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Sorption studies for mitigation of Fluoride by Bio-sorbents using Bio-waste.

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ABSTRACT
Bio-sorption is considered to be one of the favorable remediation techniques for fluoride removal from aqueous solutions. Other conventional techniques such as precipitation, reverse osmosis, ion exchange, nanofiltration etc, have several demerits such as huge initial costs, higher electricity consumption, generation of sludge, etc. The process of Bio-sorption has become an economically feasible and environmentally benign alternative technique in the treatment of water and wastewater industries owing to the disadvantages associated with above-mentioned techniques. In this regard, numerous biosorbents have been developed for their successful implementation on defluoridation. Due to various technical barriers in the Bio-sorption process which hinder its commercialization, there has been a steadily growing interest in this area of research. Of late more attention is being paid towards the development of cost-effective adsorbents using various agricultural wastes, plant biomass, bacteria, algae and fungi. In present study we prepared a biosorbents obtained from Azadirachta indica and zyzipsus mauritiana trees, sorption isotherm, and kinetics our study indicates the potentiality of such wastes as biosorbents for fluoride removal. However, it is important to determine whether these biosorbents could be used on the commercial scale which, in turn, might result in controlling pollution.
***Key Words**: Environment, Clinical manifestations, De-fluoridation Methods, Biosorbents,*

INTRODUCTION
Fluoride is highly toxic than metal and other water soluble salts such as oxalates, carbonate, sulphetes and phosphate, according to world health organization(WHO) recommendations it is ranges between 0.1 - 0.5 ppm. The standards of the United States is between 0.6 -0 .9ppm and of India 1-15ppm [1-3]. thus the requirement of fluoride content varies among countries and depends upon geography and the age of people involved, but the quantity of fluoride in drinking water is always harmful for human beings because the fluoride drinking water change the pH 0.8 of stomach and physiology of digestion so never use fluorinated drinking water, Due to intake fluorinated drinking water , fluoride being commutative bone seeking element the resultant skeletal changes are progressive [4-7]. Fluoride increases the stability of crystal lattice in bone, but makes the bone more brittle. Drinking fluoridated water will double the number of hip fractures. The International Society for Fluoride Research (ISFR) has reported studies implicating fluoride in the rising rates of Down's syndrome, chronic fatigue syndrome and sleep disorder. De-fluoridation is the process of removal of fluoride ion in drinking water. The process may be classified broadly into two categories, namely, i) Additive methods, and ii) Adsorptive methods. The different methods so far tried for the removal of excess fluoride from water can be broadly classified into four categories: A) Adsorption methods, B) Ion exchange methods, C) Precipitation methods, and D) Miscellaneous methods. Some de-fluoridation techniques developed to control fluoride content in water are reverse osmosis, adsorption using sunflower plant dry powder, steam of phytomass, Holly Oke, neem bark powder, activate cotton jute carbon, bagasse ash, burnt bone powder, phosphate-treated saw dust [8-10].

MATERIAL AND METHODS
Test solution of fluoride was prepared from fresh stock solution keeping in view in that the maximum concentration of fluoride reported in groundwater of most of the fluoride affected areas in around 45 mgl-1 (All the experiments were carried out in 250ml conical flasks with 100 ml test solution at room temperature . These flasks, along with test solution and adsorbent, were shaker at 120 rpm to study the various control parameters. At the end of desired contact time, the conical flasks were removed from shaker and allowed to stand for 2 min for settling the adsorbent. Then, samples are filtered using

Whatman no.42 filter paper and the filtrate was analyzed for residual fluoride concentration by SPADNS method, described in the Standard Methods of Examination of Water and Wastewater(APHA,1995).Batch study was conducted to determine the optimum conditions and to study the effect of pH, adsorbent dose and contact time on test on test solution. The effect of pH on fluoride was studied by adjusting the pH of test solution using 0.1 N HCl or 0.1 N NaoH on fixed quantity of adsorbent, while effect of adsorbent dose and contact time were studied by varying dose and contact time, respectively, optimum conditions were selected for further studies. The percentage removal of the fluoride and the amount of fluoride adsorbed were calculated by the following equations.

$$\% \text{ removal} = \frac{(C_i - C_e)}{Ci} \times 100$$

$$\text{Amount adsorbed } (q_e) = \frac{(C_i - C_e)}{Ci} V$$

Where Ci=initial concentration of fluoride solution in mg l -1
Ce= equilibrium concentration of fluoride solution in mg l -1
M= mass of the adsorbent in grams(g)
V= Volume of test solution in liters(l)

Material development
Fresh leaves chosen based on their crude fiber content and tress were obtained from *Azadirachta indica and* zyzipsus *maurtiana* trees.The fresh leaves were dried in hot air oven and crush mechanically.
The powder was sieved to get various particle sizes, viz. 500, 1 mm,and 1.5 mm. Leaf powder biomass was further digested by chemical methods.

Preparation of mixture of Adsorbents
The mixture of adsorbents was prepared by mixing the activated *Azadirachta indica and* zyzipsus leaves carbon according to their efficiency for Fluoride removal. The adsorbents dose which removes maximum Fluorine from standard solution was considered as the most efficient dose, for mixture
Adsorbent preparation, *Azadirachta indica and* zyzipsus leaves adsorbents mixed in two ratios 1:1 and 1:2.

Acid treatment
Leaf biomass powder sample (40 gm) and 400 ml of 1N HNO_3 (nitric acid) were taken in a 1000-ml conical flask. The mixture was gently heated on burner for 20 min after boiling starts. Treated biomass was washed with distilled water. Washing was done until maximum colour was removed and clear water obtained.

Alkali treatment
Leaf biomass powder sample (40 gm) and 400 ml 0.5 N NaOH were taken in 1000-ml conical flask. Then mixture was gently heated on burner for 20 min after boiling started. Using distilled water, the treated biomass was washed which continued until maximum colour was removed and clear water obtained.

RESULTS AND DISCUSSION
Technical studies
Successful application of the adsorption technique demands innovation of cheap, nontoxic, easily and locally available material. Biosorbents meet these requirements. Knowledge of the optimal conditions would herald a better design and modeling process. Thus, the effect of some major parameters like pH, contact, time, amount and particle size of adsorbent and concentration of fluoride ions of the uptake on adsorbent materials was investigated from kinetic viewpoint. Adsorption studies were performed by batch technique to obtain the rate and equilibrium data. Experiments were carried out by shaking 10 g/l of adsorbent dose with 50 ml of aqueous solution containing known concentration of fluoride ions and by agitating the samples on Remi shaking machine at a speed of 120 strokes/min. Samples containing fluoride ions were maintained at a desired pH by adding 0.5 N HNO3 or 0.1M NaOH. All the experiments were conducted at room temperature (25^{0}C).

Effect of pH
The pH of the aqueous solution is a controlling factor in the adsorption process. Thus, the role of hydrogen ion concentration was examined at pH values of 2, 4, 6, 8, and 10. This was adjusted by adding 0.5N HNO_3 or 0.1M NaOH with 50 ml of standard solution of 10 mg/l of fluoride for a contact time of 60 min with a dose of 10 g/l of treated biosorbent The influence of pH on the sorption rate is shown in Fig. 1. We have observed decrease in the extent of removal of fluoride ions with increase in the pH of the solution. This was investigated as 82% at pH 2 and 68 % in the case of treated biosorbents. Hence further

studies were conducted within these pH values. In the case of treated biosorbents, the percentage of adsorption increased almost linearly between 2.0 and 8.0, attaining a maximum removal at pH 2.0 in 60 min of contact time. In this case, the result may be due to neutralization of the negative charges at the surface of the treated biosorbents by greater hydrogen ion concentration at lower pH values. This reduces hindrance to diffusion of the negatively charged fluoride ions on to the increased active surface of treated biosorbents.
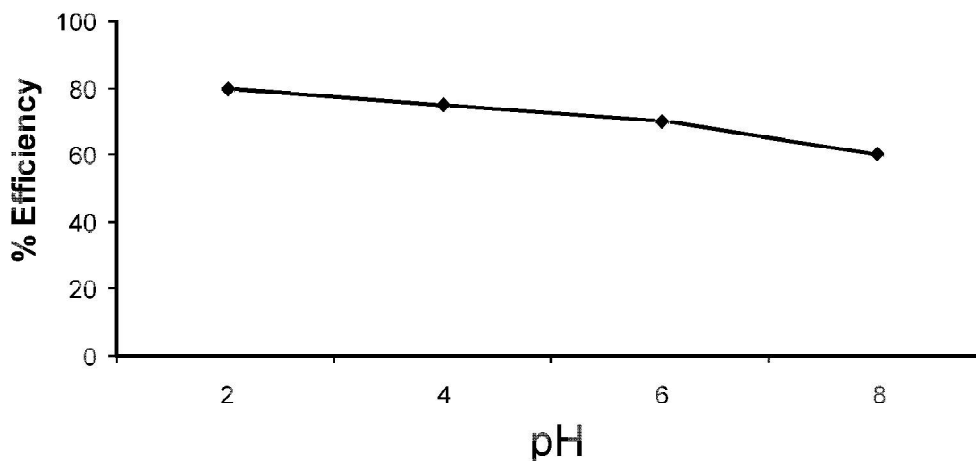
FIG.4.6 Effect of pH on the percentage removal of fluoride ion.

Effect of contact time

It is found that the removal of fluoride ions increases with increase in contact time to some extent. Further increase in contact time does not increase the uptake due to deposition of fluoride ions on the available adsorption sites on adsorbent material. Preliminary investigations on the uptake of fluoride ions on the adsorbent material at their optimum pH values indicate that the processes are quite rapid. Typically, 80% of the adsorption occurs within the first half hour of the contact for fluoride ions with an initial concentration and adsorbent dose of 10 mg/l for treated biosorbents (Fig. 2). This initial rapid adsorption subsequently gives way to a very slow approach to equilibrium and saturation is reached in 1.5 to 3 h. For further optimization of other parameters, this contact time was considered as the equilibrium time.
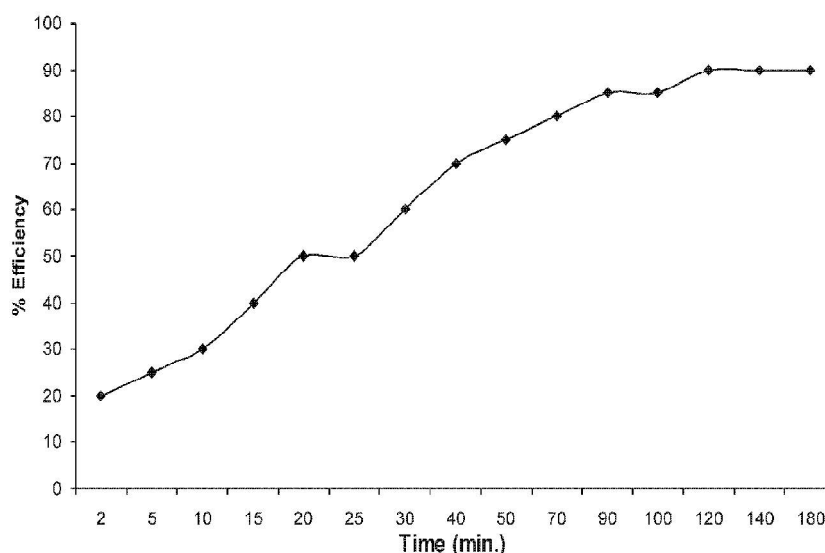

FIG. 4.7. Effect of agitation time on removal of fluoride ion.

Effect of adsorbent dose

From Fig. 3, it is observed that the removal of fluoride ions increases with an increase in the amount of adsorbent. For all these runs, initial fluoride ion concentration was fixed at 10 mg/l. The amount of adsorbent dose was varied between 0.5 and 12 g/l in aqueous solution at their optimal pH values. Results showed that treated biosorbent was efficient for 50% removal of fluoride ions, 55% at 5 g/l and

maximum removal of 85%, and 80% was observed at 12 and 10 g/l, respectively, at a room temperature of 25°C.
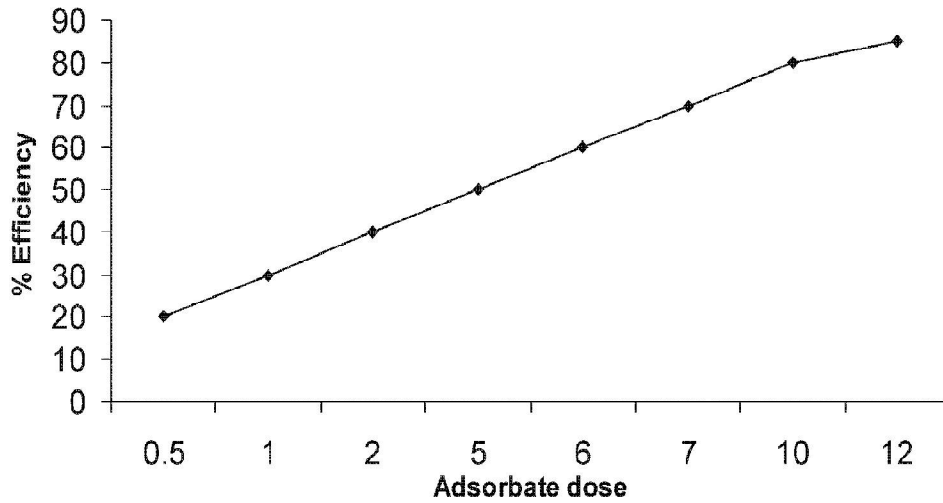

FIG.4.8. Effect of adsorbent dose on the removal of fluoride ion.

Effect of initial adsorbate concentration
For a strictly adsorptive reaction, in the optimized period of contact, the rate varies directly with the concentration of adsorbate. The capacity of the adsorbent materials gets exhausted sharply with increase in initial fluoride ion concentration (Fig. 4). The adsorption capacity of treated biosorbents was systematically studied by varying the initial concentration of fluoride ions between 2 and 15 mg/l. The per cent removal of fluoride ion is a function of initial concentration at different initial pH values.
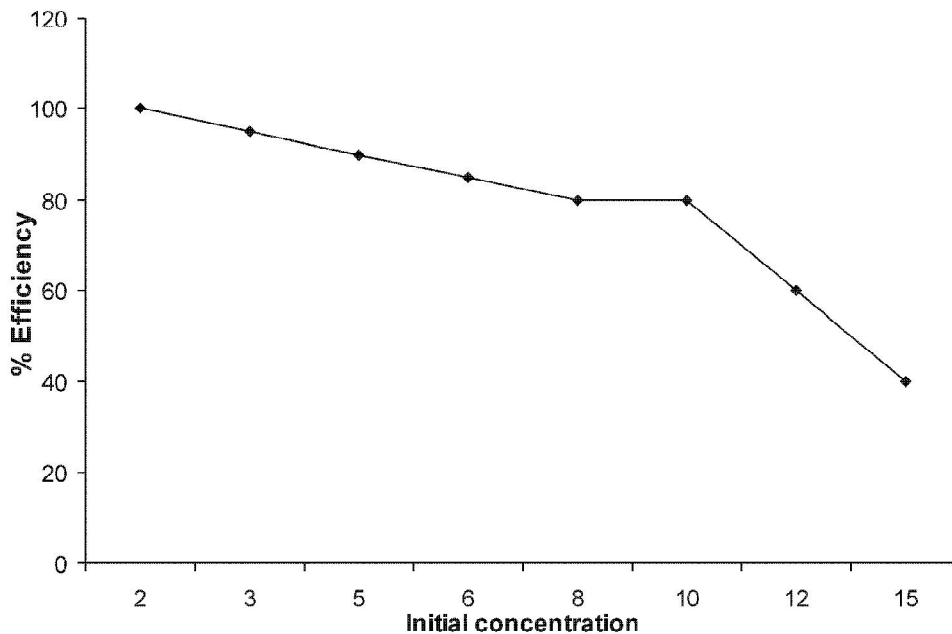

FIG. 4.9 Effect of initial concentration on the removal of fluoride ion

Effect of adsorbent particle size
Experiments were conducted to evaluate the influence of adsorbent particle size for a constant weight on the removal of fluoride ions. Particle size analysis was conducted on treated biosorbents and the percentage composition of particle size was investigated. The results obtained with the variation of adsorbent particle size and the per cent of the fluoride ions are graphically represented in Fig. 5. The uptake of fluoride ions at different adsorbent particle sizes increased with decrease in sorbent particle diameter. The presence of large number of smaller particles provides the sorption system with a larger surface area available for fluoride ion removal and it also reduces the external mass transfer resistance. Also, the time required for 50% of the total adsorption is less with the particles of smaller size. This also

gives some idea of rate-limiting step of the adsorption process. The removal of fluoride ions has been studied at a room temperature of 25°C. With the largest particle size of 1.5 mm the amount of fluoride ions adsorbed was found to be 60 and 50% treated biosorbents, respectively, 90% with smallest particle size of 500 m for an initial fluoride ion concentration of 10 mg/l, respectively. Small particle size provides more active surface area and hence such results were observed.
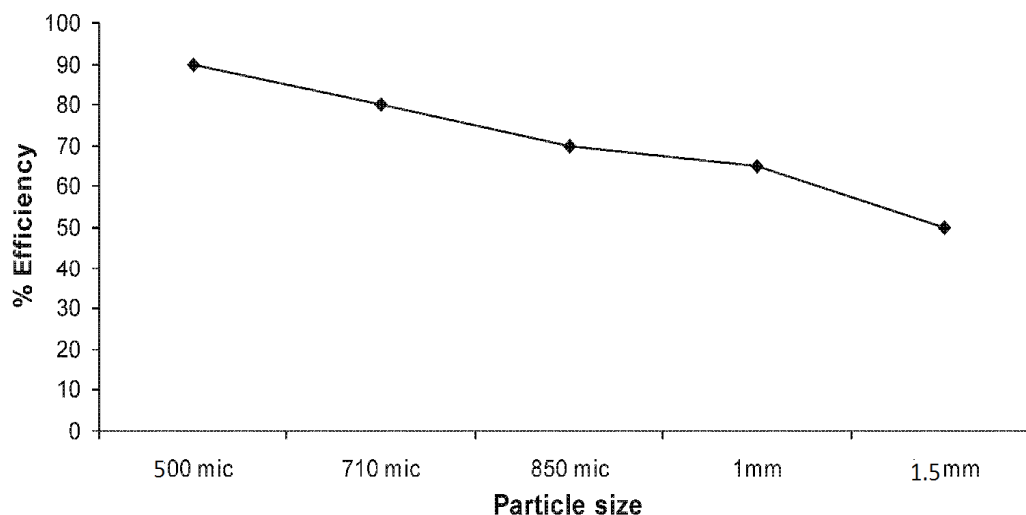

Fig. 5. Effect of particle size on removal of fluoride ion.

Sorption mechanism
The sorption data for the removal of fluoride ions have been correlated with Freundlich and Langmuir models.

Freundlich equation
It has the general form of
$$qe = K_f C^{1/n}$$
The linearised Freundlich adsorption isotherm, which is of the form log (qe) = log Kf + 1/n log Ce,
where qe is the amount of metal ions adsorbed per unit weight of adsorbents (mg g–1), Kf and 1/n are the Freundlich constants, if 1/n < 1, bond energies with surface density, if 1/n > 1, bond energy decreases with surface density and if 1/n = 1 all surface sites are equivalent. Ce is the equilibrium concentration (mg/l). Linear plots of log qe(x/m) vs log Ce at different adsorbent doses are applied to confirm the applicability of Freundlich models as shown in Fig. 6. The calculations for Freundlich model for the removal of fluoride ions are shownin Table I.

Langmuir isotherm
Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, theadsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as
$$qe = QobCe/(1 + bCe),$$
Where qe is the amount adsorbed (mg/g) and
Ce is the equilibrium concentration of adsorbate (mg/l)
Qo and b are the Langmuir constants related to capacity and   energy of adsorption, respectively.
The linear form of the Langmuir isotherm can be expressed as,

$$1/qe = (1/Qo) + (1/bQoCe).$$
When 1/qe is plotted against 1/Ce, a straight line with slope 1/bQo is obtained which shows that the adsorption follows the Langmuir isotherm as shown in Fig. 7. The Langmuir constants b and Qo are calculated from the slope and intercept with Y-axis. The essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor, and describe the type of isotherm defined by,

$$R = 1/(1 + bCo),$$

Where *b* and *Co* are terms appearing in Langmuir isotherm.

From Figs 6 and 7 it is found that the R_2 value for Langmuir model is near to unity and hence the process of defluoridation using treated biosorbents follows the Langmuir isotherm well. Table II gives the calculations of Langmuir model for the removal of fluoride ions and the various constants of this model.

Disposal of exhausted adsorbent materials

It is necessary to separate fluoride ion before its disposal. The exhausted adsorbent materials need to be dried and burned. The resultant product can be used in the manufacturing of bricks. Using various chemicals such as H_2SO_4, HCl, HNO_3, NaOH, EDTA, etc. desorption is possible.

Table1: Calculation of Freundlich isotherm

Dose (mg/1)	*Ce* (mg/1)	*Qe* (mg/mg)	1/*Ce*	1/*qe*
50	8	0.04	0.9031	1.398
100	7	0.03	0.8451	– 1.523
200	6	02	0.7782	–1.699
500	5	0.01	0.699	–2
600	4	0.01	0.6021	–2
700	3	0.01	0.4771	–2
1000	2	0.008	0.301	–2.097
1200	1.5	0.0071	01761	–2.15

Table2: Calculations of Langmuir isotherm

Dose (mg/1)	Ce (mg/1)	Qe (mg/mg)	1/Ce	1/qe
50	8	0.04	0.125	25
100	7	0.03	0.1429	33.333
200	6	0.02	0.1667	50
500	5	0.01	0.2	100
600	4	0.01	0.25	100
700	3	0.01	0.3333	100
1000	2	0.008	0.5	125
1200	1.5	0.0071	0.6667	141.18
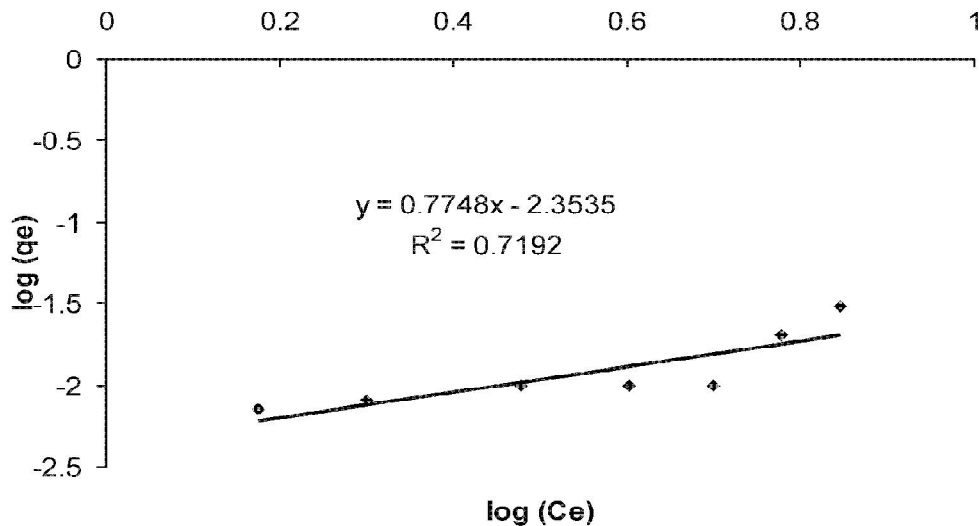
FIG. 6. Linear model of Freundlich isotherm.

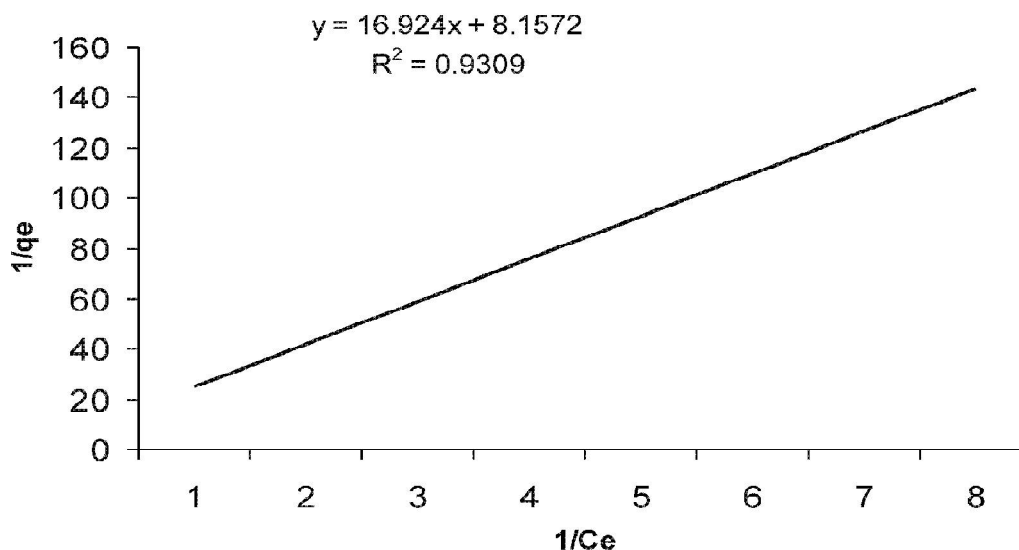$$y = 16.924x + 8.1572$$
$$R^2 = 0.9309$$

FIG. 7. Linear model of Langmuir isotherm

It shows that these low-cost biosorbents could be fruitfully used for the removal of fluoride over a wide range of concentrations. Treated biosorbents were observed to be efficient for the uptake of fluoride ions between 2.0 and 10.0 pH. Fluoride removal for a given bio-adsorbent size increased with time attaining equilibrium within 1.5 h.

In the present study both exercise was repeated with different water samples used for drinking collected from various sites, it was observed that the removal of fluoride was of the same tune as in the case of standard solutions. After removal, all physico-chemical parameters of treated water samples were checked and found in the permissible limits, which lead us to recommend this treated water for drinking and other domestic purposes.

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