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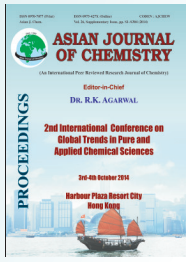

Adsorption of Fluoride Ion on Activated Carbon Prepared from *Delonix regia* Dry Fruits

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In this article, activated carbon prepared from *Delonix regia* dry fruits and applied to remove excessive fluoride from aqueous solution. The adsorption mechanism of F^- ions from aqueous media onto the surface of activated carbon with the help of different advanced technologies like X-ray diffraction, SEM-EDX, FT-IR and thermogravimetric analysis is studied. The chemistry of adsorbent surface was characterized by applying X-ray photoelectron spectroscopy.

Keywords: Activated carbon, Fluoride adsorption, *Delonix regia*.

INTRODUCTION

Fluoride has been one often called a two edged sword. In small doses it has a remarkable influence of the dental system by inhibiting dental caries, while in higher doses (> 1.5 mg/L) causes dental and skeletal fluorosis. Fluoride is more toxic than lead and just like lead, even in minute doses, accumulates in and is damaging to rain/mind development of children. Adsorptive removal with activated carbon prepared from agricultural waste material is considered as economical and simple process for the abatement of fluoride from water. The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbon production[1]. Amongst the adsorbent materials, activated carbons are unique and versatile adsorbents because of their large surface area, micro pore structure and varied adsorption effect high adsorption capacity and a high degree of surface reactivity. The carbon atoms located at the surface and edges of carbon crystallites act as active sites. These sites are activated by the treatment with acids, bases, metallic substances as activating agents in the adsorbent preparation[2].

Owing to various drawbacks associated with conventional defluoridation techniques adsorption-based fluoride removal systems are emerging as the feasible option. The objective of this study was to investigate the removal of fluoride (F^-) ion from potable water by the adsorption on activated carbon adsorbent prepared from *Delonix regia* dry fruits. *Delonix regia* is a species of flowering plant in the family fabaceae, subfamily Caesalpinioideae.

Previous studies on *Delonix regia* carbon strongly suggesting that it efficiency towards adsorption of various pollutants like dyes[3,4], metallic elements[5], gases and alkali $ZnCl_2$ activated delonix carbon in fluoride adsorption[6]. In the previous examinations authors concentrated on adsorption parameters and physical characterization of activated carbon and adsorption capacity may not exceeding 65-70 % from 5 mg/L. Hence in the present investigating study authors trying to increase the fluoride adsorption capacity by changing the carbon surface morphology by activation methods and exploring the mechanism of adsorption study with high sophisticated instruments.

EXPERIMENTAL

All reagents and chemicals used in the present investigation are AR grade purchased from Merck Co. Pvt. Ltd. India and all solution are prepared by using fluoride free double distilled water.

Adsorbent sample: Dry fruits of *Delonix regia* collected in bulk, cut into small pieces washed with double distilled water and carbonized at 800 °C in conventional muffle furnace. The raw carbon was crushed and sieved into on average 75 m particle sized. The investigations reported in this paper were conducted on sulphonated activated carbon prepared by 100 gm of carbon sample taken in 1 L round bottom flask fitted with a reflux condenser and flask filled with 0.5 M H_2SO_4 and boiled for 5 h. After refluxing the carbon sample filtered and washed thoroughly with hot double distilled water until they are free of acid content later Indigenously prepared carbon thus produced was thermally activated at 110 ºC for 1 h in an air oven.

Thermogravimetric analysis was carried out on Mettler Toledo 851e system with a heating rate of 10 °C/min. The

samples were analyzed in the temperature range 25 to1000 °C under nitrogen atmosphere with a flow rate of 30 mL/min. The adsorbents are examined using fourier transform infrared spectroscopy (FTIR). The sample discs were prepared by mixing of 1 mg of powdered carbon with 500 mg of KBr (Merck; for spectroscopy) in an agate mortar, then pressing the resulting mixture successively under a pressure of 5 tones/ cm^2 for about 5 min and at 10 tones/ cm^2 for 5 min, under vacuum. The spectra were measured from 4000 to 400 cm^{-1} on a JASCO-FTIR-5300 model. The prepared activated carbon samples were analyzed on KRATOS AXIS 165 under 10^{-9} torr vacuum with dual Al-Mg-anodes using MgK_α radiation. Pass energy of 80 eV was used in recording the spectra. X-ray excitation source Mg K (1253.06 eV) and hemi spherical electron analyzer. The samples were dried at 283 k for 24 h before the analysis. Survey and high resolution narrow scans were recorded for C 1s, O 1s and F 1s photoelectron peaks.

The surfaces of the powder carbonaceous materials have been stubbed using the double-sided adhesive carbon tape. Samples are coated with the help of platinum coater [JOEL Auto fine coater model, JFC-1600 auto fine coater, Coating time is 120 sec with 20 mA] and deposited with a thin layer of platinum on the sample. The microphotographs of these samples were recorded using SEM JEOL model, JSM-5600 equipped with EDX Analyzer, an accelerating voltage of 5 kV, at high vacuum mode. The XRD analysis on the prepared sample was made using a SCINTAG X'TRA AA85516 (Thermo ARL) X-ray diffractometer equipped with a Peltier cooled Si solid detector. Monochromatized Cu KR1 (0.150-54 nm) was used as the radiation. Diffraction patterns were collected at 45 kV-40 mA, at 0.02 °C step and count time of 0.400 sec over a range of 10.00-80.0 (2θ), at a step scan rate of 3 min^{-1}. BET-N_2 adsorption experiments were carried out manometrically using Quantachrome NovaWin-Data Acquisition and Reduction for NOVA instruments version 10.01. All samples were degassed overnight at 200 °C, prior to the adsorption experiments. The BET-N_2 surface area was obtained by applying the BET equation to the adsorption data. The pore volume of and pore size of the activated carbon's were determined by applying *t*-method.

Defluoridation method: 100 mL of standard fluoride solution (5 mg/L) was pipette out into a 500 mL beaker. To it, 1 g/L of the prepared active carbon was added and stirred at 200 rpm mechanically for 0.5 h. Then, solution was filtered through Whatman No- 42 filter paper. The F^- ion concentration in the sample after defluoridation was determined by SPADNS method[7].

Fluoride ion analysis: Fluoride ion concentrations were measured using UV-visible spectrophotometer by SPADNS method[7,8] and the percentage removal (% R) of F^- ion calculated using the following relationship:

$$\text{Removal (\%)} = \frac{(C_i - C_e)}{C_i} \times 100$$

where C_i and C_e are the initial and final concentrations (mg/L), the average values of duplicate runs were obtained and analyzed. Error in data was found to be: ± 1-2 % for percentage removal, ± 0.005-0.01 mg/g for amount adsorbed.

RESULTS AND DISCUSSION

Batch adsorption studies: Batch experiments were conducted to obtain the basic adsorption characteristics of the absorbents and during the investigation, the effects of contact time, initial adsorbate concentration and final solution pH was studied. Equilibrium studies have been made at room temperature (30 ± 1 °C).

The pH of the aqueous solution is an important controlling factor in the adsorption process. In order to obtain the optimum pH for the adsorption of F^- onto activated carbon of *Delonix regia* fruit the effects of pH were studied in range of pH 5 between 10. For adjusting pH, 0.1 N NaOH and 0.1 N HCl were used. The pH results showed that maximum fluoride removal had occurred in strongly basic medium and fluoride adsorption increases with decrease in pH. However, at neutral pH fluoride removal is considerably high, of the order of 78 %. In the alkaline range, the fluoride adsorption remains slow. Higher adsorption rate of fluoride in the basic range can be explained by the surface charge of the adsorbent.

In this analysis, initial F^- ion concentration was determined as 5 mg/L, a series of experiments has been performed to optimize the adsorption time (by varying the from 5 to 70 min) at initial concentration of 5 mg/L. The uptake capacity of F^- ion at equilibrium on activated carbon of *Delonix regia* fruit at optimum conditions with the capacity uptake of 80-90 %. The results showed that the contact time required to achieve equilibrium was about 0.5 h for adsorption. This may be due to higher surface area of activated carbon of *Delonix regia* fruit and results strongly indicate that the activated carbon used in this study is effective in removing of F^- ion.

The adsorption capacity carbon sample is systematically studied by varying the initial concentration of fluoride ions between 1 to 7 mg/L. The results showed that the amount adsorbed exponentially increases while the percentage removal exponentially decreases with the increase in initial concentration of the fluoride. All experiments were carried out at optimum conditions *viz*., 0.5 h contact time, dose 3 g/L particle diameter 75 (m) and results were given in Table-1.

Mechanism of adsorption: The removal of F^- ions by adsorption on carbon sample was found to be rapid at the initial period of contact time and then to become slow and stagnate with the increase in contact time. The mechanism for the removal of F^- ions by adsorption may be assumed to involve the following four steps. Migration of F^- ions from bulk of the solution to the surface of the adsorbent. Diffusion of F^- ions through the boundary layer to the surface of the adsorbent. Adsorption of F^- ions at an active site on the surface of activated carbon.

Surface characterization: The data obtained before and after defluoridation process with activated carbon prepared from *Delonix regia* dry fruits (DRC) presented in Table-2. The BET surface area found to be 268.306 m^2/g. It is more than some other active carbons reported in literature[12]. This feature is more important in assessing the effectiveness of adsorption process. Further, the reduction in surface area from 260.306 to 200.525 m^2/g, pore size from 17.174 to 16.859 Å, pore volume from 2.234 to 1.035 cc/g, indicated the loading of F^- ion onto the surface of activated carbon of *Delonix regia* fruit.

TABLE-1
EFFECT OF VARIOUS PARAMETERS ON ADSORPTION STUDY

Initial time (min)	Removal (%)	Initial concentrations (mg/L)	Removal (%)	Initial pH	Removal (%)
10	25.00	0.50	99.20	5.00	72.50
15	42.00	1.00	92.40	6.00	74.60
20	62.00	1.50	90.50	7.00	79.50
25	74.00	2.00	88.70	8.00	80.40
30	80.00	2.50	86.40	9.00	82.20
35	82.00	3.00	84.10	10.00	84.10
40	83.50	3.50	83.40		
45	84.00	4.00	81.70		
50	84.30	4.50	80.00		
55	84.00	5.00	79.80		
60	85.00	5.50	74.00		
65	85.20	6.00	72.40		
70	85.60	6.50	70.20		
		7.00	64.00		

TABLE-2
EDX ANALYSIS BEFORE AND AFTER TREATMENT

		wt %				At %			
	Element→	C K	O K	F K	Total	C K	O K	F K	Total
DRC	Before	82.4	17.6	0	100	82.3	17.7	0	100
	After	83.0	15.60	1.40	100	84.9	13.2	1.92	100

The examination of the SEM micrographs of the activated carbon particles showed rough areas of the surface at 1000 × magnification. EDX data was presented in Table-2. On comparing the spectrum of sample taken before and after adsorption process, a small peak pertains to fluoride could be noted with the sample after adsorption process and it was absent in the spectrum of the sample before adsorption. From the elemental analysis date presented in the Table-2, it could be noted that the oxygen element concentration was reduced after adsorption process but simultaneously fluoride concentration was increased. It might be attributed to the fact that fluoride ion would have replaced ion containing oxygen atom (OH^-) this assumption supported by effect of pH on adsorption studies.

Adsorption reactions may lead to changes in molecular and crystalline structure of 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 reaction. XRD patterns of activated carbon of *Delonix regia* fruit noted before and after adsorption process. It was evident from the spectrum that activated carbon of *Delonix regia* fruit loaded with F^- ions, exhibited variations in the crystal structure and this suggested that the fluoride ions might diffuse into micro pores and sorption was mostly by physical in nature, without altering the structure of the adsorbent. These observations corroborated well with batch sorption experiments.

Fourier transform infrared (FT-IR) spectroscopy provides evidence for the presence of specific functional groups on the surface of carbon materials. Several characteristics bands were observed in the FT-IR spectrum of activated carbon of *Delonix regia* fruit and each of the bands were assigned to specific functional group based on the previous assignments made in literature. Even though a cluster of functional groups were present on the carbon surface, the prominent among them were a sharp and intense band centered around 1660 cm^{-1} which was attributed to the carbonyl (C=O) stretching vibration of quinine[6]. Carbonyl functional groups were known to be pronounced in oxidized carbon materials rather than the original parent carbon material. In addition, a broad and intense band was observed in the range of 3200-3400 cm^{-1}, centered at 3437 cm^{-1} and it was attributable to the O-H stretching vibration of surface hydroxyl groups as well as to the adsorbed water. 1433 and 1330 cm^{-1} due to the in plane bending vibration of C-H of methylene group[9]; 1000-1300 cm^{-1} range peaks due to C-O stretching in phenols, alcohols, acids, ethers and esters[10]. The absence of specific peak pertains to C-F, suggested that the adsorption process was physisorption but not chemisorptions.

X-ray photoelectron (XP) spectra provides the relative frequencies of binding energies of electrons detected, measured in electron-volts (eV). XPS data are given in a plot of intensity *versus* binding energy. Intensity may be measured in counts per unit time (such as counts per second, denoted c/s). The high-resolution scans of XPS analysis were performed over the 280-294, 527-540 and 680-700 eV ranges (C1s, O1s and F1s spectra) for present samples before and after fluoride adsorption. XPS spectra of the C1s and O1s regions showed that the carbon-based surface oxide groups were present in the sample. The range of the main peak positions (BE) and the relative peak areas (r.p.a.) for separate peaks were estimated and presented in Table-2. Deconvolution of the C1s spectra was yielded three peaks with different binding energies representing graphitic carbon (284.65 eV), carbon present in structural hydroxy- and ether-like groups (285.96 eV), carboxyl or ester (anhydride) groups (288.36 eV). These assignments agreed well with the extensive XPS studies made on the commercially available carbons used as catalyst supports[11]. The O1s spectra for the carbon samples displayed two main peaks corresponding to the C=O (529.78 eV) and C-O (531.37 eV) moieties[11]. After the defluoridation of standard fluoride solution with activated carbon of *Delonix*

TABLE-3
TGA AND DTA ANALYSIS OF AC'S BEFORE AND AFTER DEFLUORIDATION

Parameter	TAC		Parameter	DTA	
	Before	After		Before	After
Stage 1 (°C)	72.3-252.34	55.22-310.21	Peak (°C)	440.42	444.41
Stage 2 (°C)	252.35-582.2	310.22-484.44	Onset (°C)	359.05	351.91
Stage 3 (°C)	582.2-1000	484.45-1000	Endset (°C)	507.36	514.46
Wt. loss (g)	3.131	2.762	Heat (J)	56.54	54.49
Wt. loss (%)	84.43	82.12	Heat (kJ/g)	15.25	16.2

regia fruit, the high-resolution narrow scan for F 1s was observed. The main peak at nearly 688.19 eV indicated the adsorption of fluoride on activated carbon. In the present investigation the peak in XPS spectra for fluoride was not observed before defluoridation with activated carbon of *Delonix regia* fruit. It was concluded from the obtained results that the sample was richer in carbon and oxygen than any other elements. Some F^- ions were found to be trapped at the surface of the activated carbon after defluoridation.

The thermal behaviour of chemically modified activated carbons was investigated by TGA and DTA. The Thermogram (TGA) consists of three stages (Table-3), *i.e*. the stage 1 72-250 °C for before treatment and 55-310 °C, the stage 2 ranging from 252 to 280 and 310-480 °C for before and after treated carbons, where a rapid degradation occurs and the stage 3 in the range from 580 to 1000 °C. Generally, it has been known for cellulose that the heat-treatment at lower temperature results in the depolymerization of the cellulose molecule, accompanied by the evolution of H_2O, CO_2, CO and charred residue.

It is expected that the increased oxygen content during oxidation results in higher weight loss during thermogravimetric analysis. In the present adsorption process (before and after) the weight loss up to 100 °C increased on oxidation indicating the thermo desorption of physically adsorbed materials such as water vapor, hydrocarbons and hydrocarbon in the case of residual oxidizing agents.

The oxidized carbon shows many DTA peaks demonstrating the successive loss and decomposition of various species with differing affinities at 440.4 for before 444.41 °C for after treated carbons these peaks may be resulting from the decomposition of carbonate ions.

Conclusion

The results of the experiments have shown that the percentage of fluoride removal has increased with the increase of contact time and pH. On the contrary, the percentage of removal has decreased with the increase in initial concentration of the standard fluoride solution.

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