

Examining the Efficiency of Tamarindus Indica to Aid in Fluoride Extermination from Groundwater

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Abstract

Groundwater in India is significantly contaminated by fluoride, affecting 11.7 million people across 335 districts. In this study, we analyzed the fluoride removal efficiency of Tamarind seed activated carbon (TISC) as well as Zinc Chloride coated Tamarind seed activated carbon (ZTISC) in batch mode of operation for both synthetic fluoride solution and groundwater rich in fluoride. Effect of different operating conditions including contact time, pH, adsorbent dose, adsorbate concentration was studied. The adsorption capacity of TISC was 0.8256 mg/g and that of ZTISC was 0.4963 mg/g. The maximum fluoride removal occurred at neutral pH for adsorbent dose of 1 g/L for an initial fluoride concentration of 2 mg/L. The removal efficiency of fluoride in groundwater was comparable to that of synthetic solution but reduced in the presence of co-ions like chlorides and bicarbonates. Removal efficiency for TISC was 82.4%, 70.23% and 80.2% for synthetic solution, GW1 and GW2 respectively. ZTISC showed low defluoridation ability compared to TISC. Removal efficiency for ZTISC was 49.6%, 42.6% and 51.5% for synthetic solution, GW1 and GW2 respectively. The experimental data was fit to different kinetic models and adsorption isotherms. Both TISC and ZTISC followed Pseudo first order kinetic reaction and Langmuir isotherm with correlation coefficient, $R^2 = 0.829$ and 0.75 respectively.

Keywords: Adsorption, Tamarind seed, Zinc chloride, Fluoride, Groundwater.

INTRODUCTION

Water is a vital natural resource that affects all social, economic activities and ecosystem function. Earth's surface is covered by nearly 71% of water. Although this may seem abundant, the availability of freshwater is scarce. Only 2.5% of the world's water is present as freshwater, the rest is saline and is unfit for use. Groundwater makes up about thirty percent of the world's freshwater supply which is about 0.75% of the entire world's water, including oceans and permanent ice (Jean Margat et al., 2013). About 70% of groundwater withdrawn worldwide is used for agriculture (Jean Margat et al., 2013). According to Central ground water board in India, 85% of the drinking water supply in rural area is from groundwater sources. Globally, about 38% of irrigated lands are equipped for irrigation with groundwater (S. Siebert et al., 2010). According to World Health Organization (WHO), the guideline value for fluoride in drinking water is 1.5 mg/L. The factors that control naturally occurring fluoride in groundwater are climate, hydrogeology and the composition of host rock and volcanic activity (Danni Li et al., 2018) and can also be from anthropogenic sources such as the use of phosphatic fertilizers in agriculture and by contamination from industries. In India the highest reported

fluoride concentration in groundwater is 15 mg/L.

In the case of fluoride, both its deficiency and excess concentration is harmful. Deficiency of fluoride intake leads to dental caries while excess consumption leads to dental and skeletal fluorosis, ossification of tendons & ligaments, neurological damage (Chouhan S. et al., 2010), low haemoglobin levels (Syr-Yaung Lin et al., 1966), muscle fibre degeneration, red blood cell deformation, excessive thirst, headache, depression, gastrointestinal issues, abdominal pain, reduced immunity, urinary tract disorder. Various methods for fluoride removal such as Coagulation (Dubey S, 2018), Precipitation (Huang H, 2017), Membrane Process (Ndiaye P, 2005), Ion-exchange Process (Mondal R, 2018), Electrodialysis (Djouadi Belkada F., 2018), Electro-coagulation Process (López-Guzmán M., 2019) and adsorption.

MATERIALS AND METHODS

Materials

Adsorbent

Tamarind seeds were collected from H.D. Kote, Karnataka, India and soaked in water for as long as the kernel could be removed easily. It was then washed with acid, base and distilled water to remove

any dust and was air dried for 24 hours. The dried seeds were ground in a mixer and sieved with a 600 μ m sieve followed by carbonization in a muffle furnace at 400°C for 1 hour to obtain Carbonized Tamarind seed (CTS).

Zinc Chloride coated tamarind seed carbon (ZTISC) were prepared by soaking 5g of CTS in ZnCl₂ solution prepared by dissolving 10g of ZnCl₂ in 100 mL of water for 24 hours. The Chemical ratio, which is the ratio of chemical activating agent (ZnCl₂) to the precursor, was 2:1. The residue after filtration was washed with HCl to remove excess ZnCl₂ and air dried for 24 hours.

Adsorbate: Fluoride

A stock solution of Fluoride was prepared (100 mg/L) by dissolving required amount (221mg) of Sodium Fluoride (NaF) in distilled water. The stock solution was diluted with distilled water to obtain desired concentration ranging from 1 to 7 mg/L. All the chemicals used in the study were obtained from 'The Mysore Pure Chemicals Ltd'.

Methods

Batch Studies

To understand the defluoridation capacity of TISC and ZTISC, batch adsorption

experiments were performed by contacting 0.1-1.2 g/L of the selected adsorbent samples with 50 mL aqueous solution of different initial concentration (1, 2, 3, 4, 5 mg/L) at natural solution pH. The experiments were performed in a jar test apparatus for a period of 2 hours at 125 rpm using 1000 mL jars containing 500 mL of different fluoride concentrations at room temperature. Continuous mixing was provided for the entire experimental period. The remaining concentration of fluoride in each sample after adsorption at different time intervals was determined by UV-VIS spectrophotometer after filtering the adsorbent with Whatman filter paper of 110 mm \varnothing of 40 μ m pore size. The adsorbate concentration retained in the adsorbent phase was calculated according to the following:

$$= ((C_i - C_e) V) / W \quad (1)$$

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

Where C_i and C_e are the initial and equilibrium concentrations (mg/L) of fluoride solution, respectively; V is the volume (L); and W is the weight (g) of the adsorbent. Adsorption of fluoride on the selected carbon was studied by employing different initial concentrations (1, 2, 3, 4, 5, 6, 7 mg/L). For these experiments, the

jars were stirred, keeping the pH at natural constant and agitation speed (125 rpm) for the minimum contact time required to attain equilibrium.

RESULTS

Characteristics of the adsorbent

To characterize TISC and ZTISC, the SEM, EDAX and FTIR analyses were

carried out. In the Figure 1 the presence of peaks for TISC at 3749 and 3648 cm⁻¹ indicate stretching frequency of amide (-NH₂) or alcohol (-OH) group. The peak at 1699 cm⁻¹ exhibits the stretching frequency of >C=O group and the peak at 3028 that of -CH group.

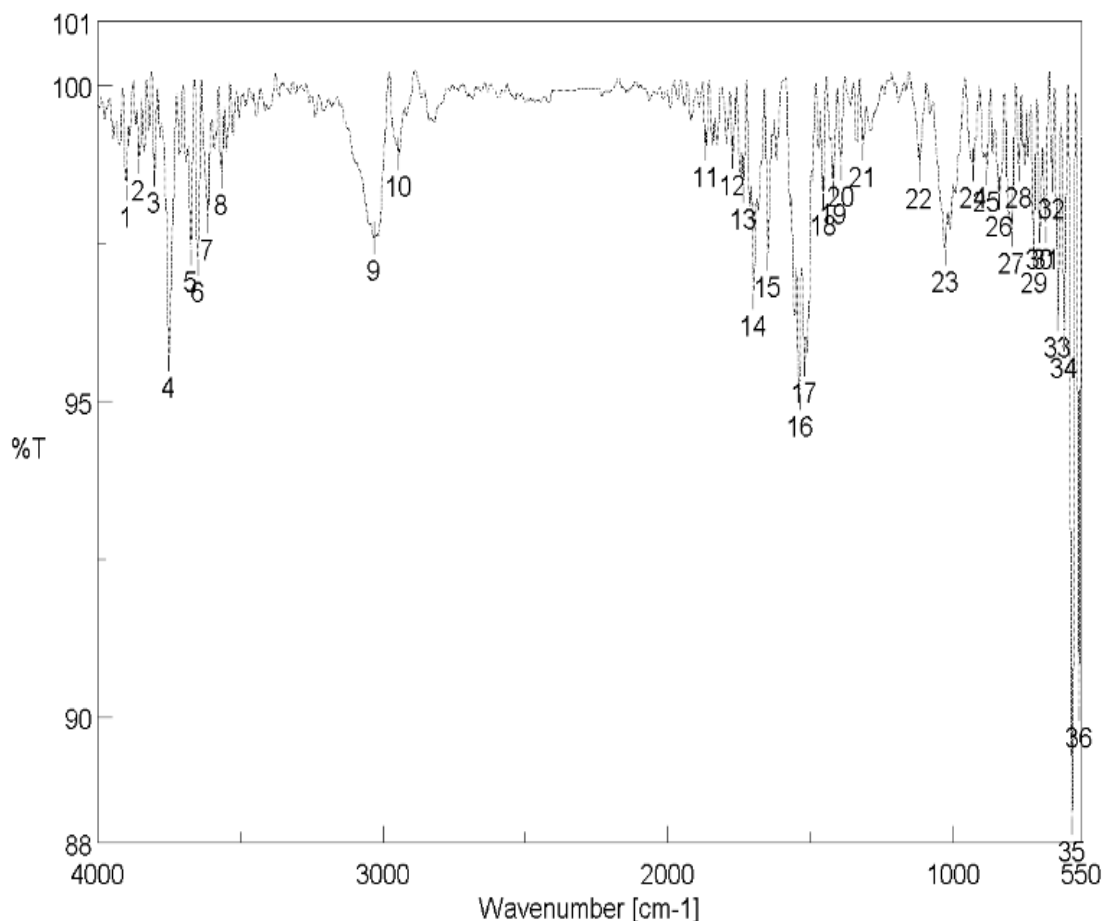


Figure 1: FTIR spectra of TISC after adsorption

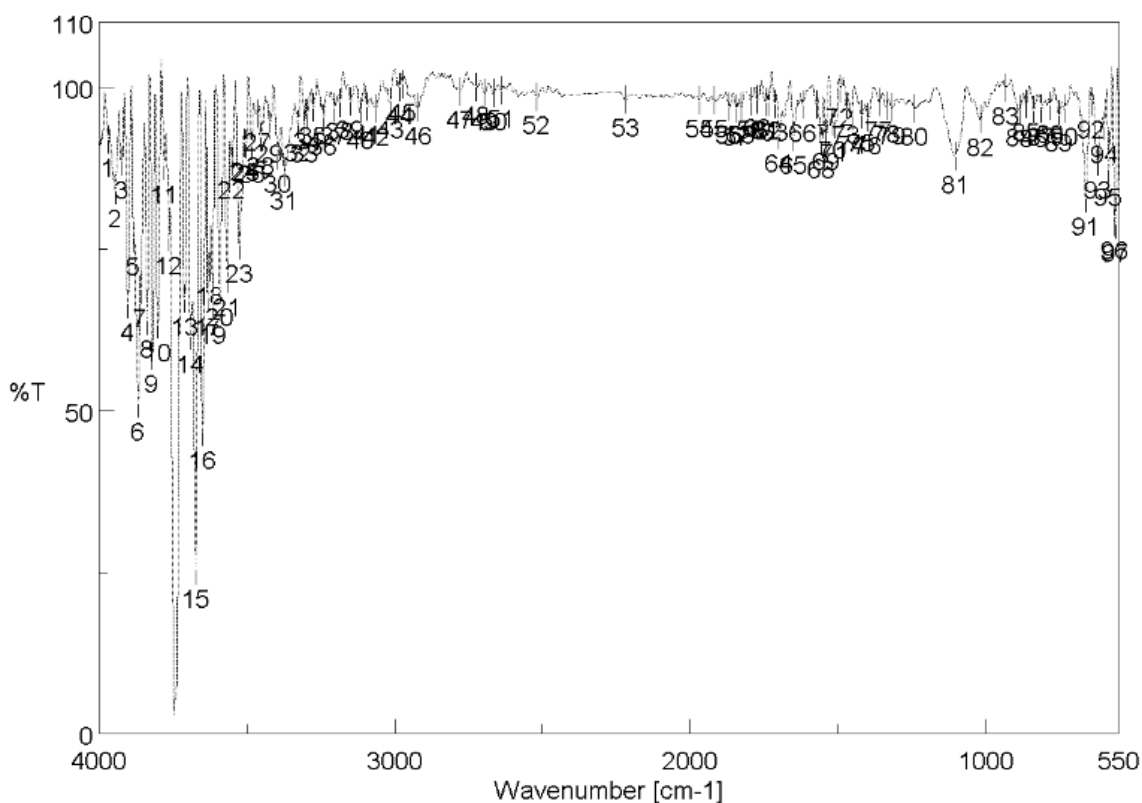


Figure 2: FTIR spectra of ZTISC after adsorption

In the Figure 2 EDAX for ZTISC shows the peaks at 3672, 3690 and 3394 indicating stretching frequency of (-NH₂) group or (-OH) group and the peaks at 1649 and 1699 cm⁻¹ indicate >C=O group. The presence of alkene in ZTISC shown by the peak at 3371 cm⁻¹ is not seen in TISC.

Surface morphology of the adsorbents was studied by SEM (SEM JEOL/MP JSM-IT300). Scanning electron micrographs have illustrated the adsorption of fluoride onto the adsorbent after the defluoridation process.

SEM images of both TISC and ZTISC as shown in Figure 3 (A-D) exist as highly aggregated irregular clusters. A change is seen in the surface morphology after the adsorption with development of pores. The pores are well developed for TISC than ZTISC confirming better sorption onto TISC.

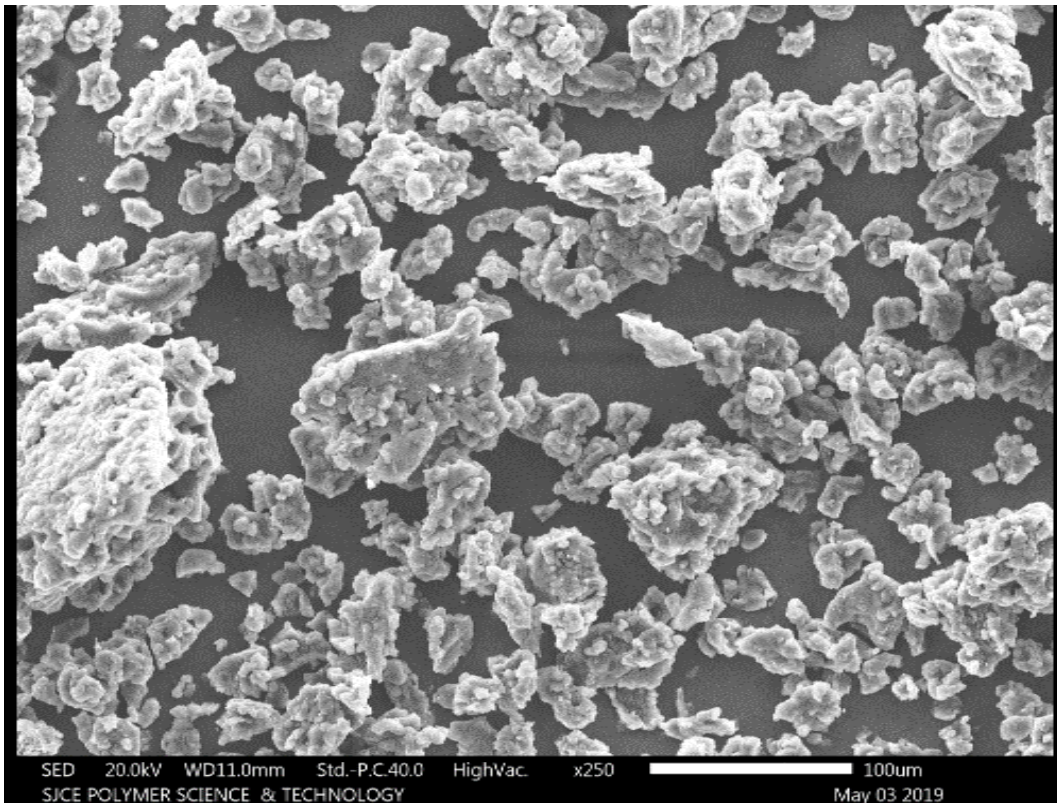


Figure 3: (A) Scanning Electron Micrograph of TISC before adsorption

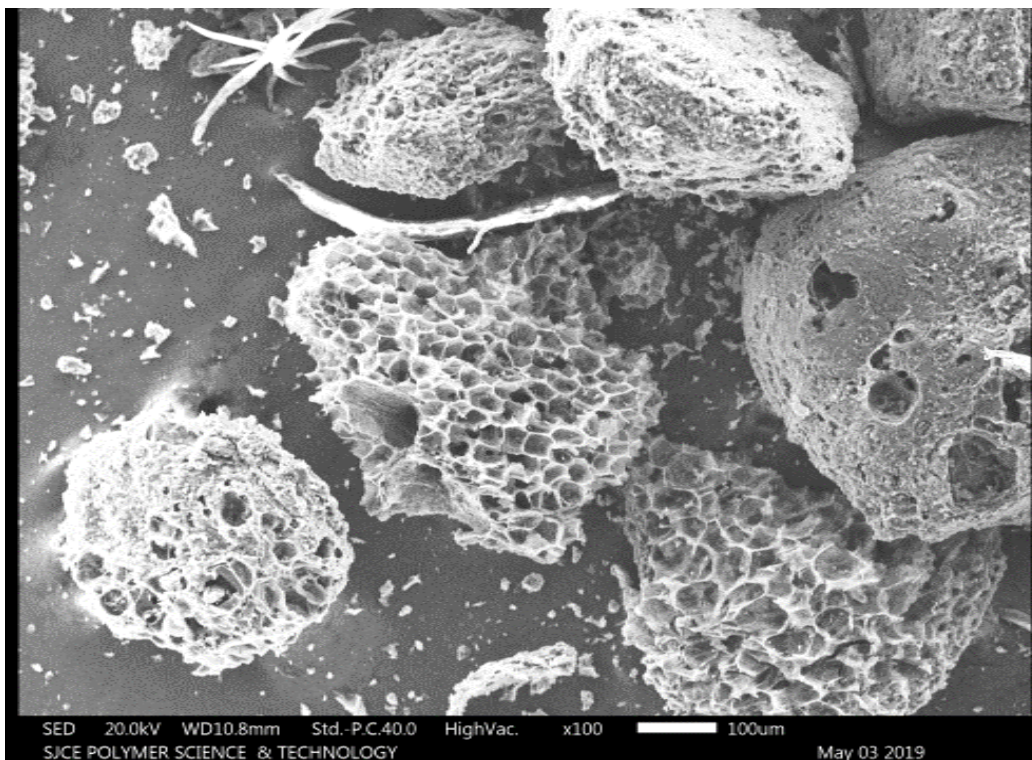


Figure 3: (B) Scanning Electron Micrograph of TISC after adsorption

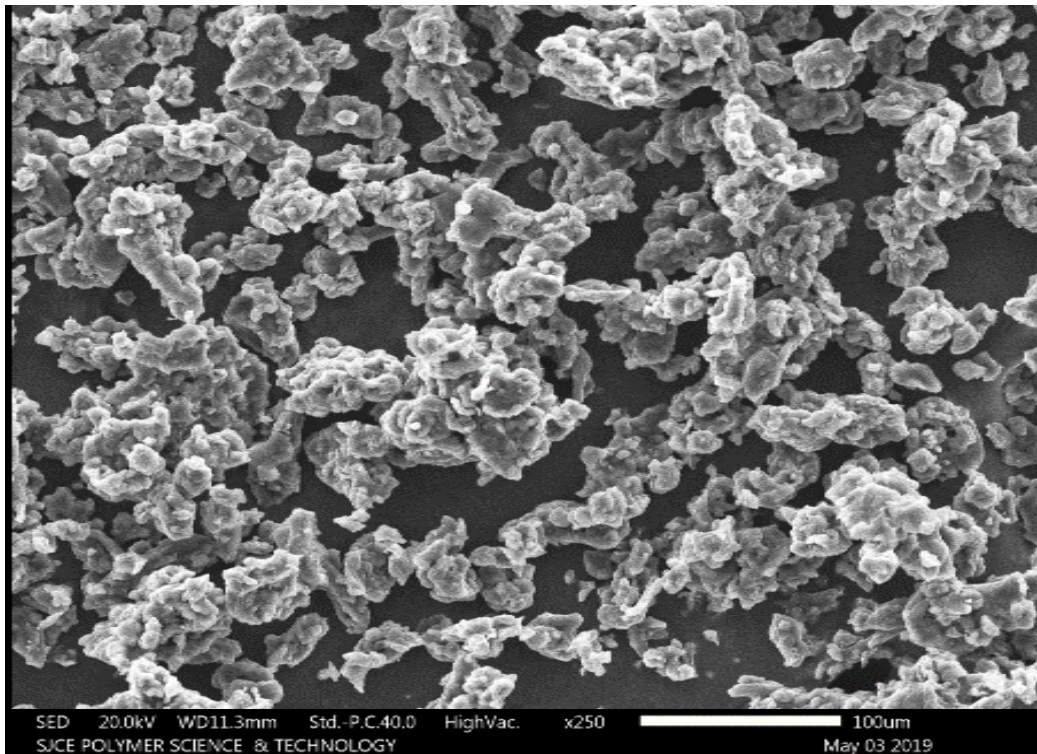


Figure 3: (C) Scanning Electron Micrograph of ZTISC before adsorption

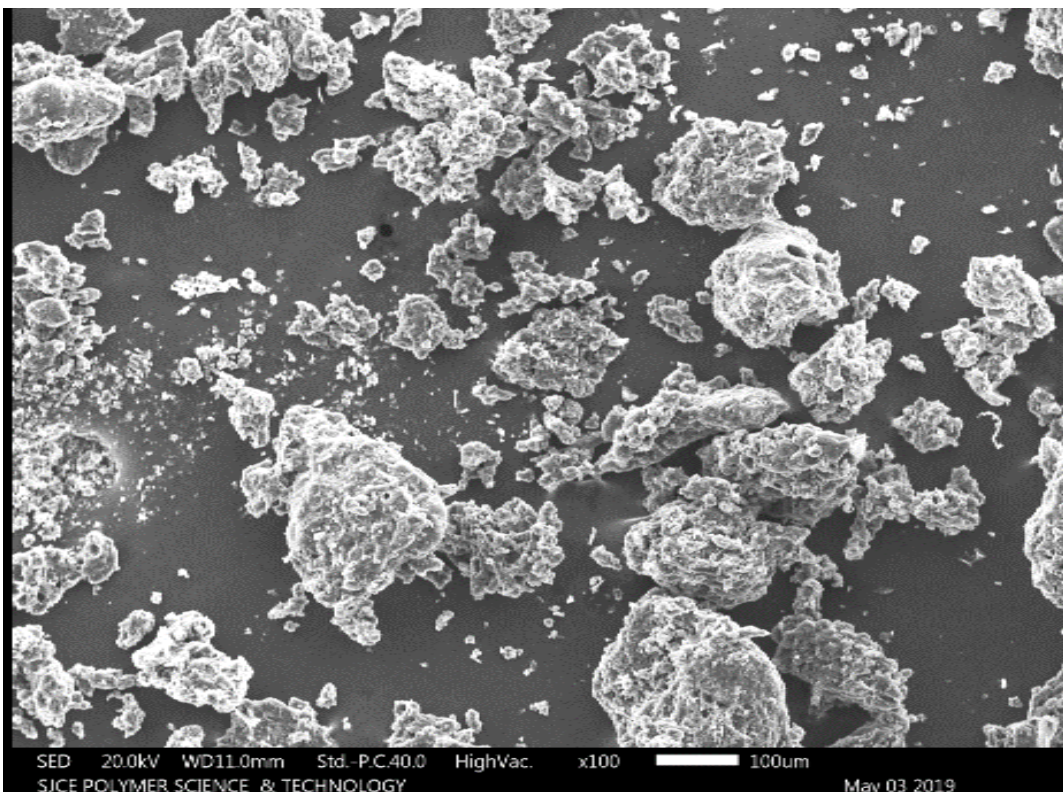


Figure 3: (D) Scanning Electron Micrograph of ZTISC after adsorption

The Energy-Dispersive Analysis of X-rays was used to analyze the elemental constituents of TISC and ZTISC. It can be seen from Figure 4 (A-D) that the chief elements in both TISC and ZTISC were Carbon and Oxygen. Phosphorous was also present in significant quantity of 2.92 and 4.09 atomic % in TISC and ZTISC respectively. Small quantities of Na, Mg,

K, Cl are present in the adsorbent before adsorption which are considerably removed following defluoridation, possibly due to ion exchange occurring to allow for sorption of fluoride at the sites where other elements were present. A small peak of fluoride is present with 0.13 and 0.06 atomic % in TISC and ZTISC respectively, indicating fluoride sorption.

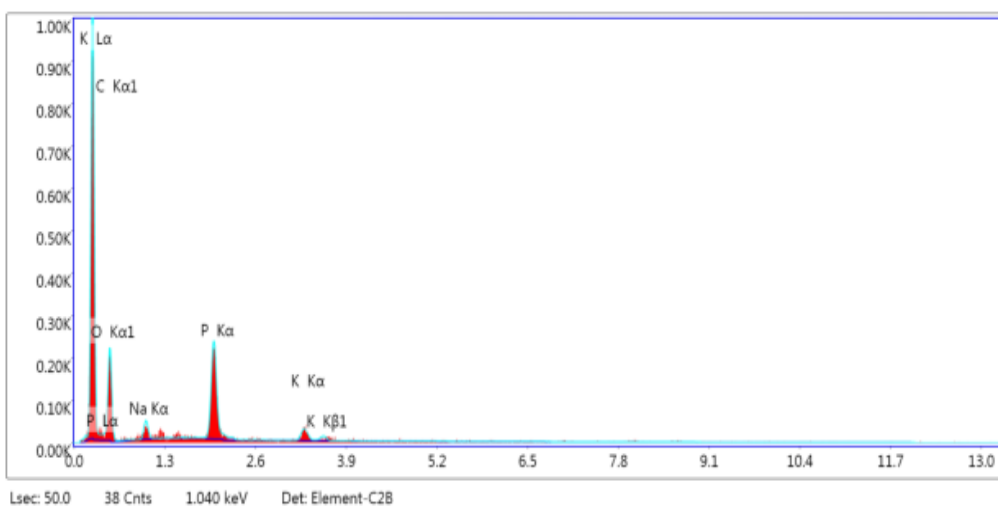


Figure 4: (A) EDAX for TISC before adsorption

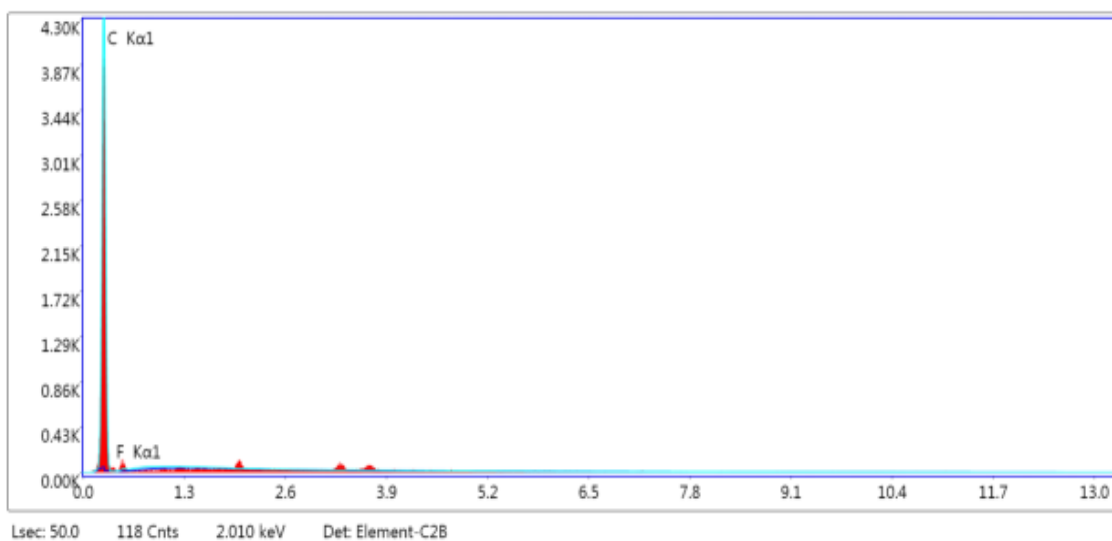


Figure 4: (B) EDAX for TISC after adsorption

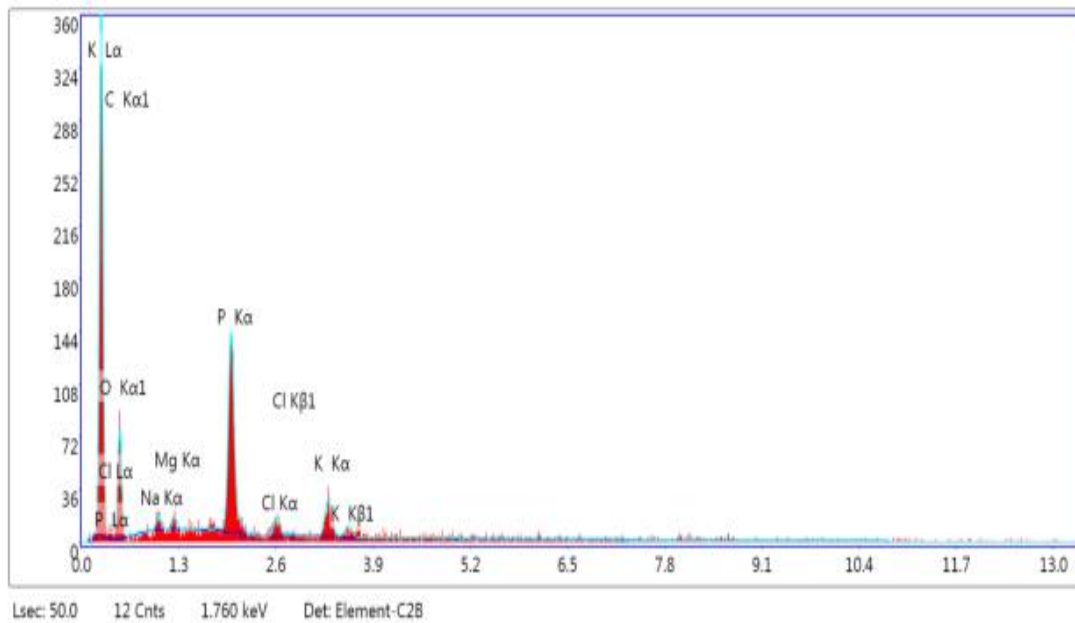


Figure 4: (C) EDAX for ZTISC before adsorption

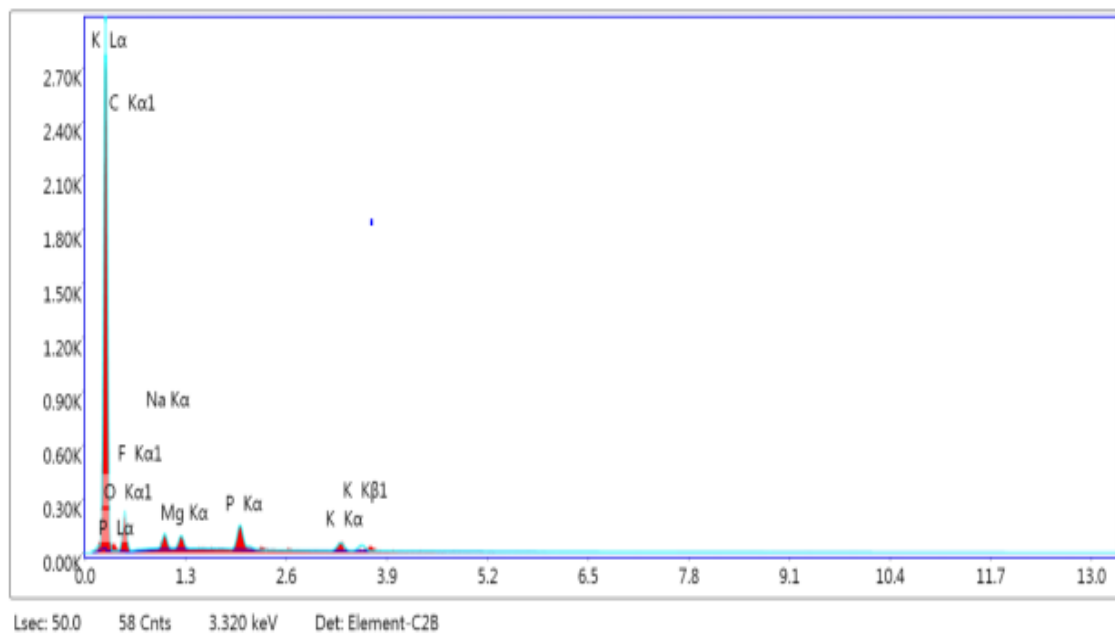


Figure 4: (D) EDAX for ZTISC after adsorption

OPTIMIZATION OF OPERATING CONDITIONS FOR ADSORPTION

Effect of contact time

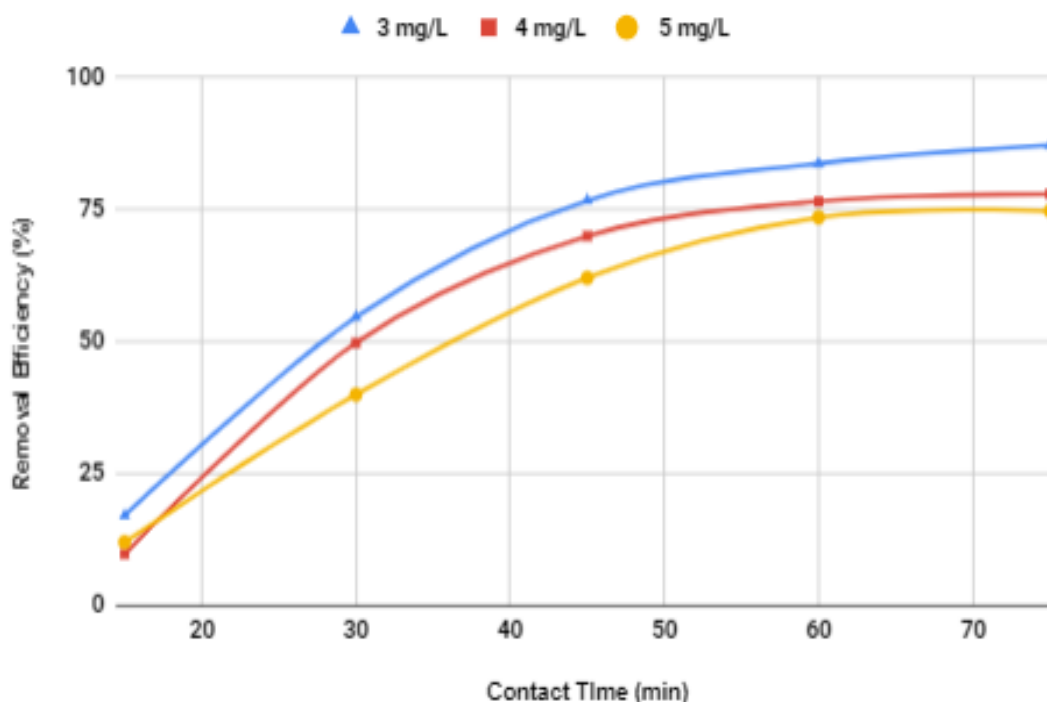
First the adsorption of fluoride on the prepared adsorbents was studied as a

function of time to find out the equilibrium time for maximum adsorption. The time profile of fluoride adsorption onto activated carbon is presented in the Graph 1 and 2 for different initial fluoride

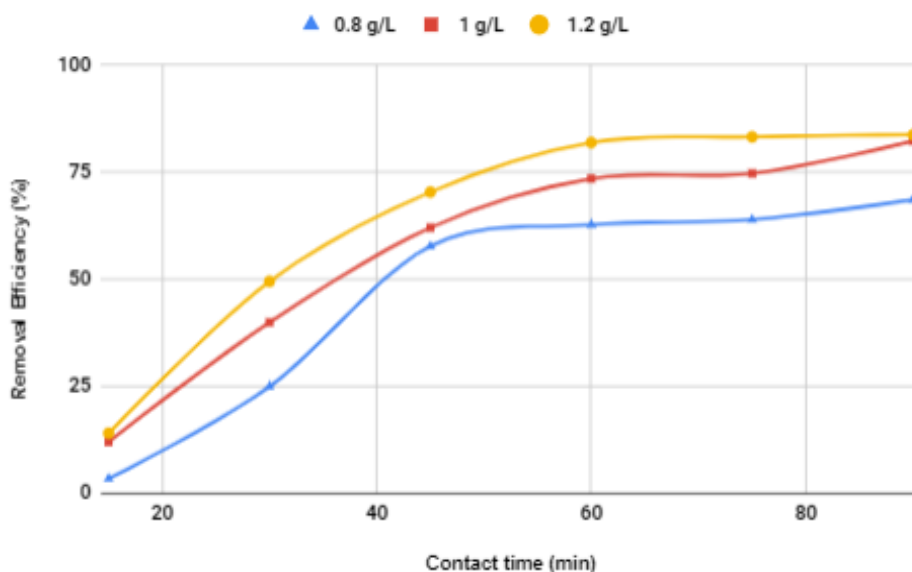
concentration and different adsorbent dose, respectively. With Tamarindus Indica seed carbon (TISC) as adsorbent the maximum removal efficiency of fluoride from synthetic solution of different initial feed concentration (3, 4 and 5 mg/L) was found at 60 min and it remained constant even with further increase in time. The steady fluoride removal is due to availability of

vacant sites for adsorption until it reaches equilibrium.

The relationship between contact time and fluoride removal efficiency with different adsorbent dose (0.8, 1, 1.2 g/L) is as shown in Graph 2. When all other conditions are kept constant the removal efficiency of fluoride increases with increase in dose resulting from availability of greater number of sites for adsorption.



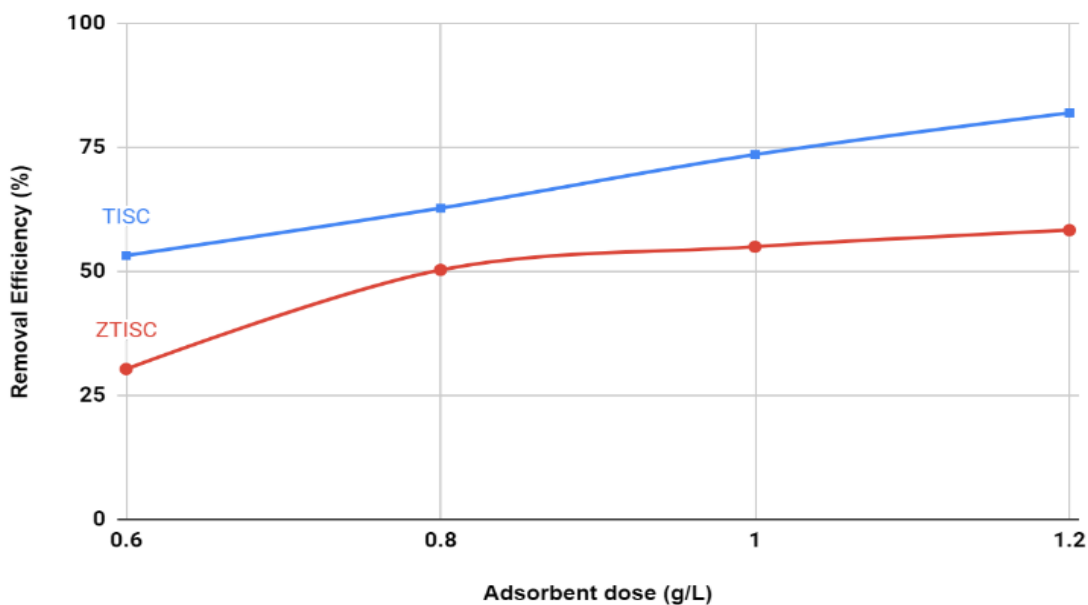
Graph 1: Effect of contact time on removal efficiency of TISC at different initial fluoride concentration at adsorbent dose 1 g/L, pH 7 at room temperature



Graph 2: Effect of contact time on removal efficiency of TISC at different adsorbent dose at initial fluoride concentration 5 mg/L, pH 7 at room temperature

Effect of dose

The effect of adsorbent dosage on the percentage removal of fluoride has been shown in the graph below. It can be seen from the Graph 3 that initially the percentage removal increases with the increase in adsorbent dosage, but it reaches a constant value for adsorbent dose of more than 1 g/L.



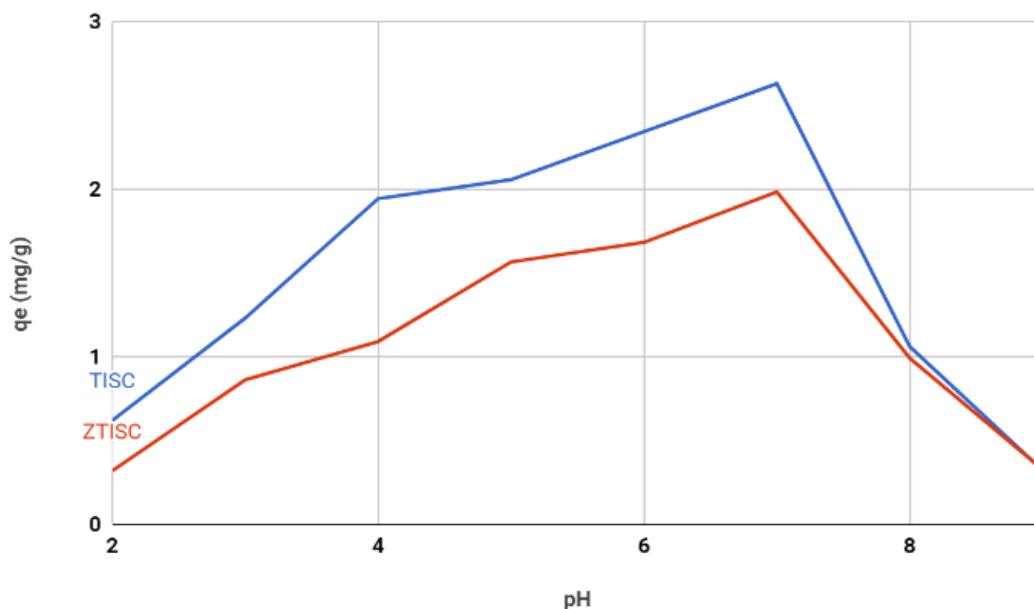
Graph 3: Effect of change in adsorbent dose for different initial fluoride concentrations, pH = 7 and contact time = 60 min

Effect of pH

The effect of pH of the solution on the fluoride removal when the initial fluoride was 5 mg/L, adsorbent dose was 1 g/L is as shown in Graph 4. pH has a strong influence on the adsorption capacity of fluoride. The adsorption experiments were conducted for pH 2 to 9 by adding 0.1N NaOH and 0.1N HCl to the solution. The fluoride removal is maximum in the neutral range. The adsorption capacity is between 2.1 and 2.6 mg/g between pH 5-7 but falls sharply to 0.3 mg/g in the alkaline solution probably due to the competition between fluoride and hydroxyl ions for sorption on the adsorbent.

COMPARISON BETWEEN FLUORIDE SORPTION FOR SYNTHETIC FLUORIDE SOLUTION AND GROUNDWATER

The groundwater samples (GW1 and GW2) collected from two monitoring wells in Mandya district were first characterized for pH, Total Hardness, Alkalinity, Chlorides, Nitrates, Sulphates and Fluoride. The results are shown in Table 2. The analyses were performed in triplicate but only the mean value is shown. The fluoride removal efficiencies for both TISC and ZTISC for one of the groundwater sample (GW2) were comparable with that of synthetic fluoride solution.



Graph 4: Variation in adsorption capacity with change in pH when initial fluoride concentration = 5 mg/L, Adsorbent dose = 1g/L, speed = 125 rpm, contact time = 90 min

The removal efficiency of TISC was 82.54% and 49.6% from synthetic water and GW2 respectively and that of ZTISC was 49.6% and 51.5% from synthetic solution and GW2 respectively. However, the removal efficiency for GW1 was

considerably lower as seen in Table 1. Which may be due to higher total hardness and chloride concentration of GW1 sample, resulting in competition between bicarbonates and chlorides with fluoride for sorption on the available sites?

Table 1: Comparison between fluoride sorption for Synthetic fluoride solution and Groundwater

	Synthetic fluoride solution		GW 1		GW 2	
	TISC	ZTISC	TISC	ZTISC	TISC	ZTISC
Removal efficiency (%)	82.54	49.6	70.23	42.6	80.2	51.5
Adsorption capacity (mg/g)	0.8256	0.4963	0.702	0.4262	0.8	0.5155

Table 2: Groundwater characterization

Characteristics	Sample 1	Sample 2	Indian Standards
pH	7.2	6.9	6.5 - 8.5
Total Hardness (mg/L)	496	368	300
Alkalinity (mg/L)	366	372	200
Chloride (mg/L)	120.7	78.2	250
Sulphate (mg/L)	60	90.5	150
Nitrate (mg/L)	3.5	4.6	45
Fluoride (mg/L)	2.1	2.6	0.6 - 1.2

Sorption Mechanism

2.303(t)

Kinetics parameters provide the knowledge for modeling and designing the adsorption process and to understand the mechanism of the adsorption reactions in terms of the order of the rate constant. To understand the sorption mechanism on TISC and ZTISC experimental data were fit to Pseudo-First order kinetic model.

Pseudo-first order model

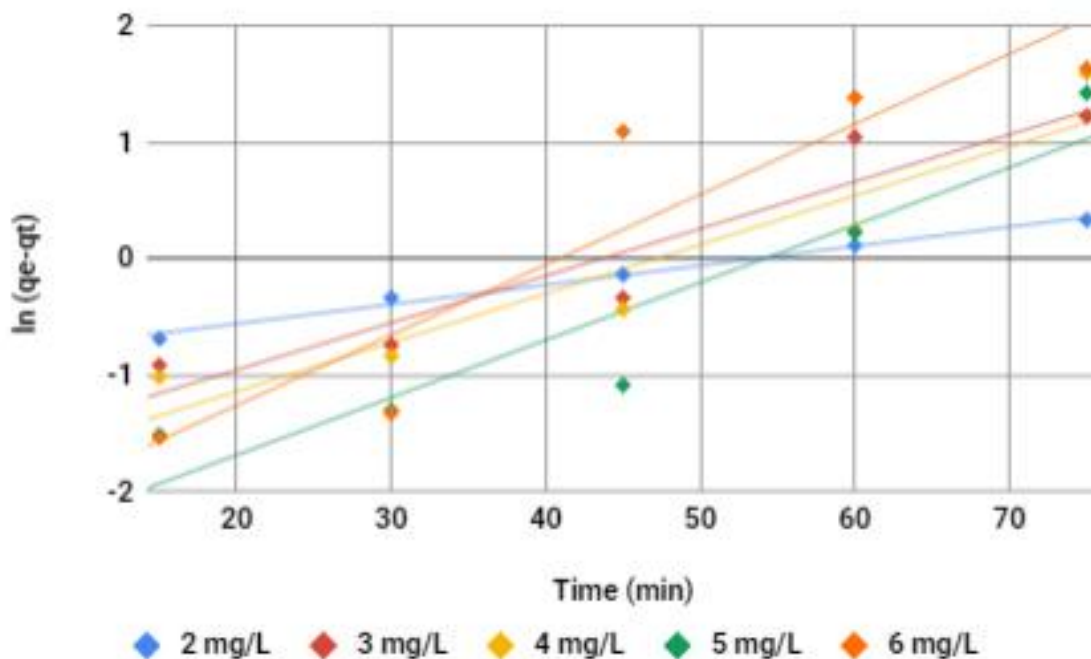
A simple pseudo-first order kinetic model is represented as:

$$\log (q_e - q_t) = \log q_e - k_{ad} t$$

(3)

Where q_t (mg/g) is the amount of fluoride sorbed on the surface of the sorbents TISC and ZTISC at time t and k_{ad} is the equilibrium rate constant of pseudo-first order sorption (min^{-1}).

The value of k_{ad} is obtained by plotting $\log (q_e - q_t)$ vs t curve for different experimental conditions. Equilibrium rate constant and correlation coefficient (R^2) were computed. Pseudo-first order model seems to hold good for TISC and ZTISC.



Graph 5: Pseudo-First order Kinetic model for different initial fluoride concentration (2-6 mg/L)

ADSORPTION ISOTHERM ANALYSIS

Langmuir isotherm

The simple Langmuir isotherm model is based on assumptions that

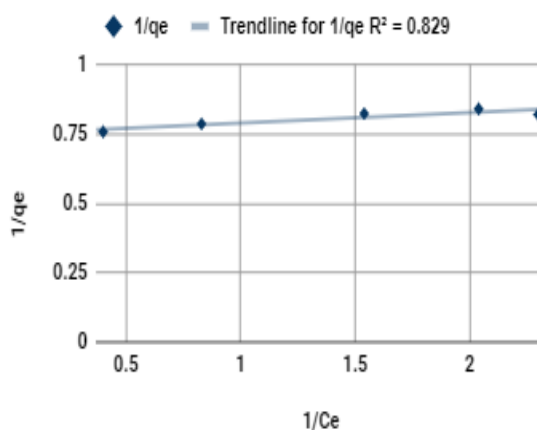
- Maximum adsorption correlates with saturated monolayer coverage of sorbent surfaces by the sorbate.
- The energy of adsorption is constant.
- There is no transmigration of adsorbed molecules in the plane of adsorbent surface.

It is expressed as,

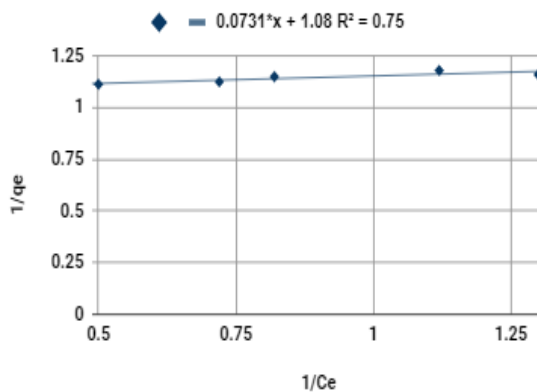
$$q_e = \frac{abC_e}{1+bC_e} \dots \dots \dots (4)$$

Where q_e is equilibrium adsorption capacity (mg/g) and C_e is the equilibrium adsorbate concentration (mg/L); a is the monolayer surface coverage (mg/g) and b is the equilibrium adsorption constant (L/mg). The linearized form of the above equation used to find the model parameters a and b is as follows. The values of a and b were calculated from the slope and intercept of the linear plot of $1/q_e$ vs $1/C_e$.

$$\frac{1}{q_e} = \frac{1}{abC_e} + \frac{1}{a} \dots \dots \dots (5)$$



Graph 5: Langmuir Isotherm for TISC (R2= 0.829)



Graph 7: Langmuir Isotherm for ZTISC (R2= 0.75)

Freundlich is otherm

The simple Freundlich isotherm model equation which is based on the multilayer adsorption of adsorbate onto the heterogeneous surfaces of an adsorbent and exponential distribution of active sites and their energies is given by

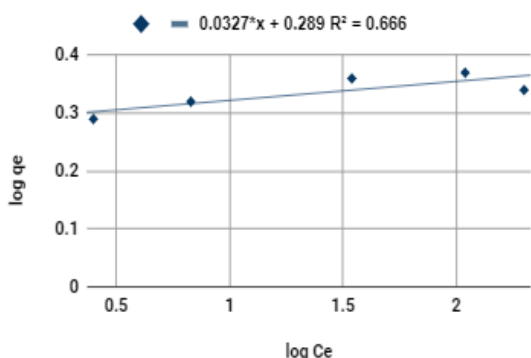
$$q_e = K_f C_e^{(1/n)} \dots \dots \dots (6)$$

where K_f and n are empirical constants related to adsorption capacity and intensity of adsorption, respectively. Freundlich isotherm indicates physisorption on the surface. The linear form of the Freundlich equation which is commonly used to describe adsorption isotherm data, is

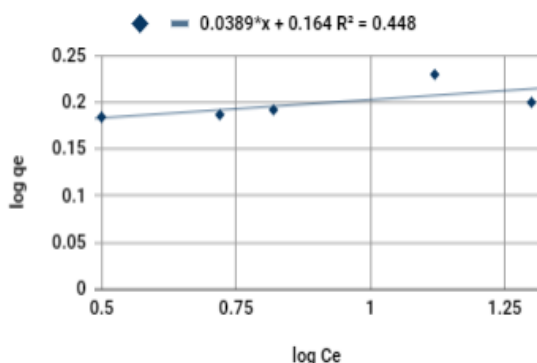
$$\text{Log}q_e = \text{log}K_f + \frac{1}{n} \text{log}C_e \quad (7)$$

n

The plot of $\text{log } q_e$ versus $\text{log } C_e$ is a linear curve, the slope and the intercept of the which gives the values of n and K_f .



Graph 8: Freundlich Isotherm for TISC (R2=0.66)



Graph 9: Freundlich Isotherm for ZTISC (R2=0.44)

CONCLUSION

This study shows that Tamarindus Indica seed carbon (TISC) can successfully remove fluoride ions from aqueous solution and groundwater and is also a cost-effective alternative since tamarind seeds are an agricultural waste product and are easily available.

- The maximum fluoride removal occurred at neutral pH for adsorbent dose of 1 g/L for initial fluoride concentration of 2 mg/L at equilibrium contact time of 60 min.
- Removal efficiency for TISC was 82.4%, 70.23% and 80.2% for synthetic solution, GW1 and GW2 respectively.
- ZTISC showed low defluoridation ability compared to TISC. Removal efficiency for ZTISC was 49.6%, 42.6% and 51.5% for synthetic solution, GW1 and GW2 respectively.
- EDAX revealed that TISC and ZTISC was composed primarily of C, O and P along with trace concentration of Na, K, Cl and Mg.

- FTIR analyses showed the presence of -NH₂, -OH, >C=O, -CH bonds on the surface of the adsorbents.
- Adsorption kinetics followed Pseudo-first order kinetic model and adsorption followed Langmuir isotherm. The Langmuir adsorption capacity of 1.5948 and 0.9234 mg/g was obtained for TISC and ZTISC, respectively with correlation coefficient >0.8.
- Good fit of equilibrium experimental data was obtained for pseudo-first order kinetic model with R²>0.9 for both TISC and ZTISC.

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