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Comparing Fluoride Removal Kinetics of Adsorption Process from Waste Water by using Mosambi Peels (Citrus Limetta Peel)& Neem Leaves (Azadirachta Indica)

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KEYWORDS

Batchwise biosorption experiment; Freundlich's model; Langmuir's Isotherm.

ABSTRACT: Fluoride contamination in groundwater is a critical issue affecting millions globally, leading to health problems such as dental and skeletal fluorosis. Conventional fluoride removal methods, while effective, are often costly and inaccessible in rural and low-resource settings. This paper presents an eco-friendly and cost-effective approach for fluoride removal using neem leaves (Azadirachta indica) and mosambi peels as a natural biosorbent. Neem leaves (Azadirachta indica) and mosambi peels (Citrus limetta peel) readily available in many regions, contain active compounds capable of adsorbing fluoride ions from water. We were performed batchwise experiments for finding the best operating condition for maximum removal of fluoride at different contact times and keeping other parameters to be constant such as initial fluoride concentration, pH and adsorbent dose. For determining the suitable adsorption mechanism, we had investigated various kinetic models such as Langmuir's Isotherm model, intraparticle diffusion model, Freundlich's Isotherm model. The rate of adsorption of fluoride on neem leaves(Azadirachta indica) and mosambi peels (Citrus limetta peel) have been determined by pseudo-first-order and pseudo-second-order rate models. The adsorption kinetics rate and mechanism is best described by the pseudo-second-order model and Freundlich's model, respectively. The result obtained from the experiments show that the neem leaves (Azadirachta indica)and mosambi peels (Citrus limetta peel) have been proved to be a low-cost biosorbent for the defluoridation of the sewage wastewater and have high fluoride removal efficiency.

Introduction

The one-third part of the earth is surrounded by the water. The major portion of the water is not consumable by the living beings. Only 2.5% of the total water available on the earth is freshwater which is present as groundwater and ice. The sources of freshwater are rivers, atmoshphere and lakes which is only 0.3% of freshwater available on earth.

Despite being called a blue planet, earth has shortage of water to sustain life. Water is essential for the living beings. So, we need to save water and use it wisely in the sustainable way for our future [1].

With the rapid growth of industries such as glass, oil refineries, electroplating etc., the amount of pollutant has been also increased. The pollutant contains both organic and inorganic impurities. It is very hazardous for both marine and terrestrial life.

Fluoride is found in the high concentration from the industrial waste water. It is also found in the ground water. It is essential for the living beings up to the limit of 0.5-1.5 mg/l and would not show any adverse effect. Beyond this limit, it shows adverse effect on humans, aquatic life and plants. Above this limit and excess of fluoride can cause severe illness in humans such as skeletal and dental fluorosis. [2].

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So, removal of fluoride is important for the wellbeing of aquatic and terrestrial life. Numerous technologies ate already present for fluoride removal from waste water such as dialysis, membrane technologies, coagulation, adsorption etc. In these technologies, adsorption is the simplest, economical method due to its high percentage removal of fluoride. [3].

Due to the availability and low cost we choose mosambi peels (Citrus limetta peel) and neem leaves (Azadirachta indica) for the biosorbent. We will optimize various parameters such as dose, pH, etc. for the kinetic study of various models.

Methods

In this study, we collected two biosorbents mosambi peels (Citrus limetta peel) and neem leaves (Azadirachta indica) from Konchabhanwar, Jhansi, Uttar Pradesh, India. We had chosen them because of their availability, cost efficient and natural biosorbent. After that, we wash it first with tap water and then distilled water to remove dirt on them at mass transfer lab, Chemical Engineering Department, Bundelkhand Institute of Engineering and Technology, Jhansi, Uttar Pradesh, India. After that, we dried it in a hot air oven at 105-115 degree Celsius for a day after which in jaw crusher dried material is crushed and screened in 50 micro meter mesh ASTM at mechanical operation lab, Chemical Engineering Department, Bundelkhand Institute of Engineering and Technology, Jhansi, Uttar Pradesh.

Preparation of stock solution

The 100 mg/L fluoride stock solution was prepared by mixing 0.221 g of anhydrous sodium fluoride in 1 L of millipore water. The 20 mg/L fluoride concentration test solution was prepared from stock solution which is the normal fluoride concentration in industrial waste water. All the experiments were carried out in 250 ml round bottom flasks, with 50 ml test solution in a conical flask at 29±1°C in horizontal incubator shaker. At the end of desired contact time, the conical flask was removed from the shaker. Subsequently, samples were filtered using Whatman no. 42 filter paper and filtrate was analyzed for residual fluoride concentration by SPADNS method, described in the standard method of examination of wastewater and water [4]. Fig. 1 shows various reactions involved in the SPANDS method for estimation of fluoride.

Reactions involved in the SPADNS method for estimation of fluoride

Recipe for SPADNS solution:

$$\frac{Mg\ of\ Fluoride}{Litre} = \frac{A}{Sample(mL)} \times \frac{B}{C}$$

Where,

A represents fluoride obtained by curve (mg)

B represents diluted sample final volume (ml)

C represents diluted sample volume worn for development of color.

$$\frac{Mg\ of\ Fluoride}{Litre} = \frac{A0 - As}{A0 - A1}$$

Where:

A_0 represents absorbance at zero fluoride concentration

A_1 represents absorbance at fluoride concentration of 1 mg/L

A_x represents absordance of the sample prepared

RESULTS AND DISCUSSIONS

PH Optimization

In this section, we discussed the effect of PH on percentage of fluoride removal. To understand this better a graph has been plotted between PH and percentage of fluoride removal which is shown in Fig.1. From the

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graph, there is clear indication that with increase in time, there is an increase in percentage of fluoride removal by these biosorbents in starting phase but once they reach equilibrium it remains more or less constant. In a study by other researchers, similar trend was observed when they used protonated chitosan beads [5]. When Biosorbents reach saturation, that pH is called their optimum PH. For mosambi peel (Citrus limetta peel) and neem leaves (Azadirachta indica) optimum pH was noted to be 4 and 5, respectively.

Dose Optimization

In this section, we discussed the effect of dose on adsorption capacity. To understand this better a graph has been plotted between contact time and adsorption capacity which is shown in Fig. 2. From the graph, there is clear indication that with increase in time, there is an increase in adsorption by these biosorbents in starting phase but once they reach equilibrium it remains more or less constant. In a study by other researchers, similar trend was observed when they used protonated chitosan beads [5]. When Biosorbents reach saturation, that dose is called their optimum dose. For mosambi peel (Citrus limetta peel) and neem leaves (Azadirachta indica) optimum dose was noted to be 0.5g/50mL and 0.6g/50mL +respectively.

Adsorption kinetics

To determine best kinetic model, we do use squared sum of errors (SSE) values. It is assumed that model which provides the lowest value of SSE is best model for that system [5,6]. To calculate SSE values, the following formula were used:

$$SSE = \sum(qe_{expt} - qe_{ca}l\ )^2 /(\ qe_{expt})^2$$

Where: $q_{e(expt)}$ and $q_{e(cal)}$ denotes the experimental sorption capacity of fluoride (mg/g) at equilibrium time and the corresponding value that were obtained from the kinetic models. In this study five simplified kinetic models namely Langmuir's Isotherm model , Weber and Morris intraparticle diffusion model, Freundlich's pore diffusion model, and the pseudo first and second order equations have been discussed to identify the rate and kinetics of sorption of fluoride onto mosambi peels (Citrus limetta peel)and neem leaves (Azadirachta indica).

Langmuir's Isotherm

The adsorption isotherm of fluoride could be expressed as Langmuir isotherms. The Langmuir isotherm equation is written as:
$C/q=1/Kb\ As + C/As$ (21)

where C is the fluoride equilibrium concentration, the parameters Kb and As are the adsorption binding constant (1/mmol) and saturation capacity (mmol fluoride/g dry wt.), respectively. [21].

Weber and morris intra-particle diffusion model

Rate of sorption is frequently used to analyze nature of the "rate controlling step," and the use of the intra-particle diffusion model has been greatly explored in this regard which is represented by the following Weber and Morris equation [10].

$$qt = k_{ip} * t^{0.5} + C$$

Where, C is the intercept, determined by the thickness of the boundary layer and kip is the intra-particle diffusion rate constant. According to this model, if adsorption of a solute is controlled by the intra-particle diffusion process, a plot of qt versus $t^{0.5}$ gives a straight line. Weber and Morris plots of q_t versus $t^{0.5}$ are shown in Fig. 4a and b for, mosambi peel (Citrus limetta peel)and neem leaves (Azadirachta indica) respectively. It is evident from the plots that there are two separate stages; first linear portion (Stage I) and second curved path followed by a plateau (Stage II). In Stage I, nearly 50% of fluoride was rapidly taken up by biosorbents within 5 minutes. This is attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surfaces. In Stage II, very slow diffusion of adsorbate from surface site into the inner pores is observed. Thus, initial portion of fluoride adsorption by carbon adsorbents may be governed by the initial intra-particle transport of fluoride controlled by surface diffusion process and later part is controlled by pore diffusion. Similar dual nature with linear and then plateau were found in the literature [11].

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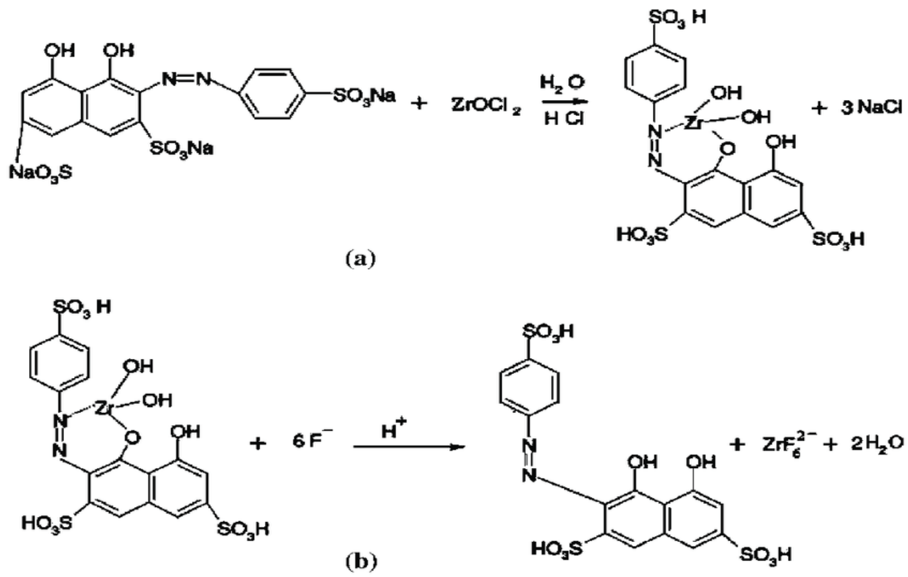

Fig. 1: (a) Formation of the SPADNS – ZrOCl2 complex.

(b) Reaction of the complex with fluoride ions

Although intra-particle diffusion renders straight lines with correlation coefficient more than 0.98 for both the biosorbents, the intercept of the line fails to pass through the origin in each case. This can be explained by difference in the rate of mass transfer in the initial and final stages of adsorption [12] and indicates some degree of boundary layer control which implies that intra-particle diffusion is not only rate controlling step [13]. The data were further used to learn about the slow step occurring in the present adsorption system using pore diffusion model.

Table 2 shows various parameters obtained by applying Weber and Morris intra-particle diffusion model to obtained data.

Freundlich's Isotherm

The Freundlich isotherm equation is written as: q=kC1/n (3) where C is equilibrium concentration, k is the saturation capacity (mmol fluoride/g dry wt. of red mud) and n is an empirical parameter. The experimental data were fitted to both Freundlich and Langmuir isotherm equations, shown in the Table 1 and Table 3 respectively. [21].

Pseudo first order model

The Lagergren's rate equation is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase [10,13]. The linear form of pseudo first-order rate expression of Lagergren is given as follows:

$$Log(qe - qt) = log\, log\, (qe) - \frac{k1t}{2.303}$$

where:

q_e - Amounts of fluoride adsorbed on adsorbent (mg/g) at equilibrium

q_t - Amounts of fluoride adsorbed on adsorbent (mg/g) at time t (min)

k_1 - Rate constant of pseudo first-order kinetics.

Fig. 6 shows the plots of linearized form of pseudo first-order kinetic model for the two biosorbents. The plots were found linear with good correlation coefficients (>0.9) indicating the applicability of pseudo first-order model in this study. The pseudo first-order rate constant (k1) and qe(cal.) values were determined for each adsorbent from the slope and the intercept of corresponding plot and are listed in Table 4.

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Pseudo second order model

The adsorption kinetics was also described as pseudo-second order process using the following equation [15],

Table 1: Various parameters obtained for different biosorbents

Name of adsorbent	Langmuir Isotherm		
	q_m	b	R^2
Mosambi Peel (Citrus limetta peel)	3.0395	1.3595	0.9884
Neem Leaves (Azadirachta indica)	2.375	1.6068	0.9941

SSE : Squared sum of errors

Table 2: Various parameters obtained for different biosorbents

Name of adsorbent	Intra particle diffusion	
	k_{id} (mg/g.min$^{-0.5}$)	R^2
Mosambi Peel (Citrus limetta peel)	0.027	0.9366
Neem Leaves (Azadirachta indica)	0.027	0.9941

SSE: Squared sum of errors

Table 3: Various parameters obtained for different biosorbents

Name of adsorbent	Freundlich Isotherm		
	n	kf	R^2
Mosambi Peel (Citrus limetta peel)	2.584	1.607	0.997
Neem Leaves (Azadirachta indica)	2.75	1.33	0.9409

SSE: Squared sum of errors

Table 4: Various parameters obtained for different biosorbents

Name of adsorbent	Pseudo first order			
	k_1 (1/min)	$q_{e(expt)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	R^2
Mosambi Peel (Citrus limetta peel)	.0599	1.925	.20511	0.981
Neem Leaves (Azadirachta indica)	.078	1.532	0.1999	.9294

SSE: Squared sum of errors

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Table 5: Various parameters obtained for different biosorbents

Name of adsorbent	Pseudo second order			
	k_2(1/min)	$q_{e(expt)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	R^2
Mosambi Peel (Citrus limetta peel)	0.67382	1.952	1.942	0.999
Neem Leaves (Azadirachta indica)	0.9903	1.532	1.54	0.9997

SSE: Squared sum of errors

$$q = \frac{1}{K2qe2} + \frac{1}{qe}$$

q_e - Amounts of fluoride adsorbed on adsorbent (mg/g) at equilibrium

q_t - Amounts of fluoride adsorbed on adsorbent (mg/g) at time t (min)

k_2 - Rate constant of pseudo second-order kinetics.

The plots of t/qt versus t for the two adsorbents are shown in Fig. 7. The values of qe(cal.) and k2 were determined for each adsorbent from the slope and intercept of the corresponding plot and are compiled in Table 5.

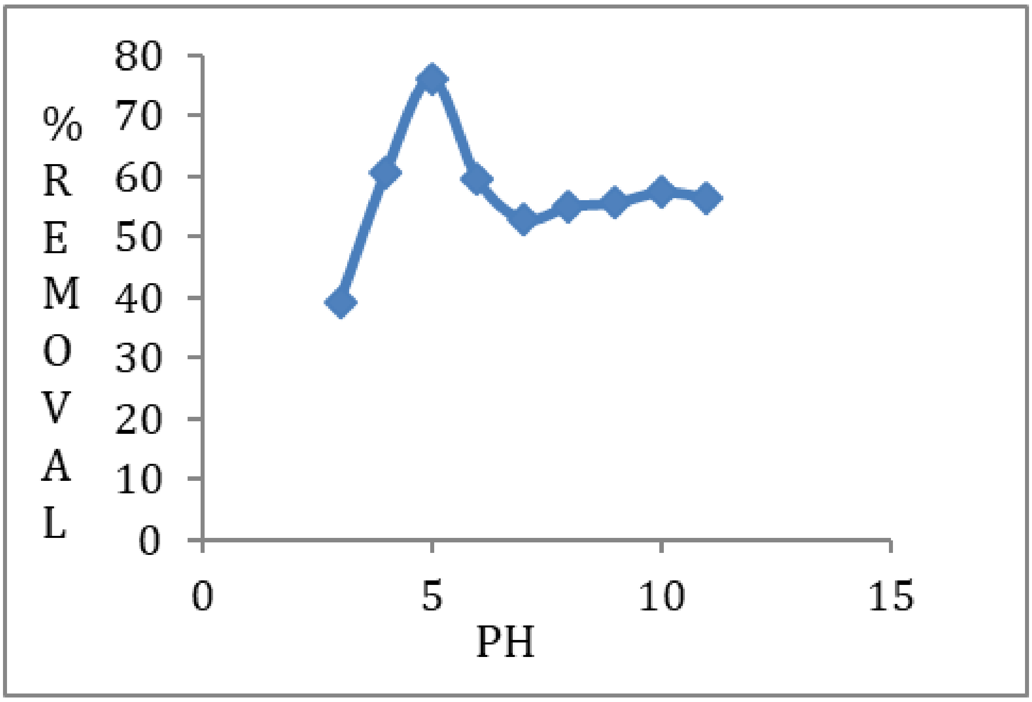

Fig.1 (a) Adsorption for neem leaves (Azadirachta indica)

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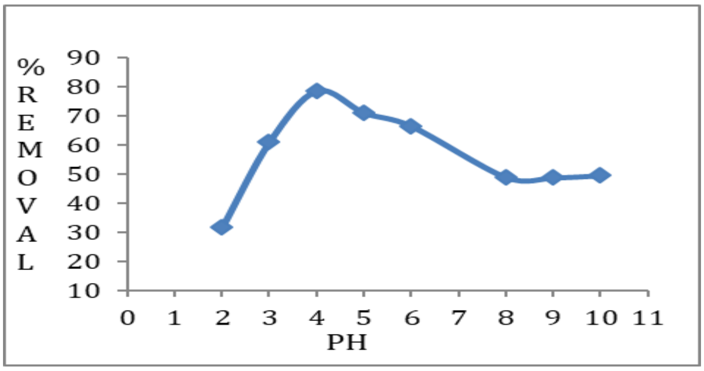
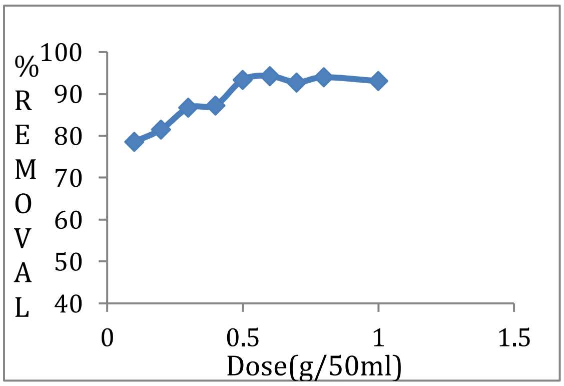


Fig.1 (b) Adsorption for Mosambi peel (Citrus limetta peel)

Fig.1(a), Fig.1(b) Effect of pH on adsorption of fluoride on neem leaves (Azadirachta indica) and mosambi peel (Citrus limetta peel)respectively.



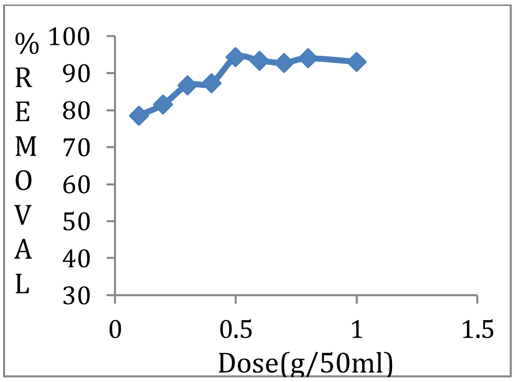
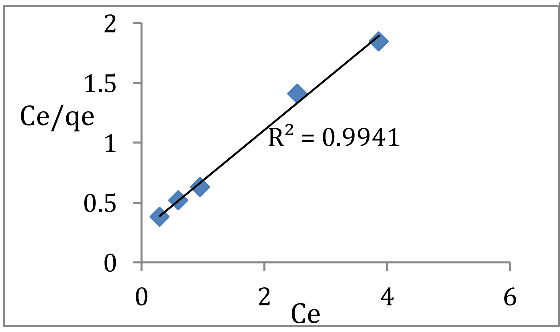


Fig.2 (a) Adsorption for Neem leaves (Azadirachta indica) **Fig.2(b) Adsorption for Mosambi peels(Citrus limetta peel)**

Fig.2(a), Fig.2(b) Effect of Dose(g/50mL) on adsorption of fluoride on neem leaves (Azadirachta indica) and mosambi peel (Citrus limetta peel)respectively



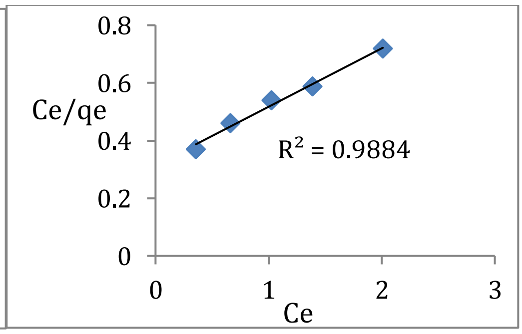


Fig.3 (a) Adsorption for Neem leaves (Azadirachta indica) Fig.3(b) Adsorption for Mosambi peel (Citrus limetta peel)

Fig.3(a), Fig.3(b) Langmuir's Isotherm Model on adsorption of fluoride on neem leaves (Azadirachta indica) and mosambi peel (Citrus limetta peel)respectively.

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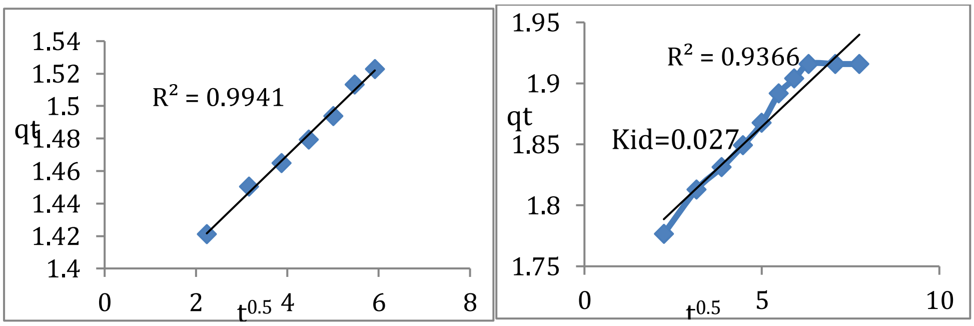

Fig.4 (a) Adsorption for Neem leaves (Azadirachta indica) Fig.4(b) Adsorption for Mosambi peel (Citrus limetta peel)

Fig.4(a), Fig.4(b) Intra Particle Diffusion Model on adsorption of fluoride on neem leaves (Azadirachta indica) and mosambi peel (Citrus limetta peel)respectively.

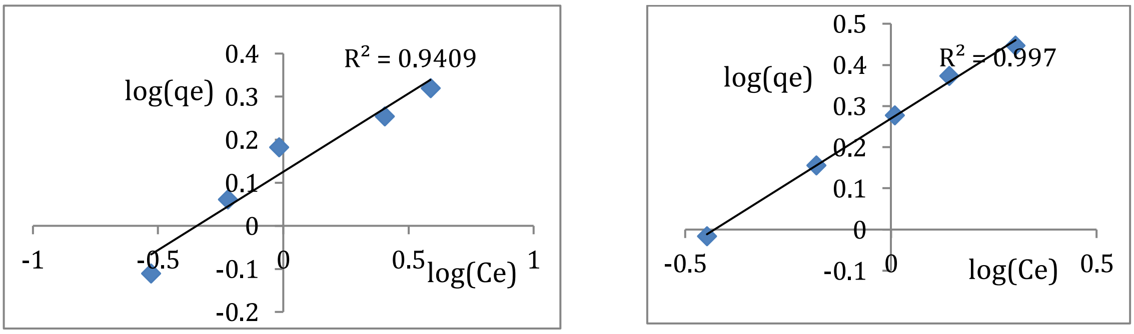

Fig.5(a) Adsorption for Neem leaves (Azadirachta indica)Fig.5(b) Adsorption for Mosambi peel (Citrus limetta peel)

Fig.5(a), Fig.5(b) Freundlich's Isotherm Model on adsorption of fluoride on neem leaves (Azadirachta indica) and mosambi peel (Citrus limetta peel)respectively.

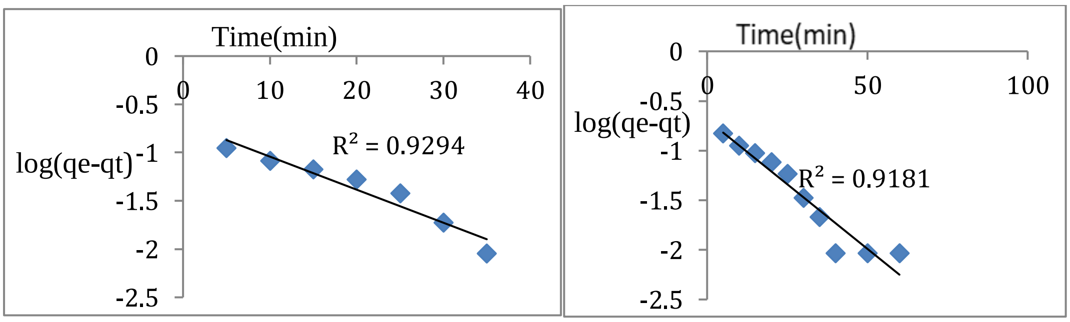

Fig.6(a) Adsorption for Neem leaves(Azadirachta indica)Fig.6(b) Adsorption for Mosambi peel (Citrus limetta peel)Fig.6(a), Fig.6(b) First Order Model on adsorption of fluoride on neem leaves and mosambi peel (Citrus limetta peel) respectively.

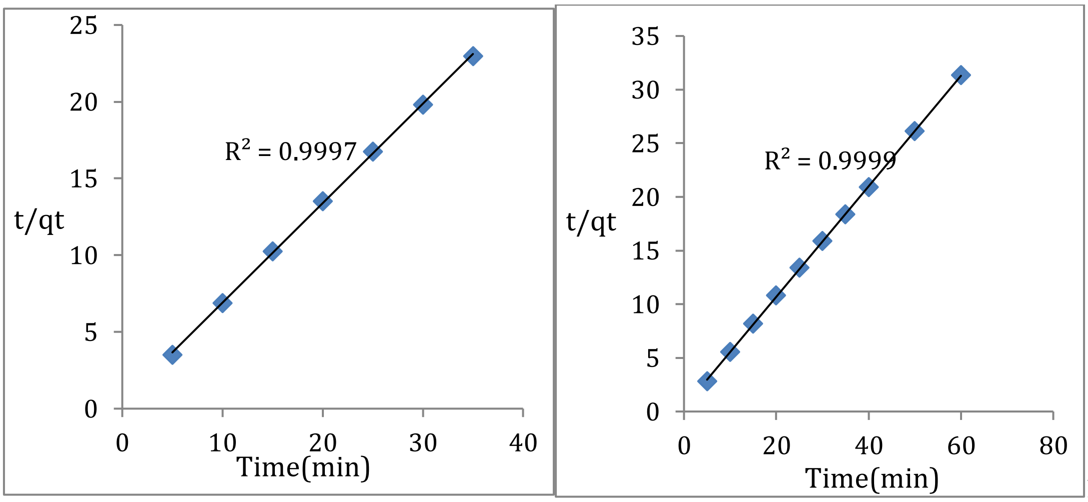

Fig.7(a) Adsorption for Neem leaves (Azadirachta indica) Fig.7(b) Adsorption for Mosambi peel (Citrus limetta peel)Fig.7(a), Fig.7(b) Second Order Model on adsorption of fluoride on neem leaves (Azadirachta indica) and mosambi peel (Citrus limetta peel)respectively.

Conclusion

In this investigation, we found that neem leaves (Azadirachta indica) and mosambi peel (Citrus limetta peel) have the high potential to remove fluoride from waste water. The dynamics of adsorption is best explained by second order model having high correlation coefficients (0.9999 & 0.9997) for mosambi peel (Citrus limetta peel)and neem leaves (Azadirachta indica) respectively. The kinetic data was best fitted with Langmuir's Isotherm model with good correlation coefficient (0.9941) for neem leaves (Azadirachta indica) & Freundlich's Isotherm model with good correlation coefficient (0.997) for mosambi peels (Citrus limetta peel)which shows that the mechanism of adsorption is controlled by pore diffusion process. It was also found that percentage of fluoride removal from waste water for neem leaves (Azadirachta indica) was optimum at 5 pH scale, dose (0.6 mg/50mL) where its removal percentage was maximum at 76.11 and 94.27 respectively. Similarly for mosambi peels (Citrus limetta peel) the parameter were optimum at 4 pH scale, dose (0.5 mg/50mL) where its removal percentage was maximum at 78.54 and 94.27 respectively. We can conclude that removal efficiency of mosambi peel (Citrus limetta peel)is higher than the neem leaves (Azadirachta indica) as biosorbent. Both neem leaves (Azadirachta indica) and mosambi peels (Citrus limetta peel)are economical, feasible, environment friendly and can seem as a viable option for a future scope.

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