

A comparative study on fluoride adsorption by Al (III) modified clinoptilolite and carbonised punica granatum carbon

Sudhanshu Kanaujia^{1*}, Sanjay K. Singh² and Bharat Singh³

¹Department of Chemistry, United College of Engineering and Research, Naini, Allahabad, 211002, U.P., India

²Department of Chemistry, Institute of Engineering and Technology, Lucknow, 211006, U.P., India

³Department of Chemistry, University of Allahabad, 211002, U.P., India

*Corresponding author

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ABSTRACT

A comparative study was done for removal of fluoride by Al (III) modified Clinoptilolite (AC) and Carbonised Punica Granatum Carbon (CPGC) through batch techniques. The fluoride removal performance of both adsorbents AC and CPGC was evaluated as a function of the initial concentration, adsorbent dose, contact time and pH. The equilibrium was attained at 90 and 75 minutes for AC and CPGC adsorbents, but percentage of removal was 76 and 65 for AC and CPGC respectively. The maximum adsorption of fluoride was found at pH 6.95 and 5.92 for AC and CPGC adsorbent respectively. The system followed the Freundlich isotherm model for both AC and CPGC with adsorption capacity 0.24 mg/g and 0.4 mg/g respectively. Copyright © 2018 VBRI Press.

Keywords: Fluoride removal, adsorption, clinoptilolite, carbonised punica granatum carbon, freundlich isotherm.

Introduction

Fluorine is the most highly reactive element of halogen family. Small amounts of it are found in seawater, bone, teeth and in ground water mainly as fluoride ion. Most fluoride associated with monovalent cations such as NaF and KF is water soluble, while the one formed with divalent cations such as CaF₂ and PbF₂ is generally insoluble.[1]

Fluoride has gained importance due to its dual influences on human beings. In lower concentrations, Fluoride is an essential nutrient which aids in the formation of bones, prevents tooth decay, etc whereas in higher concentrations it causes fluorosis, brittling of bones, curvature of bones, dwarfishness, mental derangements, cancer, etc. and in extreme cases even death.[2]

According to WHO standards, the Fluoride in drinking water should be within a range that slightly varies above and below 1 mg/L[3] In temperate regions, where water intake is low, Fluoride level up to 1.5 mg/L is acceptable. The Bureau of Indian Standards, BIS (IS-10500) [4], has prescribed a desirable limit and permissible limit of Fluoride in drinking water as 1.0 and 1.5 mg/l respectively.

Adsorption is one of the most efficient technologies for fluoride removal from drinking water when compared with other technologies such as reverse osmosis[5], nanofiltration [6], electro-dialysis[7-8] and Donnan

dialysis [9]. Many natural and low cost materials such as nirmali seeds [10], adsorption by powdered and granular red mud [11-12], zirconium impregnated coconut shell carbon[13] and clays[14] have been used as adsorbents for fluoride removal from water. Studies on various sources of activated carbon have been done by many researchers[15]. Activated carbons and modified activated carbon are potential adsorbents because of their strong affinity for fluoride[13].

The rare earth metals are usually expensive, which restricts their use in the treatment of drinking water. Because of the high electro-negativity and small ionic size of the fluoride ion, it has a strong affinity towards multivalent metal ions including Al(III), Fe(III) and Zr (IV)[16].

In the rural areas of developing countries, challenges such as access to real low-cost adsorbents, simpler processes for development of efficient adsorbent at local levels and high fluoride removal efficiency on real groundwater conditions such as the existence of neutral pH are still prevailing. These challenges have to be solved for developing efficient fluoride removal technology for rural areas.

The present paper deals with the preparation of Aluminium modified Clinoptilolite (AC) and Carbonised Punica Granatum Carbon (CPGC) and its application along with comparison for removal of fluoride from ground water.

Experimental

Materials synthesis

Aluminium (III) modified Clinoptilolite (AC)

The zeolite used in this investigation was a natural Clinoptilolite (CLI) obtained from Miyaneh region. The CLI sample was crushed up and sieved to the particle size fraction 10–20 micron. CLI sample was washed out several times with tap water and saturated in deionized water for dissolution of salts. Sample was dried in an oven at 523 K to remove any organic materials [18]. For saturation of zeolite, CLI sample was shaken in 2M NaCl solution by stirring at room temperature to saturate the exchange sites with sodium ions. Sodium saturated CLI samples were dried in air. For preparation of Al(III) modified Clinoptilolite, 50 gm CLI was transferred into 1 liter of 0.075M Al(OH)₃ solution. The mixture was intermittently agitated for 50 hours at 150 rpm shaker and washed several times using demineralised water. Finally, the Al (III) modified Clinoptilolite (AC) was dried in air.

Carbonised Punica Granatum Carbon (CPGC)

The *Punica granatum* seed (powdered sample), common name, Pomegranate, was purchased from market. Then the material was dried at 378 - 383 K for 24 hours. It was washed with doubly distilled water to remove the free acid and dried at the same temperature for 3 hours. Later, the dried adsorbent was carbonised thermally in Muffle furnace between 1073 K to 1084 K temperature ranges. The resulting product was cooled to room temperature and sieved to the desired particle sizes, namely, <55, 55 - 106, 106 - 150, 150 - 225 and 225 - 305 micron. Finally, the product was stored in vacuum desiccators until required for treatment [17].

Batch adsorption study

The batch adsorption de-fluoridation study was conducted for the optimization of various experimental conditions like contact time, initial fluoride concentration, adsorbent dose, particle size and influence of co-ions with fixed dosage. A fluoride ion stock solution (100 mg/l) was prepared by dissolving 0.221 gm anhydrous sodium fluoride and other fluoride test solutions were prepared by subsequent dilution of the stock solution. Analytical grade sodium chloride, sodium nitrate, sodium sulphate and sodium phosphate were used to prepare 1M stock solutions, and mixed at an arbitrary volume ratio to adjust the concentration of the coexisting anions in the solution.

All the experiments were carried out at room temperature. Fluoride ion concentration was measured with a specific ion selective electrode by use of total ionic strength adjustment buffer II (TISAB II) solution to maintain pH 5 - 5.5 and to eliminate the interference effect of complexing ions [19]. The pH of samples was measured by Orion ion selective equipment. All other water quality parameters were analyzed by using standard methods [20]. Effect of different initial fluoride concentrations were studied by keeping the mass of

adsorbent fixed and volume of solution at 100 ml in neutral pH.

The fluoride concentration retained in the adsorbent phase, q_e (mg/g), is calculated by following equation.

$$q_e = \frac{(C_0 - C_e) V}{W}$$

where q_e is the amount of fluoride adsorbed (mg/g); V is the volume of solution; c_o and c_e are the initial and residual concentration at equilibrium (mg/l), respectively, of fluoride and w is the weight (g) of the adsorbent.

Results and discussion

Effect of pH

The effect of pH on the adsorption of fluoride by using AC and CPGC (pH range 4.0–9.0) is shown in the **Fig. 1**. The results show that adsorption was maximum for AC and CPGC at pH 6.95 and 5.92 respectively. The fluoride removal decreases beyond this pH. The quick reduction of the amount of fluoride adsorbed in alkaline pH range should be attributed to competitive adsorption between hydroxyl ions and fluoride ions on active sites of AC.

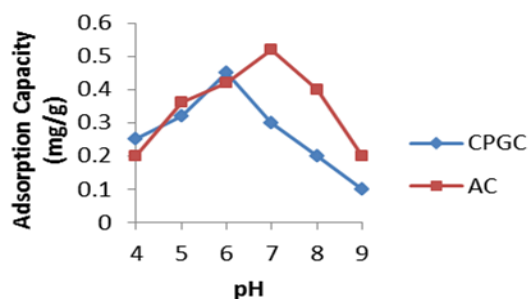


Fig. 1. Effect of pH on fluoride removal by AC and CPGC.

Effect of contact time

The sorption of fluoride ion on CPGC and AC has been investigated as a function of contact time in the range of 15–120 min. at room temperature. **Fig. 2** illustrates the percentage removal of fluoride by two considered adsorbents at different contact times. It has been observed that as contact time was increased, the percentage removal also increased. However, it gradually approached an almost constant value, denoting attainment of equilibrium. In the current case, the equilibrium times were obtained at 90 and 75 min for AC and CPGC respectively.

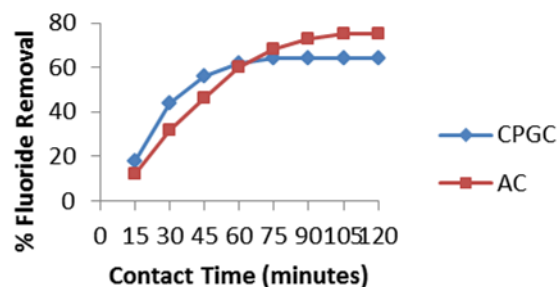


Fig. 2. Effect of contact time by AC and CPGC on fluoride removal.

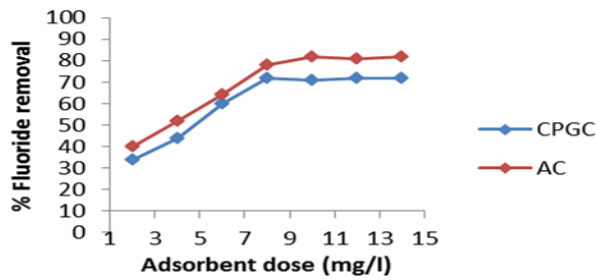


Fig. 3. Effect of adsorbent dose on fluoride removal.

Effect of adsorbent dose

An effect of adsorbent dosage on adsorption of fluoride at pH 6 and contact time of 75 min for CPGC and AC adsorbents were studied. The results are presented as fluoride removal efficiency versus function of adsorbent dosage in Fig. 3. The fluoride adsorption increased exponentially with the increasing the amount of each adsorbent due to increasing the number of active sites. It has been observed that up to certain level of higher doses of adsorbents resulted higher removal of fluoride. This might be because of higher availability of surface area and pore volume at higher doses.

Effect of initial fluoride concentration

The effect of varying the initial fluoride concentration on process of adsorption for AC and CPGC was studied and is shown in Fig 4.

It can be seen that in both the case the percentage of removal of fluoride increased with decreasing initial fluoride concentration. From Table 1, the maximum removal of fluoride was found to be 76% and 65% with an initial concentration of 5 mg/L for Al (III) Clinoptilolite and Carbonised Punica Granatum Carbon respectively.

Table 1. Effect of initial concentration (mg/L) on the adsorption of fluoride by AC and CPGC.

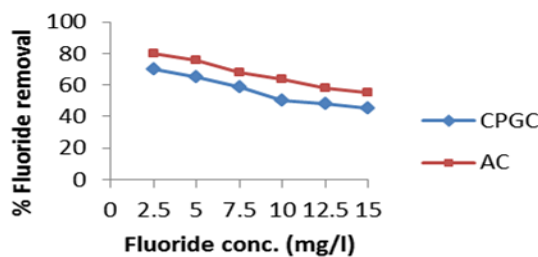


Fig. 4. Effect of initial fluoride concentration on fluoride removal of AC and CPGC.

AC		CPGC	
Initial Concentration (mg/L)	% Fluoride Removal	Initial Concentration (mg/L)	% Fluoride Removal
2.5	80	2.5	70
5.0	76	5.0	65
7.5	68	7.5	59
10.0	64	10.0	50
12.5	58	12.5	48
15.0	55	15.0	45

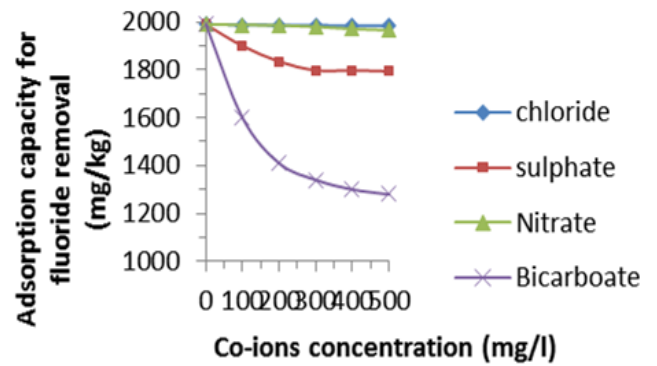


Fig. 5. Variation in adsorption capacity for different coexisting ions.

Effect of coexisting ions

The effects of coexisting ions such as sulphate, nitrate, chloride and bicarbonate on fluoride adsorption by AC and CPGC adsorbent were examined and the results are given in Fig. 5. With CPGC adsorbent chloride and nitrate ions did not noticeably interfere with fluoride removal even at a concentration of 500 mg/L, while sulphate ions began to show some adverse effects when the SO₄²⁻ concentration increased. However, bicarbonate showed great competitive adsorption with fluoride.

It is found that the percentage of fluoride removal is almost unchanged when the coexisting ion concentration is below 300 mg/L, and then decreases dramatically when the coexisting ion concentration is over 500 mg/L for Al (III) Clinoptilolite.

Adsorption isotherms

The distribution of fluoride between the liquid and solid phases can be expressed by the Langmuir and Freundlich equations in the adsorption process. The expression of the Langmuir model is given below:

$$\frac{1}{q_e} = \frac{1}{q_0 b} \times \frac{1}{c_e} + \frac{1}{q_0}$$

where c_e is the equilibrium concentration (mg/L), q_e is the adsorption capacity (mg/g), q₀ is the theoretical maximum adsorption capacity, and b (L/mg) is a Langmuir constant related to the enthalpy of adsorption. q₀ and b are determined from the slope and intercept of the plot, respectively.

The Freundlich isotherm model is expressed as follows:

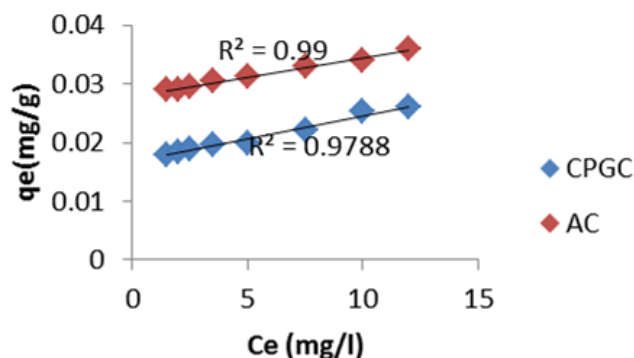
$$\log q_e = \log K_f + \frac{1}{n} \log c_e$$

where K_f and 1/n are empirical constants, indicative of the adsorption capacity and adsorption intensity respectively. The above equation is linearised and a plot of log q_e versus log C_e will give a straight line of slope 1/n and intercept K_f.

Table 2. Isotherm parameters of various adsorbents.

Isotherm Models	Adsorbents	
	AC	CPGC
Langmuir		
q_0	0.4	0.24
q_e (mg/g)	2.32	2.35
b (L/g)	1.13	5.3
R^2	0.954	0.91
Freundlich		
$1/n$	0.454	0.463
K_f	13.91	14.02
R^2	0.978	0.99

Parameters of the Langmuir and Freundlich isotherms fitting for fluoride adsorption data are listed in **Table 2**. It can be found from **Fig. 6** that the linear equation of Freundlich model shows higher correlation for AC ($R^2=0.99$) than CPGC ($R^2=0.978$). Therefore, Freundlich model is selected as the best-fit model for adsorption of fluoride on AC as well as CPGC in comparison to Langmuir model.

**Fig. 6.** Comparison of Freundlich isotherm for fluoride adsorption on AC and CPGC.

Conclusion

In this study the ability of Al (III) Clinoptilolite and Carbonised Punica Granatum Carbon was investigated for removal of fluoride from aqueous solution. The operational parameters such as pH, initial fluoride concentration, adsorbent dose and contact time were found to have an effect on the adsorption efficiency of AC and CPGC. The maximum adsorption of fluoride was found at pH 6.95 and 5.92 for AC and CPGC adsorbent respectively. According to Langmuir model the maximum adsorption capacity was found in case of AC and CPGC were 0.4 mg/g and 0.24 mg/g respectively. The equilibrium was attained at 90 and 75 minutes for AC and CPGC adsorbents, but percentage of removal was 76 and 65 for AC and CPGC respectively. The study on equilibrium sorption revealed that Freundlich isotherm model give best fit to experimental data. Therefore, the present study showed that both AC and CPGC could

be used as an adsorbent for fluoride removal but AC showed little better performance over CPGC.

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