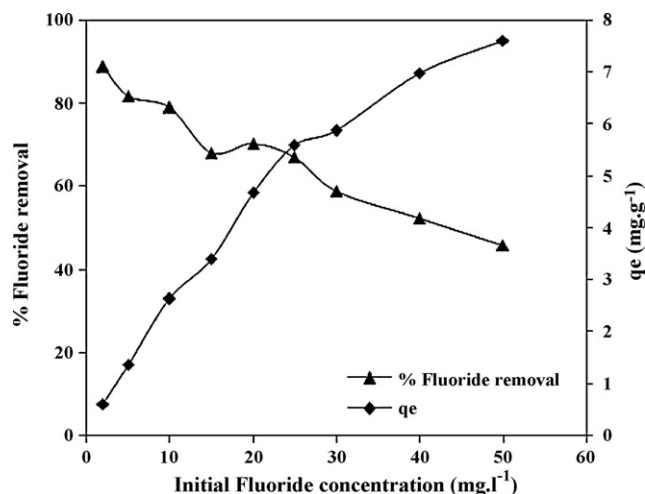


Fig. 4. Effect of Initial fluoride concentration on fluoride removal by MB.

It was observed that with increase in the initial fluoride concentration, percent removal of fluoride decreases, while the fluoride adsorption capacity increases. This decrease in the percent fluoride removal is obviously due to the availability of more fluoride ions in solution at higher fluoride concentration, which also indicates that the fluoride binding capacity of MB was almost exhausted. However, at low fluoride concentration, the ratio of surface active sites to total fluoride is high and therefore the interaction of fluoride with the active sites on adsorbent surface was sufficient for efficient fluoride removal.

3.2.4. Effect of pH

The pH of medium is one of the crucial parameters that can influence the fluoride removal efficiency significantly, and helps in understanding the fluoride uptake mechanism of the adsorbent. The effect of pH on the fluoride removal efficiency of MB was investigated over the pH range of 3–11 as shown in Fig. 5. It is evident from the results that MB showed significantly high fluoride removal efficiency over a wide range of pH 3–10. Decline of about 17% in the fluoride removal at pH > 10 was observed which may be due to the abundance of OH^- on the adsorbent surface which may affect the fluoride uptake due to extreme competition with OH^- . However, possibility of Mg incorporated clay getting slightly affected at this pH is also not ruled out.

3.2.5. Effect of co-existing ions

Fluoride contaminated ground water usually contains several other ions, which can compete with fluoride during the adsorption

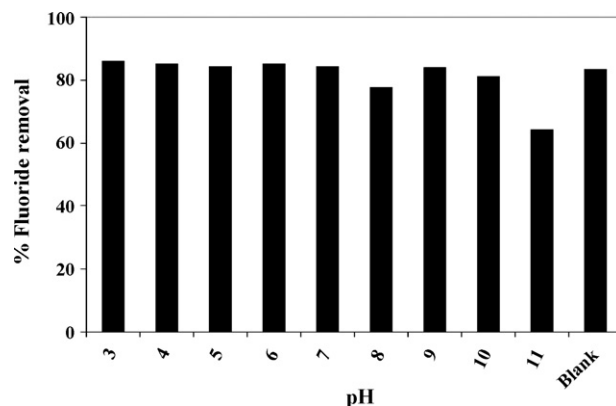


Fig. 5. Effect of pH on fluoride removal by MB.

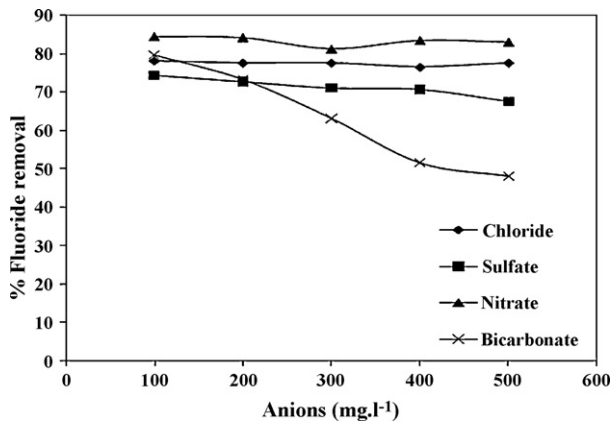


Fig. 6. Effect of different ions on fluoride removal by MB.

process. In order to study the effect of interfering ions on fluoride removal efficiency, adsorption studies were carried out in presence of varying initial concentration of Cl^- , SO_4^{2-} , NO_3^- and HCO_3^- ions by maintaining 5 mg L^{-1} as the initial fluoride concentration at optimum adsorbent dose. Fig. 6 shows the effect of co-ions on the fluoride removal efficiency of MB. It was observed that Cl^- , SO_4^{2-} and NO_3^- ions at all the concentrations studied did not affect the fluoride removal efficiency of MB. However, there was significant drop in the fluoride removal efficiency in the presence of bicarbonate ion. This decrease in the fluoride removal efficiency is due to the competition of HCO_3^- ion for active sites on adsorbent surface. Similar results for bicarbonate ion have also been reported by Karthikeyan et al. [34].

4. Adsorption modeling

The Langmuir and Freundlich equations are generally used to describe the adsorption isotherm, which explain the specific relation between the concentration and amount of adsorbate adsorb on the surface of the adsorbent. The linear equation of Langmuir adsorption isotherm [35], which is valid for the monolayer adsorption on the surface of adsorbent, is expressed as follows:

$$\frac{1}{q_e} = \frac{1}{q_{\max}K} \times \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (1)$$

where, q_{\max} is the amount of adsorbate at complete monolayer coverage (mg g^{-1}), which gives the maximum adsorption capacity of the adsorbent. K is the equilibrium constant of adsorbent at equilibrium, which indicates the affinity of adsorbate toward adsorbent. q_e and C_e are the equilibrium adsorption capacity and concentration of adsorbate in solution, respectively. The values of q_{\max} and K were calculated from the slope and intercept of the linear plots of $1/q_e$ vs $1/C_e$ (Fig. 7a) and were found to be 2.26 mg g^{-1} and $0.078 \text{ dm}^3 \text{ mg}^{-1}$, respectively.

In order to predict the adsorption efficiency of the process, the dimensionless equilibrium parameter (r) was calculated by using the equation given below:

$$r = \frac{1}{1 + KC_0} \quad (2)$$

where C_0 and K are the initial concentration of adsorbate (mg L^{-1}) and Langmuir isotherm constant. The value of r less than 1 generally indicate favorable adsorption and greater than 1 indicates unfavorable adsorption. The value of r for the initial concentration of 5.52 mg L^{-1} was found to be 0.70, which indicates that this system is favorable for adsorption.

The Freundlich adsorption isotherm [36], which is indicative of the surface heterogeneity of adsorbent, is expressed by the follow-

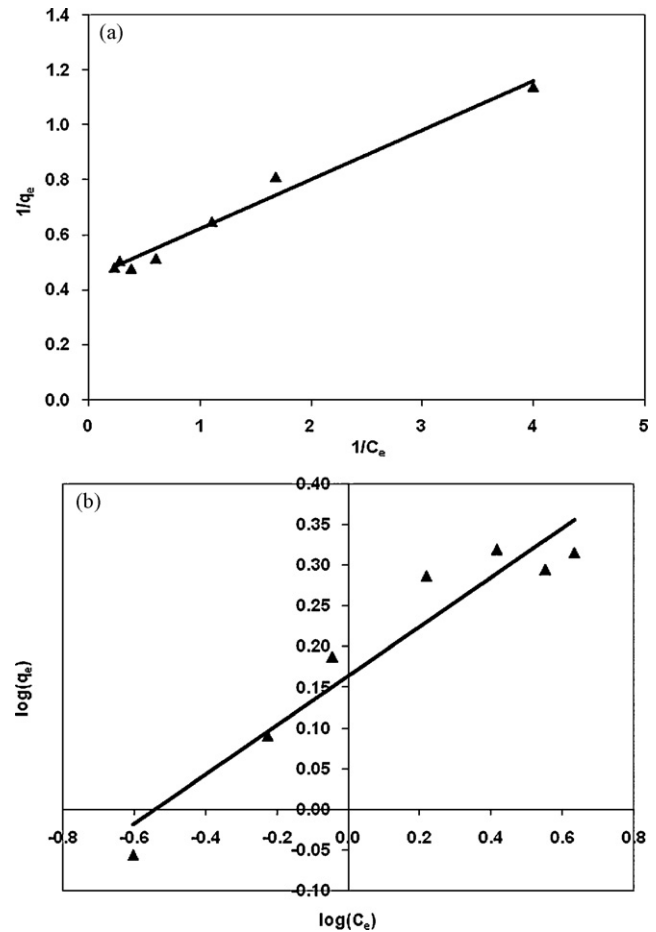


Fig. 7. (a) Langmuir and (b) Freundlich adsorption isotherms for fluoride removal by MB.

ing linearized equation:

$$\log(q_e) = \log K_F + \left(\frac{1}{n \log(C_e)} \right) \quad (3)$$

where, K_F and $1/n$ are Freundlich constants, related to adsorption capacity and adsorption intensity (heterogeneity factor), respectively. The values of K_F and $1/n$ were obtained from the slope and intercept of the linear plot of $\log(q_e)$ vs $\log(C_e)$ as shown in Fig. 7b and were found to be 1.35 mg g^{-1} and 0.16, respectively. The value of adsorption intensity observed is less than unity and therefore the present system can be considered favorable for adsorption. It is observed from the results that experimental data fit well for Langmuir adsorption isotherm, which is confirmed from the high value of $R^2 = 0.98$ as compared to $R^2 = 0.92$ for Freundlich adsorption isotherm. Better fit of Langmuir isotherm model suggests monolayer uniform adsorption on the surface of adsorbent. The Langmuir fluoride adsorption capacity of MB in the present study is found to be higher than that of unmodified bentonite (1.15 mg g^{-1}) and other low cost geomaterials reported by Srimurali et al. [29]. The Langmuir fluoride adsorption capacity of some of the geomaterials is compared and given in Table 1.

5. Adsorption kinetics

The rate of fluoride adsorption on MB was determined by studying the adsorption kinetics at different initial fluoride concentration of 5, 10 and 15 mg L^{-1} at optimum adsorbent dose. It was observed that fluoride removal increased with the lapse of time and the fluoride adsorption rate was initially rapid after which, the rate slowed

Table 1
Comparison of fluoride adsorption capacity of MB with some reported clay based adsorbents.

Adsorbents	Fluoride adsorption capacity (mg g ⁻¹)	Experimental conditions	Reference
Andosol	5.51	pH: 4.5 concentration: 0–50 mg L ⁻¹	Zevenberger et al. [43]
Titanium rich bauxite (TRB)	3.8	pH: 5.5–6.5 concentration: 5–40 mg L ⁻¹	Das et al. [45]
Modified bentonite (MB)	2.26	pH: 3–10 concentration: 5 mg L ⁻¹	Present study
Bentonite	1.15	pH: 2.8 concentration: 5 mg L ⁻¹	Srimurali et al. [29]
Charfines	0.95	pH: 2.8 concentration: 5 mg L ⁻¹	Srimurali et al. [29]
Laterite	0.85	pH: 7.5 concentration: 10–50 mg L ⁻¹	Sarkar et al. [22]
Kaolinite	0.667	pH: 6–7 concentration: 5 mg L ⁻¹	Srimurali et al. [29]
POP	0.336	pH: 3–9 concentration: 2–10 mg L ⁻¹	Gopal and Elango [25]
Tertiary soil	0.23	pH: 5–7 concentration: 10 mg L ⁻¹	Wang and Reardon [44]

down as the equilibrium approached. In order to understand the fluoride adsorption mechanism by MB, the reaction based and diffusion based models were used. The reaction-based models, which include pseudo-first-order and pseudo-second-order models, were applied to test the fitness of experimental data [37]. A pseudo-first-order kinetic rate equation given by Lagergren is represented as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303} t \quad (4)$$

where, q_t is the amount of fluoride adsorbed at time t (mg g⁻¹) and K_{ad} is the equilibrium rate constant of pseudo-first-order adsorption (min⁻¹). The values of K_{ad} for different initial concentrations of fluoride can be calculated from the slopes of the respective linear plot of $\log(q_e - q_t)$ vs t as shown in Fig. 8a. The values of K_{ad} for different initial concentrations of fluoride are given in Table 2.

The linear form of pseudo-second-order kinetic rate equation is represented as follows:

$$\frac{t}{q} = \frac{1}{K_{2ads}q_e^2} + \frac{1}{q_e} t \quad (5)$$

where q is the amount of fluoride adsorbed at time t (mg g⁻¹), q_e is the amount of fluoride adsorbed at equilibrium (mg g⁻¹), K is the second-order rate constant (g mg⁻¹ min⁻¹) and h is the initial sorption rate (mg g⁻¹ min⁻¹). The values of K and h can be calculated from the linear plots of t/q_t vs t as shown in Fig. 8b. The values of K and h for different initial concentrations of fluoride are given in Table 2. It was inferred that the value of correlation coefficient (R^2) is higher for the pseudo-first-order model as compared to the pseudo-second-order model, which suggest that the present system follows pseudo-first-order kinetic.

In order to determine the rate-limiting step in the present adsorption system, intraparticle diffusion model was also applied on the experimental data. The intraparticle diffusion model given by Weber and Morris is represented by the following equation [38]:

$$q = K_p t^{0.5} \quad (6)$$

where K_p (mg g⁻¹ min^{-0.5}) is the intraparticle diffusion rate constant. The values of K_p were calculated from the slope of the linear plot of q_t (amount of fluoride adsorb per unit mass of adsorbent) vs $t^{1/2}$ as shown in Fig. 8c. The values of K_p for different initial concentrations of fluoride are given in Table 2. A general feature of initial curved portion followed by linear curve and a plateau was observed for all the plots. The initial curved portion represents boundary

layer diffusion while linear portion reflects intraparticle diffusion after which plateau indicates that equilibrium was attained. It was also observed from Fig. 8c that the linear portion of the curve for all the plots did not pass through the origin, which suggests that fluoride adsorption mechanism of MB was rather complex one and both intraparticle diffusion and surface diffusion are involved in the rate-limiting step.

6. Thermodynamic parameters

In order to evaluate the feasibility of adsorption process, thermodynamic parameters were studied. The standard free energy change ΔG° was calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_o \quad (7)$$

where ΔG° is the free energy of sorption (kJ mol⁻¹), T is the temperature in Kelvin (K), R is the universal gas constant (8.314 J mol⁻¹ K⁻¹) and K_o is the sorption equilibrium constant. The sorption equilibrium constant K_o for the sorption reaction was determined from the slope of the linear plot of $\ln(q_e/C_e)$ vs C_e at different temperatures and extrapolating to zero C_e , according to method suggested by Khan and Singh [39]. The sorption equilibrium constant K_o can be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature and is shown below:

$$\ln K_o = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{RT} \quad (8)$$

where ΔH° is the heat of sorption (kJ mol⁻¹) and ΔS° is the standard entropy change (kJ mol⁻¹ K⁻¹). The values of ΔH° and ΔS° can be obtained from the slope and intercept of the Van Hoff's plot of $\ln(K_o)$ vs $1/T$ as shown in Fig. 9. These are observed to be 10.2 kJ mol⁻¹ and 0.11 kJ mol⁻¹ K⁻¹, respectively. The positive value of enthalpy change suggests that the fluoride adsorption process is endothermic in nature and corroborates with the findings reported in literature (Siam Sundaram et al. [40]). The negative values of free energy change -21.975 , -23.078 , -24.098 (kJ mol⁻¹) at all temperatures studied and positive value of entropy change suggests that fluoride adsorption process is favorable and spontaneous.

7. Desorption study

Fig. 10 shows desorption of adsorbed fluoride from MB using different concentrations of NaOH solution. It can be noticed that

Table 2
Lagergren, pseudo-second-order kinetic parameters and intraparticle pore diffusion model parameter for different initial F concentrations.

C_0 (mg L ⁻¹)	Lagergren parameters		Pseudo-second-order parameters			Intraparticle diffusion model	
	K_{ad} (min ⁻¹)	R^2	k (g mg ⁻¹ min ⁻¹)	h (mg g ⁻¹ min ⁻¹)	R^2	k_t (mg g ⁻¹ min ^{-0.5})	R^2
5.28 (~5)	1.8×10^{-3}	0.986	7.9×10^{-3}	1.6×10^{-2}	0.986	5.2×10^{-2}	0.985
9.8 (~10)	1.4×10^{-3}	0.991	4.5×10^{-3}	2.5×10^{-2}	0.972	7.5×10^{-2}	0.986
14.8 (~15)	2×10^{-3}	0.990	3.3×10^{-3}	3.3×10^{-2}	0.977	11.2×10^{-2}	0.993

Volume: 500 mL, temperature: 25 ± 2 °C, adsorbent dose: 3 g L⁻¹.

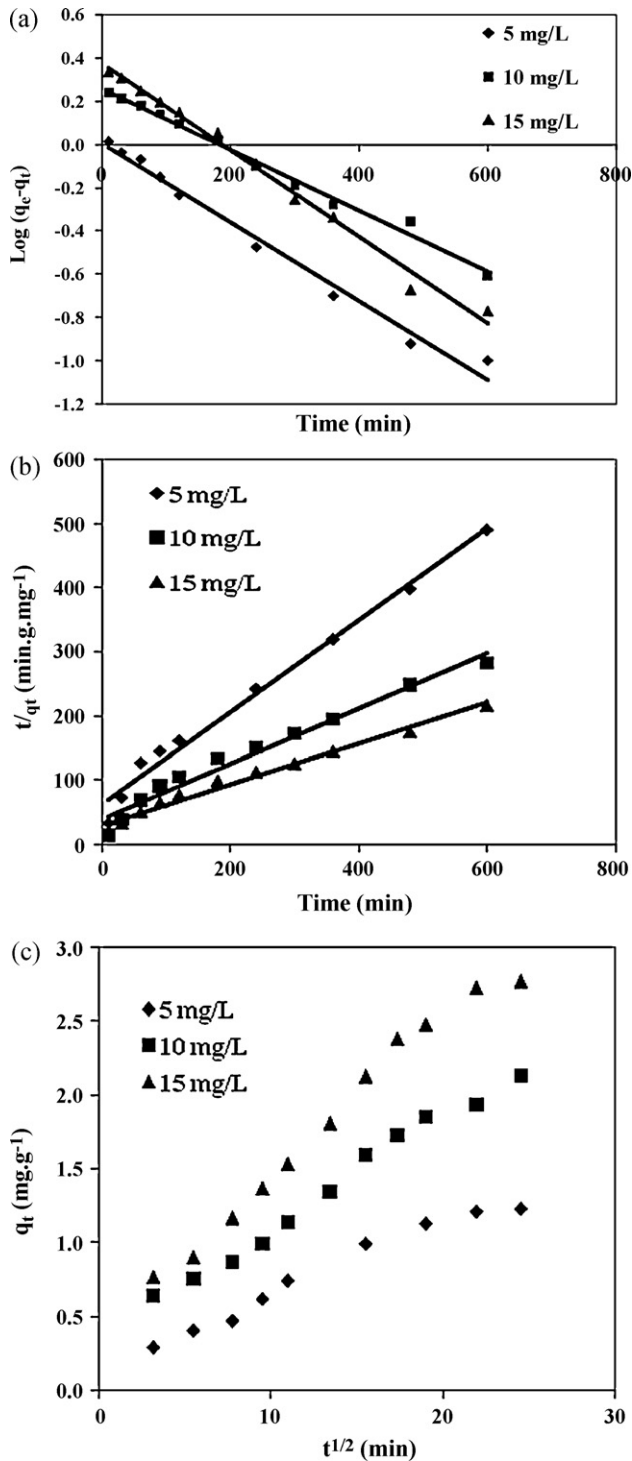


Fig. 8. (a) Lagergren plot, (b) pseudo-second-order plot, (c) Weber–Morris plots, for fluoride removal by MB.

desorption of fluoride increased with increase in NaOH concentration and almost all the fluoride (~97%) was desorbed by treating used MB with 1 M NaOH solution for 1 h. The reuse of the regenerated adsorbent showed decrease in the fluoride removal efficiency from 95.47% to 73% at an initial fluoride concentration of 5.52 mg L⁻¹. This decrease in the fluoride removal efficiency after regeneration could be due the treatment of MB with highly alkaline pH (12–13) of regenerating media. As already discussed, MB also shows lower fluoride removal at pH 11 (Fig. 5).

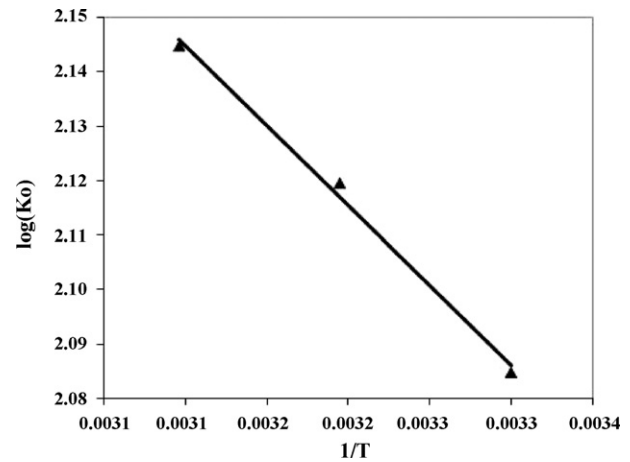


Fig. 9. van't Hoff plot for fluoride removal by MB.

8. Fluoride removal studies on field water

The potential of MB was tested in natural ground water samples collected from tube wells of fluoride-affected areas. The fluoride removal efficiency in field water was found to be slightly decreased as compared to synthetic water as shown in Fig. 11. This may be due to the presence of various competing ions in field water. The detailed characteristics of the treated and untreated water samples are given in Table 3. Slight increase in the equilibrium solution pH was also observed after treatment with MB, which may be due to the exchange between fluoride and hydroxyl ions and also due to the basic nature of the adsorbent, which is likely to get hydroxylated in water.

9. Mechanistic aspects

The predominant mechanism of fluoride sorption in several adsorbents including that activated alumina is through ion exchange between fluoride and hydroxyl groups present on adsorbent surface [41]. However, no significant fluoride removal efficiency was observed by using unmodified bentonite clay which is due to the very low anion exchange capacity of clays. The metal oxides which are usually present in interlayer spaces of layered clay based adsorbent can form aqua complex with water and develop charged surface through amphoteric dissociation [22]. At acidic pH,

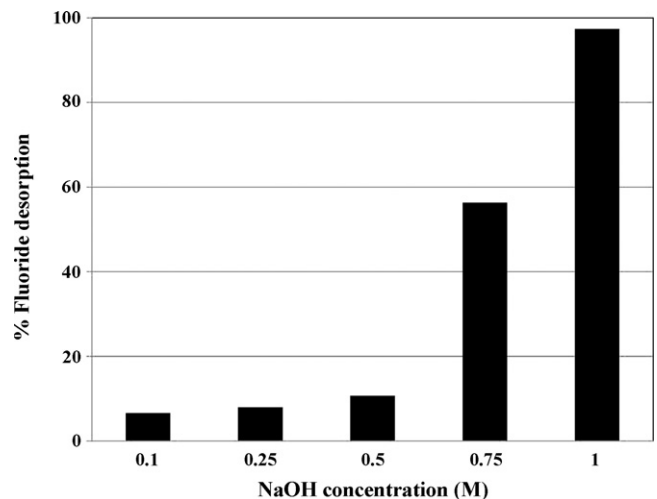


Fig. 10. Desorption of adsorbed fluoride from MB using different concentration of NaOH.

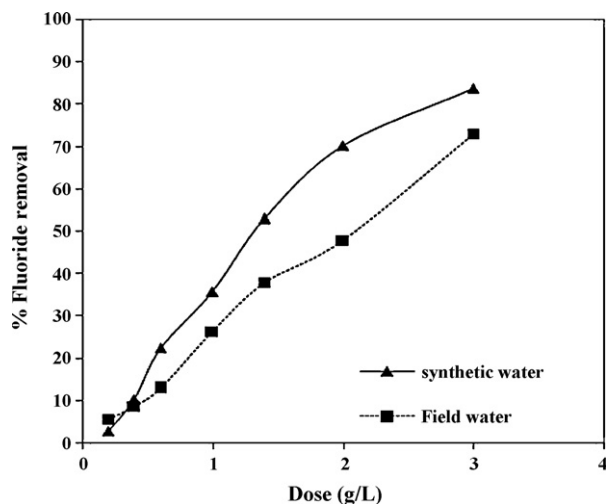
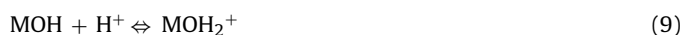


Fig. 11. Comparison of fluoride removal by MB from synthetic and field water.

more positively charged surface sites are developed which attract the negatively charged fluoride ions by electrostatic attraction, resulting in enhanced fluoride removal at acidic pH, as expressed in Eqs. (9)–(11).



Total reaction can be written as follows:



where M represents metal ion.

The magnesium oxide coated on to the surface of bentonite can form $\text{Mg}(\text{OH})_2$ in aqueous solution, which further reacts with fluoride ion to form MgF_2 by replacing hydroxide ions [42]. This exchange of fluoride and hydroxide ions is due to their similar size/comparable ionic radius, while both are also iso-electronic in nature. The presence of $\text{Mg}(\text{OH})_2$ was also supported from the XRD pattern of MB. This exchange mechanism between fluoride and hydroxide ion was further confirmed from the results that the equilibrium pH of the solution after treatment with MB slightly increases to alkaline range.



where M represents metal ion.

It therefore, appears that Mg present in interlayer spaces as well as on surface gets hydroxylated in water and replacement of these hydroxyl groups by fluoride is mainly responsible for fluoride uptake.

Table 3

Physicochemical parameters of untreated and treated ground water samples.

Parameter	Untreated sample	Treated with MB
Turbidity (NTU)	1	2
pH	8.12	9.0
Total hardness (mg L^{-1})	88	168
Total dissolved solid (mg L^{-1})	129	197
Conductivity ($\mu\text{S cm}^{-1}$)	215	328
Alkalinity (mg L^{-1})	84	164
Chloride (mg L^{-1})	12	14
Fluoride (mg L^{-1})	5.42	1.61
Nitrate (mg L^{-1})	3.47	2.96
Sulphate (mg L^{-1})	1.5	85.66

Temperature: $25 \pm 2^\circ\text{C}$, adsorbent dose: 3 g L^{-1} , contact time: 12 h.

10. Conclusion

The chemical modification of bentonite clay with magnesium oxide results in significant enhancement in its fluoride removal efficiency. It was found that modified bentonite showed significant fluoride removal efficiency over wide range of pH (3–10). Maximum fluoride adsorption capacity was found to be 2.26 mg g^{-1} at an initial fluoride concentration of 5.52 mg L^{-1} . The experimental data fitted well in Langmuir adsorption isotherm and the value of equilibrium parameter “*r*” suggests that fluoride adsorption by MB is favorable. Bicarbonate ions seem to have competing effect with fluoride at active sites and reduces the fluoride removal efficiency with increasing bicarbonate ion concentration. Kinetic study reveals that the fluoride adsorption by MB follows pseudo-first-order kinetic and both intraparticle diffusion as well as surface diffusion steps are involved in the fluoride uptake. The ΔG° and ΔH° values suggest that the fluoride adsorption by MB is a spontaneous process and endothermic in nature. Negligible leaching of metals was observed from the adsorbent and it is possible to regenerate MB with strong alkali (NaOH) treatment. Low cost of both bentonite clay and magnesium makes this material a potential candidate for defluoridation of water.

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