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Characterization and Preparation of *Artocarpus heterophyllus* bark powder and use as an adsorbent for Removal of Fluoride Ions from ground water

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ABSTRACT

Artocarpus heterophyllus bark powder was applied for the expulsion of Fluoride Ions from groundwater. Influence of pH, contact time, the dosage of adsorbent, temperature and the effect of initial concentration on the adsorption process was examined. The highest fluoride ion removal was at the range of pH of 6. Various researchers are using Freundlich and Langmuir isotherms for expulsion of fluoride Ions. The study concludes that the sufficient time for adsorption equilibrium of fluoride ion was 3 hours. *Artocarpus heterophyllus* characterization is done by using FTIR, XRD, and SEM.

Key words : *Artocarpus heterophyllus, XRD, Isotherms, Adsorption.*

Introduction

Water is a necessary natural resource for living beings. In India, more than 80 percent of the population lives in rural region. The ground water is utilized for Industrial and household purposes in the rural region (Punia *et al.,* 2018). The largest part of the population in India is dependent on ground water for drinking purpose. In ground water, fluoride enters though infiltration of fertilizers in agricultural areas, sewage treatment discharge and liquid waste from industries (Maheshwari *et al.,* 2006). Pure water is limited and is not simply accessible at all. In spite of, over the few years, unskilled consumption of water resources have degrades the water quality (Meenakshi *et al.,* 2006).

Fluoride

Fluorine is the 13th richest element on globe. The most important anthropogenic sources of fluoride is fertilizers, combusted coal and industrial waste (Farooqi *et al.,* 2008). Fluorine is maybe a necessary element for living organisms. A large population (200 million) in the world is affected by dental fluorosis (Mohan *et al.,* 2012). According to various authorities is the safe range of fluoride ion in drinking water is 1 mg/L (Ranjit *et al.,* 2015).

Recently the quality of ground water is badly affected in such a way that any person not uses water directly without proper treatment. That's why eco-friendly techniques have been used for the treatment of polluted water. Some researchers used solvent extraction, membrane filtration, chemical precipitation, and reverse osmosis, etc. techniques for

the treatment of water (Namasivayam *et al.,* 2010).

As compared to other techniques, adsorption is good purification technique because of its low cost, high efficiency. Now a days, a variety of low-cost adsorbents like orange residue, tea waste, rice husk, and coconut shells etc. has been derived from agricultural waste or natural materials (Dhakal *et al.,* 2005) and (Demirbas *et al.,* 2008). In the batch process, fluoride absorption was carried out; in this it measure various experimental factors which include pH, initial fluoride concentrations, adsorbent concentrations, temperatures. The batch process of Fluoride adsorption depends on pH. Various researcher use various model like Langmuir and Freundlich for fluoride removal all these are fitted at different temperature. In my research work Langmuir isotherm gave more accurate result for fluoride removal than Freundlich isotherm. It is observed that the adsorption process follow a pseudo-second-order kinetic model (Dutta *et al.,* 2012). Adsorption study is used by many researchers for successfully removal of fluoride from ground water. Various bio-adsorbents were examined for the expulsion of harmful complexes, which are used for drinking as well as industrial purposes. In my research work, *Artocarpus heterophyllus* (jack fruit) Tree Bark powder is used because of its low cost and easily availability. The main objective of my research work is to remove the harmful substance from ground water to make it suitable.

Experimental Methods

Adsorbent Preparation Process

The bark of *Artocarpus heterophyllus* (jack fruit tree) were collected from the Bhiwani District, Haryana State, India, and after that washed with tap water and after that washed with distilled water so that all the dust will be remove after that dried the jackfruit bark under sun for 3-5 days. After drying under sun the bark are again dried under a temperature of 105 ºC for at least 6 hours. The dried bark was grind of size near about 150 nm. Finally, the final material was stored in air tight plastic box for experimentation purpose.

Adsorbate Solution

Fluoride stock solution was prepared by dissolving 2.21 g of sodium fluoride (anhydrous) of Analytical rank in l thousand ml of double distilled water in high accuracy flask. The primary range of fluoride ion is 5.0 mg/l which is used for experimentation in laboratory (Ranjit *et al.,* 2016). The quantity of Test solution is 100 ml which is placed in 250 ml beaker. The pH of test solution was set with the help of 0.1 N Hydrochloric acid (HCL) or 0.1 N sodium hydroxide (NaOH) solutions (Poudyal *et al.,* 2015).

Plant Description

Bark of Jackfruit (*Artocarpus heterophyllus*) is a low cost adsorbent. This tree is easy available in Sonipat of Haryana (Fig. 1) The bark of the jackfruit tree is smooth and reddish-brown in color. In India, the jackfruit wood is used for house construction. The jackfruit tree wood is also used for making musical devices. The national fruit of Bangladesh is Jackfruit (Thakre *et al.,* 2015).

Fig. 1. Jackfruit on the tree showing the tree bark

Batch adsorption

For this purpose analytical reagent grade chemical were used. The beaker was rinsed with nitric acid solution and after this distilled water will be used for washing purpose. In the first step, a 100 mg F/L working solutions were prepared from the stock solution. For adjusting the pH values sulphuric acid and sodium hydroxide (0.1 N both) were used. F^- ions with dissimilar initial concentrations (5 ppm) and pH 6.0 were used for batch adsorption process and effect on adsorption capability with difference in several process parameters like as pH (2–10), temperature (30–60 °C), contact time (30–210 min) and adsorbent quantity (1-5g) was also investigated. 0.1N HCl and 0.1N NaOH solutions was used for adjusting the pH.

The sample was stirred at 100 rpm and 30 °C ± 5 °C on a stirrer for 180 minutes. The absorbance of a solution was measured at the resultant wave-

length to highest absorbance of the metal solution. The experimental work is carried out 3 times and after that the mean value is calculated. The following equation is obtained for using Adsorption capacity and percentage removal:

$$qe = (C_i — C_e)\ V/m \quad .. (1)$$

$$\% \text{ Removal} = (C_i - C_f)/C_i \times 100 \quad .. (2)$$

where C_i – initial Fluoride range[mg/L]; C_e – F^- Range at equilibrium state [mg/l], m[g] – w/t of Jackfruit bark powder, V – volume of solutions [100 ml], C_f – final concentrations of fluoride [mg/l]

Results and Discussion

Characterization of jackfruit bark powder

XRD Analysis

XRD of Artocarpus heterophyllus (Jackfruit) bark is used to see the changes in the structure of the Jackfruit. From past times XRD analysis was one of the most suitable techniques in the field of crystal study research and characteristics of materials (Waghmare *et al.*, 2015). The below Figures 2 represents XRD patterns of adsorption of fluoride ions in case of *Artocarpus heterophyllus* (Jackfruit) bark processing.

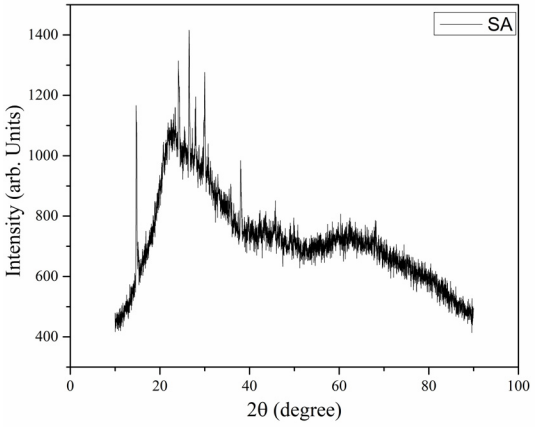


Fig. 2. XRD Analysis graph

FTIR

For the study of functional group FTIR absorption spectra is the most suitable technique. The analysis of extracted jackfruit bark powder was done from 4000 to 500 cm^{-1} which is represented in figure.

The FT-IR spectrum graphs represent the absorption values at following peaks:

- The peaks which are around 1038 cm^{-1} represents the =C-OH (stretching) vibrations.
- The peaks at 1440 and 629 cm^{-1} represents the symmetric bending of CH3 and C-O stretching of ether groups.
- The peak on 2927 cm^{-1} represents the aliphatic stretching vibration of –CH groups.
- The peak on 3843 cm^{-1} and 3742 cm^{-1} shows vibration of –OH groups.
- The peaks which is nearly equal 1613 cm^{-1} shows the C=O stretching of carboxylic acid with intermolecular hydrogen bond.

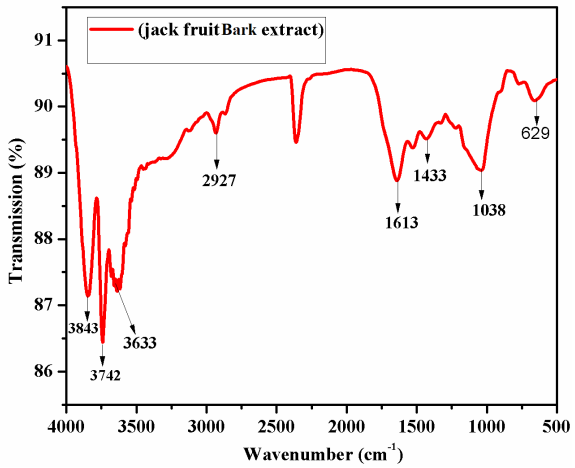


Fig. 3(a). FTIR spectra of the jackfruit

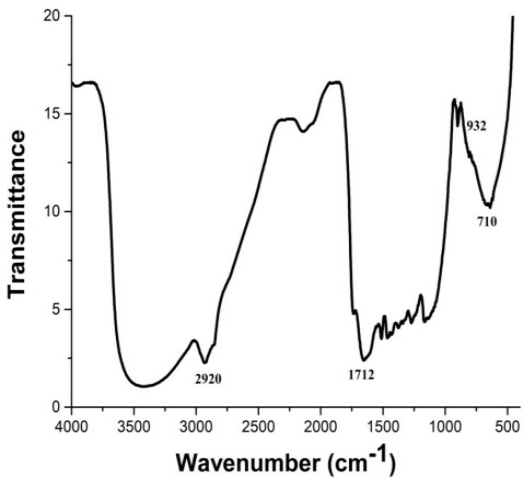


Fig. 3(b). FTIR spectra of the jackfruit bark powder after adsorption

Scanning Electron Microscopy (SEM)

The morphological structure of the JBP (Jackfruit bark powder) materials was obtained by using scanning electron micrograph (JEOL 6380, Japan). To in-

vestigate the effect of degradation methodology, surface morphology before adsorption and after adsorption were recorded as shown in Fig. 4 and these are obtained from natural *Artocarpus heterophyllus* (Jackfruit) bark. The material which we are getting have porous surface. Scanning Electron Microscopy images represent porous morphology of *Artocarpus heterophyllus* (Jackfruit) and have unsmooth surface. These may contribute to the relatively high surface area of *Artocarpus heterophyllus* (Jackfruit). The study suggests that these pores represent the active sites for adsorption of contaminants from ground water (Kannan *et al.,* 2010).

Effect of Solution pH

With the increase in pH value (ranging from 2-12) there is removal of fluoride by jackfruit bark powder as shown by graph 5. Fluoride pH value decrease from 6 to 12. The efficiency of fluoride removal increase with increase in pH value 6 for a most favorable dose of 1 g, and after that there is decrease in efficiency because accumulation takes place in the adsorption sites in the process. At pH value 6, maximum adsorption was obtained.

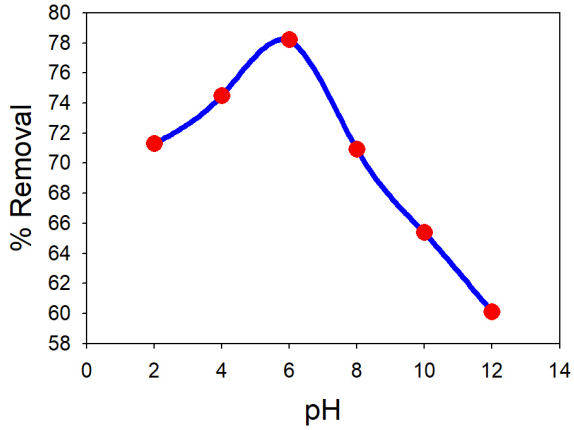


Fig. 5. pH effect on fluoride adsorption by jackfruit bark

Effect of Contact time

To examine the effect of contact time for expulsion of Fluoride jackfruit bark powder is used. This graph shows in how much percentage fluoride is removed, when we are changing contact times. This graph shows as contact time increases, initially there is increase in removal and after that as the time pass on its percentage value will decrease and after that after 180 minutes it attains a best balancing condition remains more or less constant thereafter. The highest value obtained by jackfruit powder is 78.2 percentages, within duration of 3 hour.

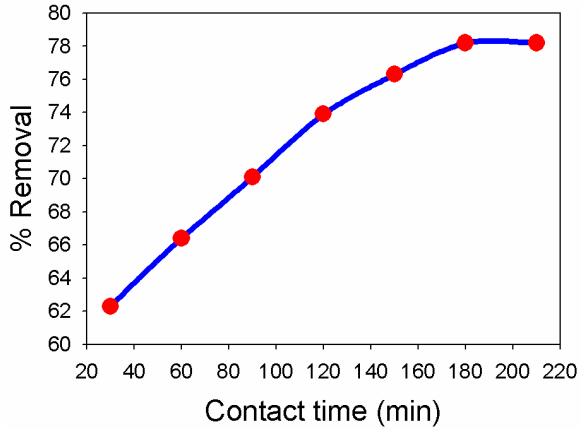
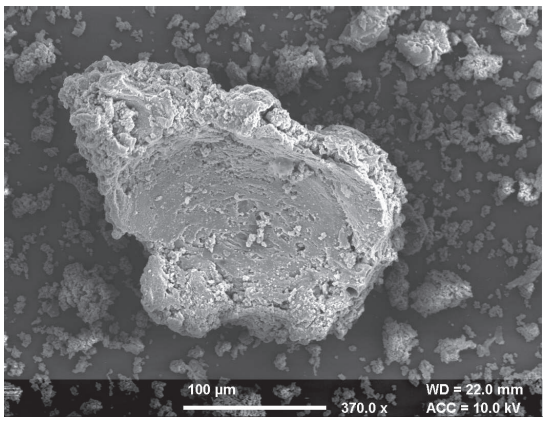
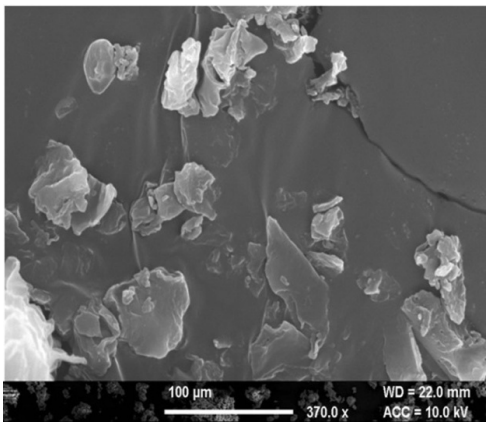


Fig. 6. Effect of agitation time on fluoride adsorption by jackfruit bark



SEM picture of jackfruit bark powder



SEM picture of jackfruit bark after adsorption

Fig. 4. SEM picture of jackfruit bark powder before and after adsorption

Effect of adsorbent Dose

Figure 7 represents the output of equilibrium adsorption process which consist a test fluoride sample of range 1.5 mg/l. As there is increase in dose the absorbed fluoride amount also got increase and by using 1g dose 78.2 % can be removed. When we take dose more than 5g then less % of fluoride is removed it may be due to the non absorbing nature of fluoride ions.

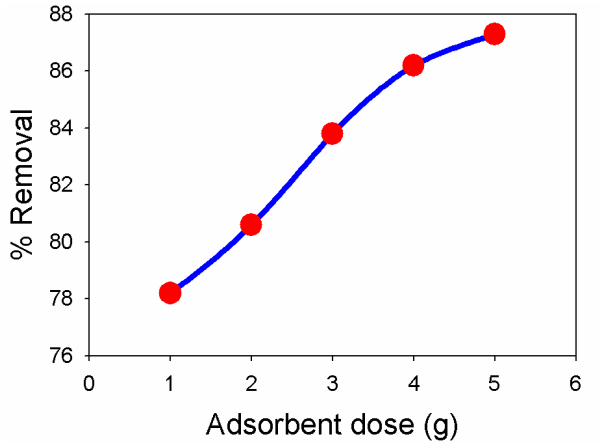


Fig. 7. Effect of sorbent dosage on fluoride adsorption by jackfruit bark

Effect of initial Fluoride concentration

Below Figure 8 represents the graph between fluoride removal efficiency and fluoride range. For adsorptive reaction, the rate changes directly with the fluoride concentration for a particular time interval. As initially fluoride concentration increase the capacity of adsorbent material concentration decrease. All the experiment is experienced by changing the initial concentration of fluoride (1.5-3.5 mg/l).

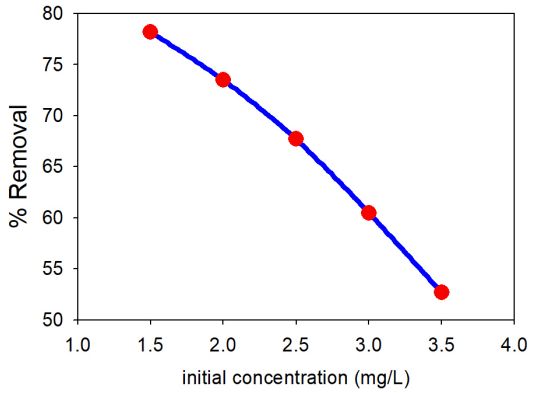


Fig. 8. Effect of initial conc. on fluoride adsorption onto jackfruit bark

Effect of Temperature on fluoride adsorption onto jackfruit bark

To study the effect of temperature on the fluoride removal efficiency, adsorption experiments were conducted at four temperatures (30, 40, 50, 60 °C). The corresponding plot of fluoride removal efficiency versus temperatures is shown in Figure 9. From the above figures we can be observed that fluoride removal efficiency increase with increasing the temperature. This indicates that adsorption is favored at higher temperature.

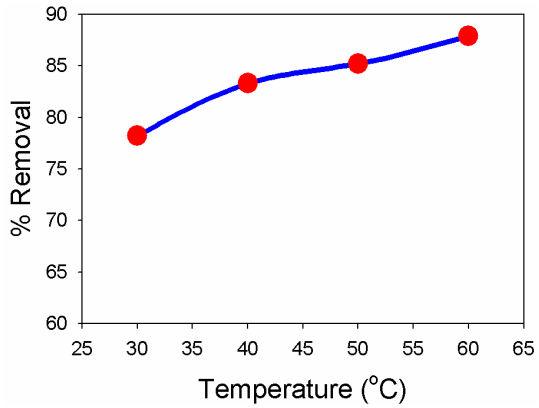


Fig. 9. Temperature effect on fluoride adsorption onto jackfruit bark

Isotherm equilibrium adsorption studies

The result of the adsorption capability and coefficients of correlation (R^2) can be calculated from Langmuir and Freundlich adsorption isotherm and there mathematical equation is given below in Table 1 (Langmuir, 1918).

Theory of Isotherm Models

The abilities of mostly used isotherms, Langmuir

Table 1. Langmuir adsorption isotherm and Freundlich adsorption isotherm model for expulsion of Fluoride by using jackfruit (*Artocarpus heterophyllus*).

Isotherm models	Parameters	Jackfruit bark
Langmuir Isotherm	*qm* (mg/g)	214.7766
	KL (b)	4.0914
	RL	0.1407
	R2	0.9973
Freundlich Isotherm	*1/n*	0.2814
	N	3.5536
	KF(mg/g)	6.0606
	R2	0.9200

and Freundlich isotherms model were examined.

Langmuir isotherm

Langmuir adsorption is most usable in all isotherms which is applied for solid and liquid systems (Langmuir, 1918). The linear form of the equation is described by:

$$C_e/ q_e = 1/bq_{max} + C_e/ q_{max}$$

Where, q_e - fluoride adsorption capacity of adsorbent, C_e - equilibrium solute conc., q_{max} -maximum adsorption capability and b - Equilibrium Langmuir constant.

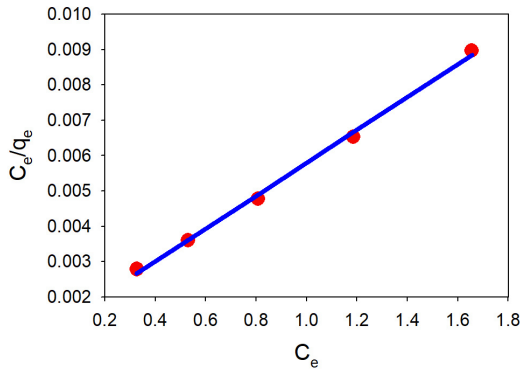


Fig. 10. Langmuir isotherm for adsorption of Fluoride

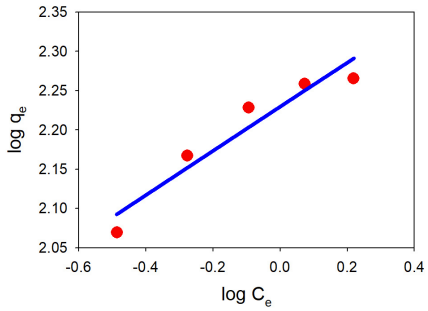


Fig. 11. Freundlich isotherms for adsorption of Fluoride

Freundlich isotherm

In Freundlich isotherm molecules are adsorbed on heterogeneous surfaces with interactions occurring among the adsorbed molecules (Freundlich, 1906). The equation is described by:

$$\log q_e = \log K_F + 1/n \log C_e$$

Where, C_e (mg L^{-1}) - Equilibrium concentration, q_e - amount of fluoride ion adsorbed at equilibrium, K_F - adsorption capacity and n - intensity of adsorption.

Table 2. "R,, value for different types of isotherm

'R' value	Isotherm types
$R > 1$	Unfavorable
$R = 1$	Linear
$0 < R < 1$	Favorable
$R = 0$	Irreversible

Kinetic study

For showing the fluoride adsorption mechanism on the surface of adsorbent, use kinetic pseudo first and second order, which are basically used to find the values of recent adsorption data for determining the parameters. Kinetic models are given as:

- Pseudo first order model - The pseudo first-order kinetic equation of Lagergren model states that the rate is proportional to the no. of unoccupied points is given as (Lagergren, 1898). The linear form of the equation:

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

where, q_e (mg/g) - amount of fluoride ions adsorbed at an equilibrium, q_t - time t (min), k_1 - rate constant of pseudo 1st order adsorption operation (min^{-1}).

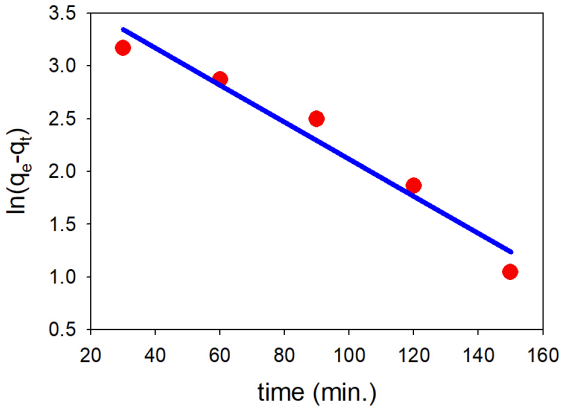


Fig. 12. Kinetic first order for adsorption of Fluoride

- **Pseudo second order model** - The pseudo second order assumes that the rate of adsorption is proportional to the square of the number of unoccupied points (Ho, 2006). Its linear form is represented as:

$$t/q_t = 1/ K_2 q_e^2 + t/q_e$$

Where, k_2 is the equilibrium rate constant of pseudo 2nd order (g mg^{-1} min^{-1})

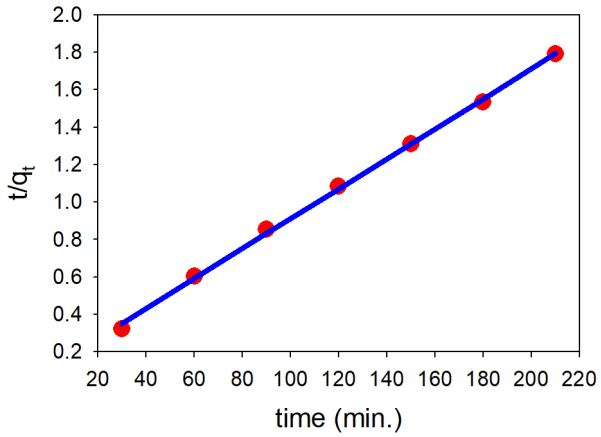


Fig. 13. Kinetic second order for adsorption of Fluoride

Table 3. Calculation of adsorption concentration on different kinetic models, parameters and Correlation co-efficient for adsorption of fluorid

Kinetic model	Parameter	Jackfruit bark
Pseudo 1st order	*qe (mg/g)*	10.5152
	K_1	0.0404
	R^2	0.9578
Pseudo second order	*qe (mg/g)*	124.89
	K_2 (g /mg min)	0.00058
	R^2	0.9987

Conclusion

In the review work large variety of adsorbent was studied which all are used for the removal of fluoride concentration. From the study it is concluded researcher use bark or wood adsorbents which have capacity of removing fluoride concentration.

- Experimental investigation has been carried out to remove fluoride from aqueous solution using jackfruit bark powder as an adsorbent. Large amount of fluoride ions were removed while taken 1g jackfruit adsorbent and volume of solution taken was 100ml.At pH 6 maximum amount of fluoride was removed. The total time required for adsorption equilibrium adsorption condition was 3 hour. The shaking speed is near about 100 rpm for maximum adsorption of F^- ions. 1.5 ppm was the most favorable starting Fluoride concentration for jackfruit adsorbent. The maximum removal efficiency observed was 78.2%. Langmuir isotherm and pseudo second order model were better fitted on adsorption data having R^2 (0.9973) and R^2 (0.9987).
- The research on defluoridation using jackfruit bark powder indicates that the equilibrium data fits better to Langmuir isotherm than Frendulich isotherm. The techniques used in my study have the advantages of high fluoride removal ability, easily operational, portability, environmental friendly and having low cost.
- At the final result, a minimal effort material is used as an adsorbent for fluoride expulsion from groundwater for daily use purpose in houses where fluoride related issues live.

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