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Defluoridation Of Water Using Aluminium Impregnated Activated Newspaper Carbon

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ABSTRACT

The capacity of aluminium impregnated activated newspaper carbon to abate fluoride ion from water was investigated by batch adsorption studies. The system variables studied include initial concentration of the sorbate, agitation time, adsorbent dose, pH, co-ions and temperature. The experimental data fitted well to the Freundlich isotherm. Thermodynamic parameters such as ΔH^0 , ΔS^0 and ΔG^0 indicate that the adsorption was endothermic and a physical process. Kinetic studies reveal that the adsorption follows reversible first order kinetics. XRD patterns of the adsorbent before and after adsorption were recorded to get a better insight into the mechanism of the adsorption process.

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INTRODUCTION

Fluorine is an important micronutrient in animals for the production and maintenance of healthy bones and teeth. Fluorine is present as fluoride ion in natural water. The health impact of ingesting water containing fluoride concentration outside the permitted limits (1.5 mg/L) is a subject that has been studied very extensively. Consumption of water with fluoride concentrations below the permitted limit accompanied by poor dental hygiene has been shown to cause cavities while ingesting water with fluoride concentrations exceeding the limits causes dental fluorosis. In an extensive bibliographic review carried on by the World Health Organization^[1], the incident of dental fluorosis was found to be intimately related to the consumption of water containing high fluoride concentration.

Excess fluoride can be removed from drinking

water using the following methods, adsorption^[2-5], precipitation^[6], ion-exchange^[7,8], electro-dialysis^[9-11] and electrochemical methods^[12-13], among these methods, adsorption is still one of the most extensively used methods for defluoridation of water. Novel adsorbents have been prepared by impregnating alumina with lanthanum(III) and ytterbium(III)^[14] and silica gel with lanthanum(III)^[15]. The adsorption capacities of impregnated aluminas were about twice that of the plain alumina while the fluoride ion capacity of lanthanum-impregnated silica gel was less than that of alumina. Impregnation of porous adsorbents has shown very promising results for preparing new adsorbents to remove fluoride from aqueous solutions^[16].

The main objective of this study is to analyze the efficiency of a new adsorbent for removing fluoride from aqueous solution. This adsorbent was prepared by impregnating aluminium with newspaper carbon. Thus, the new material is a low cost adsor-

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bent combining of the properties of large surface area of newspaper carbon with high fluoride adsorption capacity of aluminium. The capacity of newspaper carbon to abate fluoride ions from aqueous solution has already been reported by us^[16].

EXPERIMENTAL

Materials

All the reagents used were of commercially available high purity analar grade (Merck or Sd-fine, India). Stock solutions of fluoride were prepared by dissolving sodium fluoride in doubly distilled water.

Preparation of aluminium impregnated carbon. The activated newspaper carbon was prepared as reported earlier^[16]. The dried material was ground in a mortar. Further it was digested with 2% sodium bicarbonate solution for 30 minutes. After digestion, the carbon is washed free of bicarbonate and digested for 30 minutes in 40% aluminium sulphate solution. The precipitated $\text{Al}(\text{OH})_3$ was solubilised using dilute hydrochloric acid till a clear solution is obtained. This carbon was then separated washed until washings are free from Al(III) and dried at 100°C for six hours. This carbon (ANPC) was used for further studies.

Methodology

The concentration of fluoride and pH were measured using ion-selective meter (Eutech Cyberscan 2100). The XRD pattern of the adsorbent before and after adsorption was recorded at the Regional Research Laboratory, Thiruvananthapuram, S.India. The zero point charge (pH_{ZPC}) of the adsorbent was determined by pH drift method^[17] and it was found to be 6.26.

Batch adsorption experiments

Adsorption experiments were performed by agitating 500 mg of adsorbent with 50 ml of fluoride solution of desired concentration at $30 \pm 0.5^\circ\text{C}$ in different stoppered bottles in a shaking thermostat machine. The shaking speed was 120 strokes/min throughout the study. At the end of predetermined time intervals, the sorbet was filtered and the concentration of fluoride was determined. All experiments were carried out twice and the adsorbed fluoride concentrations given were the means of dupli-

cate experimental results.

Experimental variables considered were initial concentration of fluoride ions 2-10mg/L; contact time between adsorbent and the fluoride solution 5-60min; pH 3-11; dosage of the adsorbent 100-2000mg/50ml; temperature 30-50°C and co-ions viz. chloride, sulphate, nitrate and bicarbonate ions.

Data analysis

The experimental data were analyzed using Microcal Origin(version 6.0) computer software. The goodness of fit was discussed using correlation coefficient, r , and standard deviation, sd .

RESULT AND DISCUSSION

Effect of contact time and initial concentration. The equilibrium parameters for the adsorption of fluoride onto ANPC are collected in TABLE 1. The results reveal that, the amount of fluoride adsorbed per unit mass of the adsorbent increased with increase in concentration and rise in temperature. The

TABLE 1 : Equilibrium parameters for the adsorption of fluoride onto ANPC

[F] mg/L	C_e (mg/L)			Q_e (mg/g)			Fluorideremoved(%)		
	30°	40°	50°C	30°	40°	50°C	30°	40°	50°C
2	1.13	1.10	1.08	0.087	0.090	0.092	43.50	45.00	46.00
4	2.16	2.14	2.12	0.184	0.186	0.188	46.00	46.50	47.00
6	3.23	3.11	3.02	0.277	0.289	0.298	46.17	48.17	49.67
8	4.35	4.30	4.18	0.365	0.370	0.382	45.63	46.25	47.75
10	5.65	5.57	5.40	0.435	0.443	0.460	43.50	44.30	46.00

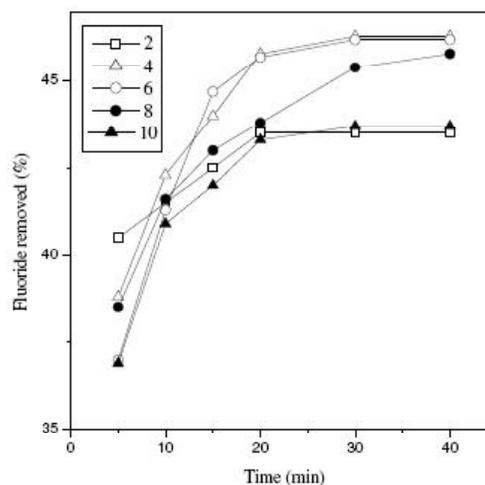


Figure 1 : Effect of agitation time and initial concentration on the adsorption of fluoride onto ANPC
Temp=30°C; pH=7

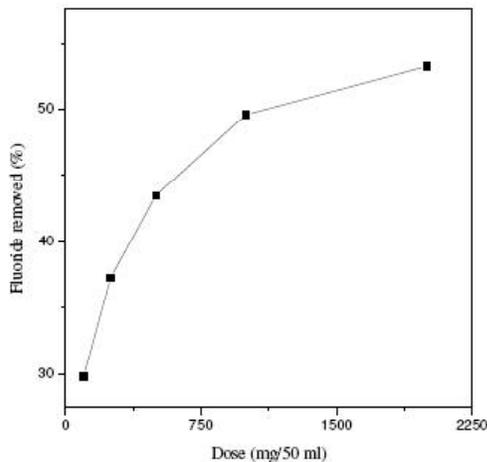


Figure 2 : Effect of dose on the adsorption of fluoride onto ANPC [F]=4mg/L; Temp=30°C; pH=7; Agitation time=60min

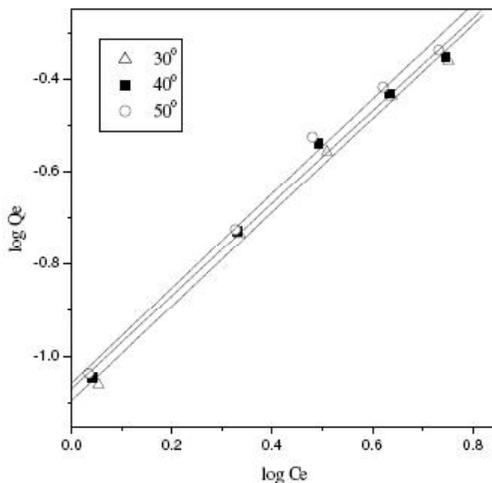


Figure 3 : Freundlich adsorption isotherms for the adsorption of fluoride onto ANPC

variation of Q_e with temperature indicates that the adsorption process is endothermic in nature. The effect of contact time between the adsorbent and adsorbate is depicted in figure 1. It is evident from the figure that the equilibrium was established after 30 min for all the concentrations. Further, the curves in figure 1 are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the fluoride on the carbon surface^[18].

Effect of adsorbent dose

The results depicted in figure 2 indicate that the removal of fluoride increases with increasing the amount of adsorbent at an initial fluoride concen-

TABLE 2 : Langmuir and Freundlich isotherm constants for the adsorption of fluoride onto ANPC

Isotherm	Statistical parameter/constants	Temp		
		30°	40°	50° C
Freundlich	r	0.99	0.99	0.99
	sd	0.03	0.03	0.03
	n	0.99	1.00	0.98
	K	0.08	0.09	0.09
Langmuir	r	0.86	0.75	0.45
	sd	0.38	0.61	0.73

tration of 4mg/L and in the adsorbent dose range of 0.1 to 2g/50ml. Further, from the result it is evident that an optimum dosage of 500mg/50ml is required for appreciable removal of fluoride and hence this amount is employed as the dose for further studies.

Adsorption isotherms

The adsorption data for the removal of fluoride have been correlated with Freundlich^[19] and Langmuir^[20] models. The following linearised Freundlich adsorption isotherm is employed.

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

Where Q_e is the amount adsorbed at equilibrium (mg/g), K and n are Freundlich constants, and C_e the equilibrium concentration (mg/L). The plots of $\log Q_e$ against $\log C_e$ are linear at different temperatures and a representative plot is shown in figure 3. The statistical results along with Freundlich constants are collected in TABLE 2. From the results it is evident that the intensity of adsorption, n is equal to one suggesting that all the surface sites are equivalent^[21].

Langmuir isotherm is based on the assumption 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 molecule at one site will not affect the adsorption of molecules at an adjacent site. The linear form of Langmuir equation can be expressed as:

$$C_e/Q_e = 1/Q^0 b + C_e/Q^0 \quad (2)$$

Where, C_e and Q_e has usual meanings and Q^0 and b are the Langmuir constants related to the capacity and energy of adsorption, respectively. The plots of

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TABLE 3: Equilibrium constant and thermodynamic parameters for the adsorption of fluoride onto ANPC

[F] mg/L	K ₀			ΔG ⁰ (kJ mol ⁻¹)			ΔH ⁰ (kJmol ⁻¹)	ΔS ⁰ (JK ⁻¹ mol ⁻¹)
	30 ⁰	40 ⁰	50 ⁰ C	30 ⁰	40 ⁰	50 ⁰ C		
2	0.77	0.82	0.85	0.66	0.52	0.43	4.12	11.5
4	0.85	0.87	0.89	0.40	0.36	0.32	1.64	4.1
6	0.86	0.93	0.99	0.39	0.19	0.04	5.72	17.6
8	0.84	0.86	0.91	0.44	0.39	0.24	3.46	9.9
10	0.77	0.79	0.85	0.66	0.60	0.43	4.11	11.3

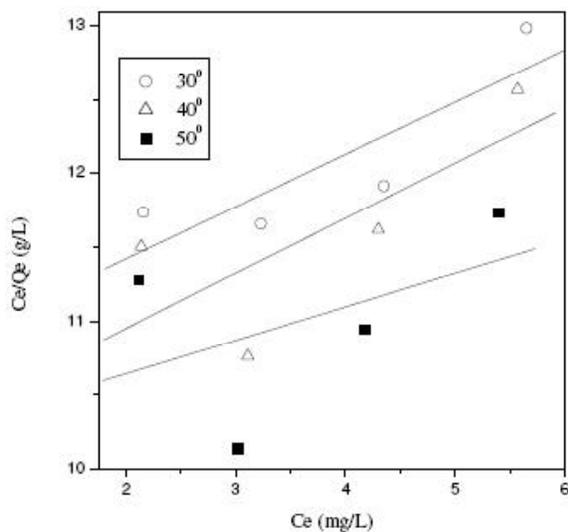


Figure 4: Langmuir adsorption isotherms for the adsorption of fluoride onto ANPC

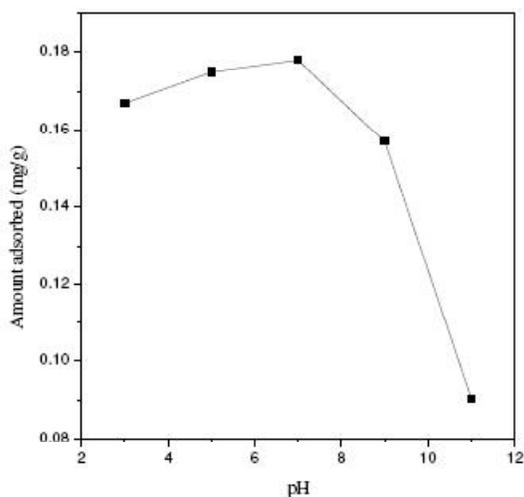


Figure 5: Effect of pH on the adsorption of fluoride onto ANPC

[F]=4mg/L; Temp=30°C; Contact time=60min

C_e/Q_e versus C_e are non linear ($r < 0.86$, TABLE 2) indicating that the adsorption process does not obey the Langmuir isotherm. A representative plot is shown in figure 4.

Thermodynamic parameters

The standard free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated from the variation of the thermodynamic equilibrium constant K_0 with temperature. The values of K_0 and other thermodynamic parameters for the adsorption process were calculated by the reported methods^[16,22] and the values computed are collected in TABLE 3.

It is evident from the results that, the endothermic nature of adsorption is indicated by increase in K_0 with rise in temperature. The ΔG^0 values are positive which mean that the reaction is non-spontaneous. The value of enthalpy of a sorption process may be used to distinguish between chemical and physical sorption^[23]. For chemical sorption enthalpy values range from 83 to 830 kJ mol⁻¹, while for physical sorption they range from 8 to 25 kJ mol⁻¹. On the basis of the above discussion it is conclude that fluoride sorption by ANPC is a physical process. Positive values of ΔH^0 suggest that the adsorption process is endothermic. As indicated in TABLE 3, ΔS^0 values for the adsorption process are positive. This observation suggests a high degree of disorderliness at the solid solution interface during the adsorption of fluoride onto ANPC. This may be due to the fact that adsorbed water molecules which are displaced by the adsorbate species gain more translational entropy than is lost by the adsorbate molecules. Thus allowing the prevalence of randomness in the system^[24].

Effect of pH. To study the influence of pH on the removal of fluoride, test mixtures containing 4mg/L of fluoride solution and 500 mg of adsorbate were adjusted to various initial pH values, both in the acidic and alkaline ranges are mixed for the equilibrium time and analyzed for final pH and residual fluoride concentrations. Figure 5 shows the effect of pH on the removal of fluoride using ANPC. As the initial pH of the fluoride solution is increased from 3 to 13, removal of fluoride is reduced from 0.167 mg/g to 0.093mg/g. The results indicate that the adsorbent exhibits a commendable defluoridation capacity in the acidic pH range. This behavior can be explained on the basis of zero point charge ($pH_{ZPC} = 6.26$) of the adsorbents. At higher pH above

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this point, the OH⁻ ions compete effectively with fluoride ions causing a decrease in the amount of fluoride removed. At a lower pH below this zero point charge, the surface of the adsorbent gets positively charged, which enhances the adsorption of negatively charged fluoride ions through electrostatic force of attraction^[25-26].

Effect of co-ions

The effect of added co-ions viz. Cl⁻, NO₃⁻, SO₄²⁻ and HCO₃⁻ on the amount of fluoride adsorbed is given in TABLE 4. The results indicate that the addition of co-ions, in the concentration range investigated, has no appreciable effect on the amount of fluoride ions removed. However, increase in the concentration of bicarbonate ions decreases the amount adsorbed. This may be due to the competition between bicarbonate and fluoride ions for the active sites on the adsorbent and a similar observation was made in the adsorption of fluoride onto activated alumina^[27] and magnesia^[28].

Kinetics of adsorption. Kinetics of sorption describes the solute uptake rate which in turn governs the residence time of sorption reaction. It must be remembered that the two important physico-chemical aspects for parameter evaluation of sorption process as unit operation are the kinetics and the equilibria. Hence in the present study, the kinetics of fluoride removal has been carried out to understand the behaviour of the adsorbent employed. The rate constants for the adsorption, k_{ad} , were determined using the expression, given by Natarajan and Khalaf, as described in the literature^[16, 29]. The rate constants were calculated from the slopes of these plots and the values are collected in TABLE 5. The values of k_{ad} were found to increase with increase in the temperature indicating the endothermic nature of the adsorption process. It is evident from the results that the forward rate constant is much lower than the backward rate constant suggesting that the rate of desorption is clearly dominant and as a result of this the adsorption process is non-spontaneous as indicated by the change in free energy values. Further, the k_{ad} values vary in a non-linear manner with increase in initial concentration of the fluoride. This is due to the fact that in cases of strict surface adsorption a variation

TABLE 4 : Effect of co-ions on the amount of fluoride adsorbed (mg/g) by ANPC

Co-ion	Concentration of co-ion, mg/L					
	0	100	200	300	400	500
Chloride	0.184	0.186	0.180	0.185	0.183	0.180
Sulphate	0.184	0.191	0.159	0.156	0.168	0.178
Nitrate	0.184	0.179	0.185	0.178	0.186	0.202
Bicarbonate	0.184	0.188	0.183	0.176	0.162	0.128

[F]=4 mg/L; Temp=30°C; pH=7; Contact time=60min

TABLE 5 : Rate constants for the adsorption of fluoride (k_{ad} , min⁻¹) and the rate constants for forward (k_f , min⁻¹) and reverse (k_r , min⁻¹) processes

[F] mg/L	10 ⁴ k _{ad}			10 ⁴ k _f			10 ⁴ k _r		
	30°	40°	50° C	30°	40°	50° C	30°	40°	50° C
2	29.5	31.1	42.8	12.8	13.9	19.7	16.7	17.1	23.1
4	25.8	80.6	101.3	11.9	37.5	47.6	13.9	43.1	53.7
6	34.1	70.0	114.7	15.7	33.7	56.9	18.4	36.3	57.7
8	10.6	58.5	64.5	4.8	27.1	30.8	5.8	3.1	33.7
10	42.1	53.9	69.1	18.3	23.9	31.8	23.8	30.0	37.3

of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial fluoride concentration and rate of reaction will not be linear. It shows that pore diffusion limits the overall rate of fluoride adsorption^[16].

Intra particle diffusion study

In adsorption studies, it is necessary to determine the rate limiting step. Therefore, the results obtained from the experiments were used to study the rate-limiting step. Since the particles were vigorously agitated during the experiments, it is reasonable to assume that the mass transfer from the bulk liquid to the particle external surface did not limit the rate. One might, and then postulate that the rate limiting step might be film or intra-particle diffusion which was tested by plotting a graph between amount of fluoride adsorbed and square root of time. The double nature of these plots may be explained as the initial curve portions are attributed to boundary layer diffusion effect, while the final linear portions are due to intra-particle diffusion effect^[30-31].

The rate constants for intra-particle diffusion, k_p for the removal of fluoride by the adsorbent were determined from the slopes of the linear portion of the respective plots. The values of k_p (mg g⁻¹ min^{-0.5}) are 0.39×10⁻², 1.16×10⁻² and 1.27×10⁻² for 30°, 40° and 50°C respectively. Further, the linear portions

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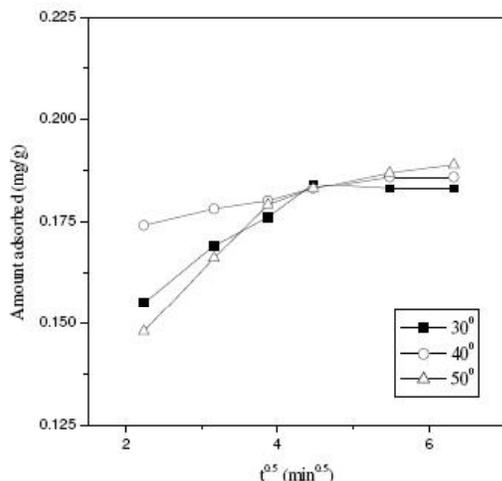


Figure 6 : Intraparticle diffusion plot for the adsorption of fluoride onto ANPC at different temperatures

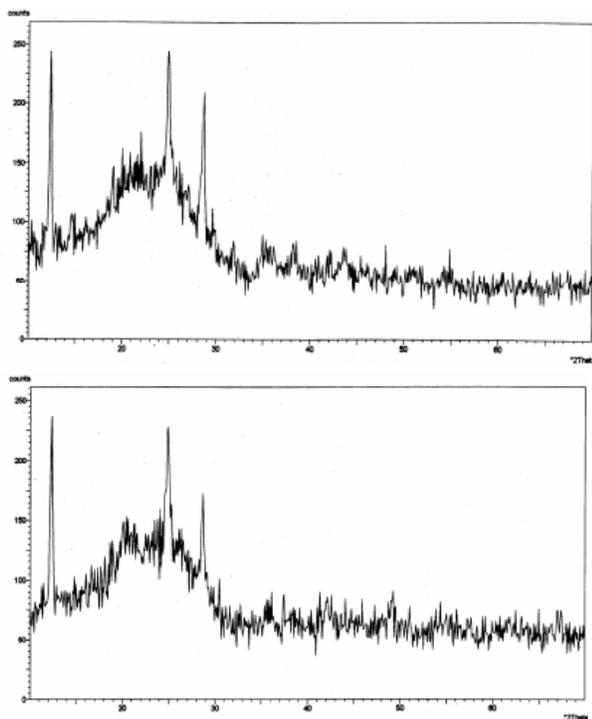


Figure 7 (a) : XRD pattern of ANPC before adsorption ;
(b) : XRD pattern of ANPC loaded with fluoride

of the curves do not pass the origin in figure 6. This indicates that mechanism of removal of fluoride is complex and both the surface adsorption and intraparticle diffusion may contribute to the rate-determining step^[32,33].

X-Ray diffraction (XRD) studies

Adsorption process may lead to changes in mo-

lecular and crystalline structure of the adsorbent and hence an understanding of the molecular and crystalline structures of the adsorbent and the resulting changes thereof would provide valuable information regarding adsorption process. Hence, XRD patterns of the adsorbent before and after adsorption of fluoride ions have been studied. The XRD patterns of the adsorbent before and after treatment with fluoride ions are shown in figure 7. It is evident from the figure that the XRD pattern of adsorbent loaded with fluoride ions exhibits no variation in the crystal structure which suggests that the fluoride ions might diffuse into micropores and sorbs mostly by physisorption without altering the structure of the adsorbent^[34]. The above observation corroborated well with batch sorption experiments and thermodynamic results.

CONCLUSION

The foregoing results indicate that the adsorption of fluoride onto ANPC is a physical process. Lower pH and higher temperatures were found as the optimum conditions for maximum fluoride adsorption by the adsorbent. The results gained from this study were extremely well described by Freundlich isotherm. The thermodynamics of the system pointed out the adsorption process is endothermic. On the basis of the kinetic and XRD studies a mechanism in which surface adsorption as well as intra-particle diffusion as rate limiting step has been proposed for the uptake of fluoride ions onto aluminium impregnated activated newspaper carbon.

It is interesting to note that, at 30°C and pH 7, for an initial fluoride concentration of 4mg/L, the amount of fluoride adsorbed by plain newspaper carbon is 0.1190mg/g^[16] however under identical conditions the fluoride uptake by ANPC is 0.184 mg/g. The increase in fluoride uptake to the tune of over 1.5 times might be due to the impregnation of aluminium. However, this increase in adsorption may be due to the interaction of fluoride with aluminium impregnated in the carbon through chemisorption in addition to physisorption as discussed earlier in this article. But, X-ray diffraction studies indicate that no difference was found between the XRD pattern of ANPC and fluoride loaded ANPC indicating that

the adsorption is a physical process. This may be due to the fact that, during impregnation with aluminium, only approximately 0.05% of the activated carbon surface area would be covered with aluminium and the carbon surface interferes greatly with the XRD measurement^[35].

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REFERENCES

- [1] World Health Organization. Fluorine and fluorides: environmental health criteria, WHO, Geneva, (1984).
- [2] Q.Zhang, H.Liang; *Environ.Int.*, **18**, 307 (1992).
- [3] A.Sivasamy, K.P.Singh, D.Mohan, M.Maruthamuthu; *J.Chem.Technol.Biot.*, **76**, 717 (2001).
- [4] Y.Ku, H.M.Chiou; *Water.Air.Soil.Poll.*, **133**, 349 (2002).
- [5] A.K.Chaturvedi, K.P.Yadav, K.C.Pathak, V.N.Singh; *Water Air Soil Poll.*, **49**, 51 (1990).
- [6] Z.Amor, S.Malki, M.Taky, B.Bariou, N.Mameri, A.Elmidou; *Desalination*, **120**, 263 (1998).
- [7] N.Azbar, A.Turkman; *Water Sci.Technol.*, **42**, 403 (2000).
- [8] K.Vaaramaa, J.Lehto; *Desalination*, **155**, 157 (2003).
- [9] C.Castel, M.Schweizer, M.O.Simonnot, M.Sardin; *Chem.Eng.Sci.*, **55**, 341 (2000).
- [10] M.Liu, R.Y.Sun, J.H.Zhang, Y.Bina, L.Wei, P.Liu, C.F.Kei; *Fluoride*, **20**, 54 (1987).
- [11] Z.Amor, B.Bariou, N.Mameri, M.Taky, S.Nicolas, A.Elmidou; *Desalination*, **133**, 215 (2001).
- [12] H.Lounici, L.Addour, D.Belhocine, H.Grib, S.Nicolas, B.Bariou, N.Mameri; *Desalination*, **114**, 241 (1997).
- [13] F.Shen, X.M.Chen, P.Gao, G.H.Chen; *Chem.Eng.Sci.*, **58**, 987 (2003).
- [14] S.S.Wasay, S.Tokunaga, S.W.Park; *Sep.Sci.Technol.*, **31**, 1501 (1996).
- [15] S.A.Wassay, M.J.Haron, S.Tokunaga; *Water Environ.Res.*, **68**, 295 (1996).
- [16] K.P.Elango, V.Gopal; *Environ.Sci.Ind.J.*, **2**, 75 (2007).
- [17] Y.F.Jia, B.Xiao, K.K.Thomas; *Langmuir*, **18**, 470 (2002).
- [18] H.Parab, S.Joshi, N.Shenoy, R.Verma, A.Lali, M.Sudarsanan, *Biores.Technol.*, **96**, 1241 (2005).
- [19] H.M.F.Freundlich; *Z.Phys.Chem. A* **57**, 385 (1906).
- [20] Langmuir; *J.Am.Chem.Soc.*, **40**, 1361 (1918).
- [21] A.V.Jamode, V.S.Sapkal, V.S.Jamode; *J.Indian Inst.Sci.*, **84**, 163 (2004).
- [22] B.Stephen Inbaraj, N.Sulochana; *Indian J.Chem. Technol.*, **9**, 201 (2002).
- [23] M.Doula, A.Ioannou, A.Dimirkou; *Adsorption*, **6**, 325 (2000).
- [24] C.Namasivayam, R.T.Yamuna; *Environ.Poll.*, **89**, 1 (1995).
- [25] N.Das, R.K.Jana; *J.Colloid Interf.Sci.*, **293**, 253 (2006).
- [26] V.Gopal, K.P.Elango; *J.Hazard.Mater.*, **141**, 98 (2007).
- [27] G.Karthikeyan, A.Sunmugasundarraaj, S.Meenakshi, K.P.Elango; *J.Indian Chem.Soc.*, **81**, 461 (2004).
- [28] V.Aravind, K.P.Elango; *Indian.J.Chem.Tecnol.*, **13**, 476 (2006).
- [29] N.Kannan, A.Vanangamudi; *Indian J. Environ. Protec.*, **11**, 241 (1991).
- [30] C.K.Lee, K.S.Low, L.C.Chung; *J.Chem.Tech. Biotechnol.*, **69**, 93 (1997).
- [31] S.J.Gregg, K.S.W.Singh; *Adsorption Surface Area and Porosity*, Academic Press, New York, (1967).
- [32] S.Rengaraj, B.Arabindoo, V.Murugesan; *Indian J.Chem.Technol.*, **6**, 1 (1999).
- [33] P.S.Syed Shabudeen, R.Venkatesh, K.Selvam, S.Madhavakrishnan, S.Pattabhi; *Res.J. Chem. Environ.*, **10**, 18 (2006).
- [34] S.Venkata Mohan, S.Krishna Mohan, J.Karthikeyan; *J.Sci.Indus.Res.*, **60**, 410 (2001).
- [35] R.L.Ramos, J.O.Turrubiartes, M.A.S.Castillo; *Carbon*, **37**, 609 (1999).