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Rapid removal of fluoride from aqueous media using activated dolomite

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Abstract

Fluoride is one of the most omnipresent groundwater pollutants. Thus the objective of this paper was to evaluate the efficiency of the thermally activated dolomite for the removal of fluoride. An inexpensive and widely available geomaterial dolomite was shown to have excellent fluoride removal property from aqueous media. The batch experiments were performed under the static and the shaken conditions using thermally activated dolomite powder where equilibrium reached just within 5 min under shaken condition with 90.87% fluoride removal. The fluoride removal capacity of the dolomite at pH 7.0 is 243.25 mg/g which is in excellent agreement with the theoretically calculated value 240.21 mg/g. The uptake of fluoride by the thermally activated dolomite mainly followed ion-exchange mechanism, pseudo second order kinetics and Freundlich isotherm. The scanning electron microscopy with energy dispersive X-ray (SEM-EDX) and X-ray diffraction studies demonstrated the thermally activated dolomite as an excellent material for fluoride removal. The proposed method is quite effective and practical for the defluoridation of drinking as well as waste water in comparison to literature reported methods.

Keywords: Activated dolomite; Fluoride removal; Ion-exchange mechanism; Pseudo second order; Freundlich isotherm

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1. Introduction

Fluoride ion is a well-known hazardous anion found in ground water in different forms [1].

The climatic and anthropogenic factors have serious impact on fluoride concentration in the ground water [2]. As crystalline and sedimentary basement rocks such as granite, mica, basalt, limestone, shale, sand stone, phosphorite, etc. contain fluoride as a constituent ion in high concentration so it enters in the ground water directly from rock weathering [3].

Therefore, fluoride-enriched water has become a major public health issue [4] as significant areas in India, Pakistan, China, Sri Lanka, Mongolia, Middle East, West Indies, Spain, Holland, Poland, Italy, Mexico, Argentina, Thailand, South Africa, Eritrea (North East Africa), West Africa, Southern Africa, and some North and South American countries have been reported to have fluoride contaminated water [5,6]. Depending on the concentrations of calcium and fluoride, CaF_2 gets precipitated which limits fluoride concentration in the ground water. Therefore, the process that decreases of Ca^{2+} concentration in water increases F^- concentration [7]. The arid climatic condition enhances evapotranspiration of the ground water and thus leads to enhancement in fluoride concentration [8]. The anthropogenic inputs also increase fluoride concentration in the ground water [9]. The commonly used agricultural pesticides and phosphatic fertilizers are significant sources of fluoride as they leach through soil profile, and thus the highest fluoride mobility has been reported in the saline soil [10]. Thus rural communities in many developing countries have been greatly affected with fluoride toxicity due to installation of deep bore-wells to satisfy their water needs [11]. An ever-increasing population and pollution has also exerted pressure to install deeper bore-wells which has ultimately been affecting human as fluoride concentration increases with the depth [11].

Fluoride enters into the human body through the drinking water, food, medicines, use of toothpaste, etc. However, the fluoride intake through the drinking water is completely

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3 absorbed and rapidly distributed throughout the human body and 99% of which gets
4 deposited on bones and teeth [12]. Thus prolonged exposure to fluoride rich ground water
5 increases the risk of dental and skeletal fluorosis [12]. Due to strong affinity towards Ca^{2+} , F^-
6 replaces Ca^{2+} from teeth and bones as well [12]. Thus children are the most vulnerable to
7 fluoride deleterious effects due to their developing teeth and bones. Seraj *et al.* have reported
8 that the exposure of children to high levels of fluoride carries the risk of impaired
9 development of intelligence [13]. Nevertheless, fluoride being contaminant in the
10 groundwater, its toxicity and deleterious consequences on muscle, brain, lung, kidney,
11 thyroid, reproduction and enzymes have been reported [14]. Therefore, the recommended
12 maximum permissible limit of fluoride in drinking water is 1.5 mg/L [15]. However, US
13 Public Health Services has recommended maximum allowable fluoride concentration range
14 with different climatic temperatures [16].
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32 The fluoride toxicity has stimulated research on water defluoridation from drinking water,
33 particularly in fluoride endemic areas [17]. Therefore the development of methods for the
34 removal of fluoride from water samples has continuously been reported in the literature
35 [5,6,14,16-26]. The methods of fluoride removal have also been reviewed which include
36 adsorption, ion-exchange, precipitation-coagulation, nano-filtration, reverse osmosis,
37 electro-dialysis and Donnan dialysis but limitations are substantial [27-30]. In the most recent
38 developed methods an excellent survey of existing methods has been presented by our
39 research group [5,6]. The electro-dialysis, reverse osmosis and nano-filtration techniques
40 require skilled operator and are quite costly. Also there are more chances of fouling, scaling
41 or membrane degradation in these methods [19,20,22,23,26]. The most popular methods for
42 fluoride removal include adsorption/ion-exchange and precipitation and have recently been
43 reviewed by Bhatnagar *et al.* [29]. The adsorption/ion-exchange involves activated carbon,
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3 clays, silica, zeolites, bio-materials [6] and nano-materials [5] while precipitation generally
4 uses aluminous or calcic compounds [29]. Most of the methods require acidic pH range for
5 the maximum efficiency towards fluoride removal. However, acidic pH becomes unsuitable
6 for drinking water defluoridation but useful in waste water treatment [27]. The use of heavy
7 metals or lanthanides loaded materials for water defluoridation have also been reported but
8 are not practical and safe due to the toxicity of heavy metals/lanthanides. Use of bio-materials
9 for fluoride removal has not been encouraged as many chemical treatments are carried out in
10 the development of bio-materials as adsorbent [6] where chances of bacterial and fungal
11 growth in treated water become prominent [31]. The methods involving activated alumina
12 have shown good removal efficiencies in favorable pH range 5.0-6.0. However, in addition to
13 generate sludge, the residual aluminum concentrations ranging 2.01 to 6.86 mg/L have been
14 reported in the treated water which is neurotoxic, causes Alzheimer's disease, and
15 carcinogenic health hazard [5,32].
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34 Fluoride is one of the most widespread groundwater pollutants. More than 200 million
35 people, from 25 nations, are suffering from fluorosis [33]. Thus the development of cost-
36 effective and environment friendly technologies for the remediation of wastewater are of
37 global interest [33,34]. Thus in our continued efforts in developing cost-effective analytical
38 techniques [35-43] and fluoride removal methods [5,6], we were looking for the most cost
39 effective method for fluoride removal from aqueous samples. With the above background this
40 paper deals with the logical approach to evaluate the fluoride removal efficiency of the
41 dolomite and evidences for ion-exchange mechanism of fluoride uptake and the removal
42 capacity of the thermally activated dolomite, an inexpensive and widely available
43 geomaterial.
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2. Materials and methods

2.1. Material development

The dolomite used in this study was collected from Balaji Chemicals, Rohini, New Delhi, India. The dolomite was grounded into fine powder and sieved on 150 μm test sieve and thermally activated in a muffle furnace at 200, 400, 600 and 800 $^{\circ}\text{C}$ for 2 h at each temperature and stored in air tight bottles for further use.

2.2. Reagents

All the reagents used in this study were of analytical reagent grade. Anhydrous sodium fluoride procured from E. Merck Ltd., India, was used throughout the experiment. 1000 mg/L fluoride stock solution was prepared by dissolving 2.21 g of sodium fluoride in 1 L of Milli-Q water. Different working standard solutions of fluoride were prepared by diluting the stock solution. 0.5 M NaOH and 0.5 M HNO_3 solutions were used to adjust the pH of the working solutions. The total ionic strength adjustment buffer (TISAB) solution was prepared using 57.0 mL glacial acetic acid, 58.0 g NaCl and adding sufficient 5 M NaOH to give a final pH 5.25 at a final volume of 4 L. The TISAB was added to the working solutions to determine fluoride concentrations.

2.3. Equipments and characterization

The experiments under the static and the shaken conditions were performed in polypropylene screw top flasks. The pH of the solutions was measured using HI 1230B pH electrode connected to HI 98172 pH meter. The multipoint calibrations of the pH meter were used for pH 4.0, 7.0 and 9.20. The fluoride concentration was determined with HI 4110 fluoride ion selective electrode (ISE) connected to HI 98172 pH/ISE meter. The calibration of ISE was carried out until a slope of 56 ± 4 mv was achieved.

The specific surface area, pore volume, pore size distribution and average pore diameter of raw and thermally activated dolomite were determined by Autosorb-AS-1 instrument (Quanta

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3 chrome USA) at Indian Institute of Technology (IIT), Kanpur, India, using Brunauer, Emmett
4 and Teller (BET) method [5] under specific conditions involving N₂ as analysis gas, cross
5 section area: 16.2 Å²/molecule, non-ideality: 6.58×10⁻⁵, nitrogen bath temp.: 77.30 K, outgas
6 temp: 200 °C, outgas time: 12 h, analysis time: 465.1 min, relative pressure P/P₀ tolerance: 0,
7 equilibrium time: 3 min.
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12 The scanning electron microscope (SEM; FEI Quanta 200F, Netherland) equipped with an
13 energy dispersive X-ray (EDX) spectrometer was used for SEM-EDX analysis at IIT
14 Roorkee, India. High vacuum mode was used and the samples were imaged using both solid
15 state back scattered electron and secondary electron detectors during SEM-EDX analysis
16 under the operating conditions: accelerating voltage of 20 kV, working distance 10.0-10.1
17 mm, resolution 2 nm, and 200 × magnification. X-ray diffraction (XRD) spectrometry was
18 used to characterize the calcination products of the dolomite.
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30 A mechanical shaker (Sciencetech, India) was used for shaking the solutions at different time
31 intervals. The concentrations of the calcium (Ca²⁺) and magnesium (Mg²⁺) ions were
32 determined using atomic absorption spectrophotometer. The titration method was applied to
33 determine carbonate ion (CO₃²⁻) concentration in the sample solutions where required.
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38 *2.4. Batch experiments*

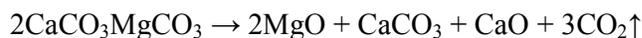
39
40 The batch experiments were conducted to investigate the effects of pH, adsorbent dose,
41 contact time and initial fluoride concentration on the rate of fluoride removal. The
42 experiments were performed in duplicate taking different amounts of adsorbent dose in 250
43 mL polypropylene screw top flasks containing 50 mL of 500 mg/L F⁻ solution. However, the
44 effect of initial fluoride concentration on the removal capacity of the dolomite was studied
45 separately in the range of 5-500 mg/L F⁻ (not shown). The experiments were performed under
46 static as well as shaken conditions. Under static condition, the solutions were left for different
47 time intervals (5, 30, 60 min and 12, 24, 48 and 72 h). Then small amount of the solution at
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3 these time intervals were taken out and the residual fluoride concentrations were determined
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5 to calculate the fluoride uptake by the dolomite. Under the shaken condition, the mixtures
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7 were shaken on mechanical shaker at 100 rpm for different time intervals (5, 30 and 60 min
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9 and 12, 24, 48 and 72 h) and filtered through Whatman filter paper no. 41. The residual
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11 fluoride concentrations in solutions were determined by fluoride ISE.
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13 14 **3. Results and discussion**

15 16 *3.1. Adsorbent material*

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18 The dolomite is a common sedimentary rock-forming mineral, consisting of the layers of the
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20 carbonate ions (CO_3^{2-}) separated by alternating layers of the calcium (Ca^{2+}) and the
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22 magnesium (Mg^{2+}) ions [44]. The thermal treatment of the dolomite at 800 °C led to change
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24 in its chemical compositions where calcite, calcium oxide and magnesium oxide are formed
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26 as shown in following chemical equation [45].
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29 The change in the chemical compositions increased in the BET surface area of the dolomite
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31 as shown in Table 1. Staszczuk et al. [45] and Walker et al. [46] have also reported many fold
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33 increase in the surface area of the dolomite after thermal treatment at 800 °C which increases
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35 its adsorption properties. The influence of thermal modification on the porosity of the
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37 dolomite was also studied. The total pore volume of raw dolomite 0.009 cc/g was increased
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39 to 0.196 cc/g for thermally activated dolomite at 800 °C i.e. D-800. At the same temperature,
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41 92.46 % increase in the macro pores was observed where average pore diameter was found to
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43 be 132.2 nm. Thus partially decomposed dolomite (D-800) was found more suitable for the
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45 de-fluoridation due to its dramatic enhanced BET surface area, pore size distribution and pore
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47 volume of this mineral.
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51 The SEM images of the raw and the thermally activated dolomite at 800 °C are shown in Fig.
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1 and 2 respectively. The SEM image of the raw dolomite clearly shows that it had a wide

range of particles size in random shapes (Fig. 1). However, upon thermal treatment i.e. on calcination at 800 °C, the particle size decreased (Fig. 2) due to cracking of the large particles because of de-carbonation of the dolomite (*cf.* above chemical equation). Thus the BET surface area of the raw dolomite 0.5 m²/g was significantly increased to 5.92 m²/g after thermal treatment at 800 °C (Table 1) while pore volume and macro pores size also dramatically increased at this temperature. Thus 800 °C was taken as the most appropriate temperature to thermally activated dolomite for fluoride removal.

Table 1. Thermal treatment of dolomite for 2 h at each temperature and the corresponding BET surface area.

Sample type	Temp. of the dolomite	BET surface area (m ² /g)
Raw dolomite (D)	-	0.5
D-200	200 °C	1.23
D-400	400 °C	1.78
D-600	600 °C	2.04
D-800	800 °C	5.92

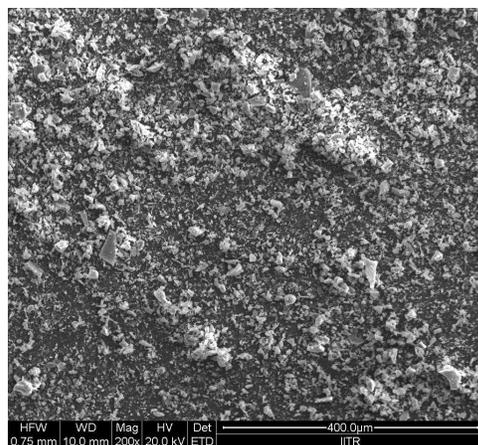


Fig. 1. SEM image of raw dolomite at 200 × magnification.

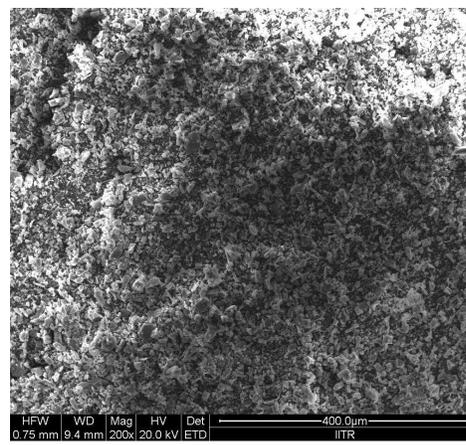
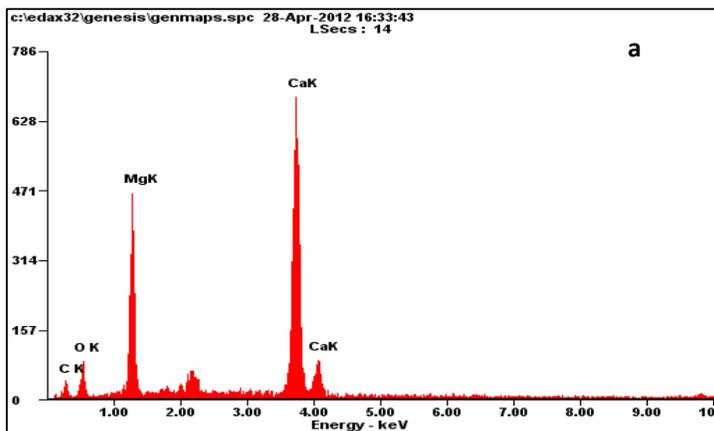


Fig. 2. SEM image of heat activated dolomite at 800 °C for 2 h at 200 × magnification.

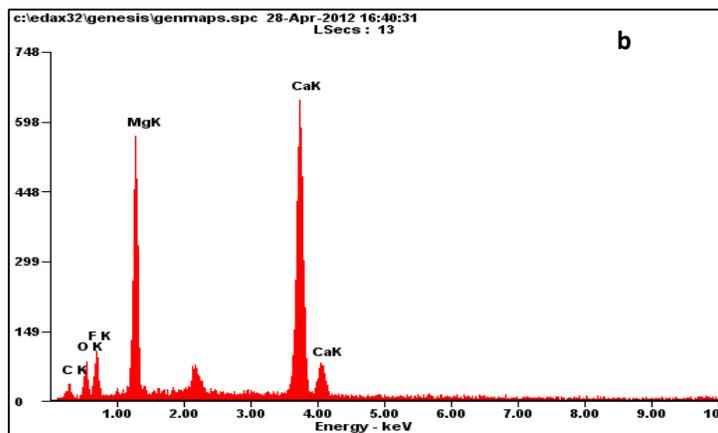
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3 is assigned to $\text{CaMg}(\text{CO}_3)_2$ i.e. the raw dolomite (Fig. 3a). The thermal treatment of the
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5 dolomite at 800 °C led to the changes in its chemical composition (*cf.* chemical equation) and
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7 thus a very different XRD pattern was obtained (Fig. 3b). The largest peak seen in Fig. 3a got
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9 shifted to 2θ 37.465 with lesser intensity count (%) 1328 and assigned to CaO (Fig. 3b). This
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11 was also confirmed by EDX spectrum of thermally activated dolomite at 800 °C shown in
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13 Fig. 4 which clearly shows that Ca was dominating over Mg. The other peaks found in Fig.
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15 3b are assigned to MgO, CaCO_3 and other elements as the EDX study shown in Fig. 4a also
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17 confirms the presence of small quantity of other elements including carbon and oxygen. No
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19 significant structural changes were observed below 800 °C as confirmed by XRD analysis at
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21 different temperatures [47]. It has also been reported that volume expansion of the calcium
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23 octahedron in dolomite is more rapid than in calcite [48]. Hence, 800 °C thermal treatment
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25 was found most appropriate for significantly increasing the surface area of the dolomite. This
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27 was also confirmed by the dramatic enhancement of BET surface area, pore size distribution
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29 and pore volume of this mineral (*vide supra*).
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36 The energy dispersive X-ray spectrometry study of the thermally activated dolomite (before
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38 fluoride treatment) showed major elemental peaks for Ca and Mg and other elemental peaks
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40 for oxygen and carbon (Fig. 4a). The elemental peak for fluoride with good weight percent
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42 was clearly observed in EDX study after 5 min contact for shaken sample (Fig. 4b) which
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44 confirmed the fluoride uptake by the thermally activated dolomite.
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Element	Weight %	Atom %
C K	08.36	16.83
O K	20.23	30.58
Mg K	27.50	26.66
Ca K	47.09	28.41
Matrix	Correction	ZAF

Z = Atomic number coefficient
A = Absorption coefficient
F = Fluorescence



Element	Weight%	Atom%
C K	07.08	13.89
O K	13.61	20.06
F K	13.65	16.93
Mg K	24.31	24.18
Ca K	38.17	22.45
Matrix	Correction	ZAF

Z = Atomic number coefficient
A = Absorption coefficient
F = Fluorescence

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Fig. 4. EDX spectrum of the thermally activated dolomite at 800°C for 2 h: (a) before fluoride treatment and (b) after fluoride treatment for 5 min.

43 3.2. Effect of pH on the fluoride adsorption

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The pH is an extremely important factor in defluoridation. Thus the effect of pH on the fluoride removal was studied under shaken condition at 500 mg/L initial fluoride concentration with sorbent dose 2 g/L for 12 h contact time in the pH range 6-10. The result on percentage removal of fluoride against pH is shown in Fig. 5 which demonstrates that the removal was excellent (92.5%) at pH 7. The slow rate of removal at higher pH may be attributed to hydroxide ion (OH⁻) competition with F⁻ for surface adsorption. Also the

solubility of the dolomite in high acidic media is the reason for its less fluoride removal efficiency at lower pH. Similarly, the maximum fluoride removal has been reported at pH 7 using calcite [49].

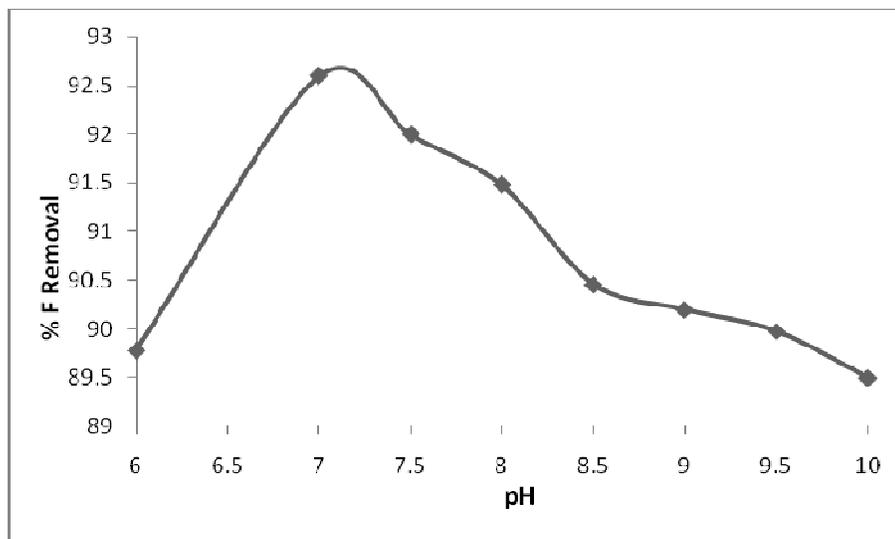


Fig. 5. Variation of fluoride removal (%) with the pH under the condition 500 mg/L F^- , 2 g/L adsorbent and 12 h contact time.

3.3. Effect of contact time

The effect of contact time on fluoride removal was studied taking 500 mg/L initial fluoride concentration with sorbent dose 2 g/L at pH 7. The results on fluoride removal under the static and the shaken conditions are shown in Fig. 6 and 7 respectively. Fig. 6 clearly demonstrates that the fluoride removal was quite slow under the static condition with only 2.5% removal in 5 min while rapidly removed in the shaken condition where 90.87 % F^- removal was achieved in the first 5 min. Under the static condition, only 2.5% of F^- was removed in the first 5 min (Fig 6) and the equilibrium reached in more than 24 h with 91.37% F^- removal which is not feasible for practical application. When the solution containing F^- and adsorbent was shaken, the intra-particle diffusion of F^- speeded up leading towards equilibrium within 5 min. Thus, the fluoride removal using thermally activated dolomite

under shaken condition was very fast where 90.87% removal achieved just within 5 min (Fig. 7). Similar results have been reported by Fan *et al.* using low cost geomaterials [50].

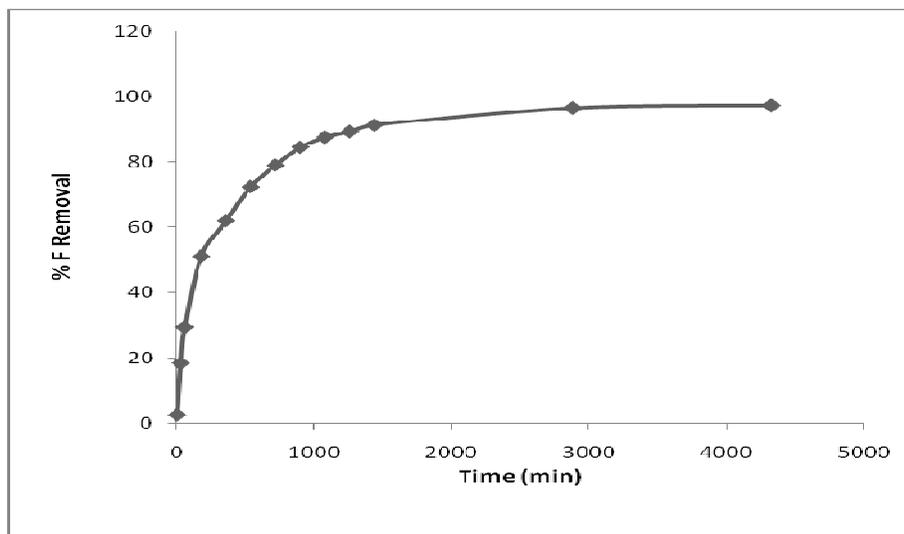


Fig. 6. Fluoride removal under static condition at 500 mg/L F^- concentration using 2 g/L adsorbent at pH 7.

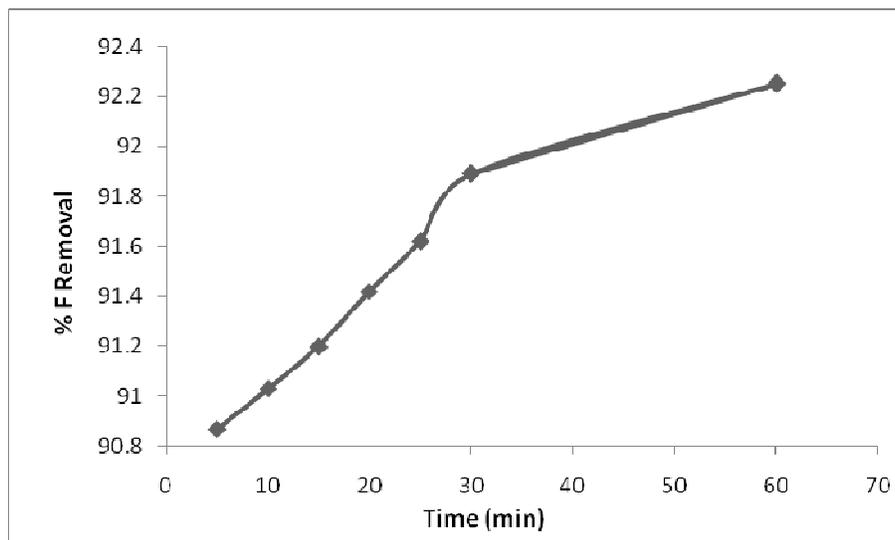


Fig. 7. Fluoride removal under shaken condition at 500 mg/L F^- concentration using 2 g/L adsorbent at pH 7.

3.4. Kinetics of fluoride removal

The Lagergren's pseudo first order [51] and pseudo second order [52] models were applied to evaluate the kinetics of the fluoride removal. The integrated pseudo first order kinetics is

shown in equation (1) where q_e and q_t are the sorption capacity (mg/g) at equilibrium and time t , respectively and k_1 is the rate constant (min^{-1}) of pseudo first order kinetics. A plot of $\log (q_e - q_t)$ versus t for pseudo first order kinetics is shown in Fig. 8 which does not show the best fit of the experimental data. The integrated pseudo second order adsorption isotherm is shown in equation (2) where k_2 is the rate constant of pseudo second order adsorption kinetics ($\text{g mg}^{-1} \text{min}^{-1}$). A plot of t/q_t versus t shown in Fig. 9 clearly shows the best fit straight line and confirms that fluoride removal by the thermally activated dolomite follows pseudo second order kinetics.

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (1)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (2)$$

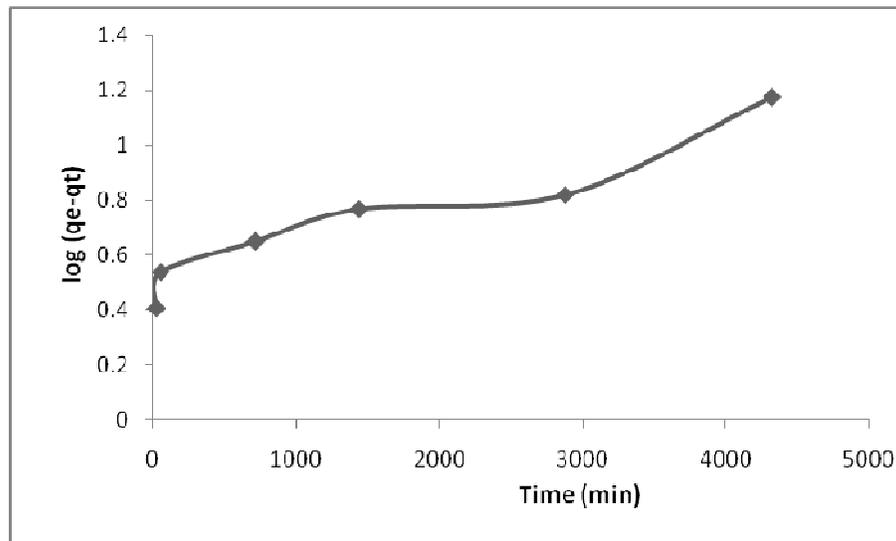


Fig. 8. Pseudo first order kinetics plot for fluoride removal at 500 mg/L F^- concentration and 2 g/L adsorbent at pH 7.

The value of correlation coefficient (R^2) for the pseudo second order adsorption kinetics is quite high (0.9998; cf. Fig. 9). The removal capacity calculated using the pseudo second order kinetics (240.21 mg/g) was also close to the experimentally determined 243.25 mg/g. The pseudo second order adsorption kinetics has also been reported for fluoride uptake onto calcite, quartz, apatite and fluor spar [50] that justified the findings in the present study.

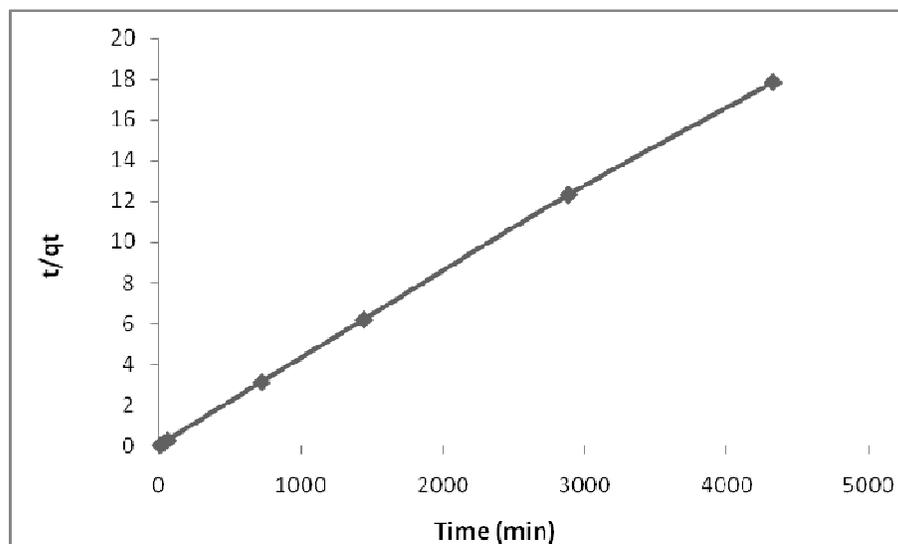


Fig. 9. Pseudo second order kinetics plot for fluoride removal at 500 mg/L F^- concentration and 2 g/L adsorbent at pH 7.

3.5. Adsorption isotherms

The adsorption isotherms have been quite useful in expressing the feasibility of an adsorbent for an adsorbate [5,6]. To study fluoride removal capacity of the thermally activated dolomite, the experiments were carried out in concentration range 5-500 mg/L F^- . The experimental data for fluoride removal using thermally activated dolomite were processed in accordance with two most widely used Langmuir and Freundlich adsorption isotherms. Freundlich adsorption model is purely an experimental model whereas the Langmuir model has certain assumptions. Langmuir isotherm model assumes that the valence active site on the surface of the adsorbent is capable of adsorbing one molecule and all the sites for adsorption have the same attraction for the molecules of adsorbate and there is no interference or effect of the adsorbed molecule at the adjacent site [5,6]. The linear form of Langmuir isotherm is expressed as: $1/Q_e = 1/(Q_0 \times bC_e) + 1/Q_0$, where Q_e is the concentration of adsorbed fluoride per unit weight of adsorbent, C_e is the concentration of fluoride ions in the aqueous phase, Q_0 is the maximum adsorption capacity per unit weight of adsorbent, b is the adsorption equilibrium constant [53]. The equilibrium data for the fluoride adsorption was plotted as $1/Q_e$ versus $1/C_e$, according to Langmuir isotherm [53]. As shown in Fig. 10, the plot $1/Q_e$ versus $1/C_e$ gave a straight line with a slope of $1/bQ_0$ and the intercept $1/Q_0$ which shows that adsorption follows Langmuir isotherm with correlation coefficient $R^2 = 0.9971$ only.

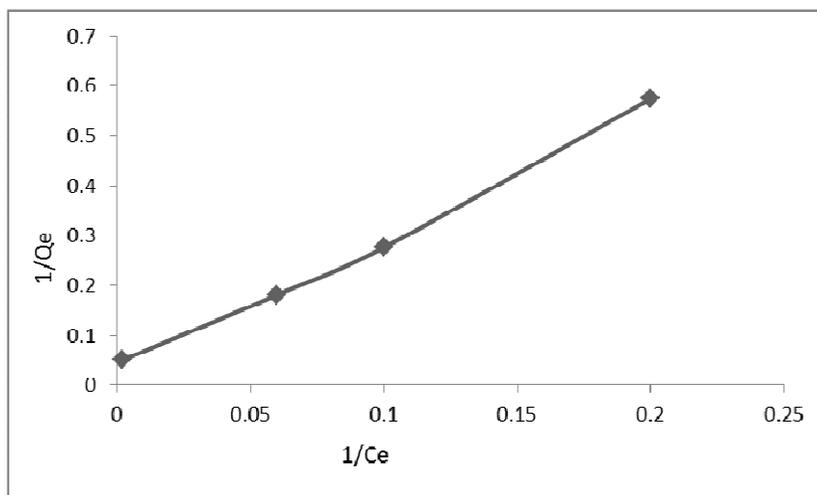


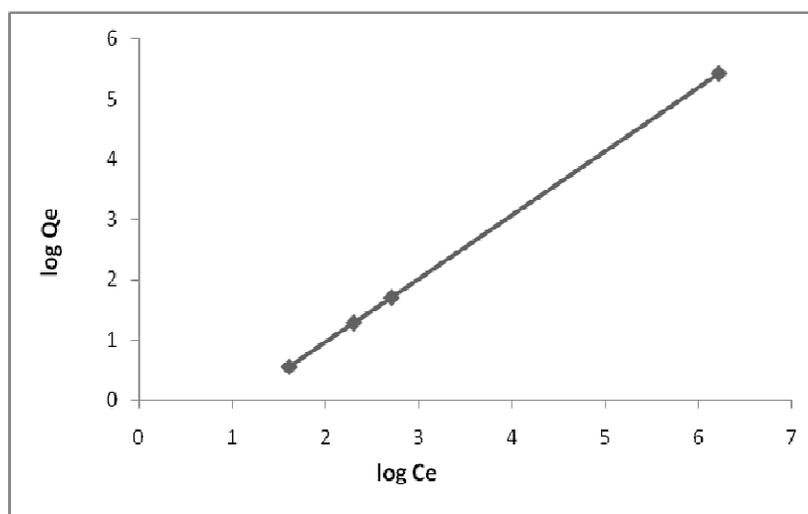
Fig. 10. Langmuir adsorption isotherm for the removal of fluoride at 2 g/L adsorbent, pH 7, contact time 5 min and varied initial concentration of adsorbate.

The experimental data were also processed in accordance with Freundlich adsorption isotherm given by $Q_e = K C_e^{1/n}$ whose liner form is $\log Q_e = 1/n \log C_e + \log K$ where Q_e is the concentration of adsorbed fluoride per unit weight (g) of adsorbent, C_e is the concentration of fluoride in the aqueous phase, K and n are empirical constants indicative of adsorption capacity and intensity, respectively [54]. The linear plot of $\log Q_e$ versus $\log C_e$ with $R^2 = 0.9999$ shows that fluoride removal by the thermally activated dolomite strictly follows Freundlich isotherm (Fig. 11) rather than Langmuir isotherm. The calculated values of K and n are 0.3152 mg/g and 0.9447 respectively. The magnitude of $1/n = 1.06$ also confirms that the fluoride removal using thermally activated dolomite followed Freundlich isotherm as it provides the best fit ($R^2 = 0.9994$) to the experimental data.

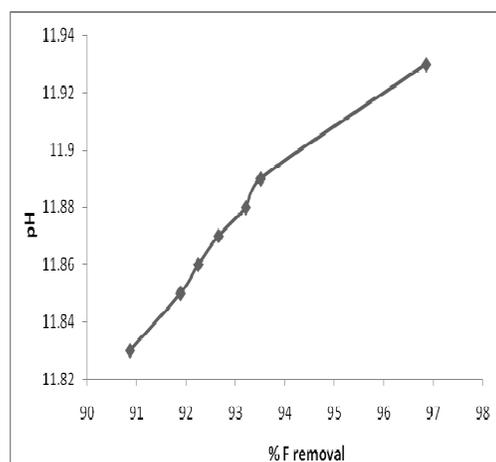
3.6. Mechanism of fluoride removal

The fluoride removal mechanism using thermally activated dolomite was studied under the static as well as the shaken conditions. Fluoride firstly transferred to the surfaces of the dolomite from bulk solutions and adsorbed at the active sites. This step, called external mass transfer of fluoride in the solutions, was very slow in static condition. Under the shaken condition, the adsorbent's particles rapidly moved around in the solutions. Thus the external

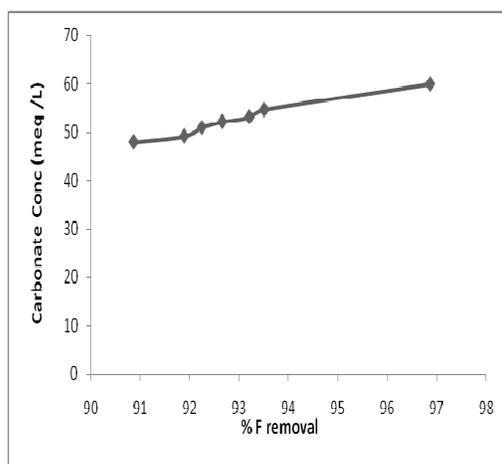
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3 mass transfer of fluoride in the shaken condition was speeded up and the equilibrium was
4 reached within 5 min. The fluoride removal reached towards equilibrium in 5 min in case of
5 the shaken condition but took much longer time in the static condition. Had the surface
6 adsorption been the only mechanism of fluoride removal then percentage removal of fluoride
7 should have been same in the both conditions at 5 min as the adsorption is an instantaneous
8 process. However, only 2.5% of fluoride was removed in the static condition at 5 min
9 indicated the operation of some other factor.
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38 **Fig. 11.** Freundlich adsorption isotherm for the removal of fluoride at 2 g/L adsorbent, pH 7,
39 contact time 5 min and varied initial concentration of adsorbate.
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3 **Fig. 12.** Change in solution pH with % F⁻ removal in shaken condition at 500 mg/L F⁻
4 concentration, 2 g/L adsorbent at pH 7.
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23 **Fig. 13.** Change in solution carbonate ion concentration with % F⁻ removal in shaken
24 condition at 500 mg/L F⁻ concentration, 2 g/L adsorbent at pH 7.
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28 The Ca²⁺ and Mg²⁺ dissolution from the dolomite surface also occurs during the experiment
29 where the relative dissolution of Ca²⁺ was found to be higher which got precipitated as CaF₂.
30 It is in conformity with Turner *et al.* who have shown evidences for fluorite (CaF₂)
31 precipitation during fluoride removal by calcite [49]. An increase in pH towards alkaline was
32 also observed after the removal of fluoride in the shaken condition. The increase in pH was
33 due to sudden increase in carbonate ion (CO₃²⁻) concentration in the solution phase because
34 of the precipitation of CaF₂. The increase in the solution pH and [CO₃²⁻] was correlated with
35 % fluoride removal and is shown in Fig. 12 & 13. The CO₃²⁻ concentration in the solution
36 was found to be 4.0 and 48 meq L⁻¹ for 5 min contact time in the static and the shaken
37 conditions, respectively which confirmed that the F⁻ diffuse into the dolomite and CO₃²⁻
38 diffuse out of the dolomite. Two F⁻ ions get transferred into the sorbent for one CO₃²⁻ ion
39 which causes high fluoride removal efficiency of the activated dolomite and thus confirmed
40 that the ion-exchange mechanism was contributing the most in the removal of the fluoride by
41 the thermally activated dolomite. The ion-exchange between F⁻ and CO₃²⁻ has also been
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reported during fluoride removal by calcite [55]. Fan *et al.* have also reported that the uptake of F⁻ on hydroxyapatite involves both; surface adsorption and ion-exchange mechanism with OH⁻ [50].

3.7. Comparison with different low cost materials

A comparison of the proposed fluoride removal method with literature reported methods is shown in Table 2 which shows that the proposed method, that utilizes inexpensive material for the removal of the fluoride from aqueous samples, is superior to many reported materials [56-67]. The optimum pH 7 is quite suitable for drinking water defluoridation. The proposed method/material has excellent fluoride removal capacity just within 5 min. The method works in a wide range (5-500 mg/L) of fluoride concentration after maintaining the pH and thus suitable for potable as well as waste water defluoridation. Only thermal treatment was applied to the proposed material while other materials especially biomaterials require chemical treatments in their development which increases the cost and may also release chemicals in the treated water. Moreover, the fluorosis affected people have been reported with calcium deficiency [68] but the presented study increases the calcium concentration in the treated water. Thus the proposed method, using widely available dolomite, is the most inexpensive, simple, rapid, efficient, healthy and applicable in a wide range of fluoride concentration.

Table 2. Comparison of proposed method with reported methods for the removal of fluoride using different low cost materials.

Material	Removal capacity (mg/g)	Contact time	Initial fluoride concentration (mg/L)	Reference
Heat activated dolomite	1.74-227.18	5 min	5-500	Present method
Calcium oxide modified activated alumina	101.01	48 h	1-1000	[56]
Quick lime	16.67	75 min	0-50	[57]
Granular ferric hydroxide	7.0	24 h	1-100	[58]

Fe-Al-Ce Oxide	178	24 h	2-110	[59]
Various graphite	0.16-3.13	60 min	2-10	[60]
modified attapulgite	41.5	48 h	20-200	[61]
Modified chitosan	22.380	24 h	10-100	[62]
Magnetic chitosan	22.49	150 min	5-140	[63]
Cross linked calcium alginate	73.6	90-120 min	10-25	[64]
Waste carbon slurry	4.306	1 h	1-11	[65]
Carbon nano-tubes	4.5	180 min	15	[66]
Nano-magnesia	267.82	90-120 min	5-200	[67]

4. Conclusion

The present study has proved beyond doubt that the thermally activated dolomite powder has excellent removal efficiency for the fluoride in aqueous media. The highest removal capacity was 243.25 mg/g with sorbent dose of 2 g/L, initial fluoride concentration of 500 mg/L in 5 min. The maximum removal of fluoride was observed at pH 7 and followed pseudo second order kinetics as well as Freundlich adsorption isotherm where an ion-exchange adsorption process was the main mechanism. The proposed method is simple, safe, the most cost effective and quick for defluoridation of drinking water.

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