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Studies on sorption of fluoride by prepared activated Kaza's carbons

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ABSTRACT

Investigations are made on the removal of fluoride from water by prepared activated carbons. Three activated carbon adsorbents, BKC, BOC and RSC are prepared from selected bio-materials of bergera koenigh, batavia orange and raphanus sativus respectively. The adsorption capacity towards adsorption of fluoride from aqueous solution was studied and was determined by using fixed amount of adsorbent(0.1g/100mL) and a known concentration of adsorbate (5mg/L) solution at 30 minutes agitating time. The data have been analyzed in the light of adsorption isotherms, adsorption kinetic equations and intraparticle diffusion model. Regeneration of adsorbents was studied.

Key words : sorption, activated carbons, fluoride removal.

INTRODUCTION

Research scientists have screened numerous substances for defluoridation efficacy and several methods have been evolved for the removal of fluoride from drinking water. Activated carbons find wide application as adsorbents catalysts or catalysis supports. Adsorption by activated carbons also provide to be the most successful and feasible technique for the removal of heavy metals and fluoride from water and industrial effluents [1,2,3]. The activated carbon adsorption has been shown to be effective and widely employed for waste water treatment technique[4]. The recent investigation reported the modification of carbon surfaces using oxidizing agents [2,4,5]. The treatment introduces three types of surface oxygen complexes as acidic, basic and neutral [6,7]. Oxygen is the dominant heteroatom in the carbon matrix and the presence of functional groups such as carbonyl, carboxyl, phenols, enols, lactones and quninones has been postulated[8]. Literature survey reveals many non-conventional biosorbents [9-12]. So we have chosen bergera koenigh, batavia orange and raphanus sativus which are easily available and biodegradable. Adsorption capacity of fluoride from aqueous solution, various parameters like the dose of adsorbents, contact time, pH etc, were studied.

MATERIALS AND METHODS

The carbon adsorbents viz, BKC, BOC and RSC are prepared from the areal parts of bergera koenigh (curry leaf seeds), batavia orange and raphanus sativus (garden raddish). The parts were dried, crushed and washed thoroughly with deionised water. They were air dried in sun light and further dried in an air oven to 100-120^{0}C for 24 hrs. then carbonized in a horizontal tube furnace in uniform nitrogen flow at 600^{0}C for 4 hrs. the prepared cabons were activated with HNO_3, H_2SO_4, HCl, NaOH solutions to adsorptive behavior in the removal of fluoride. The particle size of carbons made to 40 – 50 μ. These carbons collectively named as activated kaza's carbons after the name of Kaza Somasckhara Rao.

Standard fluoride solution is made from sodium fluoride (AnalaR grade). The fluoride content is determined spectrophtometrically by following standard SPADNS method at 570nm [13]. The adsorption of fluoride on activated carbon are carried out by agitating 0.1g of activated carbon with 100ml of 5mg/L fluoride solution for 30 minutes at room temperature (30 $\pm$ 2^{0}C). The supernatant was analyzed for the residual fluoride concentration. The effect of various experimental parameters have been investigated using batch adsorption experiments conducted at various pH values. The effect of initial concentration of fluoride, contact time, dose of adsorbent, pH on the adsorption potential have been carried out. The data have been analysed in the light of adsorption isotherms, adsorption kinetic equations and intraparticle diffusion model.

RESULTS AND DISCUSSION

The carbons were activated with 0.1M solutions of HNO_3 , H_2SO_4, HCl and NaOH.The adsorptive behavior of three activated carbons towards fluoride removal was studied and these were shown in Figure.1. for HNO_3 activated carbons the removal capacity of fluoride is 71.6-70.8%, for H_2SO_4 activated is 69.6- 67.0%, for HCl activated is 69.8 – 67.2% and for NaOH activated is 68.2 -60.4% .So the HNO_3 activated carbons were selected in these studies. Effect of initial concentration of fluoride was studied in the range 1 – 8 mg/L of fluoride solutions with 0.1g of activated carbon. The percent removal fluoride and the amount of fluoride adsorbed were calculated from the equation

$$\text{Percent removal} = 100\,(Ci - Cf)/\,Ci$$

$$\text{Amount adsorbed } qe = (Ci - Cf)\,V / M$$

Where Ci and Cf are initial and final concentration of the fluoride in mg/L, V is the volume of the solution and M is the mass of the activated carbon. The results are tabulated in Table.1 . Variation of percent removal of fluoride with increasing initial concentration is shown in Figure.2. It is clear from the results that upto 4.0 mg/L, the fluoride content is reduced to nearly permissible level i.e.,1.5 mg/L. The effect of contact time on percent removal of fluoride for these carbons was studied and the results are presented in Table. 2 . Maximum contact time observed is 30 minutes after that the percent removal is same. The effect of dose of adsorbent from 0.1g to 1.0g in the percent removal of fluoride with constant concentration of 5mg/L. The results are given in Table .3 . As the dose increases, the percent removal increases. The amount of removal of fluoride increases with increase in carbon dosage due to the availability of more surface active sites. From the results, the optimum dose of adsorbent for all carbons is 1.0g/L. Increase in adsorbent dose above 1.0g/L has no significant change in the adsorption. The effect of pH on the adsorption capacity was studied and the results are presented in Table.4 . The results indicate that the percent removal of fluoride increased with increasing solution pH since more binding sites could be exposed with negative charges, with subsequent attraction of positive charge ,with the maximum removal of fluoride observed at pH 6 particularly.

Regeneration of Adsorbents
Regeneration is an application, it may be more economical to discard the adsorbent after use. In the present study, fluoride loaded carbons were regenerated by passing 0.1N NaOH solution through the used carbon. The results of regeneration studies and the corresponding graph are shown in Figure.3 . From the results it can be concluded that when the regenerated carbon is used for standard fluoride solution it removes the fluoride from 74.1 to 47.8% .

Adsorption Isotherms
The sorption isotherms is highly significant in the removal of fluoride by adsorption technique, as it provides an approximate estimation of the sorption capacity of the adsorbent. The equilibrium data for the removal of fluoride by sorption of various adsorbents at 30±2°C is used in Freundlich and Langmuir isotherm[14]

Freundlich isotherm: $\log qe = \log K_f + (1/n)\log Ce$
Langmuir isotherm : $(Ce/qe) = (1/Q_o b) + (Ce/Q_o)$.

Where K_f and 1/n are the measures of adsorption capacity and intensity of adsorption respectively,qe is the amount of fluoride adsorbed for unit weight of adsorbent, Ce is the equilibrium conc. of fluoride and Qo and b are the Langmuir constants, which are the monolayer (maximum) adsorption capacity (in mg/g) and energy of adsorption (in g/L) respectively. The essential characteristic of Langmuir isotherm can be described by a separation factor R_L [15,16]

$$R_L = 1/(1+bCi).$$

The R_L indicates the isotherm shape and the nature of adsorption process. If $R_L > 1$,the process is unfavorable. If $R_L = 1$ linear or $R_L < 0 < 1$ favorable or if $R_L = 0$ irreversible. The derived equation parameters are shown in Table 5 and the isotherms are presented in Fig.4 & 5. The results indicate the unimolecular layer of adsorbents.

Kinetics of Adsorption
For this study, the kinetic equations
Natarajan and Khalaf : $\log(Co/Ct) = (K/2.303)t$;
Lagergran : $\log (qe/qt) = \log qe-(Kad/2.303)t$
Battacharya and Venkobachar: $\log [1-U(T)] = -[Kad/2.303]t$, were used.

The values of log Ci/Ce at log (percent removal) have been linearly correlated with time. The results of linear regression analysis (r values) and the values of rate constants are presented in Table 6. All the linear correlations have been found to be statistically significant at 95% confidence level and indicating the applicability of these kinetic equations and the first order nature of the adsorption process of fluoride on various adsorbents.

Intraparticle Diffusion Model

In a rapidly stirred batch reactor, the adsorbate species are most probably transported from the bulk of the solution to the solid phase through intraparticle diffusion which is often the rate limiting step in many sorption process[17]. The model for intraparticle diffusion is:

$$Qe = Kp\ t_{1/2} + C.$$

The values of amount of fluoride adsorbed have been correlated with the $t_{1/2}$ for various adsorbents. This has resulted in linear relationship as evidenced by the r values of Table 6, which indicate the existence of intraparticle diffusion process. The calculated value of Kp (intraparticle diffusion rate constant) for BKC is 0.0881; for BOC is 0.0958 and for RSC is 0.0884, which indicate that is maximum for BOC and minimum for BKC. The linear relation between log time versus log percent removal is shown in Fig.6.

Table 1 : Effect of initial concentration of fluoride on the extent of removal by adsorption on various adsorbents

Adsorbent Name	Initial conc. (Ci)	Final Conc. (Ce)	Percent Removal	Amount adsorbed (q_e)	Ce/q_e	Log Ce + 1.5	Log q_e + 1.5
	1.00	0.15	97.00	2.42	0.06	0.68	1.88
	2.00	0.80	84.00	2.10	1.14	1.40	1.35
	3.00	1.12	77.60	1.94	1.73	1.55	1.31
BKC	4.00	1.75	65.00	1.63	3.23	1.74	1.23
	5.00	2.30	54.00	1.35	5.11	1.86	1.15
	6.00	2.90	42.00	1.05	8.29	1.96	1.04
	8.00	4.10	18.00	0.45	27.33	2.11	0.68
	1.00	0.25	95.00	2.38	0.32	0.90	1.40
	2.00	0.60	88.00	2.20	0.82	1.28	1.37
	3.00	1.10	78.00	1.95	1.69	1.54	1.31
RSC	4.00	1.90	62.00	1.55	3.68	1.78	1.21
	5.00	2.36	52.80	1.32	5.36	1.87	1.14
	6.00	3.04	39.20	0.98	9.31	1.98	1.01
	8.00	5.38	7.60	0.19	84.95	2.23	0.30
	1.00	0.12	97.60	2.44	0.15	0.58	1.41
	2.00	0.32	93.60	2.34	0.41	1.01	1.39
	3.00	0.75	85.00	2.13	1.06	1.38	1.35
BOC	4.00	1.20	76.00	1.90	1.89	1.58	1.30
	5.00	2.07	58.60	1.47	4.24	1.82	1.19
	6.00	2.58	48.40	1.21	6.40	1.91	1.11
	8.00	5.90	18.00	1.09	39.33	2.27	0.68

Sorption Kinetics

Kinetics of fluoride ion removal was carried out to understand the behavior of activated Kazu's carbons as a low cost adsorbent material. The removal of fluoride ion is very rapid initially and decreases markedly before equilibrium is reached. Helfrich model for removal of fluoride is shown in Fig.7. The rate constant K is determined from

$$In[1-U(t)] = Kt$$

$$Where, U(t) = (Ci-Ct)/(Ci-Ce)$$

The straight line plotted between In[1-U(t)] and t indicates the applicability in aqueous system that follows reversible first order. The kinetics of sorption describing the rate of solute uptake which inturn gives the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption.

Table 2 : Effect of contact time on the percent removal of fluoride by the various adsorbents

Contact time	BKC		RSC		BOC	
(min)	**Ce mg/L**	%Rem.	Ce mg/L	% Rem.	Ce mg/L	% Rem.
1	1.99	60.2	1.97	60.6	1.82	63.6
2	1.82	63.6	1.94	61.2	1.79	64.2
3	1.71	65.8	1.92	61.6	1.76	64.8
4	1.59	68.2	1.89	62.2	1.72	65.6
5	1.48	69.8	1.83	63.4	1.69	66.2
10	1.47	70.6	1.69	66.2	1.6	68
15	1.41	71.8	1.52	69.6	1.51	69.8
20	1.29	74.2	1.41	71.8	1.39	72.2
25	1.21	75.8	1.19	76.2	1.09	78.2
30	1.02	79.6	1.18	76.4	0.99	80.2

Table 3 : Effect of dose of adsorbents on the percent removal of fluoride by adsorption on the various adsorbents

Dose of adsorbent (g/L)	BKC		RSC		BOC	
	Ce mg/L	% Rem.	Ce mg/L	% Rem.	Ce mg/L	% Rem.
0.1	1.48	70.4	1.42	71.6	1.36	72.8
0.2	1.22	75.6	1.24	75.2	1.20	76
0.3	1.18	76.4	1.20	76	1.17	76.6
0.4	1.15	77	1.17	76.6	1.15	77
0.5	1.12	77.6	1.14	77.2	1.12	77.6
0.6	1.08	78.4	1.12	77.6	1.08	78.4
0.7	1.06	78.8	1.09	78.2	1.06	78.8
0.8	1.04	79.2	1.07	78.6	1.04	79.2
1	1.01	79.8	1.02	79.6	1.01	79.8

Table 4 :Effect of pH on the percent removal of fluoride by adsorption on the various adsorbents

pH	BKC		ROC		BOC	
	Ce mg/L	% Rem.	Ce mg/L	% Rem.	Ce mg/L	% Rem.
3	1.58	68.4	1.67	66.6	1.6	68
4	1.32	73.6	1.56	68.8	1.52	69.6
5	1.22	75.6	1.43	71.4	1.41	71.8
6	1.13	77.4	1.38	72.4	1.36	72.8
7	1.33	73.4	1.32	73.6	1.32	73.6
8	1.4	72	1.46	70.8	1.49	70.2
9	1.52	69.6	1.59	68.2	1.58	68.4
10	1.72	65.6	1.79	64.2	1.82	63.6

Table 5 : Adsorption isotherm parameters of the chosen adsorbents

Model	Sample		
	BKC	RSC	BOC
Langmuir isotherm			
Q_0	3.0596	0.9586	2.4781
b	1.1879	0.3473	0.5498
Correlation Coefficient (r)	0.9381	0.9419	0.9687
Freundlich isotherm			
Slope (1/n)	8.4182	3.0282	8.179
Intercept	7.9509	4.4002	0.9808
Correlation Coefficient (r)	0.7662	0.9723	0.9578

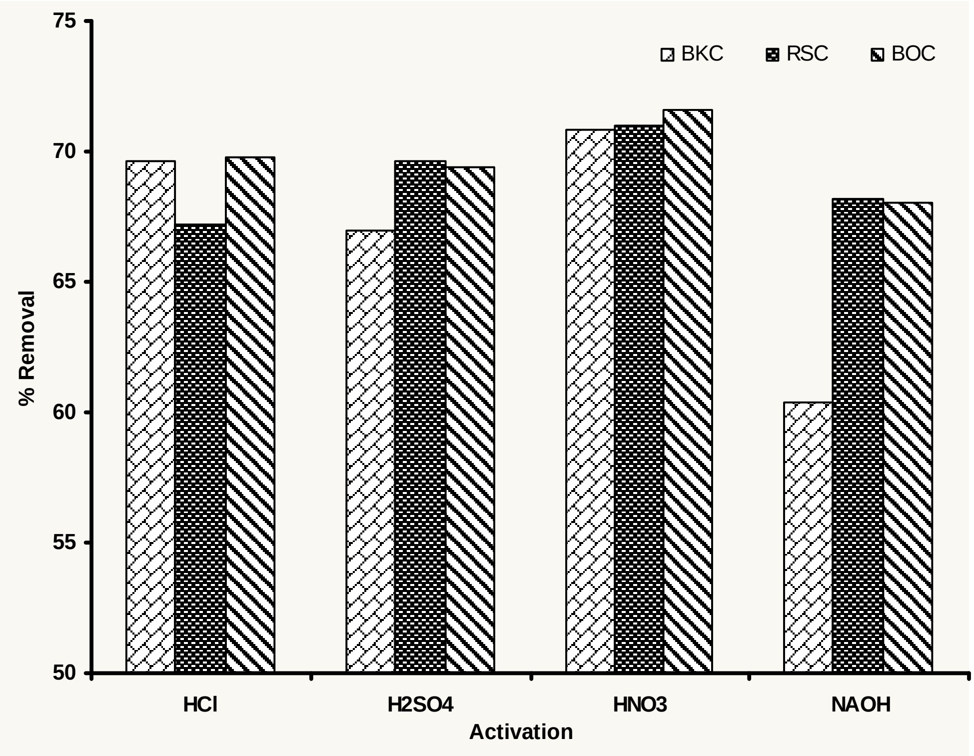


Figure 1 : Percentage fluoride removal efficiency of activated carbons as a function of various activations.

Table 6 : Statistical results of the application of the kinetic equations and models for the low cost adsorbents

Parameter	BKC	RSC	BOC
1. Natarajan & Khalaf equation			
K (min^{-1})	1.041	0.9951	1.0234
r value	0.9133	0.9869	0.949
2. Intraparticle diffusion model			
Kp ($mg\ g^{-1}\ min^{-0.5}$)	0.0881	0.0958	0.0884
Intercept	1.4815	1.3821	1.4636
R value	0.9275	0.9752	0.9177
3. Log(time) Vs Log (%rem)			
Slope	0.0348	0.0344	0.0343
Intercept	1.8668	1.8645	1.868
R value	0.988	0.9784	0.9472

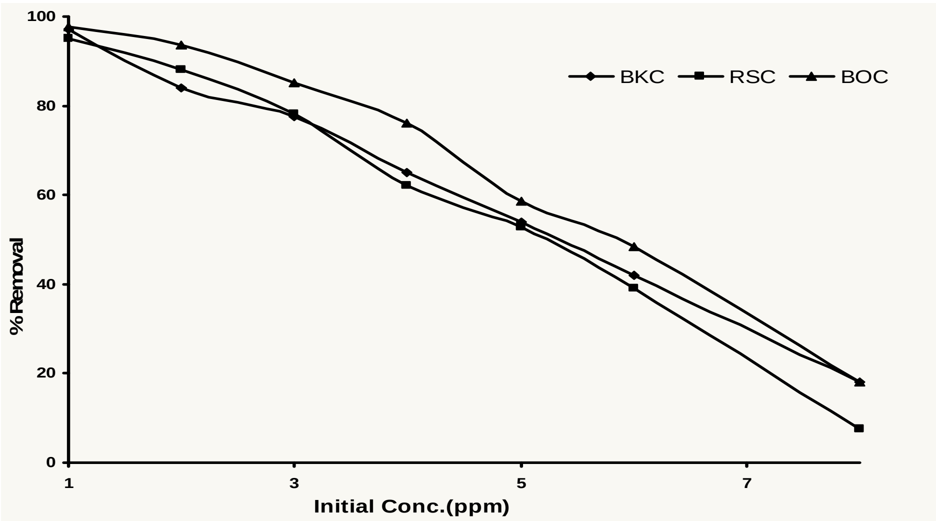


Figure 2: Variation of percent removal of fluoride with increasing initial concentration

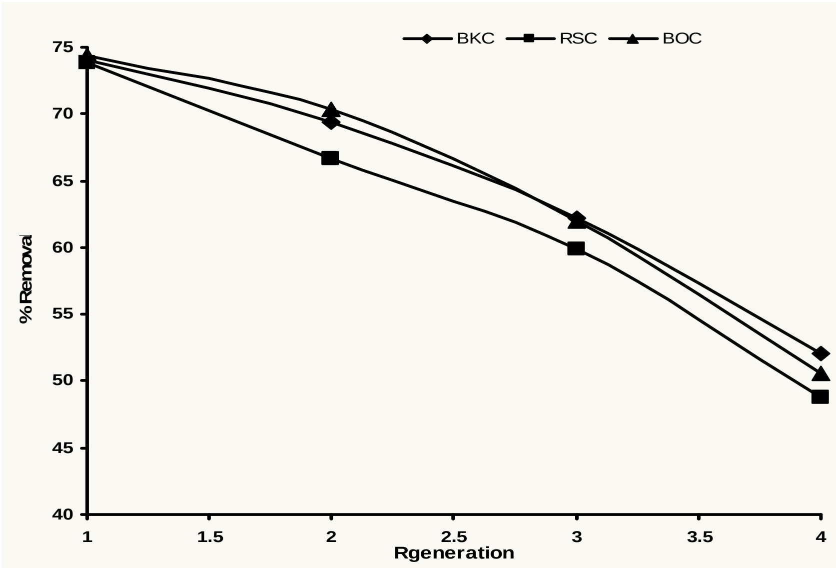


Figure 3: % Removal of fluoride by using regenerated adsorbent

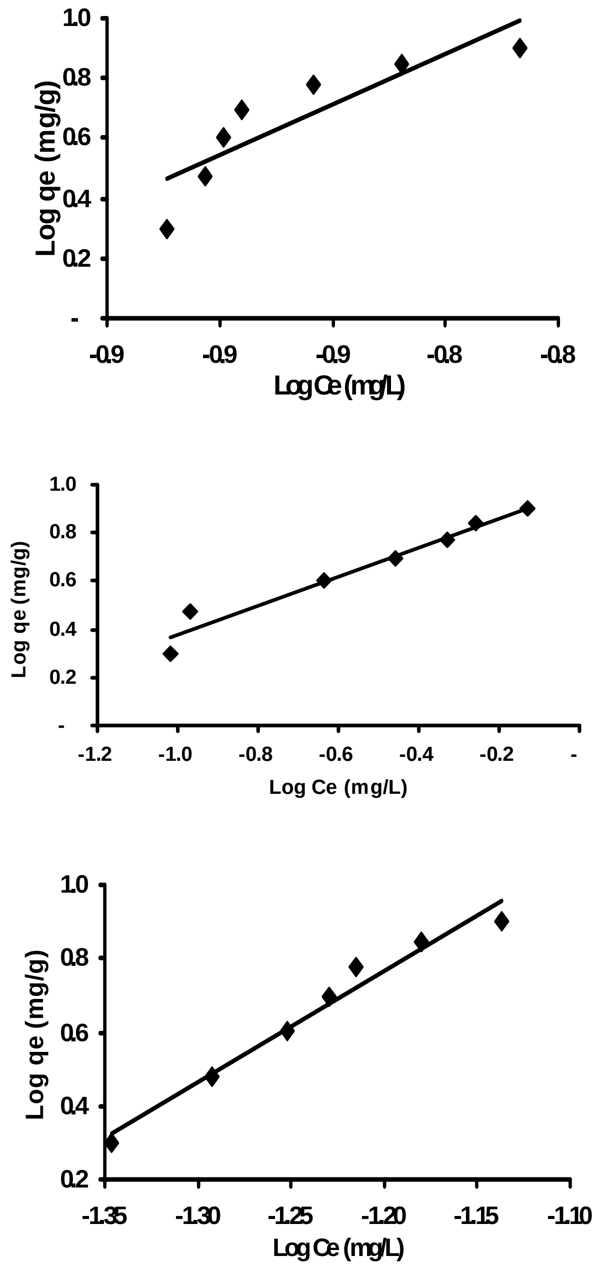
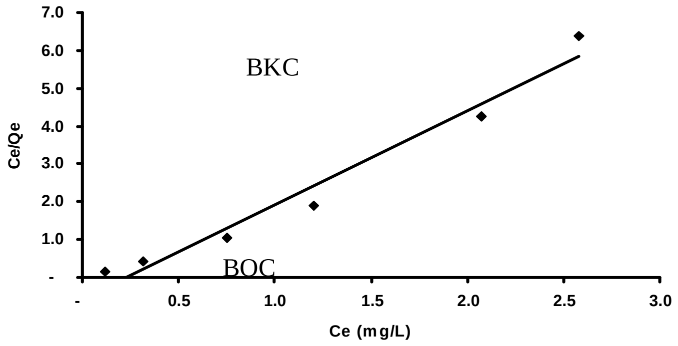
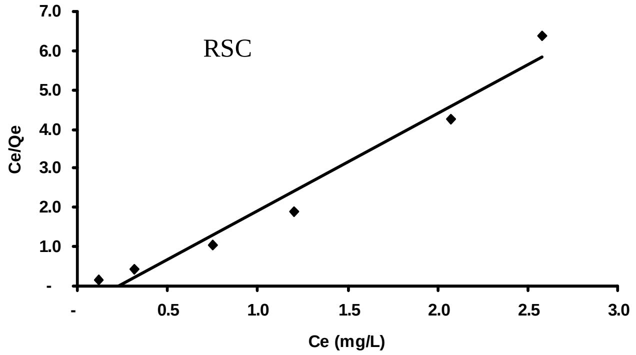
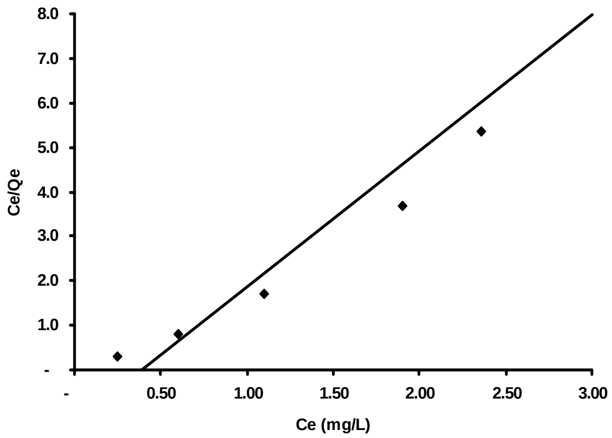


Figure 4: Freundlich isotherms for the removal of fluoride by adsorption on various adsorbents


BKC
BOC
Ce/Qe
Ce (mg/L)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
-
0.5
1.0
1.5
2.0
2.5
3.0


RSC
Ce/Qe
Ce (mg/L)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
-
0.5
1.0
1.5
2.0
2.5
3.0


Ce/Qe
Ce (mg/L)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
-
0.50
1.00
1.50
2.00
2.50
3.00

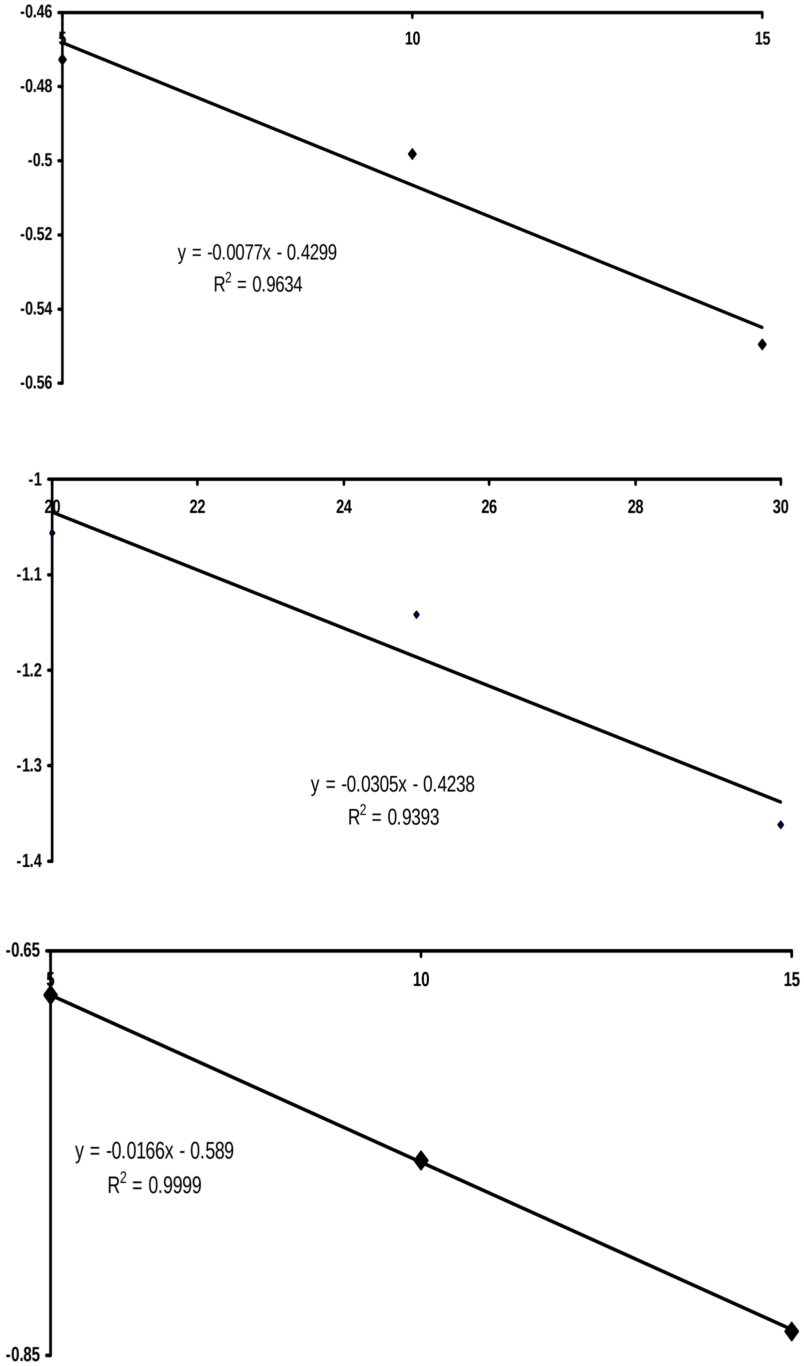


Figure 7: Calculation based on Helffrich model for removal of fluoride from fluoridated water

CONCLUSION

The prepared lowcost activated Kaza's carbons namely BKC,BOC and RSC showed good adsorption capacity towards fluoride. Good fitting of Langmuir isotherm indicates the possibility of unimolecular adsorption. The adsorbents can be used for six times for effective defluoridation.

These adsorbents are very useful and economical for the removal of fluoride ions from aqueous solution.

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