Factors influencing the removal of fluoride from aqueous solution by Pithacelobium dulce Carbon

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ABSTRACT

The aim of this research work is to develop a new method for the removal of fluoride, from aqueous solutions by using indigenously prepared low cost activated carbon like Pithacelobiumdulce carbon (PLDC). The effects various factors like pH, dose of the adsorbent, adsorbate concentration and contact time have been investigated using a batch adsorption technique. The amount of fluoride removal increased with decrease in the initial concentration of fluoride and also increased with increase in contact time, amount of adsorbent used and the initial pH of the solution. Adsorption data were modeled using the Freundlich and Langmuir adsorption isotherms and followed first order kinetic equation –dF/dt= Kr (F). The experimental results produced a straight line fit with a relatively good correlation coefficient (R^2) indicating the acceptability of the model for the studied indigenously prepared activated carbon fluoride system. The kinetics of adsorption was found to be first order with regards to intra-particle diffusion rate.

Keywords: Adsorption; Activated carbons-indigenously prepared; Freundlich and Langmuir adsorption isotherms; Intra-particle diffusion
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INTRODUCTION

Fluoride in drinking water has an intense effect on teeth and bones. Fluoride displaces hydroxide ions from hydroxyapatite, $Ca_5 (PO_4)3OH$, the principal mineral constituent of teeth (in particular the enamel) and bones, to form the harder and tougher fluoroapatite, $Ca_5 (PO_4)3F$. This will be useful in strengthening the enamel when it is present in low quantity. However, fluoroapatite is an order of magnitude less soluble than hydroxyapatite, and at high fluoride concentration the conversion of a large amount of the hydroxyapatite into fluoroapatite makes the teeth and (after prolonged exposure) the bones denser, harder and more brittle. In the teeth this causes mottling and embrittlement, a condition known as dental fluorosis. With prolonged exposure [1] at higher fluoride concentrations dental fluorosis progresses to skeletal fluorosis. Due to the industrial revolution high concentration of fluoride in water bodies causes a great damage to human life. High fluoride concentrations in groundwater, up to more than 30 mg/L, occur widely, notably in the United States of America, Africa and Asia [2-11]. Indigenously prepared activated carbons play a vital role in adsorption.

The surface chemical structure and their large surface area allow them to be used in a wide variety of industrial applications, some of the most important dealing with the environmental field and particularly with water purification

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and industrial wastewater cleaning [12-16]. De-fluoridation was reported by adsorption[17] ,chemical treatment [18,19], ion exchange [20] membrane separation [21,22], electrolytic de-fluoridation [23] and electro dialysis [24-26] etc. Among various processes, adsorption was reported to be effective [27]. Investigators reported various types of adsorbents namely activated carbon, minerals, fish bone char coal, coconut shell carbon and rice husk carbon, with different degrees of success [17,28-32] S.Venkata mohan [33] reported that fluoride is removed from aqueous phase by biosorption onto algal biosorbent spirogyra sp.IO2 and IO1.

The purpose of the present work is to study the kinetics of adsorption of fluoride on indigenously prepared activated carbon from plant materials and to compare the adsorption capacity for the removal of fluoride under optimum experimental conditions with CAC. Therefore this investigation is mainly concentrating on kinetics of adsorption of fluoride on indigenously prepared activated carbon to find out the possibility of using these carbonaceous materials as low-cost adsorbent for the removal of fluoride.

MATERIALS AND METHODS

2.1. Preparation of activated carbon.
Inorder to prepare the activated carbons the raw material were procured locally, washed with double distilled water at room temperature, dried, cut into small pieces and dried. The waste materials were carbonized in the electrical conventional heating reactor by two stages carbonization process known as low temperature carbonization and high temperature carbonization in the range of 250-600 ^{O}C and 600-800 ^{O}C respectively [34]. The materials were placed in closed stainless steel vessels by maintaining inert conditions and pyrolysis was carried out at 400 ^{O}C for 30 minutes followed by next stage to develop the pore size structure so that an accessible internal surface could be created.

The carbonized product was treated with 0.5 M nitric acid for the removal of unwanted materials. The acid washed product was thoroughly washed with hot distilled water to remove acidity. Indigenously prepared carbon thus produced was thermally activated at 120 ^{O}C for 5 hour in an air oven. The product was finally dried and sieved to get various particle sizes [35]. The material Commercial Activated Carbon (CAC) was supplied by E.Merck, India. Anhydrous sodium fluoride of laboratory reagent quality, supplied by Ranboxy Laboratories Ltd., India was used as an adsorbate and was not purified prior to use. All the other chemicals used in this study were reagent grade and supplied by BDH (India). Double distilled water was employed for preparing all the solutions and reagents.

2.2. Adsorption Experiments:
221 mg of anhydrous NaF was dissolved in one liter of distilled water to prepare the stock solution of concentration 100 mg L^{-1}. Fluoride test solution of concentration 5 mg L^{-1} was prepared from the stock solution. The normal concentration of fluoride which is present in ground water is 5mg L^{-1} and therefore this concentration was selected. All the experiments were carried out in 250 mL conical flasks with 100 ml test solution at room temperature (28 ± 3 ∘C). These flasks, along with test solution and adsorbent, were shaken in a horizontal shaker, to study the various parameters. At the end of desired contact time, the conical flasks were removed from the shaker, and allowed to stand for 5 min for the adsorbent to settle. 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 Methods of Examination of Water and Wastewater [36]. Equilibrium studies have been made at room temperature (30 ± 1^OC) by employing the batch adsorption technique. All the experiments were carried out at specified optimum conditions. Adsorption Experiments have been carried out with a view to determine the impacts of the effects like pH, contact time, dose and initial concentration of fluoride. The data have been analyzed in the light of adsorption isotherms, adsorption kinetic equations and intra particle diffusion model.

RESULTS AND DISCUSSION

3.1. Effect of pH
The pH of the aqueous solution is an important controlling factor in the adsorption process and thus the role of hydrogen ion concentration is examined at different pH levels of 4, 5,6,7,8 and 9 which is maintained by adding 1 X10^{-1}N solutions of HCl and NaOH with 50 ml of standard solution of 5ppm of fluoride with a contact time of 30 minutes and PLDC dose is 3g/L. The experimental results are present in Table 3.1 and the influence of the pH on the sorption rate is shown in figure 3.1. It is observed from the figure that the percent removal is pH dependant. The results obtained show that the maximum efficiency of percentage of fluoride removal is 81.60, for PLDC at pH 9.00, where as in case of CAC the maximum percent removal is 40.20. In all the cases the percent removal increased from acid media to basic media but after pH level 7.0 the percent removal vary very little. The percent removal of fluoride is almost double at a pH 9.00 when compared with CAC. The results agree well with those reported by others. Muthukumaran [37] reported an optimum pH of 9.0 for fluoride adsorption on to chemically activated carbon.

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Mariappan [38] reported an optimum pH of 8.5 for fluoride adsorption on to alum activated carbons and Gibbsite. Karthikeyan [39]reported an optimum pH of 7.0 for fluoride adsorption on to Activated alumina. Murugan [40] reported at an optimum pH of 7.0 for fluoride adsorption on to Indian Aloe. Prasad [41] and Kishore [42] reported an optimum pH of 9.0 for fluoride adsorption on to Eichhornia species, Mango Shells Carbon, Maize Shells carbon and Delonix regia tree dry fruit carbon respectively. Hence further studies were conducted with these pH values.

Table 3.1: Effect of adsorbate pH on the % removal of fluoride by adsorption with prepared carbon

pH	Ce		% Removal	
	PLDC	CAC	PLDC	CAC
4.00	1.77	3.60	64.60	28.00
5.00	1.45	3.30	71.00	34.00
6.00	1.20	3.16	76.00	36.80
7.00	0.99	3.09	80.20	38.20
8.00	0.95	3.01	81.00	39.80
9.00	0.92	2.99	81.60	40.20

Figure 3.1 Plots showing the relationship between pH of initial fluoride and % removal by adsorbents
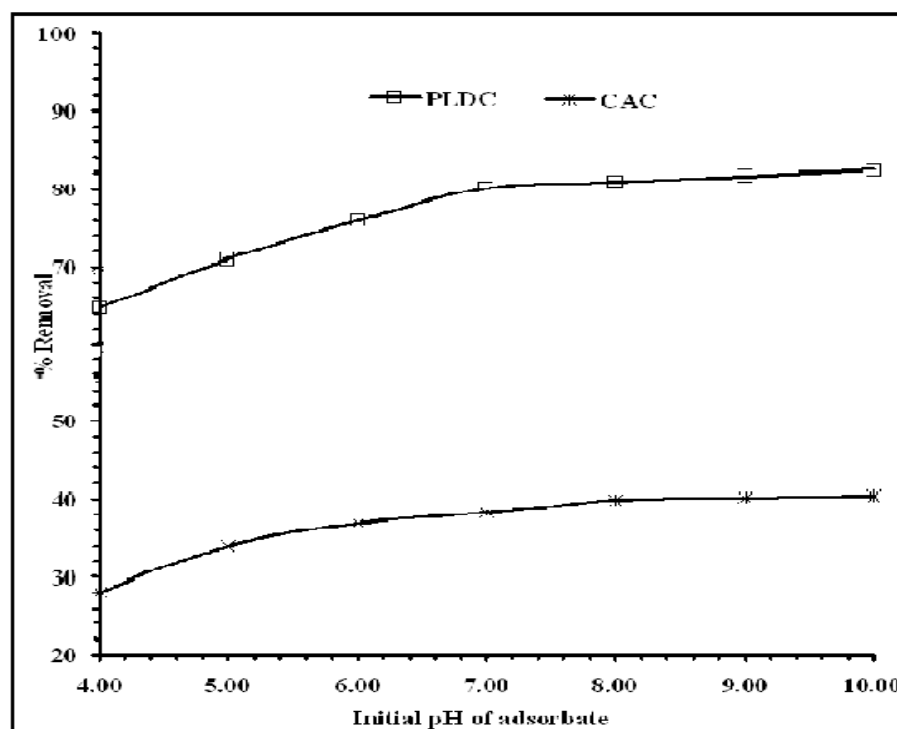
3.2 Effect of agitation time

In the adsorption system contact time plays a vital role, irrespective of the other experimental parameters that affect the adsorption kinetics. In order to study the kinetics and dynamics of adsorption of fluoride by various adsorbents, the adsorption experiments are conducted and the extent of removal of fluoride is known by varying the contact time (range: 10 - 120 minutes) by keeping pH 7, fluoride concentration of 5ppm and dose of 3g/L for PLDC, CAC and the results are given in Table 3.2

The percentage fluoride removal at different time was worked out using equation (1)

Percentage removal = $100 (C_i - C_e)/ C_i$ -------(1)

and a plot was prepared between the percentage of fluoride removal and contact time and is represented in figure 3.2. It can be noted that the percentage fluoride removal is increasing with time and attained almost an equilibrium condition (at which the rate of adsorption of solute is equal to the rate of desorption). In about 40 minutes the decreasing removal rate, particularly towards the end indicates a possible monolayer of fluoride on the outer interface of the ACs and pore (Intra-particle) diffusion on to the inner surface of the adsorbent particles through the film due to continuous agitation maintained during the experiments [43]. The removal of fluoride by these adsorbent samples is rapid at the initial period but becomes slow and almost stagnates with the increase in the contact time.

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The relative increase in the extent of removal of fluoride is substantially low after 40 minutes of contact time by the adsorbents, which is fixed as the optimum contact time. This indicates that the rate of removal of fluoride is higher in the initial stage due to the availability of adequate surface area of the adsorbent. With increase in contact time and due to the decrease in the availability of active sites the adsorption process decreases.

The higher initial rate of removal may be occurring due to the vacant adsorption sites, high solute concentration gradient and the electrostatic affinity between the adsorbent and the solute adsorbate. It is observed from the equation (2) that the rate of change of fluoride concentration is proportional to the fluoride concentration remaining (residual concentration) in solution which can be mathematically expressed according to the following first order equation [44]:

$$-dF/dt = Kr(F) \qquad ------(2)$$

Where dF/dt – rate of change in fluoride concentration in solution, mg/L, Kr – rate constant, $minutes^{-1}$, F – fluoride concentration in solution, mg/L, and 't' – contact time (minutes.).

The modified rate constant value was determined by regression analysis and found to be 0.009 / 40 minutes. With R^2 value 0.9252, defluoridation capacity of adsorbent with contact time is presented in figure 3.2.The capacity varies from 0.89 to 1.38 mg/g for PLDC, for CAC 0.28 to 0.63 mg/g for the contact time of 10 to 120 minutes. The relative increase in the extent of removal of fluoride is substantially low after 40 minutes of contact time by the adsorbents, which is fixed as the optimum contact time. The prepared carbons have 2 to 3 time's higher adsorption capacity than CAC.

Table 3.2: Effect of agitation time on the percent removal of fluoride by adsorption with prepared carbon

Time (Minutes.)	Ce		% Removal		Qe	
	PLDC	CAC	PLDC	CAC	PLDC	CAC
10	2.31	4.14	53.84	17.20	0.8973	0.2867
20	1.67	3.66	66.68	26.80	1.1113	0.4467
30	1.33	3.40	73.32	32.00	1.2220	0.5333
40	1.17	3.21	76.62	35.80	1.2770	0.5967
50	1.05	3.04	78.96	39.20	1.3160	0.6533
60	0.96	3.00	80.72	40.00	1.3453	0.6667
90	0.91	2.99	81.88	40.20	1.3647	0.6700
120	0.85	3.09	83.06	38.20	1.3843	0.6367

Figure 3.2: Effect of agitation time on the percent removal of Fluoride by adsorbents

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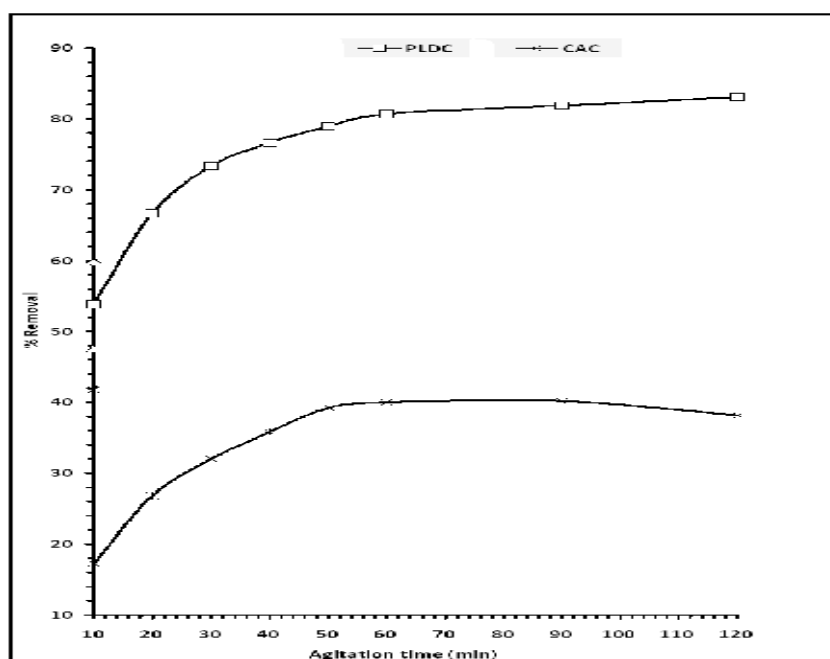
3.3. Effect of adsorbent concentration (Dose)

The percentage removal of fluoride by adsorption by the selected adsorbent is obtained with various doses of adsorbents (range: 0.5 – 9.0 g/L), with optimum initial concentration of fluoride (5 ppm) and contact time (40 minutes) at $30 \pm 1^{o}C$, pH 7. Fluoride uptake by selected adsorbents (PLDC, and CAC) as a function of adsorbent concentration (Dose) is depicted in figure 3.3 and Table 3.3.

The percentage removal of fluoride increases with increase in dose of adsorbent and it is due to the increase in the availability of number of active sites owing to the increase in the effective surface area resulting from the increase in dose of adsorbent and conglomeration of the adsorbent particles, especially at the higher doses of adsorbent [45]. Dose, at which the percentage of removal is maximum, is fixed as the optimum dose of adsorbent. The plot between the logarithmic values of percentage removal and dose of adsorbent was also found to be linear with unit correlation coefficient. The amount adsorbed was found to vary with functional power term of dose of adsorbent. In the present investigation relative percentage removal of fluoride is found to be insignificant after a dose of 3.0 gm/L for PLDC and CAC, so it is fixed as optimum dose of adsorbent.

Table 3.3: Effect of adsorbent concentration on the removal of fluoride from fluoridated water (Ce = Equilibrium concentration of adsorbate (mg/L), Qe = Adsorbent concentration (mg/g.)

Adsorbent	Dose (g/L)	Ce	% Rem.	Qe	Log (% Rem)
PLDC	0.50	1.97	60.60	6.0600	1.78
	1.00	1.64	67.20	3.3600	1.82
	1.50	1.41	71.80	2.3933	1.85
	2.00	1.24	75.20	1.8800	1.87
	2.50	1.15	76.96	1.5392	1.88
	3.00	1.08	78.40	1.3067	1.89
	3.50	1.03	79.40	1.1343	1.89
	4.00	0.97	80.60	1.0075	1.90
	4.50	0.91	81.80	0.9089	1.91
	5.00	0.85	83.00	0.8300	1.91
	7.00	0.79	84.20	0.6014	1.92
	9.00	0.78	84.40	0.4689	1.92
CAC	0.50	4.60	8.00	0.8000	0.90
	1.00	4.06	18.80	0.9400	1.27
	1.50	3.60	28.00	0.9333	1.44
	2.00	3.33	33.40	0.8350	1.52
	2.50	3.12	37.60	0.7520	1.58
	3.00	2.90	42.00	0.7000	1.62
	3.50	2.80	44.00	0.6286	1.64
	4.00	2.68	46.40	0.5800	1.67
	4.50	2.60	48.00	0.5333	1.68
	5.00	2.54	49.20	0.4920	1.69
	7.00	2.54	49.20	0.3514	1.69
	9.00	2.54	49.20	0.2733	1.69

3.4. Effect of initial adsorbate concentration

For a strict adsorptive reaction in the optimized period of contact the rate varies directly with the concentration of adsorbate. The capacity of the adsorbent materials gets exhausted sharply with increase in initial fluoride concentration

The adsorption capacity of treated bio-adsorbent was systematically studied by varying the initial concentration of fluoride between 1-8mg/L by keeping pH 7, dose of 3g/L for PLDC,CAC. The effect of initial concentration of fluoride on the extent of removal of fluoride in terms of amount of the fluoride adsorbed on PLDC and CAC are given in Table 3.4 and figure 3.4 The amount adsorbed exponentially increases while the percentage removal exponentially decreases with the increase in initial concentration of the fluoride. This indicates that there exists a reduction in immediate solute adsorption owing to the lack of available active sites on the adsorbent surface, compared with the relatively large number of active sites required for the high initial concentration of fluoride. The results in Table3.4 indicate that when PLDC is used as adsorbent, the percent removal decreases from 89.00 to 72.50 mg/g and the amount adsorbed increases from 0.2967 to 1.9333 mg/g. But in the case of CAC, the percent removal decreases from 32.00 to 10.00 mg/g . Similarly the amount adsorbed increases from 0.1067 to 0.2667 mg/g.

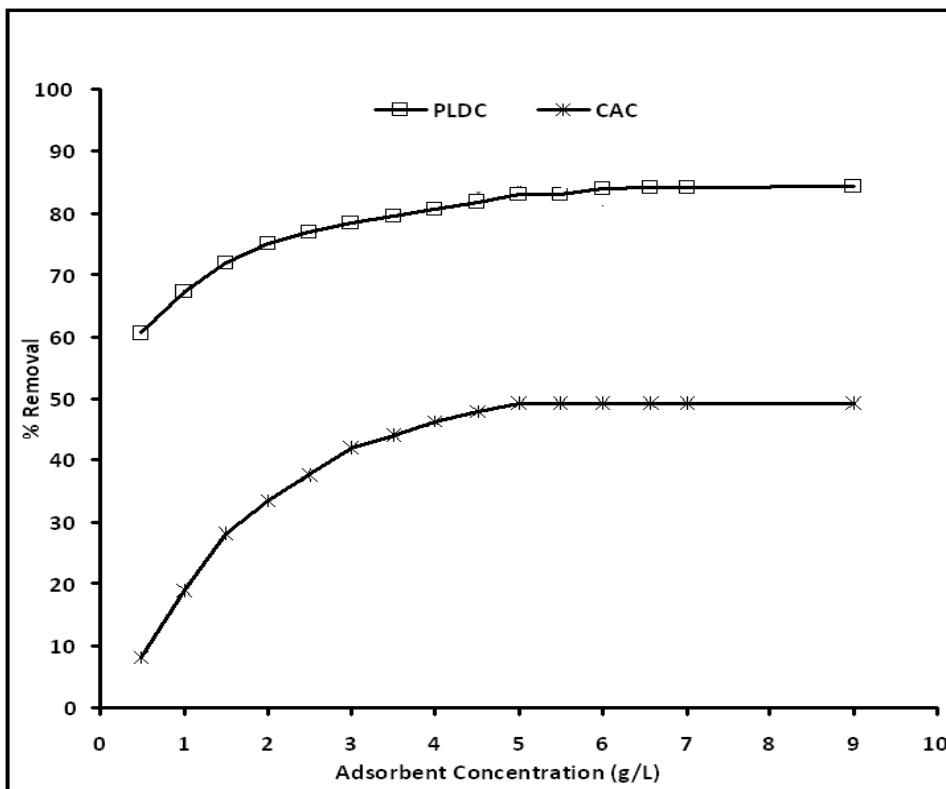_____

Figure 3.3: Effect of Dose on the percent removal of fluoride

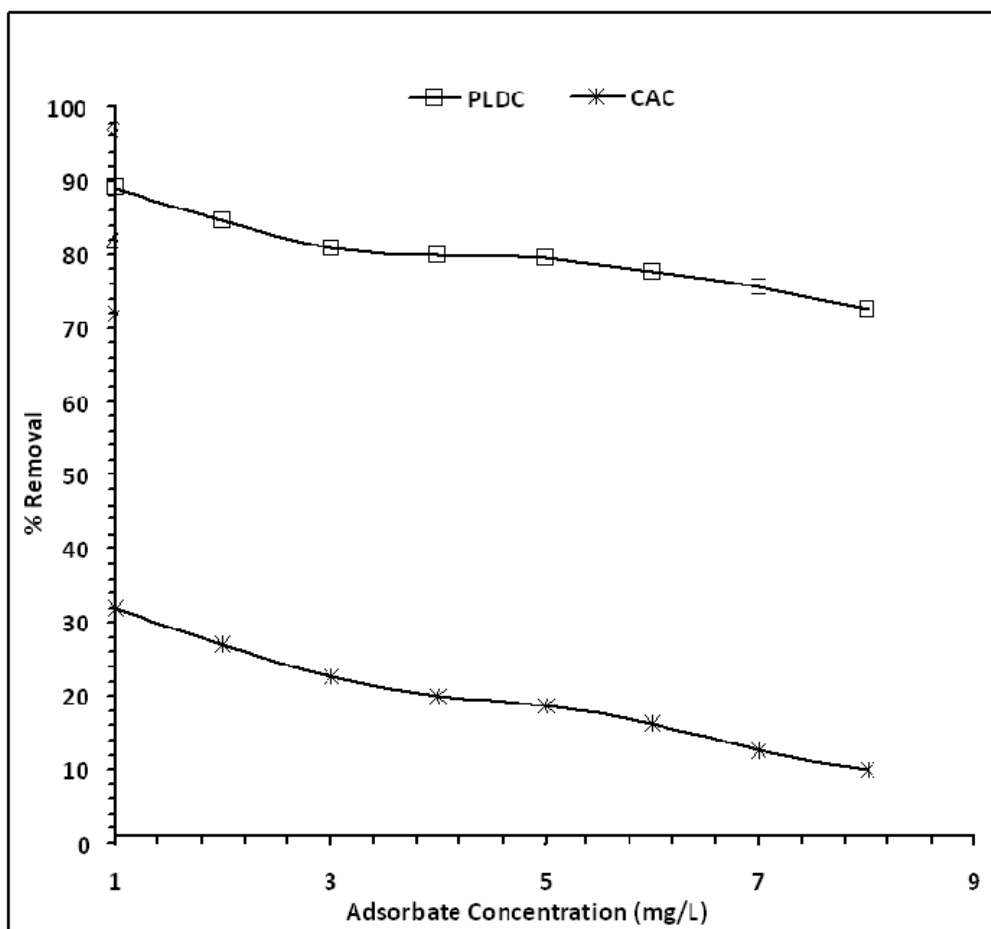**Figure 3.4: Effect of adsorbate concentration on the percent removal of fluoride**

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Table 3.4: Effect of Adsorbate concentration on percent removal of fluoride and calculation of adsorption isotherms

Adsorbent Name	Ci	Ce	%Removal	Qe	Ce/Qe	Log(Ce)	Log(Qe)
PLDC	1.00	0.11	89.00	0.2967	0.3708	-0.9586	-0.5277
	2.00	0.31	84.50	0.5633	0.5503	-0.5086	-0.2492
	3.00	0.57	81.00	0.8100	0.7037	-0.2441	-0.0915
	4.00	0.80	80.00	1.0667	0.7500	-0.0969	0.0280
	5.00	1.02	79.60	1.3267	0.7688	0.0086	0.1228
	6.00	1.34	77.67	1.5533	0.8627	0.1271	0.1913
	7.00	1.72	75.43	1.7600	0.9773	0.2355	0.2455
	8.00	2.2	72.50	1.9333	1.1379	0.3424	0.2863
CAC	1.00	0.68	32.00	0.1067	6.3750	-0.1675	-0.9720
	2.00	1.46	27.00	0.1800	8.1111	0.1644	-0.7447
	3.00	2.32	22.67	0.2267	10.2353	0.3655	-0.6446
	4.00	3.20	20.00	0.2667	12.0000	0.5051	-0.5740
	5.00	4.07	18.60	0.3100	13.1290	0.6096	-0.5086
	6.00	5.02	16.33	0.3267	15.3673	0.7007	-0.4859
	7.00	6.12	12.57	0.2933	20.8636	0.7868	-0.5326
	8.00	7.20	10.00	0.2667	27.0000	0.8573	-0.5740

3.5. Adsorption isotherms:
Adsorption isotherms are essential to know how fluoride concentration will interact with prepared carbons and are useful to optimise the use of activated carbon as an adsorbent. It also provides an approximate estimation of the sorption capacity of the adsorbents. Therefore, empirical equations (Freundlich and Langmuir isotherm model) are important for adsorption data interpretations and predictions. Both Freundlich and Langmuir isotherm models were used for the evaluation of experimental results.

3.5.1 Freundlich isotherm*:*
The general form of Freundlich isotherm is as follows [46-48]

$$q_e = K_f C^{1/n} \qquad\qquad\qquad -----(3)$$

The linearised Freundlich adsorption isotherm, is of the from

$$\log (q_e) = \log K_f + (1/n) \log C_e \qquad ------(4)$$

where, K_f and $1/n$ are the Freundlich constants, q_e is the amount of fluoride adsorbed per unit weight of the adsorbent (in mg/g) and C_e is the equilibrium concentration of fluoride (in mg/L) [49]. In the present adsorption study the $1/n$ value for PLDC is 0.6145 and for CAC is 0.1620. Linear plots of log Ce Vs log qe at different fluoride concentrations are applied to confirm the applicability of Freundlich isotherm model for the removal of fluoride are shown in figure 3.5 and Table 3.5.

3.5.2 Langmuir isotherm [40, 48, 49, 50, 51]
Langmuir isotherm is based on the assumption of that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as;

$$qe = a\, b\, Ce / (1 + b\, Ce), \qquad ----------- (5)$$

where qe is the amount adsorbed (mg/g) and Ce, is the equilibrium concentration of adsorbate (mg/L), a and b are the Langmuir constants related to capacity and energy of adsorption, respectively. The linear form of the Langmuir isotherm can be expressed as,

$$1/qe = (1/ a) + (1/ b\, a\, Ce) \qquad --------------- (6)$$

When $1/qe$ is plotted against $1/Ce$, a straight line with slope $1/ba$ is obtained which shows that the adsorption follows the Langmuir isotherm as shown in figure.3.6 The Langmuir constants '*b*' and '*a*' are calculated from the slope and intercept with Y-axis. The isotherm parameters along with the correlation coefficients (r-values) for adsorbents are calculated. The observed linear relationships as evidenced by r-values close to unity (0.99) confirm that these two adsorption isotherms are applicable.

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Figure 3.5: Calculation of Freundlich isotherm for the removal of fluoride, Ce = Equilibrium concentration of adsorbate in mg/L, Qe = Amount of fluoride ion adsorbed by the adsorbent (mg/g)
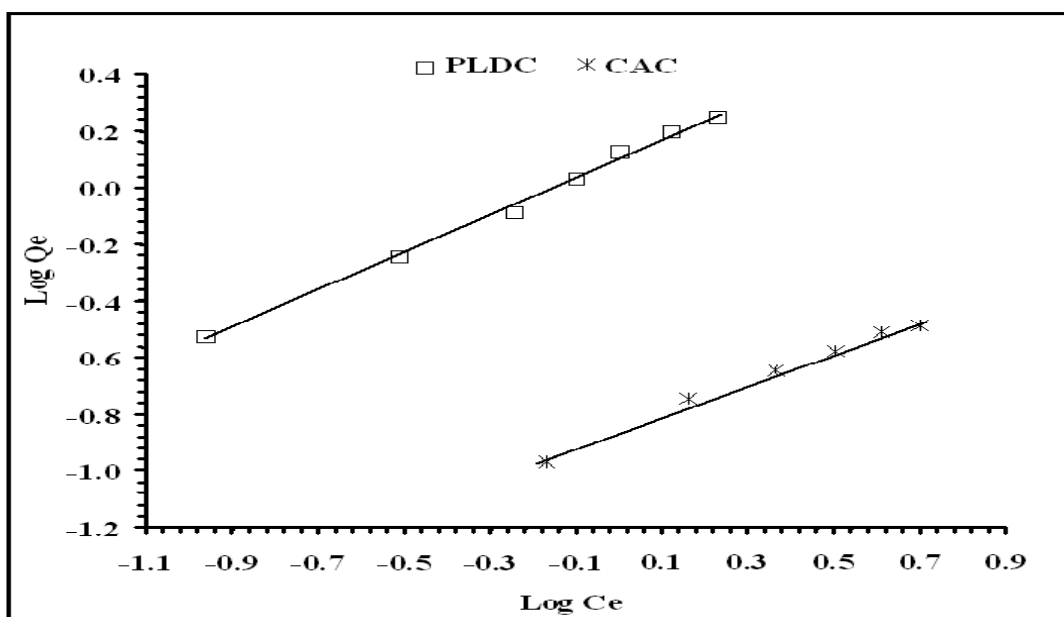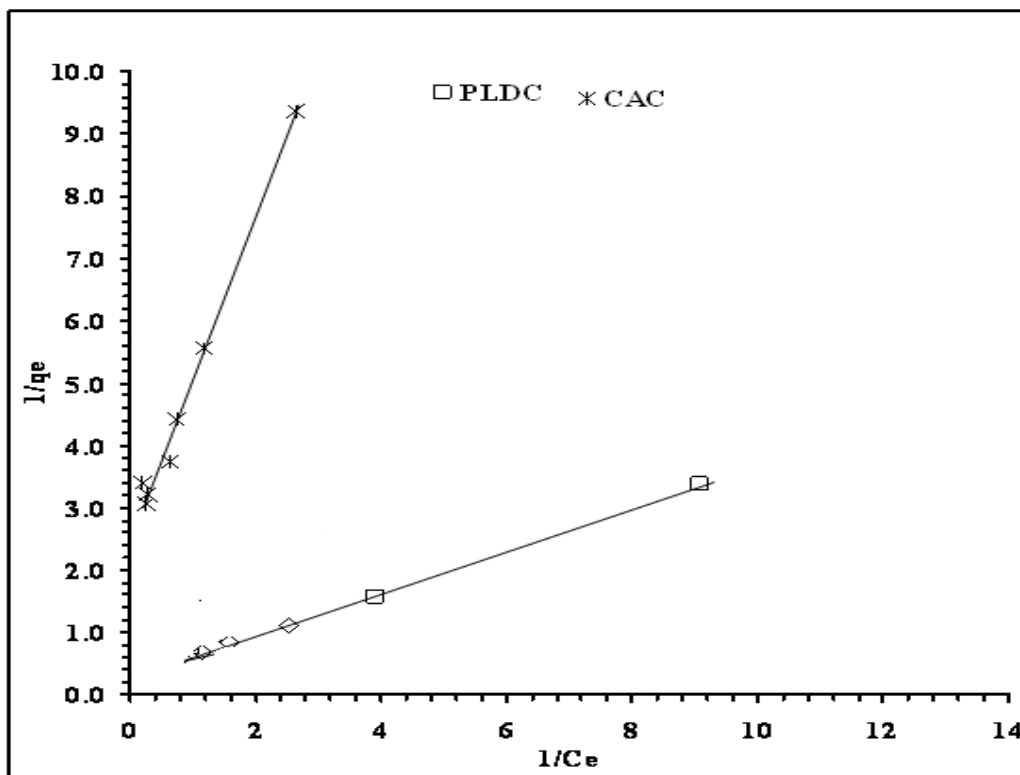

Figure 3.6: Calculation of Langmuir isotherm for the removal of fluoride, Ce = Equilibrium concentration of adsorbate in mg/L, Qe = Amount of fluoride adsorbed by the adsorbent (mg/g)

The applicability of Langmuir isotherm model indicates the formation of monolayer coverage of adsorbate on outer surface of the adsorbent. Further, the essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor, and described the type of isotherm defined by

$$R_L = 1/ (1 + b\, C_i) \qquad \text{--------------- (7)}$$

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where, C_i is the initial concentration of fluoride (in mg/L) and b is the Langmuir constant (in g/L). The separation factor R_L indicates the isotherm's shape and the nature of the adsorption process as unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$). In the present study the value of R_L for PLDC is 0.4202. The value indicates that the sorption process is favourable for low cost adsorbent BMC than commercially activated carbon (CAC). From Table 3.5 it is found that the R^2 value for Langmuir model is near to unity (0.99) and hence the process of defluoridation using treated bio-sorbent follows the Langmuir isotherm well. Table 3.5 gives the calculations of Langmuir model for the removal of fluoride and the various constants of this model.

Table 3.5: Adsorption isotherm parameters of the chosen adsorbents

Isotherm Parameter	Symbol Constant	PLDC	CAC
Freundlich isotherm	K_f	0.0204	0.6390
	$1/n$	0.6145	0.1620
	r	0.9984	0.9973
	R^2	0.9967	0.9946
Langmuir isotherm	a (mg/g)	0.0700	0.1105
	b (g/L)	0.2760	0.2350
	r	0.9993	0.9154
	R_L	0.4202	0.4597
	R^2	0.9909	0.9912

Figure 3.7: Calculations of Lagergren model for the removal of fluoride from fluoridated water
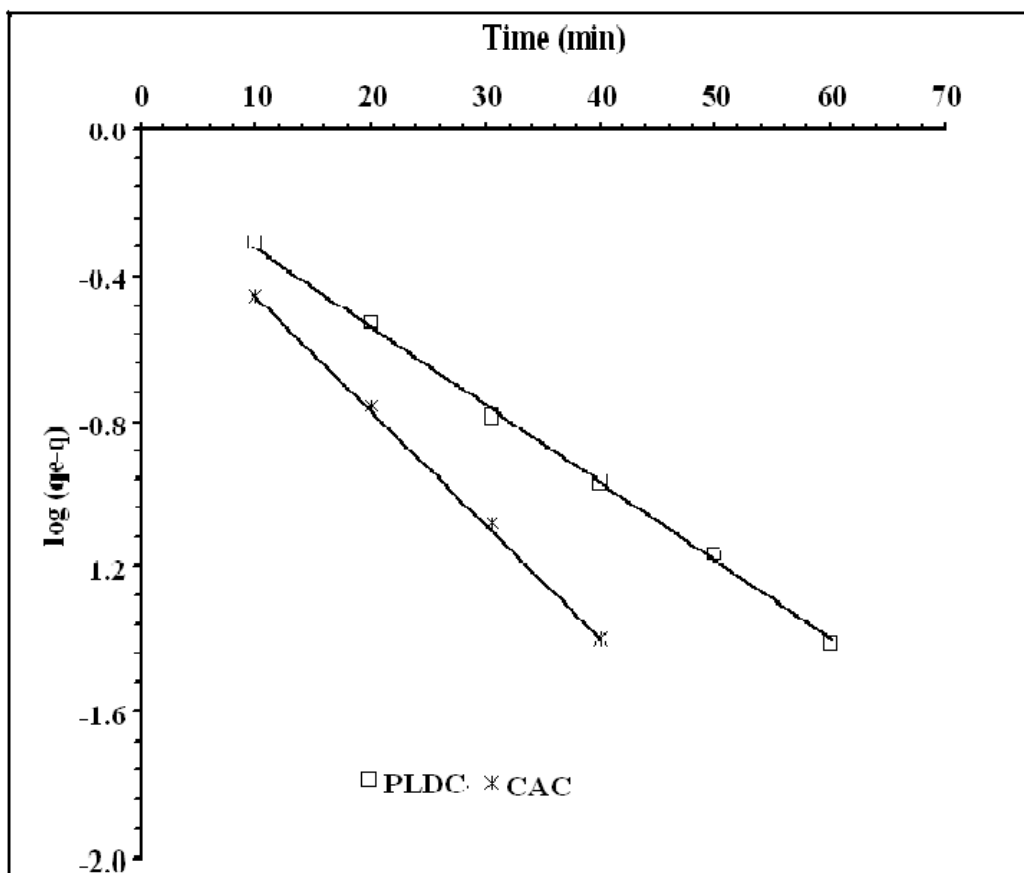
3.6 Adsorption Kinetics
3.6.1 Lagergren model
Adsorption of various compounds in aqueous system on to adsorbent is time dependant process. Adsorption of solute on to sorbent can be described by three consecutive steps. First the adsorbate migrates through the solution to the exterior surface on the adsorbent particles by molecular diffusion, i.e. film diffusion. Secondly, the solute move from particles surface into interior site of particle by pore diffusion and finally the adsorbate is adsorbed onto the active sites at the interior surface of the adsorbent particle. As the final adsorption step is very rapid the overall rate

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of adsorption will be controlled either by film diffusion or by internal diffusion. The adsorption of solute from the liquid phase to the solid phase can be considered as a reversible reaction with equilibrium established between the two phases. The Lagergren first order rate expression (equation 8) that follows for both the systems and the same has been used for the determination of a specific rate constant as shown in figure.3.7.

Log (qe-q) = log qe – (k $_{ad}$. t) / 2.303   ------ (8)

where qe and q (both in mg/g) are the amount of solute adsorbed solute adsorbed at any time, t (minutes) and at equilibrium time respectively..

3.6.2 Intra-particle diffusion model: [41, 42, 48]
In a rapidly stirred batch reactor, the adsorbate species are most probably transported from the bulk of the solution to the solid phase through Intra-particle diffusion, which is often the rate limiting step in many sorption processes. Applying the following intra-particle diffusion model also tests the presence of intra-particle diffusion process in the present adsorption system.

The mode for Intra-particle diffusion is:
$$q_e = k_p t^{1/2} + C \qquad \text{--------- (9)}$$

where, q_e is the amount of fluoride adsorbed per unit mass of the adsorbent (in mg / g) at time t; k_p and c are respectively the Intra-particle diffusion rate constant (mg/g. minutes$^{-1/2}$) and the intercept. The values of amount of fluoride adsorbed have been correlated with the t$^{1/2}$ (minutes$^{1/2}$) for various adsorbents which are presented in figure 3.8. This has resulted in linear relationship as evidenced by the r-values which indicate the existence of intraparticle diffusion process. The calculated value of k_p for PLDC is (0.0953) and for CAC is (0.0837) which indicate that the intra-particle diffusion process is more significant in PLDC system than in CAC system. The values of intercept (C) give an idea of boundary layer thickness, i.e., the larger the intercept, the greater the boundary layer effect [52]. The values of intercept decrease in the order PLDC > CAC.

Figure 3.8: Intra-particle diffusion plots for the removal of fluoride by adsorption on various adsorbents

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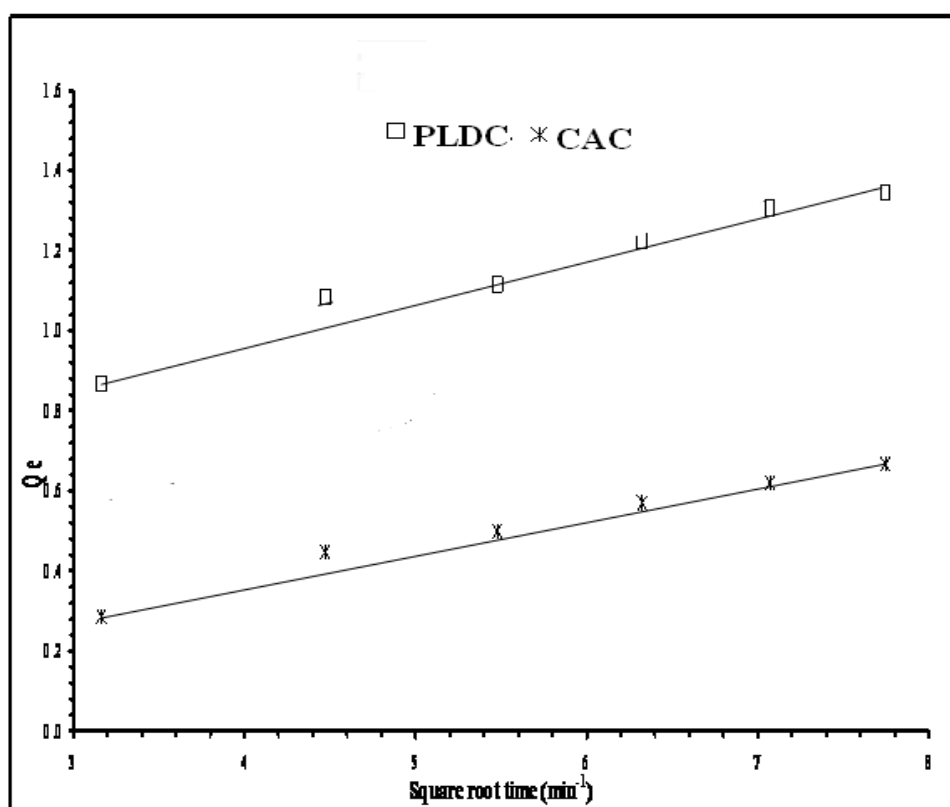
CONCLUSION

In the present study, indigenously prepared low cost aadsorbents were studied for removal of fluoride from synthetic, as well as from groundwater sample. The percentage of removal of fluoride from aqueous solution by PLDC and CAC are 81.60 and 40.20 respectively. The capacity of the removal of fluoride depends not only on the pH of the solution but also on the dose of the adsorbent, temperature etc., Isothermal data fitted well with the Langmuir's adsorption isotherm model.Adsorption of fluoride on all studied adsorbents from aqueous solution followed first order reaction, and the mechanism of fluoride removal on adsorbents was found to be complex. The surface adsorption as well as intra-particle diffusion contributes to the rate-determining step. Comparison of PLDC with CAC reveals that this adsorbent is economically viable for the removal of fluoride.

REFERENCES

[1] C.B. Dissanayake, *Int. J. Environ. Stud.* **1991**, 19, 195–203.

[2] W.Czarnowski, K. Wrzesniowska, J.Krechniak, *Sci. of the Total Environ,* **1996**, 191, 177–184.

[3] N. Azbar, A. Turkman,*Water Sci. and Technol*, **2000**, 42, 403–407.

[4] W.Y. Wang R.B.Li, J.A.Tan, K.L. Luo L.S.Yang, H.R.Li, Y.H.Li, *Fluoride.,* **2002**, 35, 122–129

[5] M.,Agarwal, K.Rai, R.Shrivastav, S.Dass, *J. Cleaner Produc.*, **2003**,11, 439–444.

[6] G.Moges, F.Zewge, , M.Socher. *J. Afr. Earth Sci.,* **1996**,21, 479–482

[7] S.J. Gaciri, T.C.Davies, *J. Hydrol.*, **1992**,143, 395–412.

[8] T.Chernet, Y.Trafi V.Valles, *Water Res.,* **2002**, 35, 2819–2832.

[9] H. Mjengera, G. Mkongo, 3rd WaterNet Symposium Water Demand Management for Sustainable Development., **2002.**

[10] W.K.N.Moturi, M.P.Tole, T.C.Davies, *Environ. Geochem. and Health.,* **2002,** 24, 123–130.

[11] Apambire, W.B., Boyle, D.R., Michel, F.A, *Environ.Geol*, **1997,**33, 13–24.

[12] D.C Bansal, J.B. Donnet, and H.F Stoeckli, Active Carbon, Marcel Dekker, New York **1988.**

[13] H.Jankowska ,A.Swiatkowski , J.Choma . Active Carbon, Chinchester: Ellis Horwood; **1991**.

[14] E. Bernardo, R. Egashira, J. Kawasaki, *Carbon* , **1997,**35 ,1217–1221,

[15] I. Gaballah, J. Hager, R. Solozabal (Eds.), *Metals and Materials Society, USA,* **1999**.

[16] A.H. El-Sheikh et al. ; *J. Anal. Appl. Pyrolysis* , **2004,**71**,** 151–164 . S.Rio, A. Delebarre, V. Hequet, P. Le, J. Blondin, *Journal of Chemical Technology and Biotechnology*, **2002,** 77 ,382–388.

[17] A.M. Raichur, M.Jyoti Basu, sep.*Purif. Techn.*, **2001,**24,121-12.

[18] E.J.Reardon, Y.Wang, *Environ.Sci.Technol.,***2000,**34,3247-3253.

[19] S. Saha, *Water Res.,* **1993,**27**,** 1347–1350.

[20] G. Singh, B. Kumar, P.K. Sen, J. Maunder, *Water Environ. Res.* , **1999,**71, 36– 42.

[21] A. Dieye, C. Larchet, B. Auclair, C. Mar-Diop,*Eur. Polym. J.,* **1998**, 34 ,67–75,

[22] Z. Amer, B. Bariou, N. Mameri, M. Taky, S. Nicolas, A. Elimidaoui, Desalination, **2001,** 133**,**215–223.

[23] N. Mameri, H. Lounici, D. Belhocine, H. Grib, D.L. Prion, Y. Yahiat, *Sep. Purif. Technol.,* **2001,**24,113–119,

[24] M. Hichour, F. Persin, J. Sandeaux, C. Gavach, *Sep. Purif. Technol.,* **2000,** 18, 1–11,

[25] M. Hichour, F. Persin, J. Sandeaux, C. Gavach, *Rev. Sci. Eau.,* **1999**, 12**,** 671–686,

[26] S.K. Adikari, U.K. Tipnis, W.P. Harkare, K.P. Govindan, *Desalinatio.,* **1989**,71,301–312,

[27] S. Venkata Mohan, N. Chandrasekhar Rao, J. Karthikeyan, *J. Hazard. Mater,* **2002**,90 (2) ,189–204,

[28] K.S. Jayantha, G.R. Ranjana, H.R. Sheela, R. Modang, Y.S. Shivananni, *J. Environ. Sci. Eng.*, **2004**, 46 (4) ,282–288.

[29] N. Prabavathi, T. Ramachandramoorthy, R. EdisonRaja, B. Kavitha, C.Sivaji, R. Srinivasan, *IJEP,* **2003**, 23 (3)**,** 304–308.

[30] S. Srimurali, A. Pragathi, J. Karthikeyan, *J. Environ. Pollut.,* **1998**,99, 285–289.

[31] K. Muthukumaran, K. Balasubramanian, T.V. Ramakrishna, *IJEP.,* **1995**,15 (7) ,514–517.

[32] D.J. Killedar, D.S. Bhargava, *Ind. J. Environ. Health,* **1993,**35 (2) 81–87,

[33] S. Venkata Mohan, S.V. Ramanaiah, B. Rajkumar , P.N. Sarma „*Journal of Hazardous Materials,* **2007**,141,465–474.

[34] Ruchi Malik, Manisha Mukherjee, Aditya Swami, S.Dilip Ramteke and Rajkamal Sarin. **2004**, 5(2), 75-80.

[35] U. S. Environmental Protection Agency "Process Design Manual for Carbon adsorption; Technology Transfer EPA, **1973,**625, 1-71-0029.

[36] APHA, 1998. Standard Methods for Examination of Water and Wastewater, 20ᵗʰ edition. American Public Health Association, Washington, DC, USA.

[37] K.Muthukumaran, N.Balasubramanian and T. Ramakrishna,Indian Journal of Environmental protection, **1995**, 15 (7), 514 – 517.

_____

[38] P.mariyappan,V.Yegnaraman and T.vasudevan , IJEP, **2003**,23(9),975-985.

[39] G.Karthikeyan; Defluoridation studies of activated alumina and other adsorbents, LSI; National work shop on defluoridation technologies for fluorosis control, Sri Krishnadevaraya University, Ananthapur- Andhrapradesh, India, proceedings., **1997,**   23 – 26 .

[40] M.Murugan and E.Subramanian,Indian Journal of Environmental protection ., **2002**, 22 (9), 970 – 977.

[41] N.V.V.S Prasad Ph.D thesis, **2004.**

[42] Kishore, M.Phil, thesis, **2004**.

[43] D.S.Bhargava and D.J.Killidar,Res.J.WPF. **1991**,63(6),848-858.

[44] Wu, Yeun C. and Anan Nitya, ASCE, Env.Eng., **1979**, 105 (EE2),357-367.

[45] N. Kannan and K. Karuppasamy, Indian J. Environ.Prot., **1998,**683-686.

[46] M.Sarioglu, Zeolite. *Seperation & Purification Technology*. **2005,** 41,1-11.

[47] A.V.Jamode et al.,*Pol.Res.,***2004,** 23 (2): 239 – 250.

[48] K. Somasekhara Rao et al., *IJEP*, **2005,** 25(9):824-828.

[49] N.Kannan and M.Meenakshi sundaram.. *IJEP* ,**2002**,22(5): 495-499.

[50] N.Kannan. et al. *Fresenius Env.Bulletin,***2001**.

[51] S.Goswami et al., *Chem.Env.Res*. **2004,**13(1&2): 117-126.

[52] W.J. Weber, Jr., Physico ,Wiley Inter science, New York **1972**.