

Defluoridization Using a Natural Adsorbent, *Strychnos Potatorum*

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Abstract

The study assessed the suitability of low-cost natural adsorbent to effectively remediate fluoride contaminated water. The removal of fluoride from aqueous solution by using *Strychnos Potatorum* was studied in batch technique. Influence of pH, adsorbent dose, contact time, co ions, speed and initial concentration on the adsorption were investigated. The maximum removal of fluoride ion was obtained at pH 7. The removal of fluoride was expressed with Langmuir and Freundlich isotherm. It was found that the sufficient time for adsorption equilibrium of fluoride ion was 1 hour. The removal of fluoride ions was maximum for the adsorbent dosage of SP is 50mg/50ml. The fluoride adsorption was maximum at 60minutes. The adsorption of F⁻ ion was maximum in the shaking speed of 120 rpm. The presence of interfering ions such as nitrate and carbonate showed positive effect while sulphate and chloride showed little negative effect and phosphate showed high negative effect for the adsorbent. The optimum initial fluoride concentration for SP adsorbent was 1mg/50ml.

Key words : Fluoride, SP- *Strychnos Potatorum* , fluoride, low-cost natural adsorbent

I. Introduction

Water is an essential natural resource for sustaining life and environment that we have always thought to be available in abundance and free gift of nature. However, chemical composition of surface or subsurface is one of the prime factors on which the suitability of water for domestic, industrial or agricultural purpose depends. Freshwater occurs as surface water and groundwater. Though groundwater contributes only 0.6% of the total water resources on earth, it is the major and the preferred source of drinking water in rural as well as urban areas, particularly in the developing countries like India because treatment of the same, including disinfection is often not required. It caters to 80% of the total drinking water requirement and 50% of the agricultural requirement in rural India. But in the era of economical growth, groundwater is getting polluted due to urbanization and industrialization. Over the past few decades, the ever-growing population, urbanization, industrialization and unskilled utilization of water resources have led to degradation of water quality and reduction in per capita availability in various developing countries. Due to various ecological factors either natural or anthropogenic, the groundwater is getting polluted because of deep percolation from intensively cultivated fields, disposal of hazardous wastes, liquid and solid wastes from industries, sewage disposal, surface impoundments etc. [1–4]. During its complex

flow history, groundwater passes through various geological formations leading to consequent contamination in shallow aquifers. Presence of various hazardous contaminants like fluoride, arsenic, nitrate, sulphate, pesticides, other heavy metals etc. in underground water has been reported from different parts of India [5–12]. In many cases, the water sources have been rendered unsafe not only for human consumption but also for other activities such as irrigation and industrial needs. Therefore, now there is a need to focus greater attention on the future impact of water resources planning and development taking into consideration all the related issues. In India, fluoride is the major inorganic pollutant of natural origin found in groundwater. So far various researchers have used plant materials and other materials as adsorbents for the removal of fluoride ions [13 – 27]

1.1 About the study

The aim of the present study was to examine the feasibility of using low cost natural adsorbents such as *Strychnos Potatorum*, in Fluoride removal using adsorption technique. Adsorption characterisation was done by using SEM, XRD and FT-IR techniques. The effect of adsorbent dosage, contact time, pH, co-ions, initial fluoride concentration and shaking speed were determined.

II. Experimental

2.1 Fluoride Adsorption Experiments

A stock solution (100 mg/L) was prepared by dissolving 221mg NaF (analytical grade) in 1 L of distilled water. All the solutions for fluoride removal experiments and analysis were prepared by an appropriate dilution from the stock solution. Adsorption studies were carried out for each desired initial fluoride concentration solution in a conical flask immersed in a temperature-controlled water bath and shaken with a mechanical shaker (Tai Tec, Thermo Minder Mini-80, Japan) for the required time at a rate of 120 cycles/min. Fluoride analysis was carried out with photocolourimetry using the SPADNS indicator. The adsorption isotherm at $\text{pH } 6.90 \pm 0.10$ was studied by varying the initial fluoride concentration from 5 to 100 mg/L. The effect of pH was investigated by adjusting the pH from 2 to 12 using 0.1 M NaOH and HCl solutions under an initial fluoride concentration of 10 mg/L. A kinetic study at $\text{pH } 6.90 \pm 0.10$ was carried out at different time intervals with an initial fluoride concentration of 10 mg/L. Finally, the effects of a number of competing ions (Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-}) were observed using, 20-200 mg/L solutions at $\text{pH } 6.90 \pm 0.10$ over 1 hour

2.2 Physical characterizations:

The surface morphology and size distribution of the ayurvedic adsorbent powders were observed by means of a SEM, XRD and FTIR spectral analysis. The ayurvedic adsorbent powders before and after treated batch adsorption experiments was characterized using XRD and SEM. A representative experiment was carried out under the given conditions: 30°C , initial F⁻ concentration = 1mg/50ml, shaking speed = 120 rpm and contact time = 1 hour respectively, for the preparation of XRD and SEM samples. The X-ray diffraction patterns was recorded using X-ray diffractometer, Model (Phillips, 'X' Pert). The sample was scanned for 2θ range from 0° to 60° . The SEM analysis was carried out using Jeol, XA-840 A. The FTIR spectra were recorded on a Nicolet 560 FTIR spectrophotometer.

2.3 Chemical Used

Stock solution of fluoride was prepared by dissolving 221mg of sodium fluoride in 1 L distilled water. The measuring cylinder, volumetric flask and conical flask used. The sodium fluoride used was an analytical grade (Merck, Germany). The required concentration of fluoride solution was prepared by serial dilution of 100 mg/L Fluoride solution. Indicator was SPANDS reagent.

2.4 Theory of Isotherm Models

The abilities of four widely used isotherms, the theoretical Langmuir, empirical Freundlich, Temkin and Redlich-Peterson isotherms, to model the

adsorption equilibrium data were examined. To express the mechanism of fluoride adsorption onto the surface of adsorbent, the kinetic models pseudo first order, pseudo second order, intra particle diffusion and Elovich models are used to analyze the present adsorption data to determine the related kinetic parameters.

Langmuir adsorption isotherm is perhaps the best known of all isotherms which is often applied in solid/liquid system to describe the saturated monolayer adsorption. It can be represented as:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (1)$$

Where C_e is the equilibrium concentration (mg/L); q_e is the amount of ion adsorbed (mg/g); q_m is q_e for a complete monolayer (mg/g); K_a is adsorption equilibrium constant (L/mg). To evaluate the adsorption capacity for particular range of adsorbate concentration, the before mentioned equation Eq. (1) can be used as a linear form as follows :

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \quad (2)$$

The constants q_m and K_a can be determined from a linearised form of Eq. (2) by the slope of the linear plot of C_e/q_e versus C_e .

Freundlich adsorption isotherm based on adsorption on heterogeneous surface is the earliest known relationship describing the adsorption equilibrium and is given by:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where q_e is the amount of ion adsorbed (mg/g); C_e is the equilibrium concentration (mg/L); K_F and $1/n$ are empirical constants, indicating the adsorption capacity and adsorption intensity, respectively. The Eq. (3) may be converted to a linear form by taking logarithms.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

The plot of $\log q_e$ versus $\log C_e$ of Eq. (4) should result in a straight line. From the slope and intercept of the plot, the values for n and K_F can be obtained.

Temkin Isotherm, the simple form of adsorption isotherm model, has been developed considering the chemisorptions of an adsorbate onto the adsorbent represented as

$$q_e = a + b \log C_e \quad (5)$$

where q_e and C_e have the same meaning as noted previously and the other parameters are called the Temkin constants. The plot of q_e versus $\log C_e$ will generate a straight line. The Temkin constants a and

b can be calculated from the slope and intercept of the linear plot.

Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. It can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (6)$$

Eq. (6) can be converted to a linear form by taking natural logarithms:

$$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln (C_e) + \ln (B) \quad (7)$$

Three isotherm constants, A, B, and g ($0 < g < 1$), can be evaluated from the linear plot represented by Eq. (7) using a trial and error optimization method.

III. Results and Discussion

3.1 Effect of Adsorbent dosage

The results of the effect of an increase in the adsorbent dose from 50-500mg/50ml were presented in Fig.1.

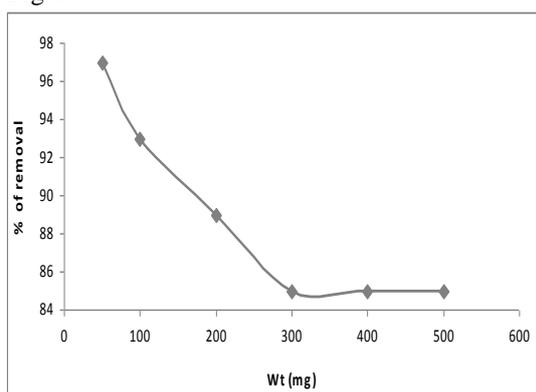


Fig.1. Effect of Adsorbent dosage

From the results, it was observed that the fluoride removal decreased while increasing the adsorbent dosage. This is due to the non-adsorbability of fluoride ions as a result of sorbent-sorbate interaction. The optimum adsorbent required was 50 mg/50ml. It was used for further study.

3.2 Effect of contact time

The effect of contact time while varying the agitation speed is shown in Fig.2. It was observed that initially while increasing the agitation time, the adsorption of fluoride also increased. When the time reaches at 60 minutes the adsorption became maximum. After that the adsorption decreased significantly because of the most of the adsorption took place initially.

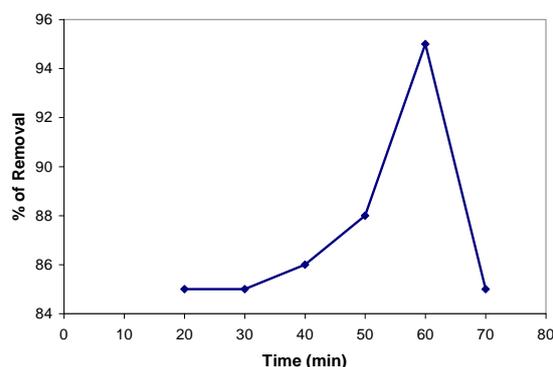


Fig.2. Effect of contact time

3.3 Effect of pH

The effect of pH on fluoride removal by SP was assessed using pH sweep experiments. The effect is shown in Fig.3. It shows that that fluoride removal reactions in SP powder was dependent on pH. It was evident from the results that the F⁻ ions removal was high at neutral pH. As the pH varied, defluoridization capacity dropped down. It might be because of the competition between OH⁻ and F⁻ ions.

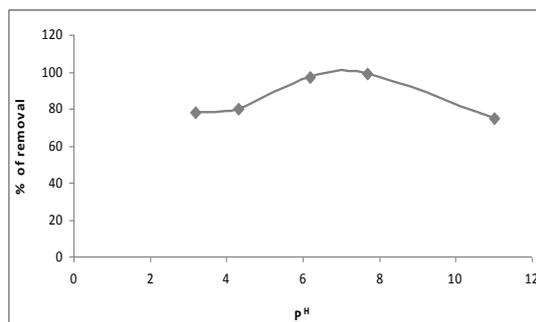


Fig.3. Effect of pH

3.4 Effect of Co-ions

Fluoride contaminated water contains several other ions which can equally compete in the adsorption process. In order to investigate the effect of interfering ions on F⁻ removal, adsorption studies were carried out in the salt solutions of chloride, carbonate, nitrate, sulphate and phosphate independently at an adsorbent dose = 50mg/50ml, shaking speed = 120 rpm and contact time = 1h. The effect of these co-existing ions on F⁻ removal is shown in Fig.4. From this results, it was observed that carbonate nitrate ions showed little negative effect, but chloride, sulphate and phosphate showed more negative effect in the adsorption of fluoride. This is might be due to competing effect of these co-ions for the active sites of the adsorbent.

Table – 1 Effect of Co-ions

No	Salts	%F ⁻ removal
1	NaCl	85
2	NaCO ₃	89
3	NaNO ₃	89
4	Na ₂ SO ₄	85
5	NaH ₂ PO ₄	75
6	Blank	93

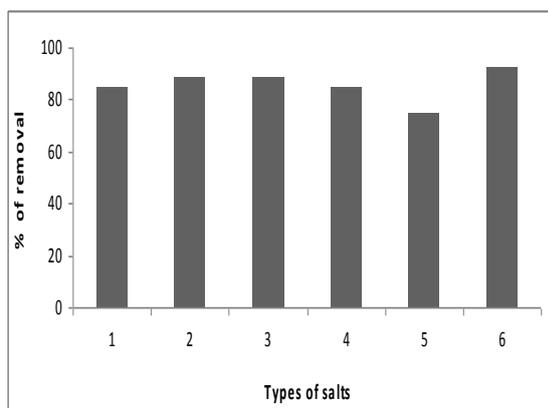


Fig.4. Effect of Co-ions

3.5 Effect of speed

The adsorption of effect of speed were studied by increasing the agitation speed from 100 rpm – 300 rpm. The results are shown in the Fig.5. It was noticed that on increasing the shaking speed the F⁻ removal decreased. The F⁻ removal was found to be maximum at 120 rpm because at this shaking speed, the collision frequency between adsorbent & adsorbent might be maximum [1].

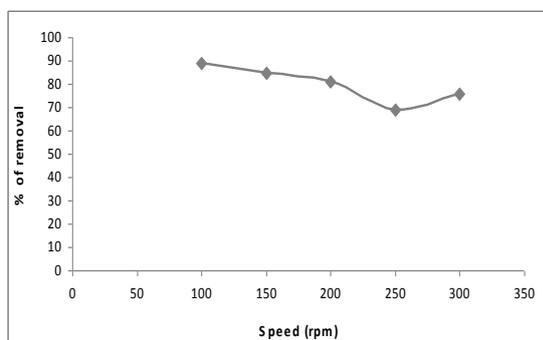


Fig.5. Effect of speed

3.6 Effect of initial fluoride concentration

Adsorption of fluoride varied with the increasing the initial fluoride concentration. These effect was shown in Fig.6. It was observed that while increasing the fluoride concentration the uptake of fluoride ion

decreased. This is due to the lack of active sites of the adsorbent for high concentration of fluoride.

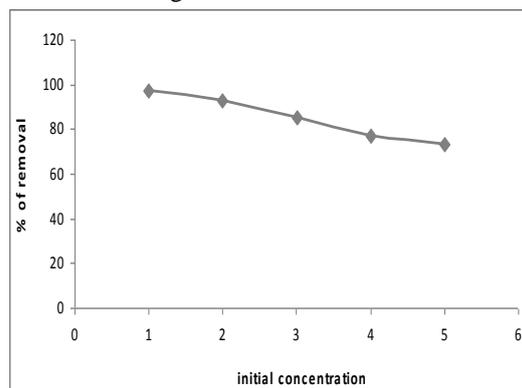


Fig.6. Effect of initial fluoride concentration

3.7 Adsorption Characterization

The XRD patterns of SP before (untreated) and after treatment (treated) with F⁻ ions are shown in Fig.8 (a) & (b) and the XRD data are given in the Table.2 & 3. It was evident from the XRD studies that the crystal structure of the SP showed significant changes after the adsorption of F⁻ ions. The SEM micrographs shows irregularly shaped particles with surface agglomerates of small size particles adhered on bigger particles.

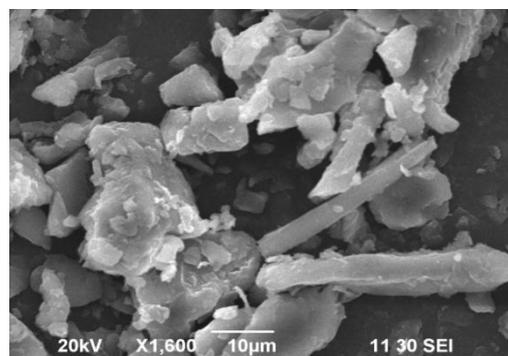


Fig.7.(a) Before treatment

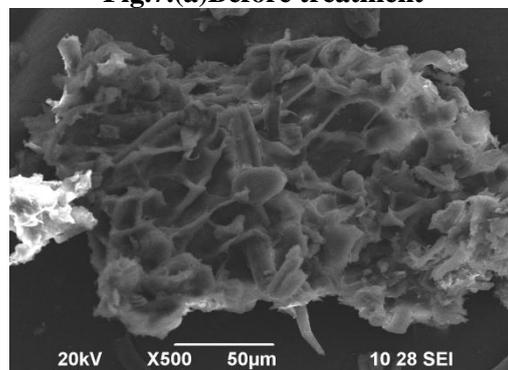


Fig.7. (b) after treatment

Table . 2. XRD data before adsorption of SP

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
18.1106	62.85	0.4291	4.89427	100.00
19.8916	44.99	0.7872	4.46359	71.57
23.4649	47.31	0.3717	3.78820	75.28
45.4859	30.48	1.5744	1.99416	48.49
48.5752	32.37	0.7422	1.87276	51.50
77.0995	23.18	0.1785	1.23605	36.88

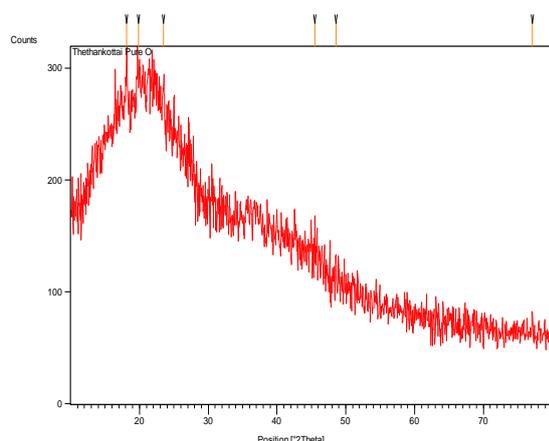


Fig.8 (a) XRD diagram before adsorption of SP

Table – 3 XRD data after adsorption of SP

Pos. [°2Th.]	Height [cts]	FWH [°2Th.]	d-spacing [Å]	Rel. Int. [%]
21.374	29.87	1.6797	4.1537	64.11
26.780	46.59	0.6437	3.3262	100.00
48.306	17.74	0.7200	1.8825	38.07

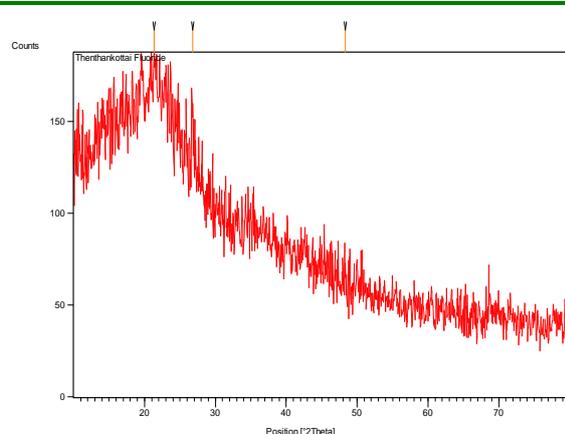


Fig.8 (b) XRD diagram after adsorption of SP

Analysis of isotherm data is important for predicting the adsorption capacity of the sorbent, which is one of the main parameters required for the design of an adsorption system. Several isotherm model equations have been used for this purpose. The distribution of fluoride between the liquid and solid phase is a measure of the position of equilibrium in the adsorption process and can be expressed by the Freundlich and Langmuir equations.

The applicability of Freundlich and Langmuir models that deal with physicochemical adsorption on heterogeneous surfaces and monolayer coverage and constant adsorption energy respectively, was studied. An experiment was carried out under the given conditions to study the adsorption modeling. The linearized Freundlich isotherm (Fig.9), which was indicative of surface heterogeneity of the adsorbent was given below:

$$\log q_e = \log K + 1/n (\log C_e) \quad (8)$$

where K and 1/n are the Freundlich constants related to adsorption capacity and intensity respectively. The values of K and 1/n are 0.1823 mg/g and 0.9793 with a regression coefficient, $R^2 = 0.9895$, which were obtained from the slope and intercept of the linearized Freundlich plot of $\log C_e$ vs. $\log q_e$. Since the value of adsorption intensity (1/n) was less than unity, the adsorption was a favorable one [20].

The linearized Langmuir model, which deals with the monolayer coverage was given below.

$$1/q_e = ((1/q_0b) (1/C_e)) + 1/q_0 \quad (9)$$

where q_0 is the maximum amount of fluoride ion per unit weight of SP powder and 'b' is the equilibrium constant which indicates the affinity of binding sites of SP powder. The values of the Langmuir parameters, q_0 and b are 24.94 mg/g and 0.2193 L/mg respectively with the regression coefficient, $R^2 = 0.9963$, which were obtained from the slope and intercept of the linear plots of $1/q_e$ vs. $1/C_e$ (Fig.10)

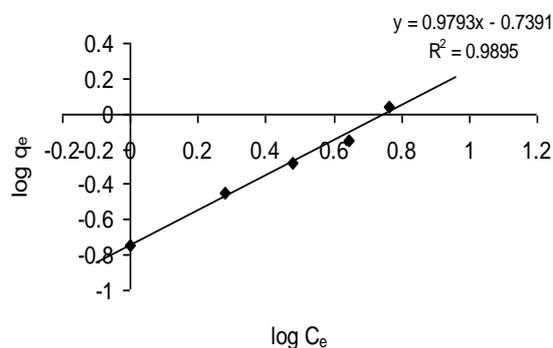


Fig.9 Freundlich adsorption isotherm, $\log C_e$ vs. $\log q_e$

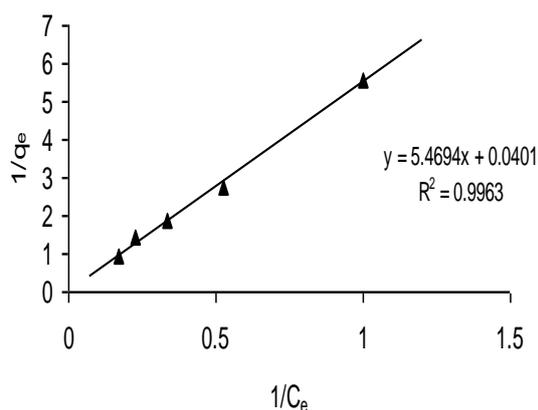


Fig.10 Langmuir isotherm, $1/C_e$ vs. $1/q_e$

In order to predict the adsorption efficiency of the process, the dimensionless equilibrium parameter (r) was calculated by using the following relation [21]:

$$r = 1/(1+C_0b)$$

where C_0 and b are initial fluoride concentration and the Langmuir isotherm constant. A value of $r < 1$ represents favorable adsorption while $r > 1$ represents unfavorable adsorption. The value of ' r ' was found to be 0.0436, which indicates that the system is favorable adsorption.

3.9 Kinetics

The kinetics of adsorption was investigated to explain the fluoride removal mechanism of SP powder. It was noticed that the fluoride removal increases with the lapse of time. However, the rate of fluoride adsorption was initially rapid and the equilibrium was attained within 60 minutes. The rate constant (K_{ads}) for sorption of fluoride on the SP powder was studied by applying Lagergren first-order rate equation [20,22]:

$$\log (q_e - q_t) = \log q_e - K_{ads} (t/2.303) \quad (10)$$

where q_e and q_t (both in mg/g) are the amounts of fluoride adsorbed at equilibrium and at time t , respectively and K_{ads} is the rate constant (min^{-1}). The values of K_{ads} for fluoride sorption were calculated from the slope of the linear plot of $\log (q_e - q_t)$ vs. time as shown in Fig.50. They were found to be 3.0×10^{-4} , 4.0×10^{-4} , 4.0×10^{-4} , 3.0×10^{-4} and 1.0×10^{-4} for initial fluoride concentration of 100, 200, 300, 400 and 500 mg/L respectively. For strict surface adsorption, the variation in adsorption rate should be proportional to first power of concentration. However, the relationship between initial solute concentration and the rate of adsorption will not be linear when pore diffusion limits the adsorption process. The possibility was studied in terms of graphical relationship between the amount of fluoride adsorbed and square root of time as shown in Fig.12. In order to investigate the contribution of intraparticle diffusion in the adsorption process, the rate constant

for intra particle diffusion, K_p ($\text{mg/g min}^{-1/2}$) was calculated using the following relation:

$$q = K_p t^{1/2} \quad (11)$$

where K_p ($\text{mg/g min}^{-1/2}$) is the intraparticle diffusion rate constant. The value of K_p were calculated from the slope of the linear plot of q_t against the square root of time ($t^{1/2}$) as shown in Fig.12. They were found to be 1.1×10^{-3} , 3.7×10^{-3} , 4.4×10^{-3} , 4.4×10^{-3} and 3.3×10^{-3} $\text{mg/g min}^{-1/2}$ at initial fluoride concentration of 100, 200, 300, 400 and 500 mg/L respectively. It is evident that all the plots have the same general features (i.e. initial curved and subsequent linear portion). The initial curved portion was attributed to the film or boundary layer diffusion while the linear portion reflects the intra particle diffusion. However, it is also evident from Fig.13 that the linear portion of the curve did not pass through the origin, which indicates that the mechanism for fluoride removal by SP powder was a complex one and both surface adsorption as well as intra particle diffusion contribute the rate determining step [23].

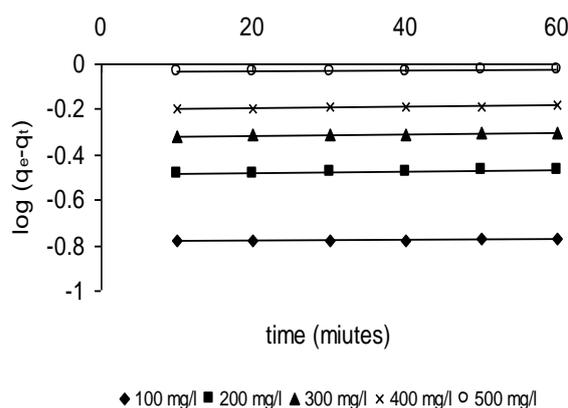


Fig. 11 Adsorption kinetics, time vs. $\log (q_e - q_t)$ with initial fluoride concentration of 100 mg/L

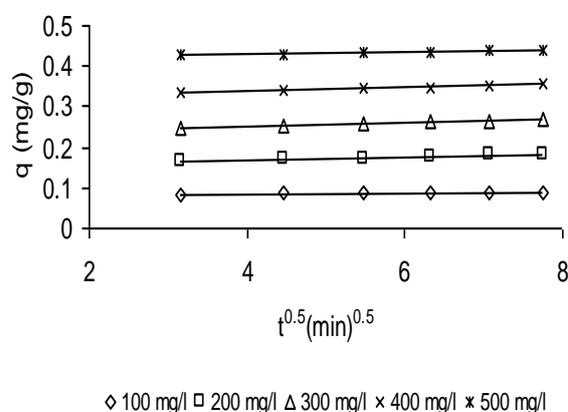


Fig.12 Graphical relationship between the amount of fluoride adsorbed and square root of time

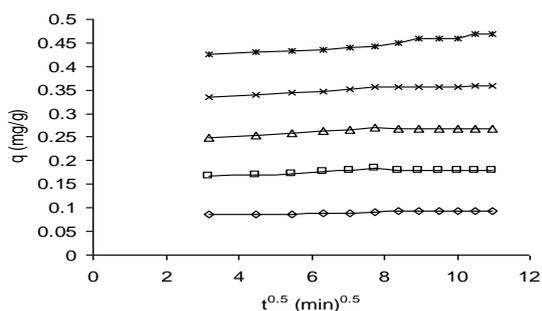


Fig.13 Intraparticle mass transfer curve for the adsorption of fluoride

3.10 FT-IR Spectral studies

The results suggested that the adsorption of fluoride ions onto SP may be a complex one involving both physisorption and chemisorption. To get a better insight into the nature of the mechanism, the FT-IR spectra of the adsorbents before and after adsorption were recorded and representative spectra are given in Fig. 14. (a) & (b). Most of the peaks showed no significant variation in position. This might be due to the fact that replacement of Cl⁻ by more electronegative F⁻ might have caused the shift to a lower wave number [21].

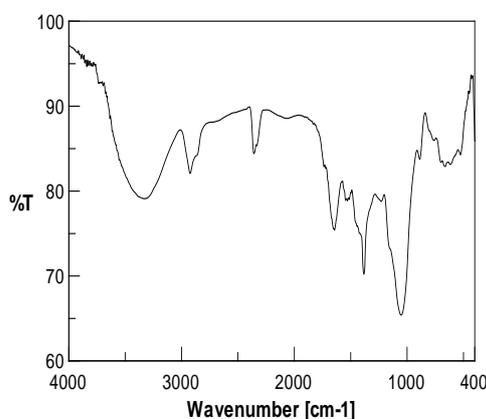


Fig.14 (a) FT-IR spectra for SP before adsorption

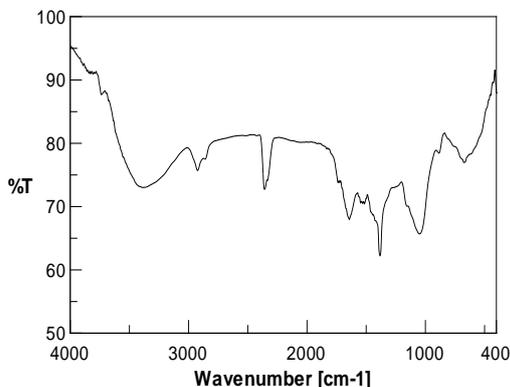


Fig.14 (b) FT-IR spectra for SP after adsorption

IV. Application

This method can be applied for removal of fluoride ions in presence of foreign ions in contaminated water. Among the foreign ions, nitrate, carbonate, sulphate, chloride and phosphate showed negative effect on fluoride removal by SP powder. This might be due to a change in pH and also because of competition between the competing ions and fluoride ions for the active site of SP powder.

V. Conclusion

The removal of fluoride ions was maximum for the adsorbent dosage of SP 50mg/50ml. The fluoride adsorption was maximum at 60 min for the adsorbent. The adsorption of F⁻ ion was maximum in the shaking speed of 120 rpm. The presence of interfering ions such as nitrate, carbonate, sulphate and chloride showed little negative effect and phosphate showed high negative effect for the adsorbent. In the pH = 7, the F adsorption was maximum for SP. The optimum initial F concentration for SP adsorbent was 1mg/50ml.

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