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# Adsorptive removal of fluoride from aqueous media using *Citrus limonum* (lemon) leaf

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## ABSTRACT

A novel, the most inexpensive, easily available and eco-friendly analyte (fluoride) adsorbent of treated *Citrus limonum* (lemon) leaf has been developed and evaluated its feasibility for fluoride ion removal from aqueous environment. The adsorption of fluoride ion was affected by pH, adsorbent dose, contact time and initial fluoride concentrations. Batch experiments were performed to study the influence of various experimental variables such as pH of aqueous solution (2–8), adsorbent dose (1–10 g/50 mL fluoride solution), contact time (5–145 min), initial fluoride concentration (2–15 mg/L) and the presence of few competing anions on the adsorption of fluoride on *C. limonum* (lemon) leaf adsorbent. The optimal value of pH 2 was observed where the adsorbent showed the maximum defluoridation capacity of 70% of 2 mg/L fluoride ion. The experimental data revealed that both the Langmuir and Freundlich isotherm models fitted with the fluoride sorption process but very well followed Freundlich isotherm model. The reproducibility of the method was validated by removing and analyzing various samples by our method under the optimized conditions. The proposed method was compared with literature reported methods and found to be more effective. The present study demonstrated that treated powdered *C. limonum* leaf could effectively remediate fluoride contaminated water.

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## 1. Introduction

Fluorine is well recognized as an element of public health concern. Fluoride is important for mineralization of body tissues. It also plays a role in bone health [1–4]. The American Dietetic Association professionals routinely monitor and promote the use of systemic and topical fluorides, especially in children and adolescents, which has resulted in major reductions in dental caries and its associated disability [4,5]. Fluoridation of public water supplies i.e. water fluoridation at recommended intake levels has been the most effective dental public health measure [4,5]. Although the benefits of water fluoridation for dental health are widely accepted, concerns remain about possible adverse effects, particularly effects on bone. Increased rates of hip fracture in places with high concentrations of fluoride in drinking water have also been suggested by several investigators but this finding has not been consistent [6]. There is a low risk of hip fracture for people ingesting fluoride in drinking water at concentrations of about 1 mg/L [6]. Thus fluoride ion in drinking water is known for both beneficial and detrimental effects on health. The prevalence of fluorosis is mainly due to the intake of large quantities of fluoride through drinking water

owing to more than 90% bioavailability [7]. Thus fluoride in drinking water has a profound effect on teeth and bones. Fluoride up to a small level of 1.0–1.5 mg/L, strengthens the enamel. Concentrations in the range of 1.5–4.0 mg/L result in dental fluorosis whereas with prolonged exposure at still higher fluoride concentrations (4–10 mg/L) dental fluorosis progresses to skeletal fluorosis [8]. Thus fluorosis is one of the most frequently occurring diseases that develop in the population who depends on water containing high fluoride concentrations for their daily drinking [9]. Therefore the World Health Organization as well as many countries has set 1.5 mg/L of fluoride as the upper limit in drinking water [10–12].

High fluoride concentrations in ground water up to 30 mg/L occur widely in many parts of the world including India, Pakistan, China, Sri Lanka, West Indies, Spain, Holland, Poland, Italy, Iraq, Iran, Sudan, Uganda, Kenya, United Republic of Tanzania, Mexico, Thailand, Serbia, Ethiopia, Eritrea (North East Africa), West Africa, Southern Africa and North and South American countries [2,7,8,10,11,13–38]. According to reported statistics more than 1.34 million people have suffered from skeletal fluorosis due to high fluoride drinking water and another 30 million are exposed to it in China [10,15,16,37,38]. India is one among the twenty three nations in the world, where fluoride contaminated groundwater is creating health problems [39]. Excessive fluoride concentrations have been reported in ground waters of more than nineteen states in India alone where people are facing acute fluorosis problems [19]. The most seriously affected areas are in Andhra Pradesh,

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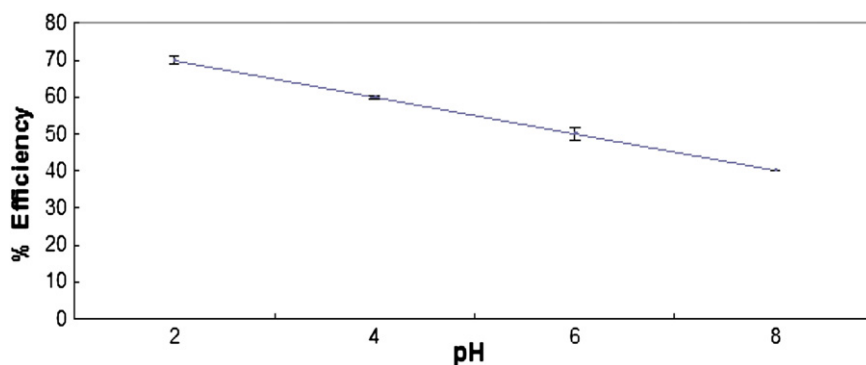


Fig. 1. Effect of pH on removal of fluoride at initial fluoride concentration of 2 mg/L, adsorbent dose of 10 g/50 mL and contact time of 145 min.

Assam, Chhattisgarh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh [7,8,10,14,17,20,22,33–36] while the highest fluoride concentration of 48 mg/L has been reported in Rewari district of Haryana state [10,35]. Hence defluoridation of water has been taken as an important public exercise. Therefore many defluoridation techniques have been reviewed [8] and reported which include membrane separation processes [40,41], adsorption [20,42–48], ion-exchange [49,50], precipitation-coagulation [51,52], nano-filtration [53,54], reverse osmosis [41,55,56], electrolytic defluoridation [57–59], electrodialysis [60,61] and Donnan dialysis [62–64]. Many of these methods did not get used on large scale because of various unfavorable factors such as high operational and maintenance cost, generation of toxic by-products (pollution) and due to complex treatment. On the other hand membrane process is expensive in terms of installation and operation cost, there are also more chances of fouling, scaling or membrane degradation. The electrochemical techniques are not popular due to high cost during installation and maintenance [65].

It has also been reported that the total fluoride intake is higher in subjects of low socioeconomic status [66]. Hence the adsorption technique has been found to be quite cost effectiveness for fluoride removal [15,67] where many types of adsorbents like aluminum based materials [45,49,51,68–70], fly ash [71], alum sludge [45,72], algal biosorbent [73], chitosan beads [20,74–79], red mud [48], synthetic compounds/amberlite resin/zeolite [46,47,80,81], calcite [82], hydrated cement [83], hydrotalcite-like compounds and their calcined products [84], double layer oxides [9], clays and soils [14,15,22,44,85–88], carbon based materials [67,89–91], synthetic hydroxyapatite [77,79,92,93], and quick lime [94] have been tried. However, majority of these methods generate large amount of sludge, disposal of which becomes a problem.

While continuous efforts have been directed towards adsorptive removal of fluoride from water samples using different low cost adsorptive materials i.e. the cheap alternative and eco-friendly materials [22,95,96], we came across that various plant leaves and stem extracts have been used for the adsorptive removal of heavy metals [97] as well as corrosion inhibitors [98,99]. After our most recent review on the adsorptive removal of fluoride [65] and while surveying for cheap and effective defluoridating agents we found that the orange waste loaded with multivalent metal ions ( $\text{Al}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Sn}^{4+}$  and  $\text{V}^{4+}$ ) has been used for the adsorptive removal of fluoride from aqueous solution where adsorption gels for fluoride ion were prepared by saponification and used [100] but metal loading makes the process cumbersome. Most recently, we have reported from our laboratory the removal of fluoride from water sample using Zr–Mn composite material [101]. With continuous report in fluoride contamination in drinking water in rural habitations of Central Rajasthan, India [29], we continued our work in search of further cheap and effective defluoridating materials which led us to evaluate the feasibility of fluoride removal using acid and alkali treated lemon (*Citrus limonum*)

leaf powder under varying conditions and is reported in the present communication.

## 2. Experimental

### 2.1. Materials and equipment

All the reagents used were of analytical reagent grade and used without further purification. Anhydrous sodium fluoride with 99.5% purity was purchased from E. Merck Ltd. India and 1000 mg/L fluoride stock solution was prepared by dissolving appropriate amount of NaF in 1 L of distilled deionized water from a Milli-Q water system. Different standard fluoride solution was prepared from stock solution. For quality control, a total ionic strength adjustment buffer (TISAB) solution for the determination of fluoride ion concentration was provided with fluoride ion meter make Eutech model: ECION270042GS was used. Fluoride ion meter was used for the fluoride ion determination during studies. Remi Shaker model RS-2492203 was used for samples shaking. Hanna Instruments pH meter model S358236, using BDH buffer for standardization, was used for the measurement of pH of all the solutions during adsorption studies. The residual fluoride concentrations in solutions were measured by the fluoride meter equipped with Orion fluoride ion selective electrode (Thermo Scientific Orion, USA).

### 2.2. Adsorbent material development

Fresh lemon i.e. *C. limonum* leaves were obtained from lemon tree. Leaves were washed carefully with distilled deionized water and sun-dried for 3 days. The dried *C. limonum* leaves were manually grounded using mortar pestle and sieved to obtain leaf powders below 1.5 mm of diameter. The powdered samples of *C. limonum* leaves were subjected to acid and alkali treatment before being used as an adsorbent. For the acid treatment, the *C. limonum* leaf biomass powder sample (40 g)

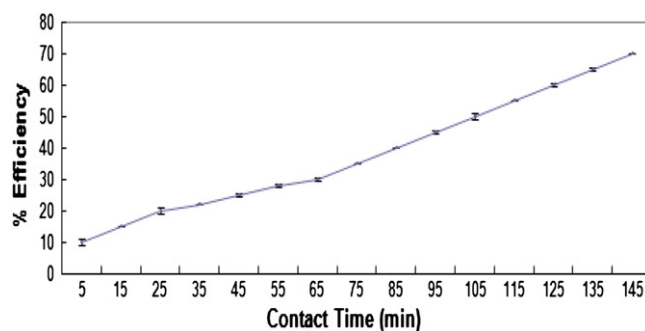


Fig. 2. Effect of contact time on the removal of fluoride ion at adsorbent dose of 10 g/50 mL (2 mg/L fluoride), temp of 30 °C and pH 2.

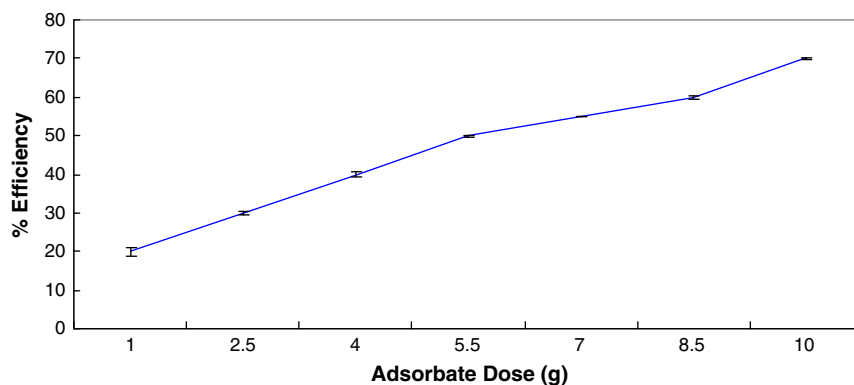


Fig. 3. Effect of adsorbent dose on the removal of fluoride ion at initial fluoride concentration of 2 mg/L, temp of 30 °C, contact time of 145 min, and pH 2.

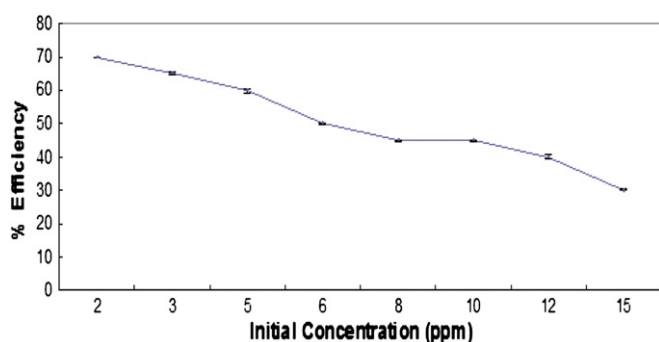


Fig. 4. Effect of initial fluoride concentration on the removal of fluoride ion at adsorbent dose of 10 g/50 mL, temp of 30 °C, pH 2, and contact time of 145 min.

and 400 mL of 1 M HNO<sub>3</sub> (nitric acid) were taken in a 1000 mL conical flask. The mixture was gently heated on burner for 20 min and then biomass was filtered out and washed with distilled water. Washing was carried out until maximum color was removed and clear water obtained. The acid treated *C. limonum* leaf biomass powder sample was then subjected to alkali treatment with 400 mL of 0.5 M NaOH in a 1000 mL conical flask. The mixture was gently heated on burner for 20 min. The treated biomass was washed repeatedly with distilled water and continued until maximum color was removed giving clear water showing pH ~7 when filtered out. After careful washing with deionized water, the adsorbent materials were dried at 110 °C in an electric oven for 3 h. The treated *C. limonum* leaf biomass powder sample was cooled in air to room temperature.

### 2.3. General procedure of adsorption studies

Batch techniques were used for studying the adsorption process for fluoride removal rate and equilibrium data. Experiments were carried out by taking different amounts of adsorbent dose (*vide infra*) in 250 mL polypropylene flasks containing 50 mL of fluoride solution of different known concentration. The samples were shaken on a Remi Shaker model RS-2492203 at the speed of 200 strokes min<sup>-1</sup> at the constant temperature of 30 °C for 145 min except where the effect of the contact time was studied. While studying the effect of different variables on the rate of fluoride adsorption, the pH of the solution was maintained by adding 0.5 M HNO<sub>3</sub> or 0.1 M NaOH to obtained desired pH. After each batch of the sorption experiment, the adsorbent was separated from the solution by filtration using Whatman filter paper no. 42. The residual fluoride concentration in solution was measured by a fluoride meter equipped with Orion fluoride ion selective electrode (Thermo Scientific Orion, USA).

## 3. Results and discussion

Various batch experiments were conducted to evaluate the feasibility of fluoride removal using *C. limonum* leaf under varying conditions. The adsorption of fluoride on the powdered samples of *C. limonum* leaf was studied at 30 °C by batch experiments. The fluoride removal efficiency of adsorbent depends on various factors which have been discussed in the following sections.

### 3.1. Influence of pH

The pH of the aqueous solution is an important controlling factor in the fluoride adsorption process. Thus the effect of pH was studied by

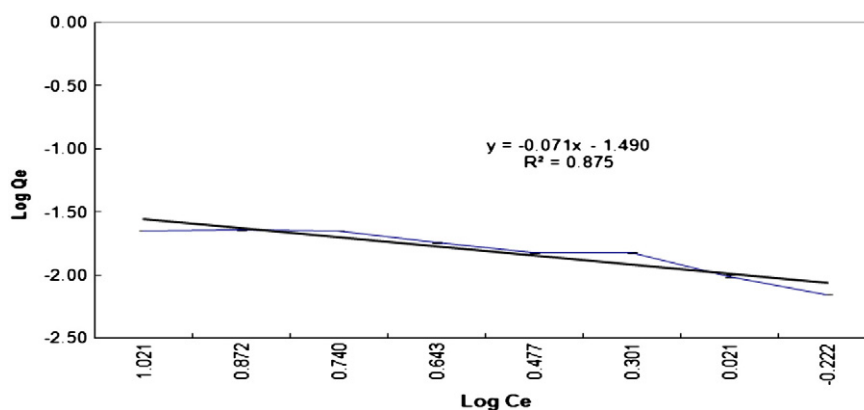


Fig. 5. Linear model of Freundlich isotherm for removal of fluoride at 10 g/50 mL volume, pH 2, temp of 30 °C, contact time of 145 min and varied initial concentration of adsorbate.

**Table 1**

The values of Freundlich and Langmuir isotherm parameters of adsorbent.

Langmuir isotherm			Freundlich isotherm		
$1/Q_0 = 14.086$	$1/b = 0.895$	$R^2 = 0.779$	$K_f = 0.0323$	$1/n = 0.0714$	$R^2 = 0.875$
$Q_0 = 0.070$	$b = 1.117$			$n = 14.005$	

varying the pH of the adsorption media as 2, 4, 6 and 8. In different sets of 250 mL polypropylene flasks containing 50 mL of fluoride solution of known concentrations were taken. Then the pH of each solution was adjusted so that the flask sets had desired pH values. This was followed by the addition of 10 g of powdered *C. limonum* leaf adsorbent to each flask. The flasks were then sealed, placed into a thermostatically controlled shaker and for shaking at the speed of 200 strokes  $\text{min}^{-1}$  at 30 °C for 145 min. The pH was maintained at desired value by adding 0.5 M  $\text{HNO}_3$  or 0.1 M  $\text{NaOH}$  to the dose of 10 g of powdered *C. limonum* leaf in 50 mL fluoride solution 2 mg/L. As shown in Fig. 1, a decrease in the removal of fluoride ions was observed with increase in the pH of the solution. This may be due to better adsorption of fluoride ion at low pH. This may be attributed to large number of  $\text{H}^+$  ions present at low pH values, which in turns neutralizes the negatively charged  $\text{OH}^-$  ions on adsorbed surface thereby reducing hindrance to the diffusion of fluoride ions. At higher pH values, the reduction in adsorption may be due to abundance of  $\text{OH}^-$  ions causing increased hindrance to diffusion of fluoride ions. Thus the adsorption and desorption of fluoride ion followed ligand exchange mechanism. The highest adsorption i.e. removal of fluoride ion in the studied pH range was observed at pH 2 which was used for subsequent dependence studies.

### 3.2. Influence of contact time

The influence of the contact times on the defluoridation capacity of adsorbent i.e. the powdered samples of *C. limonum* leaf were studied by varying the contact time from 5 to 145 min under the adsorbent dose of 10 g/50 mL (2 mg/L fluoride), pH 2 and temp of 30 °C. It was found that the removal of fluoride ions increased with the increase in contact time. The results are presented in terms of percentage efficiency in Fig. 2. Further increase in contact time did not increase the fluoride uptake (not shown in Fig. 2) due to sufficient deposition of fluoride ions on the available adsorption sites on adsorbent materials. The results show that the uptake of fluoride ions on the powdered *C. limonum* leaf adsorbent material, at the optimum pH 2, is quite rapid at the initial stage of the defluoridation. Similar results have been reported in the literature by us as well as various researchers [17,20,74,101].

### 3.3. Effect of adsorbent dose

To study the effect of the increased adsorption dosages on the percentage removal of fluoride, the amount of adsorbent dose was varied between 1.0 and 10.0 g/50 mL. The pH of the adsorption media was maintained at 2 while initial fluoride ion concentration was fixed at 2 mg/L and contact time was kept 145 min. The observation shown in Fig. 3, revealed an increase in the removal efficiency with simultaneous increase in adsorbent dose. The results show that 70% fluoride removal efficiency took place at adsorbent dose of 10 g/50 mL which is a very good defluoridation efficiency provided by inexpensive adsorbent materials. This may be due to the increase in surface area with increase adsorbent dose, and hence more active sites were available for the adsorption of fluoride. Similar results have been reported in the literature by us as well as various researchers [17,20,101]. Thus based on the present study 10 g/50 mL of the adsorbent was selected as for further experiments as the optimum dosage.

### 3.4. Effect of initial fluoride concentration

The effect of the defluoridation capacity of inexpensive, easily available and eco-friendly treated *C. limonum* leaf powder was studied with different initial fluoride concentrations in the range of 2 to 15 mg/L at pH 2, temp of 30 °C for 145 min and the results are shown in Fig. 4. It was observed that the defluoridation capacity increased at lower initial fluoride ion concentration but decreased at higher concentration which indicates that the capacity of the adsorbent material gets exhausted sharply with increase in initial fluoride ion concentration. It may be attributed to the presence of more fluoride ion than the adsorption capacity of the adsorbent and similar results have been reported by us in our recent study as well as by other researchers [17,20,101].

### 3.5. Equilibrium sorption isotherm methods

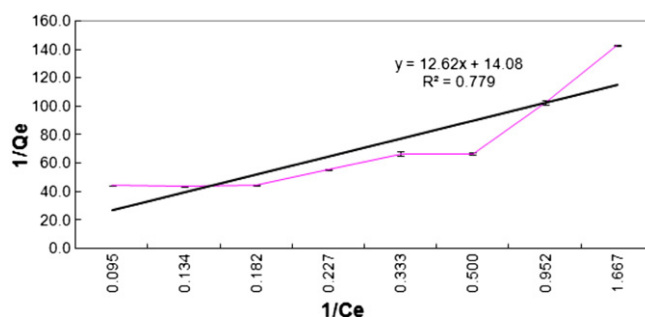
Freundlich and Langmuir isotherms are useful models for the description of adsorption process by different adsorbents [102–104]. Thus alignment of adsorption process with Freundlich and Langmuir isotherms were also studied for the equilibrium adsorption of fluoride ion at eight different concentrations ranging from 2 to 15 mg/L at pH 2. Then the adsorption data for defluoridation of water have been correlated with Freundlich and Langmuir models. The defluoridation capacity of powdered *C. limonum* leaf adsorbent was calculated using Eq. (1) where  $Q_m$  is amount adsorbed (mg/g),  $C_0$  is the initial concentration in solution (mg/L),  $C_e$  is the equilibrium concentration in solution (mg/L),  $V$  is the solution volume (L), and  $M_s$  is the weight of the adsorbent (g).

$$Q_m = (C_0 - C_e)V/M_s \quad (1)$$

Freundlich isotherm is a commonly used isotherm model to analyze adsorption data. The general formula of Freundlich equation [102,103] is given by Eq. (2).

$$Q_e = K_f C_e^{1/n} \quad (2)$$

One taking logarithm of Eq. (2) shows that linear form of Freundlich isotherm model can be written as Eq. (3) where,  $Q_e$  is the total amount of fluoride ion adsorbed/total weight of adsorbents (mg/g). The Freundlich constant  $K_f$  characterizes the adsorption capacity of adsorbent



**Fig. 6.** Linear model of Langmuir isotherm for removal of fluoride at 10 g/50 mL volume, pH 2, temp of 30 °C, contact time of 145 min and varied initial concentration of adsorbate.



**Table 2**

Comparison of adsorption studies with different adsorbents as low cost materials.

Type of adsorbent used	Fitted adsorption isotherms; removal [F] level (mg/L); optimum pH; contact time; comments	Capacity/efficiency (mg/g or %)	Ref.
Kaolinite, bentonite, charfines, lignite and nirmali seeds	Adsorption isotherms not studied; 5.0 mg/L; pH 2.8, time = 120 min	Highest removal capacity is 33%	[22]
Hydroxyapatite > Fluorspar > Quartz activated using ferric ions > Calcite > Quartz	Adsorption isotherm not studied; 2.0 mg/L at natural pH	Highest removal capacity of 38 and 46%	[95]
Multani matti and red soil	Langmuir and Freundlich adsorption isotherms; 2.0 mg/L, pH 6.5 for Multani matti, pH 5.0 for red soil, 15 min	50–70% of fluoride in the concentration range of 1–4 mg/L	[14]
Bentonite/chitosan beads	Freundlich adsorption isotherm; pH 5.0	Bentonite of 0.895 mg/g whereas chitosan beads of 0.359 mg/g	[96]
Bark of babool	Langmuir and Freundlich adsorption isotherms; 5.0 mg/L; pH 8.0; 8 h.	77.04%	[105]
Spent pot liner leachate (a hazardous solid waste)	Adsorption isotherms not studied; 1.0 mg/L; pH 7.0–10.0	100% at 6 mL/min flow rate through the ion exchanger	[50]
Algal biosorbent ( <i>Spirogyra</i> IO2)	Good fit with the Langmuir's adsorption isotherm; 5.0 mg/L; pH 7.0	5 mg fluoride/0.1 g biosorbent	
Orange waste loaded with multivalent metal ions	Metal loading makes the process cumbersome.	Acceptable level of environmental standard	[100]
Powdered <i>Citrus limonum</i> leaf	Both isotherms studied but best fit with the Freundlich isotherm; 1.4 mg/L (70% of 2.0 mg/L); pH 2.0; 145 min; the most inexpensive.	70% at the optimum pH 2	Present work

and the Freundlich constant  $1/n$  reflects the adsorption intensity of adsorbent while  $C_e$  is the concentration at equilibrium.

$$\log Q_e = 1/n \log C_e + \log K_f \quad (3)$$

Using the experimental data, the linear form of Freundlich isotherm plot has been plotted between  $\log Q_e$  and  $\log C_e$  and is shown in Fig. 5. An excellent linearity of Freundlich isotherm plot confirms the applicability of the Freundlich model for defluoridation of water at different initial concentration. The fitting curve of Freundlich adsorption isotherm for fluoride adsorption using powdered *C. limonum* leaf adsorbent is shown in Fig. 5. The calculated Freundlich parameters from fitting curve of Freundlich model are listed in Table 1.

Langmuir isotherm is applicable for single layer adsorption and it assumes that all the adsorption sites have equal affinity for adsorbate molecules but there is no transmigration of adsorbate molecules in surface plane. Langmuir isotherm equation [103,105] can be expressed as in Eq. (4) where,  $Q_e$  shows the adsorbed amount (mg/g).

$$Q_e = Q_0 b C_0 / (1 + b C_e) \quad (4)$$

$C_e$  is the equilibrium constant of adsorbate (mg/L),  $Q_0$  and  $b$  is Langmuir constant. Linear form for Langmuir isotherm can be expressed as in Eq. (5).

$$1/Q_e = (1/Q_0) + (1/bQ_0 C_e) \quad (5)$$

A plot  $1/Q_e$  against  $1/C_e$  is shown in Fig. 6 where the straight line has a slope of  $1/bQ_0$ . It shows that the adsorption follows the Langmuir isotherm. Langmuir constants  $b$  and  $Q_0$  have been calculated from the slope and intercept in Fig. 6 and are shown in Table 1.

Higher correlation coefficient ( $R^2$ ) value in case of Freundlich model showed that the adsorption data could be well described by Freundlich isotherm model, which suggested that the powdered *C. limonum* leaf adsorbent was a heterogeneous adsorbent. The magnitudes of  $1/n$  lying between 0 and 1 suggested that the adsorption of fluoride onto developed adsorbent was quite favorable. In other words the adsorption method follows the Freundlich isotherm more strictly than the Langmuir isotherm.

### 3.6. Comparison of proposed methods with different adsorbents as low cost materials

A comparison of the proposed low cost adsorption method for the removal of fluoride ion with other published methods using low cost materials with their general characteristics is shown in Table 2. Some methods are having good adsorption capacity sensitivity but some are time consuming (8 h) [105] while other uses the hazardous solid waste as adsorbent material [50]. The present proposed procedure uses the most inexpensive, easily available and eco-friendly adsorbent treated *C. limonum* (lemon) for the analyte (fluoride) removal. Moreover, the proposed procedure removes fluoride at the 1.4 mg/L. Thus the method is quite sensitive, effective and rapid (145 min) as compared with literature reported methods and found to be more effective.

## 4. Conclusions

The powdered *C. limonum* leaf material as an adsorbent for fluoride removal from water was successfully used. The adsorption of fluoride was dependent on pH, initial fluoride concentration, adsorbent dose as well as contact time which were optimized. The uptake of fluoride ions is possible between pH of 2 and 8 whereas the maximum fluoride removal was achieved at pH 2. The removal rate increased with the increase in adsorbent dose and contact time while the rate decreased with the increase in fluoride concentration and pH. The adsorption by adsorbent followed strictly the Freundlich isotherm. The present study concluded that the powdered *C. limonum* leaf material as an adsorbent can be effectively utilized for the removal of fluoride from aqueous environment.

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