Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2015, 4 (1): 166-177

(International Peer Reviewed Journal)

Adsorption of Fluoride from Aqueous Phase by Bombax Malabaricum Carbon (Kaza's Carbon)

K.A.Emmanuel[1*], A.Veerabhadrarao[2], T.V.Nagalakshmi[3], Ch. Sureshbabu[4]
and K. Somasekhara Rao[5]

1. Department of chemistry, Sir C.R.R.College, Eluru,W.G.District, A.P. **INDIA**
2. Department of Physics, Sir C.R.R.College, Eluru,W.G.District, A.P. **INDIA**
3. Department of Chemistry, P.P.D.C.E.T, Nunna, Krishna District, A.P. **INDIA**
4. Department of Eng. Chemistry, Eluru College of Enng & Tech, Eluru-7, **INDIA**
5. Department of Chemistry, Nagaland University, Lumami, Nagaland, **INDIA**

Email: kaekola@gmail.com

Accepted on 16th January 2015

ABSTRACT

The endeavor of this research work is to intend and develop a novel gainful strategy for fluoride removal, applicable to rural areas of developing countries. This contribution presents results concerning to the adsorptive studies carried out on removal of fluoride by low cost adsorbent Activated Kaza's carbon prepared from Bombax malabaricum ***(BMC)****. Batch sorption studies were executed and the results showed that biosorbent demonstrated ability to adsorb the fluoride. The dependence of fluoride adsorption on various factors such as pH of the solution, adsorbent dose and concentration of the fluoride were investigated. Sorption interaction of fluoride onto BMC obeyed the first order rate equation. Experimental results showed good fit with the Langmuir's adsorption isotherm model. The removal of fluoride was found to be dependent on the pH of the aqueous solution and the adsorption of fluoride was observed to be greater at pH 7. Maximum fluoride sorption was observed at operating 30°C operating temperature. Considerable changes in the FT-IR spectra was observed after fluoride sorption which is investigative of the involvement of surface functional groups associated with hydrogen atoms in the carboxylic groups in sorption interaction. From X-ray photoelectron spectroscopy (XPS) analysis a marginal increase in the area for the binding energy peak at 287.4 eV was observed which could be due to the formation of –C–F– bonds.*

Keywords: Biosorption; *BMC*; Biosorbent; Kinetics; Adsorption–desorption; Isotherms; SEM; FT-IR; XPS.

INTRODUCTION

Inconsistent presence and absence of fluoride in water is an issue of solemn health concern. The recommended concentration of fluoride in drinking water is between 0.5 and 1.5 mg L^{-1}. Excess fluoride in drinking water was reported from different geographical regions. More than 200 million people worldwide are affected by excess concentration of fluoride, in their drinking water [1]. The problem of excessive fluoride in ground water in India was detected in Guntur of Andhra Pradesh [2]. According to an estimate, 25 million people in 19 states and union territories have already been affected and another 66 million are at risk including 6 million children below the age of 14 years [3]. Though fluoride enters the body mainly through water, food, industrial exposure, drugs cosmetics, etc. drinking water is the major source (75%) of daily intake [4]. A fluoride ion is attracted by positively charged calcium in teeth and bones, due to its strong electro negativity. Major health problems caused by fluoride are dental fluorosis (teeth mottling) skeletal fluorosis (deformation of bones in children and also in adults) and non skeletal fluorosis [5, 6]. It can interfere with carbohydrates, lipids, protein, vitamins, enzymes and mineral metabolism when the dosage is high. In some parts of India, the fluoride levels are below 0.5 mg/l, while at certain other places, fluoride levels are as high as 35 mg/l [7,8].

Removal of fluoride was reported by adsorption [9], chemical treatment [10, 11] electrolytic de-fluoridation [12], and electro dialysis [13-15], membrane separation [16, 17], ion exchange [18] etc. Among various processes, adsorption was reported to be effective [19]. Different types of adsorbents reported such as activated carbon, minerals, fish bone charcoal, coconut shell carbon and rice husk carbon, with different degrees of success were reported by the researchers with fruitful results [9, 20–24]. Of late there is a lot of interest being shown on the application of biosorbent materials for removal of various pollutants. Biosorbent materials can passively bind large amounts of metal(s) or organic pollutants, a phenomenon commonly referred to as biosorption [25–32]. Biosorbents generate a keen interest because of naturally occurring biomass (es) or spent biomass (es) can be effectively utilized [25]. In addition, biosorption is useful because of cost efficiency, lesser utilisation of chemicals and the process of disposing the biological sludge is made easier. It also offers low cost operative solution for industrial wastewater management [33]. Literature survey shows reveals that only a limited number of studies were available on the treatment by BMC (fresh and marine water) in spite of their omnipresent distribution and their key role in the turnover and fixation of carbon [34-36]. In light of the above mentioned points, batch adsorption of studies was executed on the removal of fluoride from aqueous phases using BMC which is available in plenty. The adsorption studies carried out under various experimental conditions and the results obtained are presented in this paper. The sorption mechanism elucidation was also carried out by employing instrumental techniques, viz., X-ray photoelectron spectroscopy (XPS), Fourier transform infra red spectroscopy (FT-IR) and scanning electron microscope (SEM). The adsorbent BMC can be obtained from agriculture waste and requires no additional investment. Therefore usage of BMC is eco-friendly and cost effective.

MATERIALS AND METHODS

Chemicals: 2.21 g of sodium fluoride (AR grade) was dissolved in 1000 mL of distilled water for the preparation stock solution fluoride. The stock solution was then appropriately diluted to get the desired fluoride concentration.

Biosorbent: In this study an attempt is made to evaluate the adsorption capacity of the BMC from aqueous phase. 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. 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 h in an air oven. The product was finally dried and sieved to get various particle sizes [37].

Batch sorption experiments: Equilibrium studies have been made at room temperature (30 ± 1^{O}C) 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.

The effect of pH on the removal of fluoride was observed by adjusting the reaction mixture to different initial pH values from 4 to 10 (concentration, 5mg F L^{-1}); biomass, 3.0 g; temperature, 30 ◦C; agitation, 100 rpm; contact time, 40 min). Isothermal studies to determine the sorption capacity and intensity were carried out by adding various doses of sorbent (0.5–9.0 g at an increment of 0.5 g) and agitating the reaction mixture for the equilibrium time [temperature, 30 ◦C; agitation, 100 rpm; biosorbent mass, 3.0 g; concentration, 5mgF L^{-1} ; adsorption (contact) time, 40 min; pH 7.0]. Sorption kinetics were determined by analyzing uptake of the fluoride from aqueous solution at different time intervals of 10, 20, 30, 40, 50, 60, 90, 120, min.

Analysis: The residual fluoride concentration in the aqueous phase was analyzed colorimetrically using SPADNS method on a UV–vis spectrophotometer (Chemeto, model no:UV-2600) according to the procedures outlined in Standard methods of APHA [38]. FT-IR spectra of *BMC* were obtained by using a Thermo Nicolet Nexus 670 FT-IRS Spectrometer by KBr (0.1 g) keeping of dry biomass (0.1 g). X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Analytical (AXIS 165). For scanning electron microscope, biosorbent sample was washed with 0.9%. NaCl solution followed by phosphate buffer (pH 7.0) and subsequently the biomass was incubated in 3% glutaraldehyde (2 h). Incubated culture was serially treated with 10–90% alcohol for dehydration after transferred into absolute alcohol and subjected to SEM (Hitachi S-3000N) analysis.

RESULTS AND DISCUSSION

Characterization of the biosorbent

Physical characteristics: The physico chemical properties of activated carbons were studied. pH(7.84),Electrical conductivity(65), Lose of ignition(89.78), density(0.2779), pHzpc(7.50), decolourizing power(87mg/g) and surface area(9919.85Å)

Surface morphology: The scanning electron micrograph clearly revealed the surface texture and morphology of the biosorbent (Fig.1). It was subjected to 2000× maginification SEM images clearly show the surface morphological changes of the adsorbent materials before and after defluoridation.

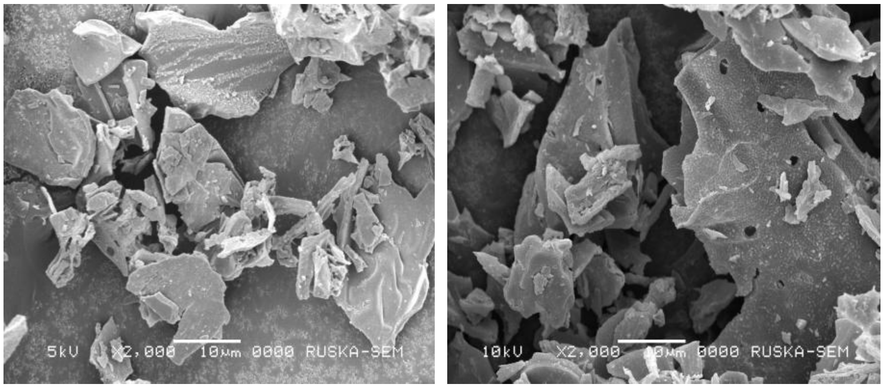

Figure 1. SEM image of BMC before and after defluoridation

Sorption kinetics: The two important physical and chemical aspects for parameter evaluation of the sorption process as a unit operation are kinetics and the equilibria of sorption. Kinetics of sorption, describes the solute uptake rate, which in turn governs the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption.

Helffrich model: In the present study, kinetics of fluoride removal was carried out to understand the behaviour of acid biosorbent as a low cost adsorbent material. Uptake of fluoride on to acid treated sorbent as a function of time. The removal of fluoride was very rapid initially and decreases markedly before equilibrium was reached. The rate constant (k) is determined using the following Helffrich model. The rate constant (k) can be determined using Helffrich equation

$$\ln (1-U(t)) = kt \qquad \text{-------(1)}$$

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

Ci, Ct, Ce are the concentrations (mg/L) of adsorbent samples initially, at any time 't', and at equilibrium respectively. The straight line plotted between ln (1-U (t)) and't indicates the applicability in aqueous system that follows reversible first order which is represented in figure 2. When a single species is considered on heterogeneous surface, the two important physico chemical aspects for parameter evaluation of the sorption process as a unit operation are kinetics and the equilibrium of the sorption. Also kinetics of sorption described the rate of solute uptake, which in turn gives the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption.

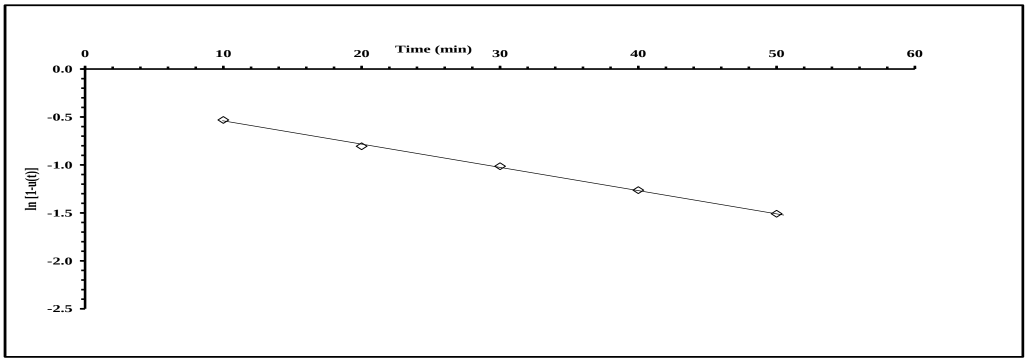

Figure 2: Calculations of Helffrich model for the removal of fluoride from fluoridated water

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 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 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.

$\log (qe-q) = \log qe - (k_{ad}. t) / 2.303$ --------2)

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.

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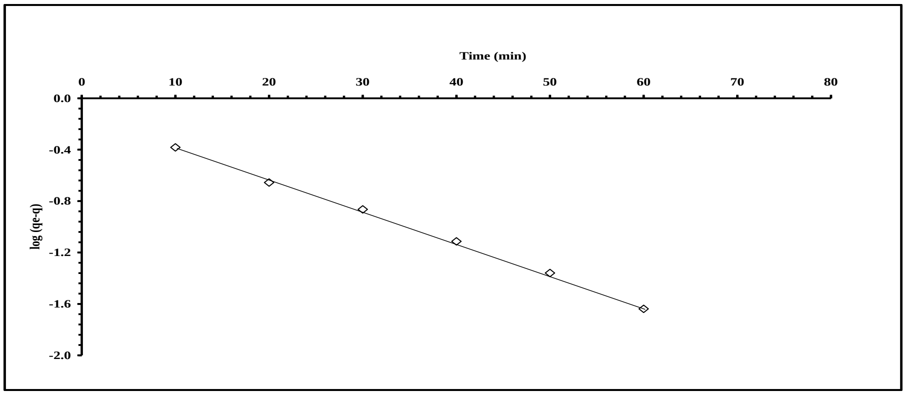

Figure 3: Calculations of Lagergren model for the removal of fluoride from fluoridated water

Intra-particle diffusion model: [39,40,41]: 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:

$$q_e = k_p t^{1/2} + C, \qquad \text{-----------------(3)}$$

where, q_e is the amount of fluoride adsorbed per unit mass of the adsorbent (in mg g^{-1}) at time t; k_p and c are respectively the Intra-particle diffusion rate constant (mg g^{-1}. 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 the adsorbent. This has resulted in linear relationship as evidenced by the r-value which indicates the existence of intraparticle diffusion process. The value of intra-particle diffusion rate constant (k_p) calculated for BMC and the value is 0.0836. The value of intercept (C) gives an idea of boundary layer thickness, i.e., the larger the intercept, the greater the boundary layer effect [42]. Intra-particle diffusion plot for the removal of fluoride by adsorption on the adsorbent is shown in figure 4. The highest percentage removal was observed at 3.0 g of biomass. The sorption kinetic data obtained from fluoride BMC system was studied with different kinetic models [43, 44] namely the intraparticle diffusion model [19, 44, 45,] Lagergren model, Helffrich model [44]. The sorption kinetic data were correlated with the linear forms of the three models, respectively.

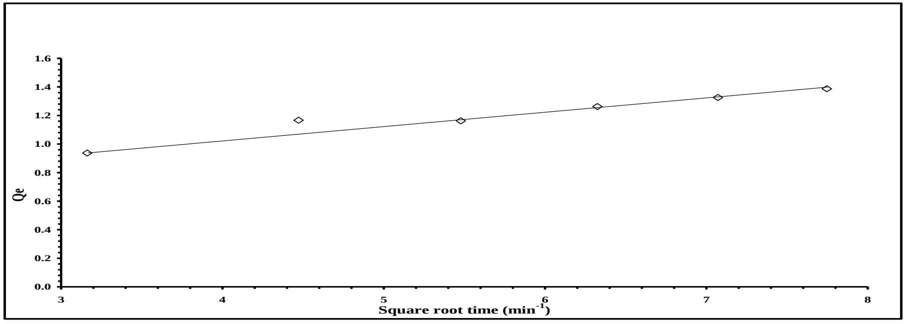

Figure 4: Intra-particle diffusion plot for the removal of fluoride by adsorption on the adsorbent

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.

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

$$q_e = K_f\, C^{1/n} \qquad \text{-----(4)}$$

The linearised Freundlich adsorption isotherm, is of the from

$$\log (q_e) = \log K_f + (1/n) \log C_e \qquad \text{------(5)}$$

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^{-1}) and C_e is the equilibrium concentration of fluoride (in mg L^{-1}) [49]. In the present adsorption study the 1/n value for BMC is 0.2979. 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 5 and table 1.

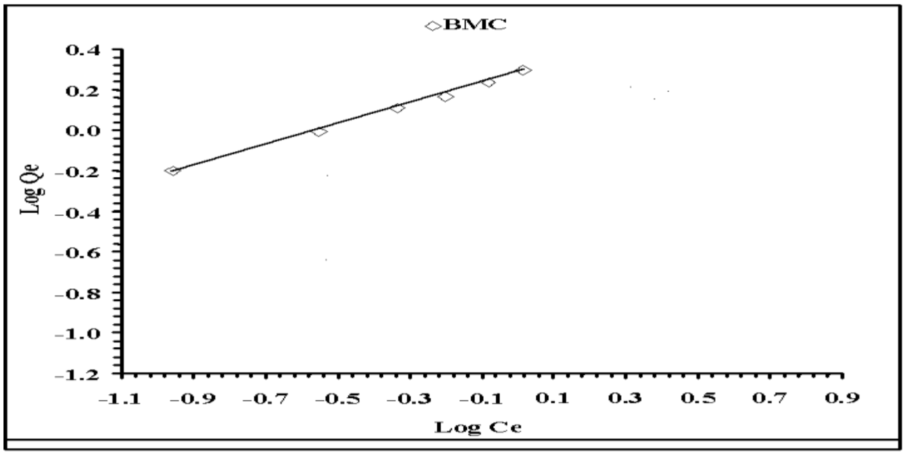

Figure 5: Calculation of Freundlich isotherm for the removal of fluoride, Ce = Equilibrium concentration of adsorbate in mg/L, Qe = Amount of fluoride ion adsorbed by the adsorbent (mg/g).

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;

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

where qe is the amount adsorbed (mg/g) and Ce, is the equilibrium concentration of adsorbate (mg L^{-1}), 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,

$$1/qe = (1/ a) + (1/ b\, a\, Ce) \qquad \text{--------------- (7)}$$

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 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.

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

$$R_L = 1/ (1 + b\, C_i) \qquad \text{--------------- (8)}$$

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 values of R_L for BMC is 0.4298. The value indicates that the sorption process is favourable for low cost adsorbent BMC than commercially activated carbon (CAC). From Table 1 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 1 gives the calculations of Langmuir model for the removal of fluoride and the various constants of this model.

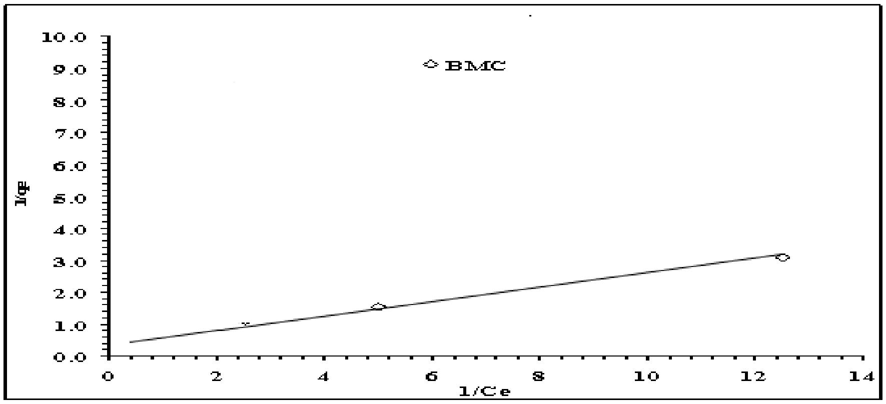

Figure 6: Calculation of Langmuir isotherm for the removal of fluoride, Ce = Equilibrium concentration of adsorbate in mg/L, Qe = Amount of fluoride adsorbed by the adsorbent (mg/g).

Table 1: Adsorption isotherm parameters of the chosen adsorbents

Isotherm Parameter	Symbol Constant	BMC	CAC
Freundlich isotherm	K_f	0.0345	0.6390
	1/n	0.2979	0.1620
	r	0.9972	0.9973
	R^2	0.9945	0.9946
Langmuir isotherm	a (mg/g)	0.0686	0.1105
	b (g/L)	0.2653	0.2350
	r	0.9998	0.9154
	R_L	0.4298	0.4597
	R^2	0.9935	0.9912

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 a dose of 3g L^{-1} and the particle size kept at 45µ the maximum efficiency of percentage of fluoride removal is 85.10 at 9 pH. The results are represented in Table 2. The percent removal increased from acid media to basic media but after pH level 7 the percent removal vary very little and is represented in figure 7. The results agree well with those reported by others Muthukumaran [52]Mariapan[53]Karthikeyan[54] Murugan [55] Kishore [40] and Prasad[41].

Table 2: Effect of adsorbate pH on the % removal of fluoride by adsorption with prepared carbon

pH	Ce		% Removal	
	BMC	CAC	BMC	CAC
4.00	1.52	3.60	69.60	28.00
5.00	1.25	3.30	75.00	34.00
6.00	0.97	3.16	80.60	36.80
7.00	0.78	3.09	84.40	38.20
8.00	0.75	3.01	85.00	39.80
9.00	0.74	2.99	85.10	40.10
10.00	0.73	2.98	85.10	40.10

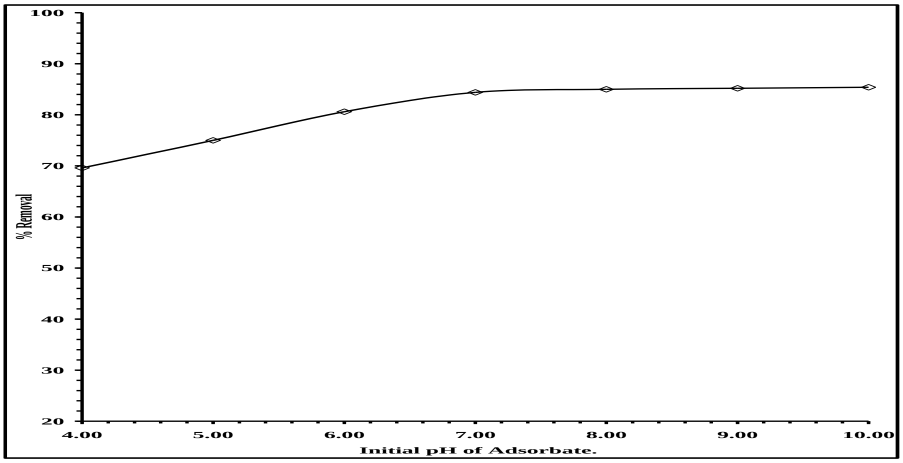

Figure 7. Plot showing the relationship between pH of initial fluoride and % removal by adsorbent

Sorption elucidation

FT-IR analysis: FT-IR spectra were obtained for the BMC before and after acid treatment and after fluoride adsorption were recorded. Interpretations of the spectra were based on the information acquired from literature [56-62]. Significant changes in the FT-IR spectra after the fluoride sorption were found at the wave numbers of 3855,2854,1383,1000,872,439 and 427cm^{-1}. Display of strong broad O–H stretch carboxylic bands in the region 3855 cm^{-1} and carboxylic/phenolic stretching bands in the region of 2854 cm^{-1} was observed. The band appeared in the region 1383 cm^{-1} might be attributed to C=O stretch. The band appearing in the region 1000 cm^{-1} indicated the presence of –C–F stretch group. FT-IR results indicated that mainly hydrogen atoms in the carboxylic groups were involved in fluoride ion sorption and are represented in figure 8.

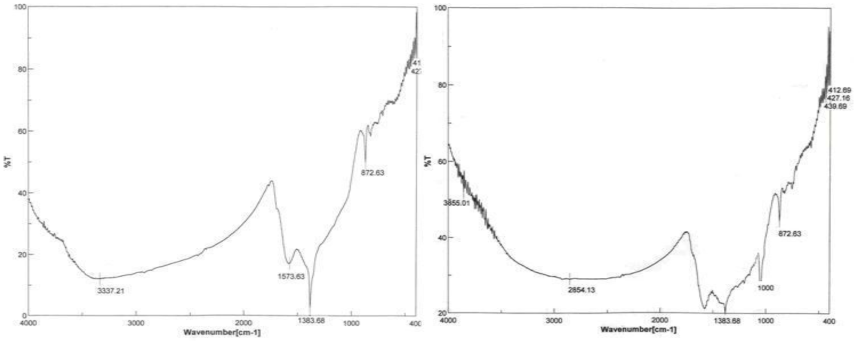

Figure 8: FT –IR image of activated carbon [BMC] before and after defluoridation

XPS analysis: Surface properties play an important role in numerous important technologies. X-ray photoelectron spectroscopy (XPS) is a widely used method for surface analysis of materials, due to its surface sensitivity and chemical specificity. From the XPS spectra, the elements present and their chemical state (valence) can be determined. Since only electrons emitted from atoms near the surface escape without losing energy, this technique is surface sensitive. Subtle changes in peak positions and shape can yield important information on changes in surface chemistry, giving XPS the ability to determine the elemental composition on the surface of materials. Analysis of the XPS data gave an idea about the local oxidation states and chemical bonding environment of the composing material. In virgin biosorbent the observed C 1s peak could be convoluted into three peaks. In XPS for BMC (284.6eV,285.6eV,287.5eV), (figure 9) which could be attributed to the presence of C–C/C–H, –O–C–O–, and carboxylic group (–O–C$=$O–) respectively [63]. XPS of BMC samples loaded with fluoride showed peaks in addition to the above peaks a peak at around 685- 686 eV which could be attributed to F 1s that is adsorption. After sorption with fluoride BMC the C 1s showed peak at 290.39 eV, (figure 10). This peak can be attributed due to the carbon on which fluoride is adsorbed. This peak is not observed in the virgin samples. F 1s spectra of BMC after deflouridation is shown in figure 11. The figure after deflouridation clearly indicates the adsorption of fluoride on the activated carbons.

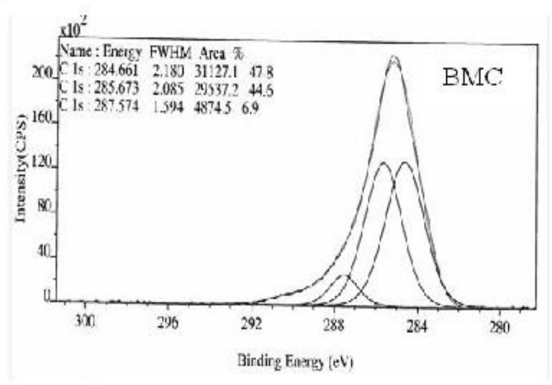

Figure 9: C 1s spectra of BMC before deflouridation

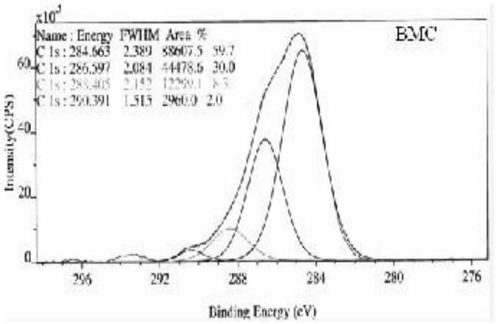

Figure 10: C 1s spectra of BMC after deflouridation

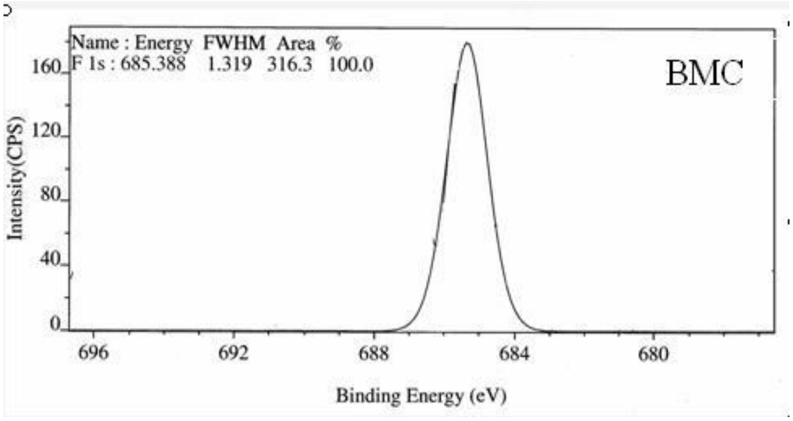

Figure 11: F 1s spectra of BMC after deflouridation

APPLICATIONS

Bore wells and Hand pumps water samples have been collected from Guntur District for investigation and chemical analysis. The defluoridation studies reveals that all samples having desirable limits of fluoride after defluoridation with indigenously prepared BMC carbon except when samples were treated with Commercial Activated Carbon(CAC).

CONCLUSIONS

In the present study, agricultural biomass based adsorbents were studied for removal of fluoride from aqueous solutions. It is found that BMC is effective in the removal fluoride from aqueous solutions. 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. With a view to understanding fluoride BMC mechanism, FT-IR spectral studies and X-ray photoelectron spectroscopy (XPS) analysis were done on virgin and fluoride loaded biosorbent.

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