

A Study on Removal of Fluoride Ions from Drinking Water using a Low- Cost Natural Adsorbent

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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 *Vetiveria Zizanioides* was studied. Influence of pH, adsorbent dose, contact time, co-ions, speed and initial concentration on the adsorption process was investigated. The maximum removal of fluoride ion was maximum at the range of pH of 6 to 7. The removal of fluoride was expressed with Langmuir and Freundlich isotherms. 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 200mg/50ml. The adsorption of F⁻ ion was maximum with the shaking speed of 120 rpm. The presence of interfering ions such as chloride, nitrate and carbonate showed little negative effect and sulphate and phosphate showed high negative effect for the adsorbent. The optimum initial F⁻ concentration for better adsorbent efficiency was found to be 1mg/50ml. The kinetics of F⁻ removal was investigated and discussed

Keywords— Fluoride, *vetiveria zizanioides*, low cost 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 [5–7]. 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 as adsorbents for the removal of fluoride ions [8–22]

B. About the Study

The aim of the present study was to examine the feasibility of using low cost natural adsorbents such as *vetiveria zizanioides*, 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

A. 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 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 photocolormetry using the SPADNS indicator. The adsorption isotherm at pH 6.90 ± 0.10 was studied by varying the initial fluoride concentration from 5 to 50 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 pH 6.90 ± 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^- ,

SO_4^{2-} , PO_4^{3-} and $\text{S}_2\text{O}_3^{2-}$) were observed using, 20-200 mg/L solutions at pH 6.90 ± 0.10 over 1 Hr

B. 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 =50 mg/L, shaking speed =150 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.

C. 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.

D. 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:

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

(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 :

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

(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:

$$q_e = K_F C_e^{1/n}$$

(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.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

(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 chemisorption of an adsorbate onto the adsorbent, is represented as

$$q_e = a + b \log C_e$$

(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:

$$q_e = \frac{AC_e}{1 + BC_e^g}$$

(6)

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

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

(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. RESULT AND DISCUSSION

A. Effect of Adsorbent dosage

To study the effect of an increase in the adsorbent dosage on removal of fluoride experiments were conducted employing adsorbent doses ranging from 100-500mg/50ml. The results are presented in Fig.1, where it could be seen that fluoride uptake was high for 200mg/50ml of the adsorbent. This might be due to the fact that dose concentration of 200mg/50ml of adsorbent, more sorbent surface and pore volume would be available for the adsorption interaction and this result in higher fluoride ion removal [23].

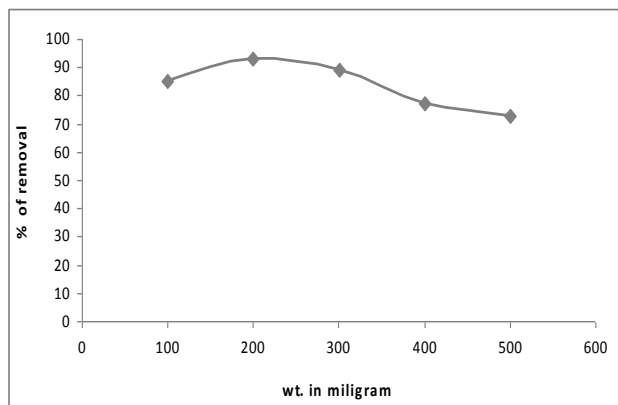


Fig.1. Effect of adsorbent dosage

B. Effect of pH

The pH controls the adsorption at the water-adsorbent interfaces. The effect of the pH was shown in the Fig.2. It showed that the removal of fluoride was maximum at the range of pH of 6 – 7.

The lower defluoridation efficiency at pH below 6 was possibly due to protonation of fluoride. This result could be attributed to the formation of weakly ionized hydrofluoric acid [24]. Above the pH of 7, there may be the competition between the OH⁻ and F⁻ ion

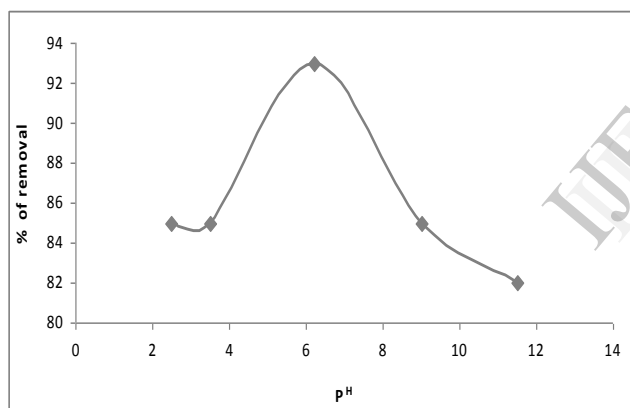


Fig.2. Effect of pH

C. Effect of contact time

The percentage of fluoride absorbed in different intervals of time was studied. The effect of contact time is shown in Fig.3. It was observed that on increasing the time by 10 minutes, the F⁻ ion removal initially increased. After 60 minutes it attained equilibrium due to the decrease in adsorption sites.

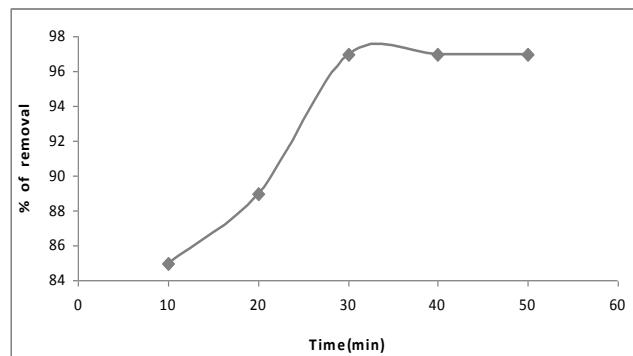


Fig.3. Effect of contact time

D. Effect of Co-ions:

The fluoride removal from drinking water was affected by the different kinds of co-ions present in it. The effect of co-ions were studied and its result is shown in Fig.4.

It was observed that sulfate ions showed the positive effect and chloride ion, nitrate ion, carbonate ion showed little negative effect, but phosphate ion showed a very high negative effect. It entirely reduced the absorption of fluoride from 93% to 13%. This might be due to the competing effect of these co-ions for the active sites of the adsorbents [25].

Table – 1 Effect of co-ions

S.No	Co-ions	% F ⁻ removal
1	NaCl	89
2	NaCO ₃	81
3	NaNO ₃	85
4	NaS ₂ O ₃	93
5	NaH ₂ PO ₄	13
6	Blank	93

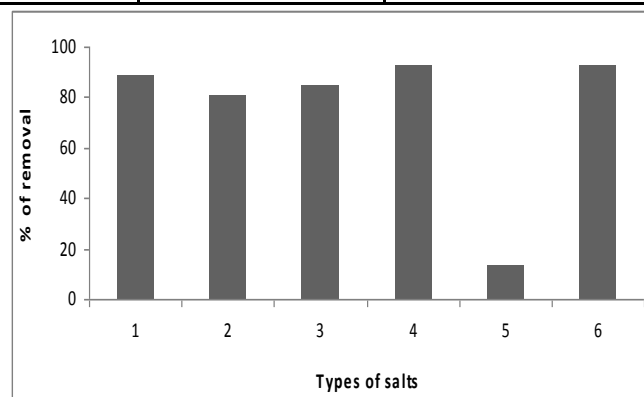


Fig.4. Effect of co-ions

E. Effect of speed

The effect of speed on Fluoride ion adsorption was studied by increasing the agitation speed from 100 rpm – 300 rpm. The results are shown in the Fig.5.

From the results, it was observed that increasing the agitation speed decreased the adsorption of fluoride ions. The optimum agitation speed for this adsorbent was 120 rpm. This is due to the collision frequency was maximum at 120rpm only. Hence the shaking speed of 120 rpm was chosen for further study.

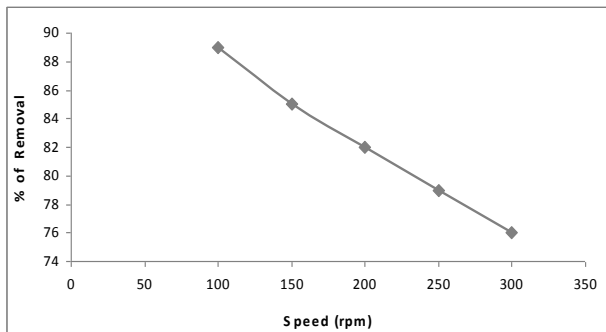


Fig.5 Effect of speed

F. Effect of initial concentration

Experiments were carried out by changing the initial concentrations of Fluoride. The results are shown in Fig.6. It was observed that the maximum fluoride removal decreased with the increase in initial concentration of fluoride ions. This indicated that there exists a reduction in immediate solute adsorption owing to the lack of available active sites on the adsorbent surface [25].

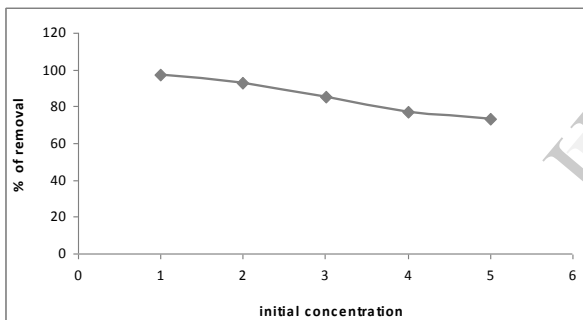
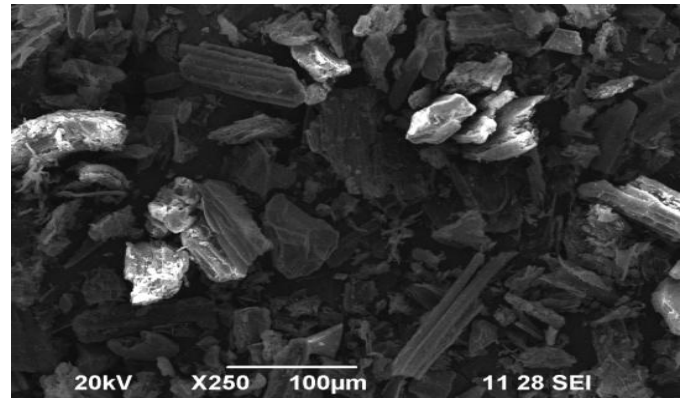


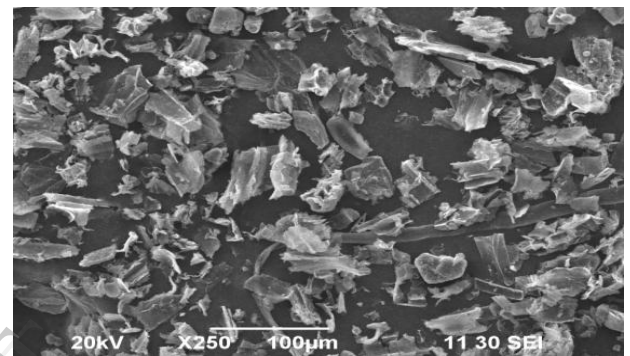
Fig.6. Effect of initial concentration

G. Adsorbent Characteristics

The SEM patterns of the VZ before (untreated) and after treatment (treated) with F^- ions are shown in Fig.7 (a) & (b) and the XRD data are given in the Fig 8 (a) & (b). It is evident from the XRD studies that the crystal structure of the VZ showed significant changes after the adsorption of F^- ions. This also suggests that the uptake of F^- ions by VZ was due to chemisorption and precipitation, with alternation in the crystal structure of VZ. The SEM micrographs shows irregularly shaped particles with surface agglomerates of small size particles adhered on bigger particles.



(a)



(b)

Fig.7. (a) SEM before treatment, (b) After treatment

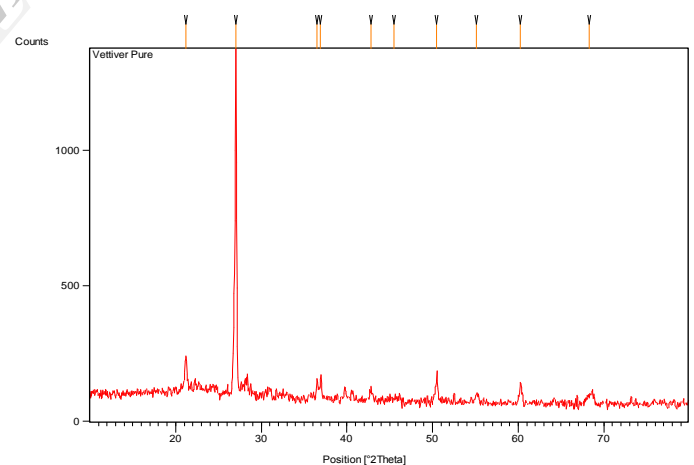


Fig.8 (a) XRD data for the VZ before treatment

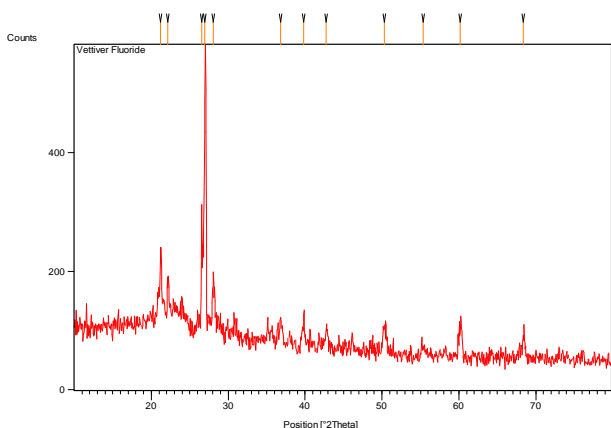


Fig.8 (b) XRD data for the VZ after treatment

H. Mathematical Modelling of the Adsorption Isotherm

The ability of VZ to adsorb fluoride from aqueous solution was evaluated from the general nature of the adsorption isotherm plot (C_e against q_e , Fig.9). The equilibrium adsorption data were fitted to the Langmuir and Freundlich isotherm models that have been used most frequently to describe equilibrium adsorption data. For a solid-liquid system, the Langmuir isotherm is expressed in linear form as

$$1/q_e = (1/QbC_e) + 1/Q \tag{8}$$

where q_e is the amount of solute adsorbed ($mg\ g^{-1}$) at equilibrium and C_e is equilibrium solute concentration ($mg\ dm^{-3}$) in solution. The values of empirical constants Q and b , denoting monolayer capacity and energy of adsorption respectively, are evaluated ($20.7\ mg\ g^{-1}$ and $0.155\ dm^3\ mg^{-1}$, respectively) from the slope and intercept of the linear plot of $1/q_e$ against $1/C_e$ (Fig.9).

The Freundlich model is expressed as

$$Q_e = K_f (C_e)^{1/n} \tag{9}$$

where K_f and $1/n$ are the characteristic isotherm constants of the system. The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. For linearization of the data, the Freundlich equation is written in logarithmic form as

$$\ln q_e = \ln K_f + (1/n) \ln C_e \tag{10}$$

A linear plot of $\ln q_e$ against $\ln C_e$ yields a slope of $1/n$ and intercept of $\ln K_f$ (Fig.10). The value of K_f ($0.29\ mg\ g^{-1}$) is roughly an indicator of adsorption capacity and the value of $1/n$ (1.0056) indicates the adsorption intensity.

Evaluation of the preferred isotherm model, judged from the regression coefficient value (R^2), indicates that either the Langmuir (0.9942) or Freundlich (0.9893) equation is applicable to fluoride-VZ interaction. The influence of isotherm shape evaluated from 'r', a dimensionless constant, defined as:

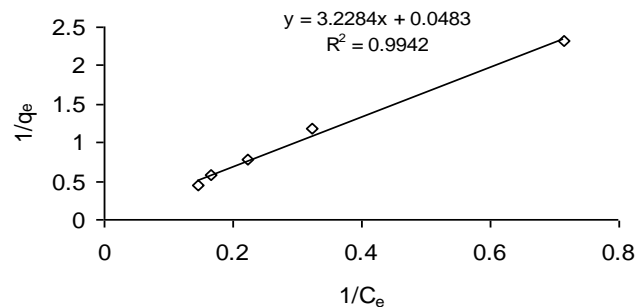


Fig.9. Langmuir isotherm curve

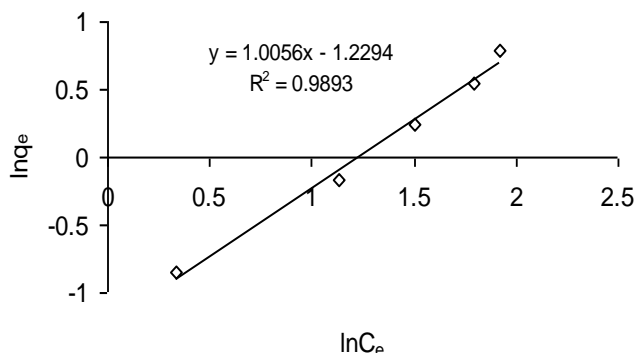


Fig.10. Freundlich isotherm curve

$$r = 1 / (1+bC_0) \tag{11}$$

where b is the Langmuir constant and C_0 is the initial fluoride concentration ($100mg/l$). The parameter 'r' indicates the shape of the isotherm accordingly:

Table – 3 'r' value for different types of isotherm

'r' value	Type of isotherm
$r > 1$	Unfavourable
$r = 1$	Linear
$0 < r < 1$	Favourable
$r = 0$	Irreversible

Favourable adsorption is predicted in the present case from the r value of 0.06.

I. Kinetics and Rate Parameters

In order to understand the kinetics of the process, the data were fitted to a pseudo-first-order rate expression, the Lagergren rate equation, as

$$\ln (q_e - q_t) = \ln q_e - K_1 t \tag{12}$$

where q_e and q_t are the amounts of fluoride ($mg\ g^{-1}$) on Vetiveria Zizanioides at equilibrium and at time 't', respectively, and K_1 (min^{-1}) is the first-order rate constant. A plot of $\ln (q_e - q_t)$ against time (t) should yield a straight line (Fig.11), and the rate constant K_1 was evaluated from the slope and was found to be 6.0×10^{-4} , 3.0×10^{-4} , 0.9×10^{-4} , 1.0×10^{-4} and $1.0 \times 10^{-4}\ min^{-1}$ for the concentration of fluoride ion, 100, 200, 300, 400 and 500 mg/l respectively. The values of K_1 were found to decrease with increase in the initial concentration of fluoride from 100 to 300 mgL^{-1} and then a

small increase was found at F⁻ concentration of 400 mgL⁻¹. An examination of the effect of fluoride ion concentration on the K₁ helps to describe the mechanism of removal taking place. In cases of strict surface adsorption, a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationships between initial solute concentration and the rate of reaction will not be linear. Hence, it seems likely that pore diffusion limits the overall rate of fluoride adsorption [26].

The data may be fitted to the pseudo-second-order expression

$$t/q_t = (1/K_2) (1/q_e^2) + t/q_e \tag{13}$$

applying the boundary conditions of t=0 to t=t and q_t=0 to q_t = q_t. A plot of t/q_t against 't' should yield a straight line (Fig.12) with K₂ (g mg⁻¹ min⁻¹), the second order rate constant, obtained from the intercept.

The applicability of a particular rate expression for the fluoride-VZ system was evaluated from the goodness of data fit and regression coefficient value (R²). In the present situation the Lagergren first-order equation gives a lower regression value (R² > 0.9605) than the second-order equation (R² > 0.9928), showing adherence to the pseudo-second-order rate law.

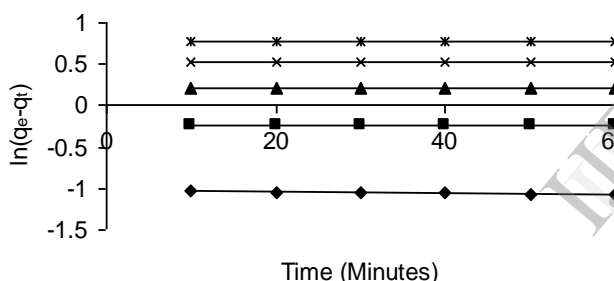


Fig.11. Lagergren equation plot

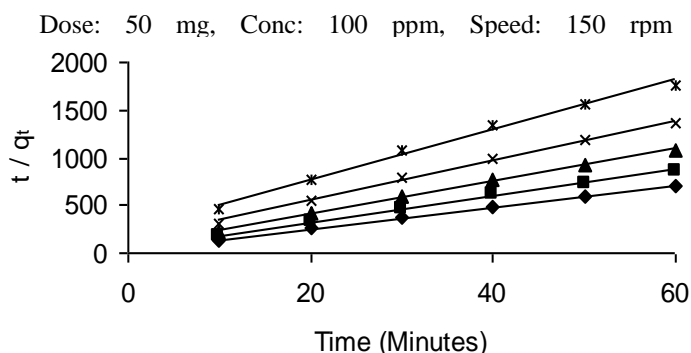


Fig.12. Second-order rate equation plot

J. FT-IR studies

The foregoing results suggested that the adsorption of fluoride ions onto VZ may be a complex one involving both physic- and chemi-adsorption. 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.13. (a) & (b).

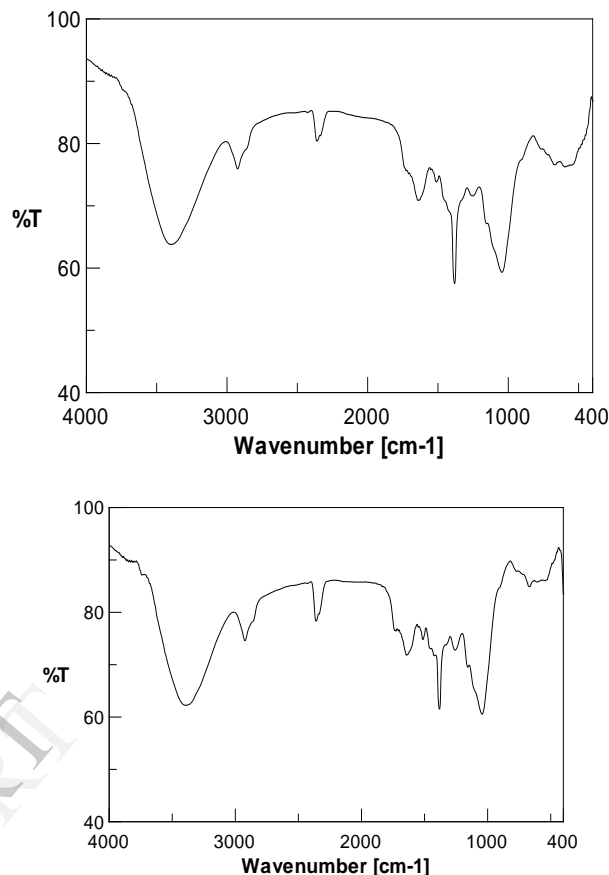


Fig.13. (b) FT-IR spectra for after adsorption

IV.CONCLUSION

The removal of fluoride ions is maximum for the adsorbent dosage of VZ is 200mg/50ml. The maximum removal of fluoride ion was at the range of pH of 6 to 7. The sufficient time for adsorption equilibrium of fluoride ion was 30 minutes. The adsorption of F⁻ ion is maximum in the shaking speed of 120 rpm. The optimum initial F concentration for VZ adsorbent is 1mg/50 ml. The presence of interfering ions such as Chloride, Nitrate and Carbonate showed little negative effect and Sulphate, Phosphate showed high negative effect for the adsorbent.

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