

# Feasibility of Acid Activated *Moringa Oleifera* Leaves as an Adsorbent for Defluoridation of Water

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**ABSTRACT:** Fluoride contamination of water is a major problem worldwide. This investigation reports the use of acid treated *Moringa oleifera* leaves as a defluoridating agent. The suitability of *Moringa oleifera* leaves for the removal of fluoride was assessed by batch method and optimized various parameters viz., contact time, adsorbent dosage, pH, initial fluoride ion concentration that influence the sorption was explained using Langmuir, Freundlich and Temkin isotherms.

**KEYWORDS :** Adsorption, fluoride, Freundlich isotherm, Langmuir isotherm, *Moringa oleifera*, Temkin isotherm.

## I. INTRODUCTION

Water is most abundant and is an essential component of our life supporting system. But today most of the countries are facing drinking water problems. In India, drinking water is contaminated at many places by various pollutants such as fluorides, nitrates, iron etc. About 71% of the earth surface is occupied by water of which only about 0.05% is accessible for human consumption while the bulk of the remaining comprises of the inaccessible seawater, groundwater, swamps and frozen polar ice caps [1]. The scarcity of water is due to rapid population growth, increased industrialization and decreased amounts of rainfall in the previous decades [3]. Fluoride is present universally in almost every water (higher concentrations are found in ground water), earth crust, many minerals, rocks etc. It is also present in most of everyday needs, viz. toothpastes, drugs, cosmetics, chewing gums, mouthwashes, and so on. Though a small amount of it is beneficial for human health for preventing dental carries, it is very harmful when present in excess of 1 mg/L. According to World Health Organization norms, the upper limit of fluoride concentration in drinking water is 1.5 mg/l (WHO, 2008). The Bureau of Indian Standard which is the main regulatory agency for drinking water in India specifies that the desirable limit of fluoride in drinking water is 0.6 mg/l to 1 mg/L. The high fluoride levels in drinking water and its impacts on human health have increased the importance of defluoridation studies [4]. The magnitude of the problem is sinking in and efforts are being made towards defluoridation of drinking water, combating the debilitating fluorosis and taking steps to prevent and control the disease [5]. Chemical coagulants like Aluminum sulphate (alum), FeCl<sub>2</sub> are used in Municipal drinking water treatment plant for purification process. This excess use of amount of chemical coagulants can affect human health e.g. Aluminum has also been indicated to be a causative agent in neurological diseases such as pre-senile dementia [6]. The conventional method of fluoride removal includes: ion-exchange, reverse osmosis and adsorption [7].

Due to rich biodiversity of India, a large number of plant species are available for treatment of various toxicities. Research reports indicate that herbal and low cost plant products may be used for mitigation of fluoride toxicity [8]. The objective of the present study is to investigate the effectiveness of naturally occurring and low-cost materials like *Moringa oleifera* for removal of fluorides from water.

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In the present study, the efficiency of removal of fluoride by using low cost bio-adsorbents like *Moringa oleifera* was investigated. The study assesses the suitability of in- expensive bio-adsorbents to effectively remediate fluoride contaminated water.

## II. LITERATURE SURVEY

**Temkin and Pyzhev (1940)**, studied the synthesis and decomposition of  $\text{NH}_3$  technical Fe catalysts promoted by  $\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}$  at  $400^\circ\text{--}450^\circ$  and 1 atm. pressure and  $\text{H}_2\text{:N}_2$  ratios of 0.5 up to 8.5, the rate constants are  $k=1.04\times 10^3$  at  $400^\circ$  and 7.78 at  $450^\circ$ .

**Diwedi et al (2014)** Present investigation focused on the bioadsorption of fluoride from aqueous solution by *Ficus religiosa* (peepal) leaves. Removal of fluoride has been investigated as a function of pH, bioadsorbent dose, temperature, time and equilibrium initial fluoride ion concentration. Batch study exposed that the bioadsorption of fluoride on *Ficus religiosa* (peepal) leaves were strongly pH dependent, and maximum fluoride removal was found to occur at equilibrium pH of 7.

**Tiwari et al., (2014)** In this present study, formaldehyde and sulphuric acid treated two agricultural adsorbents; potato peel and neem bark are used to adsorb methylene blue. On the whole, the acid-treated adsorbents are investigated to have high sorption efficiency compared to HCHO treated adsorbents.

**Parlikar and Mokashi (2013)** used *Moringa oleifera* for defluoridation of water. Using colorimetric method, tests were conducted to get optimal values of pH of water in acid and alkali treated powder of *Moringa oleifera*.

Aravind et al., (2015) investigated fluoride removal efficiency of various low-cost bio-adsorbents such as *Moringa oleifera* (MO), Rice husk Activated Charcoal (RHAC) and Activated Vertiver Root (AVR) using an experimental column study. Among these, MO was found to be most efficient bio-adsorbent for fluoride removal.

## III. EXPERIMENTAL METHODS

### (i). Collection and Preparation of Adsorbent and Adsorbate

*Moringa oleifera* leaves were used as adsorbent and were collected from local trees and were washed with water many times to remove dirt and then sun dried for 3 days. The dried sample was then ground to powder using a pestle and mortar, the dried sample powder was then sieved to select the particle size of  $350\text{ }\mu\text{m}$  and was then used as an adsorbent. 40 gm of the powder sample was added to 400 ml of 1N  $\text{HNO}_3$  for acid treatment [9]. The mixture was boiled for about 20 minutes on a sand bath. Washing of the powder sample was carried out by using distilled water until maximum colour was removed and clear water was obtained. Finally, it was dried again in an oven at  $50^\circ\text{C}$  for 6 hours.

The preparation of adsorbate was carried out by preparing a standard solution of 2 ppm fluoride by dissolving 2 mg of anhydrous sodium fluoride in 1000 ml of distilled water.

### (ii). Preparation of the reagent

The SPADNS solution, 0.003721 M was prepared by dissolving 0.4750 g of SPADNS reagent in 250 ml deionized water. The Zirconyl chloride acid solution, 0.0375 M was prepared by dissolving 0.0665 g of  $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$  in 25 ml of deionized water. Then 25 ml of HCl was added and deionized water was added until the total volume of the solution was 250 ml. The concentration of zirconyl acid-SPADNS reagent was prepared by mixing the two solutions in the ratio of 1:1. This reagent was further diluted.

### (iii). Sorption Experiment

Synthetic fluoride bearing water sample having initial fluoride ion concentration of 2 mg/L was used. This fluoride solution was filtered by using Whatmann's filter paper no.41 to this filtrate, SPADNS and zirconyl acid solution of 5 ml each was used. The sample was checked for fluoride detection using spectrophotometer at wavelength 570 nm.

The fluoride removal studies by adsorption were conducted in 250 ml conical flask using 100 ml of synthetic water sample. To these conical flasks acid treated (activated) adsorbent was added and after giving a required contact time of 1 hour the contents of the flask were then filtered using whatmann's filter paper no. 41. The filtrate was used for

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fluoride ion estimation using SPADNS method. The fluoride content in the filtrate was determined by UV- Visible spectrophotometer. The values of percent fluoride removal by adsorbent was calculated using the following relation.

$$\% \text{ removal} = \frac{C_0 - C_i}{C_0} \times 100$$

Where,  $C_0$  is initial fluoride ion concentration and  $C_i$  is the final fluoride ion concentration.

## Langmuir Isotherm

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm model is described as

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e$$

Where,

$q_{\max}$  = The monolayer adsorption capacity of the adsorbent (mg/g)

$K_L$  = The Langmuir adsorption constant (L /mg)

$C_e$  = Equilibrium concentration of the solution in (mg/L)

$q_e$  = Amount adsorbed per unit weight of adsorbent (mg/g)

Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor,  $R_L$ , which is defined by the following equation,

$$R_L = [1/(1+bC_i)]$$

Where  $C_i$  is the initial concentration of the fluoride solution and  $b$  is the Langmuir constant related to energy of adsorption ( $L \text{ mg}^{-1}$ ).  $R_L$  value indicates the adsorption nature to be either unfavourable if  $R_L > 1$ , linear if  $R_L = 1$ , favourable if  $0 < R_L < 1$  and irreversible if  $R_L = 0$ .

## Freundlich Isotherm

It is applicable to both monolayer and multilayer adsorption and is based on assumption that adsorbate adsorb onto heterogeneous surfaces of an adsorbent. The linear form of Freundlich equation is expressed as

$$q_e = K_f C_e^{1/n}$$

Where,

$q_e$  = Amount adsorbed per unit weight of adsorbent (mg/g).

$C_e$  = Equilibrium concentration of the solution in (mg/L).

$K_f$  and  $n$  are Freundlich Isotherms constants which is a measure of adsorption capacity or fundamental effectiveness of the adsorbent.  $K_f$  and  $n$  can be determined from the linear plot of  $\log q_e$  versus  $\log C_e$  as shown in equation. The adsorption process is said to be favorable when the value of 'n' satisfies the condition  $1 < n < 10$  which indicated favorability of adsorption and the degree of heterogeneity, otherwise it is unfavorable.

## Temkin Isotherm

This isotherm contains a factor that explicitly takes into account of adsorbent–adsorbate interactions. the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed  $q_e$  against  $\ln C_e$  and the constants were determined from the slope and intercept. The model is given by the following equation:

$$q_e = B \ln A_T + B \ln C_e$$

$A_T$  = Temkin isotherm equilibrium binding constant (L/g)

$b_T$  = Temkin isotherm constant

$R$  = universal gas constant (8.314J/mol/K)

$T$  = Temperature

$B$  = Constant related to heat of sorption(J/mol)

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## IV. PROPOSED METHODOLOGY AND DISCUSSION

Understanding of adsorption technique is possible with knowledge of the optimal conditions, which would herald a better design and modeling process. Thus, the effect of some major parameters like pH, contact time, dose of adsorbent and initial concentration of fluoride ions uptake on adsorbent materials were investigated from kinetic viewpoint. Adsorption studies were performed by batch technique to obtain the equilibrium data. The experimental data from batch experiment were analyzed using adsorption isotherm equations (Langmuir, Freundlich, and Temkin), in which linear regression analysis was used to evaluate whether the theoretical models have better or worse fit for the experimental data.

### (i). Effect of pH on Defluoridation

The pH of the aqueous solution is a controlling factor in the adsorption process. The experiments were carried out for acid treated *Moringa oleifera* leaves powder for determining optimum pH. The pH was varied from 1 to 10. The adsorbent having 350  $\mu\text{m}$  size, acid treated, was used to determine optimal pH at which the adsorption was maximum. For these experiments initial fluoride ion concentration was 2 mg/L, with adsorbent dose of 2.5 g/L and contact time of 1 hour. As shown in Table 1, the acid treated adsorbent showed the maximum removal efficiency 83 % at pH 1[10].

**Table 1:** Effect of pH on sorption of fluoride

S.No.	pH	Acid treated powder	
		Absorbance (A)	% Removal
1.	1	0.020	83
2.	2	0.023	81
3.	4	0.031	74
4.	6	0.044	63
5.	8	0.057	53
6.	10	0.059	51

### (ii). Effect of contact time on Defluoridation

The adsorbent dose of 2.5 g/L was taken and kept constant throughout the experimental work. The contact time was varied from 0.5 to 2.5 hours for acid treated *Moringa oleifera* leaves powder of particle size 350 $\mu\text{m}$ . The experimental study was carried out to determine optimal contact time using acid treated adsorbent with same particle size. The pH was 8 and dose was 2.5 g/L for the study.

**Table 2:** Effect Of Contact Time On Defluoridation

S.No.	Time (minutes)	Acid treated powder	
		Absorbance (A)	% Removal
1.	30	0.015	87
2.	60	0.013	89
3.	90	0.012	90
4.	120	0.006	95
5.	150	0.002	98

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## (iii). Effect Of Adsorbent Dose On Defluoridation

In case of acid treated *Moringa oleifera* leaves powder, the % removal of fluoride decreases with increase in dose due to maximum absorbance (97 %) achieved with in short span of time, and further addition of adsorbent results in overcrowding which in turn decreases the efficiency. Unit adsorption of fluoride is decreased in all cases after increasing dose. This can be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [11].

**Table 3:** Effect of adsorbent on sorption of fluoride

S.No.	Adsorbent Dose (mg)	Acid treated powder	
		Absorbance (A)	% Removal
1.	100	0.003	97
2.	200	0.006	95
3.	300	0.008	93
4.	400	0.010	91

## (iv). Effect of initial fluoride ion concentration

Studies on the effect of initial fluoride concentration were conducted by varying it from 0.5 to 2 mg/L keeping adsorbent dose of 2.5 g/L, pH of 8, and contact time of 1 hour.

**Table 4:** Effect of Fluoride Ion Concentration On Defluoridation

S.No	Fluoride ion concentration (mg/l)	Acid treated powder	
		Absorbance (A)	% Removal
1.	0.5	0.017	86
2.	1	0.010	91
3.	1.5	0.007	94
4.	2	0.002	98

The response of different fluoride ion concentration on the removal of fluoride is presented in Table 4. For acid treated powder, the observations reveal that with the increase in fluoride ion concentration the % removal of fluoride also increases. With increase in initial concentration of fluoride the driving force for transport of fluoride from the bulk to the surface of adsorbent increases, which results in more adsorption of fluoride per unit mass of adsorbent[12].

## IV. EXPERIMENTAL RESULTS

### Adsorption Isotherms

In the present study, adsorption isotherm study was carried out on three isotherm models: Langmuir, Freundlich and Temkin. The applicability of isotherm models to the adsorption study done was compared by observing the correlation coefficients,  $R^2$  value. Adsorption isotherm helps in determining the feasibility of acid treated *Moringa oleifera* leaves powder for treating fluoride ion in water. Langmuir, Freundlich and Temkin isotherms were plotted to provide deep insight to the adsorption of fluoride ion on *Moringa oleifera* leaves powder.

From Table 5, it is clear that acid treated adsorbent responded good behaviour with all three types of isotherm models but Langmuir's isotherm fitted best with them which is also well explained by the good regression coefficient of 0.97. The Langmuir's model described the monolayer sorption nature of the adsorbent.

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**Table 5** : Langmuir, Freundlich and Temkin equation values for adsorption of fluoride with respect to initial fluoride ion concentration

Adsorbent	Langmuir				Freundlich			Temkin		
	$Q_{max}$ (mg/g)	$R_L$	$K_L$ (L/mg)	$R^2$	$K_f$ (mg/g)	Value of 'n'	$R^2$	B (J/mol)	$A_T$ (L/g)	$R^2$
Acid treated	1.1441	0.003589	138.79	0.971	0.6546	17.543	0.885	-0.042	$1.951 \times 10^{-7}$	0.983

From the Table 5, adsorption of fluoride on the adsorbent have values of linear regression coefficient,  $R^2$  (0.885 ), demonstrating that the experimental data fitted well with the Freundlich isotherm equation. Moreover, it was reported that the Freundlich isotherm constant can be used to explore the favorability of adsorption process. As observed in Table 5, the value of n for the adsorption of fluoride on acid treated *Moringa oleifera* leaves is situated outside the range of 1 - 10 indicating unfavorable adsorption process.

It is well defined from the Table 5, that Temkin isotherm data fitted quiet well. The value of  $R^2$  was 0.897 , which gave a close fit to the adsorption of fluoride on acid treated *Moringa oleifera* leaves powder. Furthermore, it can also be observed in Table 5, B= -0.042 which is an indication of heat of adsorption.

In the present study, the value of  $R_L$  is greater than 0-1 indicating that Langmuir isotherm is favourable. While the value of n is greater than 10 indicating unfavourable adsorption process.

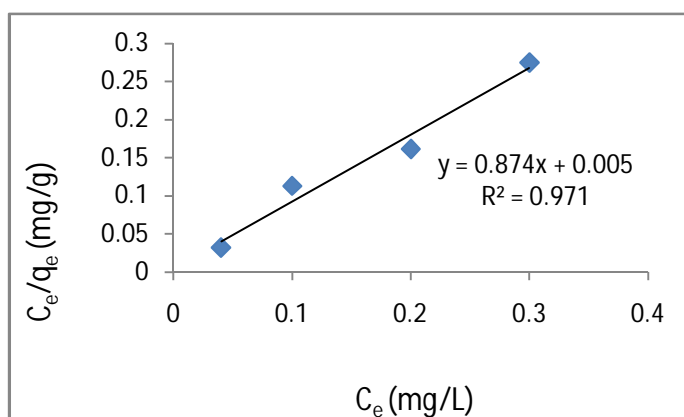


Fig.1(a) Langmuir Isotherm for effect of initial fluoride ion concentration on defluoridation

From Table 5 and Fig 1(a) and by further calculating the values of  $R_L$  for acid treated adsorbents are found to be 0.003589 . The values of  $R_L$  satisfies the following condition  $0 < R_L < 1$  and thus indicates that the adsorption was favourable.

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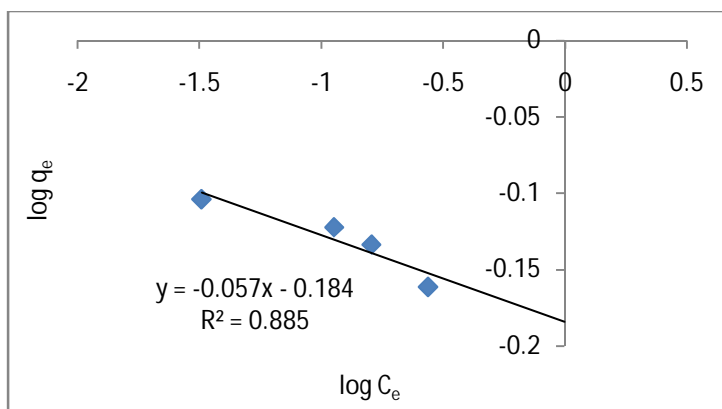


Fig. 2(a) Freundlich Isotherm for effect of initial fluoride ion concentration on defluoridation

From the Figure 2(a), the value of  $\frac{1}{n}$  is 0.057 and further calculating the value of  $K_f$  is 0.6546 As observed in Table 4.8,  $n = 17.54$  for the adsorption of fluoride on acid treated *Moringa oleifera* leaves which is situated outside the range of 1 - 10 indicating unfavorable adsorption process[13] .

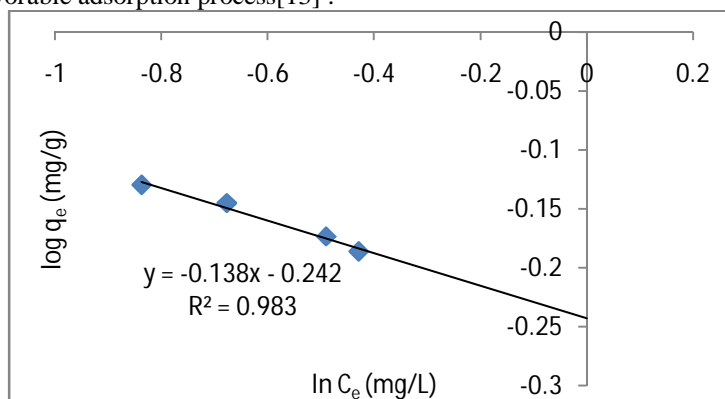


Fig. 3(a) Temkin Isotherm for effect of initial fluoride ion concentration on defluoridation

From Fig. 3(a) it can be observed that the values of  $R^2$  is 0.983, which gave a close fit to the adsorption of fluoride on acid treated *Moringa oleifera* leaves powder. This outcome suggests that the experimental data fitted better with the Temkin isotherm model. Furthermore, it can also be observed in Table 5 that the heat of adsorption of fluoride on acid treated *Moringa oleifera* leaves is  $-59979$  kJ/mol.

Through the adsorption equilibrium study employing Langmuir, Freundlich and Temkin isotherms models, the maximum adsorption capacity was determined where the adsorption of fluoride with acid treated *Moringa oleifera* leaves powder was 1.1441 mg/g .

## V. CONCLUSIONS

The correlation coefficient,  $R^2$  value for the acid treated adsorbent indicated that all three Isotherms (Langmuir, Freundlich and Temkin) showed a good fit to the experimental data. The Langmuir Isotherm was slightly better than Freundlich and Temkin Isotherm. It is concluded by referring to the data obtained that the acid treated *Moringa oleifera* leaves powder was efficient as an adsorbent in removing fluoride from water.



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