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Fluoride adsorption onto activated carbons prepared from indigenous materials

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ABSTRACT

The adsorption of fluoride ions on activated carbon prepared from low cost materials has been studied by batch process. The influences of contact time, dosage, pH, pH zpc and co-ions on the fluoride sorption were studied. Adsorption was explained using Langmuir and Freundlich isotherms with the help of Chi-square analysis. Thermodynamic parameters like ΔS^0, ΔH^0 and ΔS^0 were calculated to understand the nature of adsorption. The surface morphology of the adsorbent material before and after fluoride sorption was observed using scanning electron microscope(SEM) and X-ray diffraction studies(XRD). The performance of the activated carbons has been tested with field samples collected from fluoride endemic areas.

KEYWORDS

Adsorption;
Activated carbons;
Langmuir;
Freundlich isotherm;
Chi-square analysis;
Intraparticle diffusion.

INTRODUCTION

Endemic skeletal fluorosis continues to be a public health problem in several parts of the world including India, where drinking water contains naturally occurring soluble fluoride much above the permissible limit of 1.5mg/L[1]. Fluoride exists adequately in the earth's crust and can enter groundwater by natural process such as natural weathering and leaching. Many states in India such as Rajasthan, Gujarat, Andhra Pradesh, Orissa, Karnataka and Tamil Nadu report fluoride concentration in water above the permissible limits[2]. This available statistics indicate that all over India more than 6 million people are seriously affected by fluorosis and another 6 million are exposed to it[3]. A number of defluoridation techniques have been suggested for the removal of excess fluoride. Depending upon their mode of action they are classified into three major types viz., those based on chemical addition, adsorption processes, and ion exchange mechanism[4,5,6,7]. Membrane processes such as reverse osmosis, nanofiltration, electro dialysis and Donnan dialysis were recently investigated to reduce fluoride in water[8,9,10,11]. The most economical adsorbent for fluoride removal from drinking water is activated alumina. In recent years, much effort has been devoted to the investigation and development of other, more cost effective, fluoride adsorbents such as fly ash and bauxite, silica gel, bone charcoal, spent catalyst, and bentonite[12]. A locally available and cost effective fluoride adsorbent will be highly desirable.

This paper narrates the fluoride adsorption behaviour of the materials which efficiently remove of fluoride from aqueous solutions at a relatively low level which are low cost and easily available. Activated carbons prepared from *Recinius Communis Linn*(RC), *Carica Papaya Linn*(CP) and *Morinda pubescence*s (MP) are used to adsorb fluoride by batch experiments. The main objective of this study was to analyze the efficiency of these adsorbents for removing fluoride ions from aqueous solutions.

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TABLE 1 : Characteristics of the activated carbons

S.no	Parameters	Adsorbents		
		RC	CP	MP
1	Particle size (mm)	0.15	0.11	0.14
2	Density (g/cc)	0.54	0.56	0.58
3	Ash content (%)	2.04	1.98	2.11
4	Moisture content (%)	1.64	1.34	1.50
5	Loss of ignition (%)	82.00	85.10	88.30
6	Water soluble matter	0.17	0.31	0.24
7	pH of aqueous solution	7.5	7.2	7.0
8	pH (zpc)	7.1	6.9	6.7
9	Iodine number (mg/g)	204	236	190

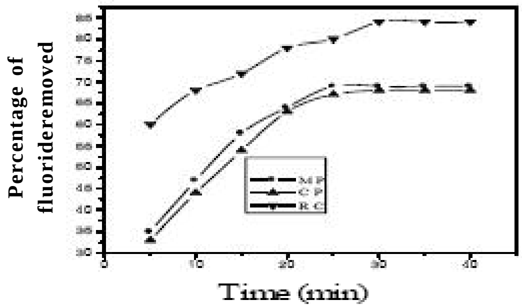


Figure 1: Effect of contact time

EXPERIENTIAL

The preparation of activated carbons RC, CP and MP consisted of carbonization of the respective plant materials. Each dried raw material was cut into small pieces and the carbonization was conducted in a muffle furnace at 400^{0}C, 450^{0}C and 500^{0}C for RC, CP and MP respectively. The heating period was 2 hours for all materials. After carbonization, the carbon was ground using domestic mixie. The material was sieved using BSS 52 to have uniform particle size. The activated carbons obtained were kept in a desicator and were characterized for the physical parameters which are shown in TABLE 1.

Adsorption studies

The three activated carbons shown in Table 1 were used to study adsorption of fluoride. Adsorption equilibrium study of fluoride was carried out in 250ml stoppered Iodine flask by adding 300mg RC, 400mg CP, and 2g of MP activated carbon to 50ml of 3ppm Fluoride solution. Fluoride determination was done using an expandable ion analyzer, EA 940, and fluoride ion-selective electrode BN 9609 (all Orion USA made). The pH measurements were done with same instrument with a pH electrode. The concentrations of NO_3^-, SO_4^2, were determined by UV visible spectrometer (Perkin Elmer Lambda 35) and the concentration of Mg^{2+} and Ca^{2+} ions were determined by an atomic adsorption spectrophotometer AAS (Perkin Elmer A Analyst 100). pH_{ZPC} (pH of zero point charge) was determined by pH drift method (13). All other water quality parameters were analyzed by using standard methods. The surface morphology of the raw and treated activated carbon was visualized by SEM with a HITACHI-S-3000H model. XRD pattern was recorded using X^1 per PRO(model), PAN analytical(make). Computations were made using Microcal Origin, (version 6.0) software. The goodness of the fit is discussed using the regression, correlation and coefficient (R).

RESULT AND DISCUSSION

Effect of contact time

The fluoride removal efficiency of the activated carbons was determined by varying the contact time. It is evident from figure 1. That the maximum fluoride removal time for RC is 35 min, CP 30 min and for MP is 25mins. The results show that the percentage of fluoride adsorption increased with increasing time of equilibration. This study does not claim any kinetic evaluation of the adsorption process, but it has shown that the equilibrium was attained.

Effect of dosage

The experiments were carried out with different dosages of activated carbon with 3ppm initial fluoride concentration which is shown in figure 2. A significant increase in percent removal with increase in dosage of activated carbons was done to bring down the fluoride

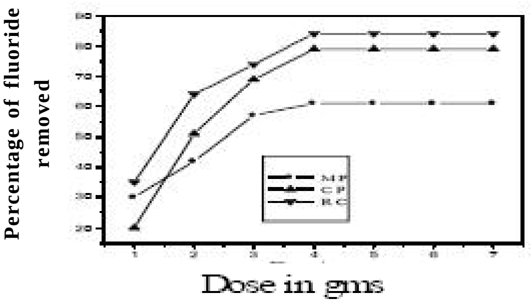


Figure 2 : Effect of dose

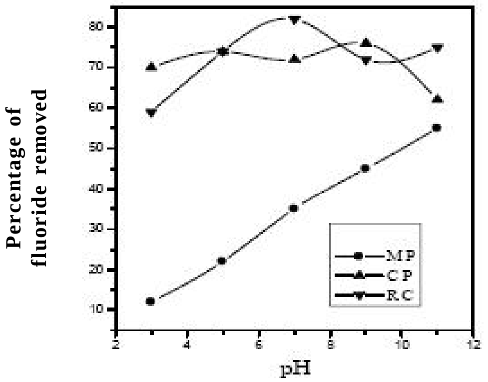


Figure 3 : Effect of pH

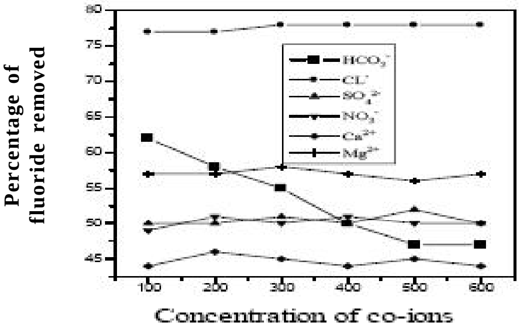


Figure 4 : Effect of co-ions

level to 1ppm which is the tolerance limit for fluoride. Finally 300mg for RC, 400mg for CP and 2g for MP was fixed as optimum dose.

Effect of pH

The pH controls the adsorption at the water interfaces. The removal of fluoride ion from aqueous solutions was highly dependent on the solution pH in many cases. The defluoridation efficiency of the activated carbons were determined at five different pH levels viz., 3, 5 ,7 , 9 and 11 and the results are given in figure 3. The pH of the solution was adjusted by adding HCl/NaOH solution. It is evident from the figure that RC, and CP carbons have no significant effect on the defluoridation efficiency. Efficiency remains the same in both alkaline and acidic medium. But MP has higher efficiency at higher pH.

Effect of co-ions

The dependence of the activated carbon on the presence of other co-ions that are commonly present in water, namely Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, Ca^{2+} and Mg^{2+} was investigated with varying initial concentrations of these ions viz., 100, 200, 300, 400, 500 and 600 mg/L by keeping fluoride concentration as same. All ions except bicarbonate ions do not have any significant effect on the removal of fluoride by these activated carbons and this is evident from figure 4.

Adsorption isotherms

Two commonly used isotherms, namely Langmuir and Freundlich isotherms, have been adopted to quantify the fluoride sorption capacity of the activated carbons.

Langmuir isotherm

The Langmuir isotherm model can be represented in the form of equation

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \qquad (1)$$

TABLE 2 : Langmuir and frendlich constants

	Langmuir constants							Freundlich constants				
	Temp K	Q_o	b	R^2	Sd	R_L	χ^2	1/n	K_f	R^2	Sd	χ^2
	303	0.452	8.445	0.967	0.0386	0.637	0.5691	0.892	2.090	0.996	0.0334	0.0071
RC	313	0.444	5.445	0.967	0.0396	0.579	0.2543	0.897	1.833	0.999	0.0123	0.0041
	323	0.432	7.880	0.981	0.0430	0.687	0.1964	0.883	1.828	0.998	0.0670	0.0029
	303	1.604	0.288	0.979	0.0230	0.664	0.4123	0.652	2.823	0.998	0.0141	0.0057
CP	313	1.269	0.475	0.994	0.0147	0.513	0.3478	0.595	2.467	0.994	0.0262	0.0044
	323	1.287	0.599	0.993	0.0172	0.455	0.2987	0.529	2.202	0.995	0.0254	0.0027
	303	0.695	3.374	0.978	0.0350	0.759	0.6591	0.991	2.004	0.995	0.0326	0.0121
MP	313	0.347	6.289	0.967	0.0784	0.581	0.4896	0.811	1.41	0.991	0.0444	0.0058
	323	0.139	4.691	0.987	0.0281	0.961	0.3698	0.636	1.37	0.996	0.0380	0.0049

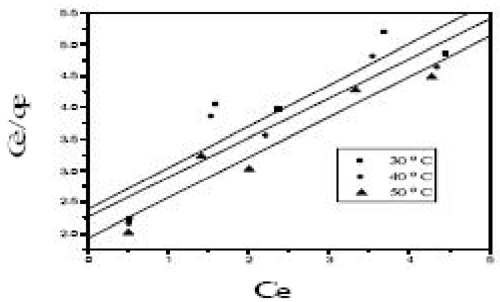


Figure 5(a): Langmuir plot for R C

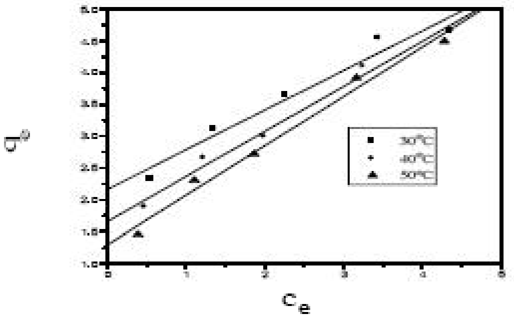


Figure 5(b) : Langmuir plot for C P

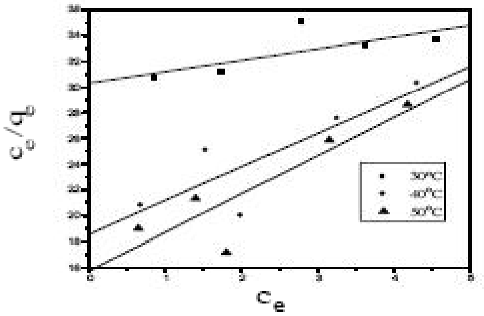


Figure 5(c) : Langmuir plot for M P

where Q_0 is the amount of adsorbate at complete monolayer coverage (mg/g), which gives the maximum sorption capacity of the adsorbent and b is Langmuir isotherm constant that relates to the energy of adsorption. The respective Langmuir isotherms of RC, CP and MP are shown in figure 5a, b and c. Langmuir constants were calculated and listed in TABLE 2. The linear plots of Ce/qe vs Ce indicate the applicability of Langmuir adsorption isotherms occurring through monolayer coverage of fluoride ions on the outer surface of the adsorbent materials.

In order to find out the feasibility of the isotherm, the essential characteristics of Langmuir constants can be expressed in terms of dimensionless constant, separation factor or equilibrium parameter R_L[14,15].

$$R_L = \frac{1}{1 + bC_0} \tag{2}$$

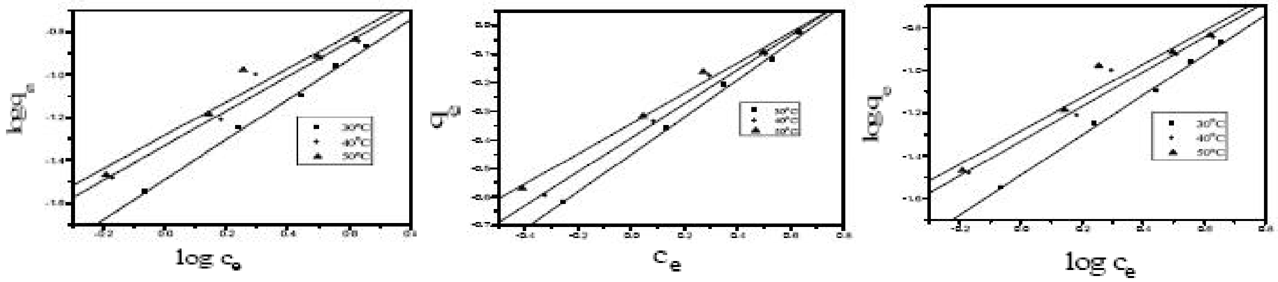
where b is Langmuir constant and C_o is the initial concentration of fluoride mg/L. The R_L values at different temperatures were calculated and given in TABLE 2. The R_L values between 0 and 1 indicate favourable adsorption for all concentrations and temperatures studied.

Freundlich isotherm

The linear form of the Freundlich isotherm can be represented by the equation

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

where q_e is the amount of fluoride adsorbed per unit weight of the adsorbent(mg/g), C_e is the equilibrium concentration of fluoride in solution(mg/L), K_f is the measure of adsorption capacity and 1/n is the adsorption intensity. Freundlich isotherms of RC, CP and MP are shown in figure 6a, b and c. Freundlich constants for the three activated carbons were calculated and presented in TABLE 2. The linear form of the Freundlich isotherm with high correlation coefficient values, R^2 indicates physisorption as the governing force in the fluo-



(a): Freundlich plot for R C **(b): Freundlich plot for C P** **(c): Freundlich plot for M P**

Figure 6

ride sorption reaction with the adsorbent. In all cases the value of K_f decreased with increase in temperature, showing the temperature dependence of the rate of adsorption. Values of 1/n are between 0.1 and 1.0 and the n values lie in the range of 1 to 10 and fulfill the favourable conditions for adsorption[16,17,18].

Chi-squared analysis

Identification of a suitable isotherm model for fluoride adsorption on activated carbons was done using chi-square tests which is basically the sum of the squares of the difference between the experimental data and that data obtained by calculating from models, with each squared difference divided by corresponding data obtained by calculation from the models[19]. The equilibrium mathematic statement is

$$\chi^2 = \sum \frac{\left(q_e - q_{e,m}\right)^2}{q_{e,m}} \qquad (4)$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from model(mg/g) and q_e is experimental data on the equilibrium capacity(mg/g). If data from the model are similar to the experimental data, χ^2 will be small number while if they differ χ^2 will be a bigger number. Therefore, it is also necessary to analyse the data set using the non linear chi-squared test to confirm the best fit isotherm for the sorption system[20]. The χ^2 values for the systems studied here were calculated and presented in TABLE 2. The Freundlich isotherm has higher χ^2 values with small standard deviation than the Langmuir isotherm. This indicated that the Freundlich isotherm fits well for the adsorption of fluoride on all activated carbons.

Adsorption dynamics

From a mechanistic point of view, to interpret the experimental data, prediction of the rate-limiting step is an important factor to be considered in the sorption process. Though kinetic and equilibrium isotherm studies help to identify the adsorption process, predicting the mechanisms is required for design purpose. For a solid-liquid sorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both.

The sorption dynamics can be described by three consecutive steps as follows:

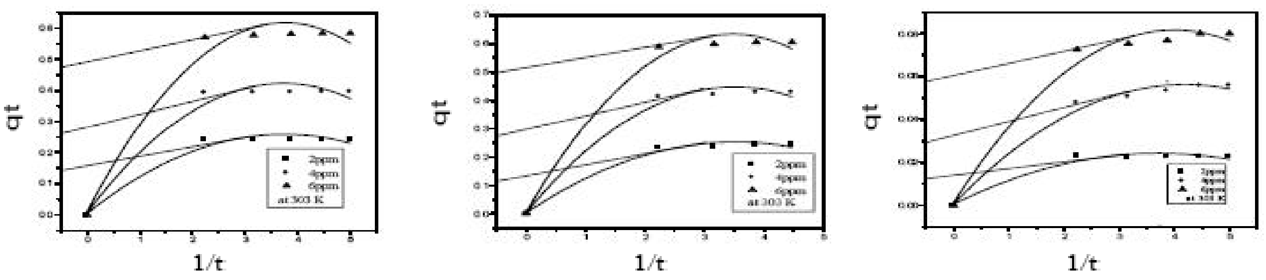
- Transport of the solute from bulk solution through liquid film to the adsorbent exterior surface
- Solute diffusion into the pore of adsorbent except for a small quantity of sorption on the external surface; parallel to this intraparticle transport mechanism of the surface diffusion
- Sorption of solute on the interior surfaces of the pores and capillary spaces of the adsorbent

The last step is considered to be an equilibrium reaction of the three steps, the third step is assumed to be rapid and considered to be negligible.

The overall rate of sorption will be controlled by the slowest step, which would be either film diffusion or pore diffusion. However, the controlling step might be distributed between intraparticle and external transport mechanisms. Whatever be the case, external diffusion will be involved in the adsorption process. The adsorption of fluoride onto the activated carbon may be controlled due to film diffusion at earlier stages and as the adsorbent particles are loaded with fluoride ions, the sorption process may be controlled due to intraparticle diffusion. But for design purposes, it is necessary to calculate the slowest step involved in the sorption process. For the adsorption process, the external mass transfer controls the adsorption process for the systems that have poor mixing, dilute concentrations of adsorbate, small particle sizes of adsorbent and higher affinity of adsorbate for adsorbent whereas the intraparticle diffusion will control the sorption process for a system with good mixing, large particle size of adsorbent, high concentration of adsorbate and low affinity of adsorbate for adsorbent. The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting the experimental data in an intraparticle diffusion plot. Previous studies by various researchers showed that the plot of q_t versus $t^{1/2}$ represents multi linearity which characterized the two or more steps involved in the sorption process. According to Weber and Morris, an intraparticle diffusion coefficient is defined by the equation.

$$q_t = K_p t^{1/2} \qquad (5)$$

q_t = the amount of fluoride adsorbed per unit mass of adsorbents at any time; $t^{1/2}$=square root of time; K_p=



(a): Intra particle diffusion for R C **(b): Intra particle diffusion for C P** **(c) : Intra paticle diffusion for M P**

Figure 7

Intraparticle diffusion rate constant.

The plots of intraparticle diffusion curves show initial curved portion followed by linear portion and a plateau. The first sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption where the intraparticle diffusion is rate controlled. The third portion is final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentration in solutions[21]. The plots for RC, CP and MP are shown in figure 7a, b and c.

Evidence for intraparticle diffusion (K_p)

A preliminary appraisal of the sorbent - sorbate system may provide information indicating the sorption mechanism. For instance, there are several chemical groups on the sorbent which can undergo chemical reaction to form a chemical bond. Acid groups on the sorbent could provide ion exchange sites for metal ions and ionic dyes. Amine groups can provide a lone pair of electrons for chelation with metal ions etc. Relatively inert sorbent surfaces may only provide physical sites for diffusional controlled bond formation.

In order to identify the exact mechanism it is necessary to carry out experiments to study several system variables, namely, initial concentration, sorbent particle size, solution temperature, solution pH and agitation and analyse the data for different order kinetic reactions or for pore/solid phase diffusion mechanisms.

If equilibrium is achieved within three hours, the process is usually kinetic controlled and above twenty four hours, it is diffusion controlled. Either or both kinetic and sorption processes may be rate controlling in the three to twenty four hour period. Another very general guide line is that changes in pH have a greater effect on the sorption of solutes in reaction controlled sorption processes. A more appropriate quantitative approach to distinguish between kinetic and diffusion rate control is to perform the square root of contact time analysis according to equation[5]. A plot of the amount of pollutant adsorbed, q_t, against the square root of time, $t^{1/2}$, yields a straight line plot of slope K_p, a diffusional rate parameter. This straight line, passing through the origin, indicates intraparticle diffusion control. This approach has been successful in many cases[22,23,24]. In cases of adsorbents whose pore size range is extensive including micro-, meso and macro pores up to three linear sections have been obtained[25,26]. Additional confirmation of a diffusion mechanism can be obtained by analysing the effect of the system variables on K_p. The values of K_p are given in TABLE 3.

TABLE 3 : Values of K_P

Temperature(K)	Values of Kp		
	RC	CP	MP
303	0.251	0.143	0.245
313	0.237	0.253	0.261
323	0.233	0.189	0.263

For intraparticle diffusion controlling systems K_p should vary linearly with reciprocal particle diameter; the product of K_p times sorbent mass should vary linearly with sorbent mass.

Thermodynamic parameters

Thermodynamic parameters such as standard free energy, (ΔG^0) standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) of the sorption process were calculated as follows and the values are given in TABLE 4.

The free energy of sorption process, considering the sorption equilibrium constant K_0, is given by the equation.

$$\Delta G^0 = -RT\ln K_0 \qquad (6)$$

TABLE 4 : Thermodynamic parameters for sorption of fluoride at different temperatures

Adsorbent	ΔG(kjmol^{-1})			ΔH(kjmol^{-1})	ΔS(kjmol^{-1})
	303K	313K	323K		
RC	-2.50	-2.68	-2.94	15.98	0.059
CP	-2.44	-2.26	-2.70	19.67	0.073
MP	-1.66	-1.26	-1.70	13.29	0.084

where ΔG^0 is the free energy of sorption (kJ mo1^{-1}), T is the temperature in Kelvin and R is the universal gas constant. (8.314Jmol^{-1}k^{-1}). The sorption distribution coefficient K_0 for the sorption reaction was determined from the slope of the plot of $\ln(q_e/C_e)$ Vs C_e at different temperatures and extraploting to zero C_e according to method suggested by Khan and Singh[27].

The adsorption distribution coefficient may be expressed in terms of enthalpy change (ΔH^0) and entropy change (ΔS^0) as function of temperature

$$\ln K_0 = \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (7)$$

where ΔH^0 is heat of adsorption (KJmol^{-1}) and ΔS^0 is standard entropy change(KJmol^{-1}). The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of a plot of lnk Vs 1/T[28].

Instrumental analysis

Surface morphologies of the carbons before and after the fluoride sorption were studied using SEM images. SEM images of the activated carbons RC, CP and MP before and after fluoride adsorption are shown in figures 8, 9 and 10. Comparison of the SEM images reveals that the surface texture and porosity of the adsorbents has holes and small openings, which constitute the contact areas facilitating pore diffusion during adsorption. XRD patterns of the raw and treated carbons also show significant changes in the peak intensity. Figures 11, 12 and 13 indicate the decrease in the peak intensity values of RC, CP and MP respectively, after the fluoride adsorption[29].

Field trial

The three activated carbons used in this study were also employed as defluoridating media using field samples from fluoride endemic areas. The experimental results are presented in TABLE 5. All the activated carbons were observed to significantly reduce fluoride from water. However, other common water quality parameters remained largely unaltered.

TABLE 5 : Field trial results

Water quality parameter	Before treatment	After treatment		
		R C	C P	M P
pH	8.5	7.9	8.0	8.1
EC (ms/cm)	0.98	0.86	0.91	1.11
Cl^- (mg/L)	66.50	65.4	68.5	60.9
TH (mg/L)	120	140	165	150
TDS (mg/L)	750	740	700	720
F^- (mg/L)	2.85	0.92	1.01	1.10

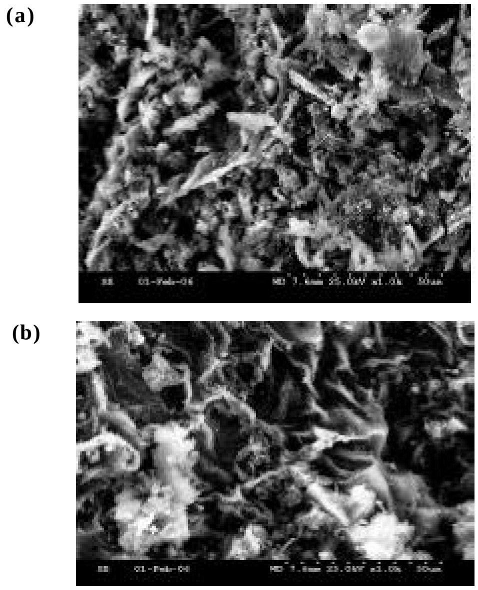


Figure 8 : (a) SEM for RC before treatment (b) SEM for RC after treatment

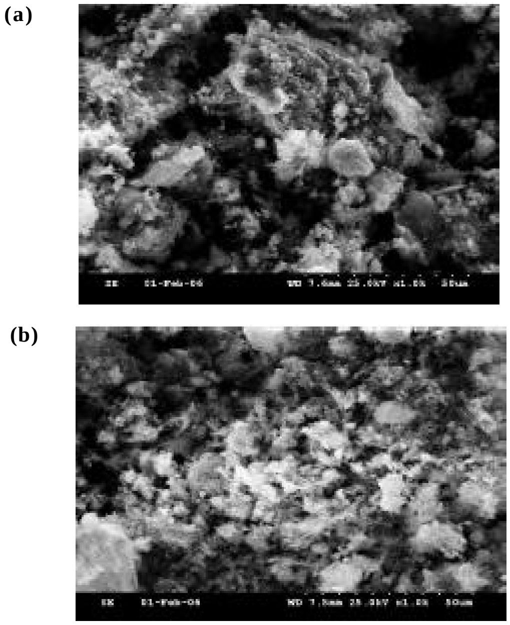


Figure 9 : (a) SEM for CP before treatment (b) SEM for CP after treatment

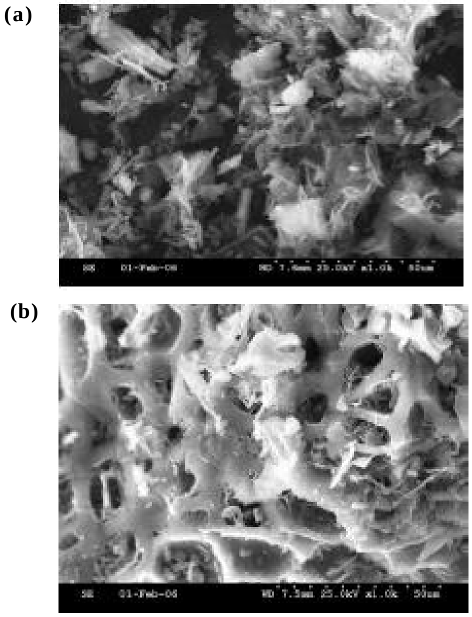


Figure 10 : (a) SEM for M P before treatment (b) SEM for M P after treatment

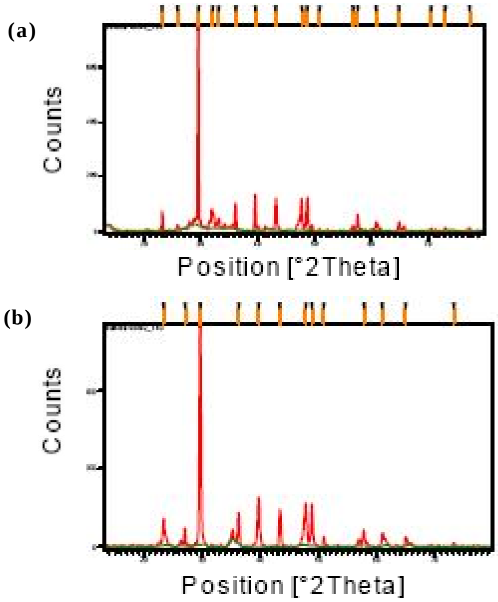


Figure 12 : (a) XRD for C P after treatment (b) XRD for C P before treatment

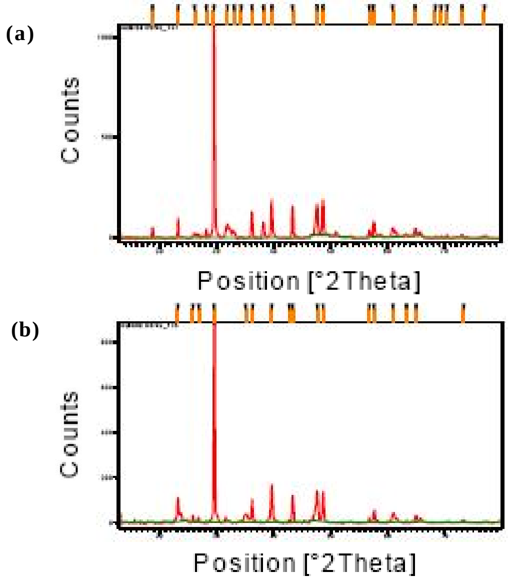


Figure 11 : (a) XRD for RC before treatment (b) XRD for RC after treatment

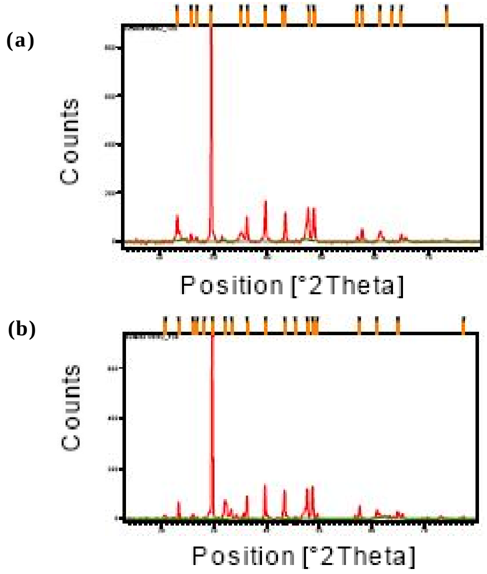


Figure13 : (a) XRD for M P before treatment (b) XRD for M P after treatment

CONCLUSION

All the three activated carbons, viz., RC, CP and MP exhibited considerable adsorption of fluoride from water. The fluoride sorption process depended on the adsorbent dosage, contact time, co-ions, temperature and pH. The equilibrium data of adsorption are in good agreement with adsorption isotherm models irrespective of the temperature or concentration. The adsorption dependence of fluoride on temperature was investigated and the thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0 were calculated. The negative ΔG^0 values indicated the feasibility of the adsorption and its spontaneous nature. The value of ΔH^0 is positive and it confirms the endothermic nature of the reaction. The positive value of S^0 shows the increased randomness at the solid - liquid interface. SEM and XRD studies revealed that fluoride adsorption is predominantly a surface phenomenon. Field trial studies show that these adsorbents can be used as defluoridation agents, which exhibited promising applications.

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