IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399.Volume 12, Issue 4 Ver. II (April. 2018), PP 43-48
www.iosrjournals.org

Removal of Fluoride from Synthetic Water Using Chitosan as an Adsorbent

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Abstract: *Adsorption is the technique used for removal of pollutants from water. Treatment for removal of fluoride from synthetic water is studied by adsorption process. In this present work, biopolymer Chitosan in its powder and solution form has been employed as a technically economical and viable medium for removal of fluoride. The effects of various physico-chemical parameters like contact time, solute concentration, mixing speed, adsorbent dose are studied. The fluoride concentration decreased with the increasing adsorbent doses, contact time and mixing speed. The optimal condition for removal of fluoride was found to be of 2.5 g of Chitosan in powder form at 60 rpm mixing speed. Of different dosages of Chitosan in solution form, 15 ml of 0.1 g Chitosan solution proved to be the optimum dosage which was found to be exceptionally good in achieving an efficiency of 65-70%. Chitosan as powder and solution form proved to be very effective in the removal of fluoride from synthetic water. The experimental data of adsorption fit well with Freundlich adsorption isotherm for fluoride removal using Chitosan as an adsorbent.*

Keywords - *Fluoride removal, Synthetic water, Chitosan, Adsorption.*

Date of Submission: 21-04-2018 Date of acceptance: 08-05-2018

I. Introduction

Fluoride is a chemical that occurs naturally within many types of rock. The fluoride rich minerals in the rocks and soils are the cause of high fluoride content in groundwater. Rural drinking water supply is mainly dependent on groundwater. Excess fluoride in drinking water is prevalent in 150 districts of 17 states of the country. The drinking water sources have been reported with fluoride concentration within permissible limits is beneficial for the production and maintenance of healthy bones and teeth while excessive intake of fluoride causes dental and skeletal fluorosis. WHO permissible limit for fluoride in drinking water is 1.5 mg/L (Jagtap et.al, 2011). Runoff and infiltration of chemical fertilizers in agricultural areas, septic and sewage treatment system discharges in communities with fluoridated water supplies, liquid waste from industrial sources also constitutes for fluoride sources.

Adsorption in general is the process of accumulating soluble substances that are in solution on a suitable interface. Adsorption is one of the most widely used treatment technique for the removal of pollutants from water and wastewater. Adsorption on natural polymers and their derivatives are known to remove pollutants from water.

Chitosan is a linear polycationic polymer, biodegradable and non- toxic extract from shellfish shells used in a variety of water purification applications. This biopolymer has drawn attention as a complexing agent due to its low cost as compared to activated carbon and its high content of amino and hydroxyl functional groups showing high potentials for a wide range of molecules, including phenolic compounds, dyes and metal ions (Crini, 2005).

II. Materials And Methodology

2.1 Materials

Chitosan, in the flake form was procured from Kerala. The cost of Chitosan is around Rs 750/kg. Synthetic water was also used for the experiments prepared by adding sodium fluoride to 1L of tap water to get the required concentration of fluoride (6 mg/L). The sample is taken in a 500 ml beaker and a thorough mixing is done using jar test apparatus. After treatment, the treated samples are analyzed for Fluoride (UV spectrometer), SPADNS method.

2.2 Adsorption Batch Studies

Adsorption studies were carried out in batch process in Jar test apparatus with a stirrer for agitation. The Chitosan flakes procured were used to treat the synthetic water sample. Chitosan in its powder and solution form were used as an adsorbent for removal of fluoride. The Chitosan powder was added in the dosages of 1.5 g, 2 g, 2.5 g and 3 g to 250 ml of the synthetic water sample. Chitosan was also used in the solution form. 3% acetic acid was prepared by diluting 3 ml of 0.1 N acetic acid to 100 ml using distilled water. The Chitosan flakes were then dissolved in the 100 ml acetic acid solution in dosages of 0.01 g, 0.05 g and 0.1 g. The resulting solution called the Chitosan solution was added in volumes of 10 ml and 15 ml, to treat every 250 ml of synthetic water sample. The jar test apparatus with a stirrer was made to run at speed of 60 rpm for agitation and the samples were drawn at every 5 minutes of contact time. A number of parameters such as reaction time, adsorbent dosages as a powder and solution form were varied in order to optimize the removal process.

III. 3. Results And Discussions

3.1 Treatability studies using Chitosan in Powder form and in Solution form

Physicochemical parameters such as adsorbent dosage, agitation rate and contact time on fluoride removal studied in the batch reactor are tabulated in the Table 3.1 and Table 3.2

Table 3.1: Experimental results using Chitosan powder

Parameter Mixing speed 60 rpm (Synthetic water)	Dosage in powder form (g)	Time (min)				% Removal
		0	5	15	30	
Fluoride (mg/L)	1.5	6	4.97	3.29	2.14	56.94
	2	6	4.90	3.17	1.97	59.95
	2.5	6	3.92	2.27	1.12	71.17

Table 3.2: Experimental results using Chitosan solution

Parameter Mixing Speed 60 rpm Synthetic water	Dosage in solution form	Time (min)				% Removal
		0	5	15	30	
Fluoride (mg/L)	0.01 g					
	10 ml	6	4.76	4.23	3.65	39.16
	15 ml	6	4.24	3.97	3.04	49.33
	0.05 g					
	10 ml	6	4.08	3.42	2.56	57.33
	15 ml	6	4.02	3.11	2.17	63.38
	0.1 g					
	10 ml	6	4.12	3.09	2.03	66.16
	15 ml	6	4.01	2.97	1.8	70

3.2 Effect of Agitation Rate

Effect of agitation rate on % removal of fluoride onto Chitosan powder and solution form was studied over an agitation speed of 30, 45 and 60rpm, the removal efficiency increases with increase rotation speed. Hence, the agitation speed of 60 rpm was maintained throughout the study. Increase of the agitation speed enhances the turbulence and decrease of thickness of the liquid boundary layer.

3.3 Effect of Adsorbent dosage with Contact Time

In order to optimize the adsorbent dose a series of experiments were conducted by varying the adsorbent dosages. The removal of fluoride increased with increase in adsorbent dose due to availability of greater amount of active sites of adsorbent. Figure 3.1 shows the plot for removal of fluoride versus time for Chitosan in powder form. It was observed that fluoride removal was rapid during first 15 minutes and then onwards it was gradual. This can be attributed to the availability of more vacant sites within the sorbent and high concentration gradient between the solution and the solid phase. Figure 3.2 shows the plot for removal of fluoride versus time for both Chitosan in its powder and solution form. It can be observed that maximum removal efficiency was achieved at 2.5 g of Chitosan dosage (powder form) from initial concentration fluoride of 6 mg/L was reduced to 1.12 mg/L. With 15 ml of 0.1 g of Chitosan dosage (solution form), the initial concentration of fluoride of 6 mg/L was reduced to 1.8 mg/L.

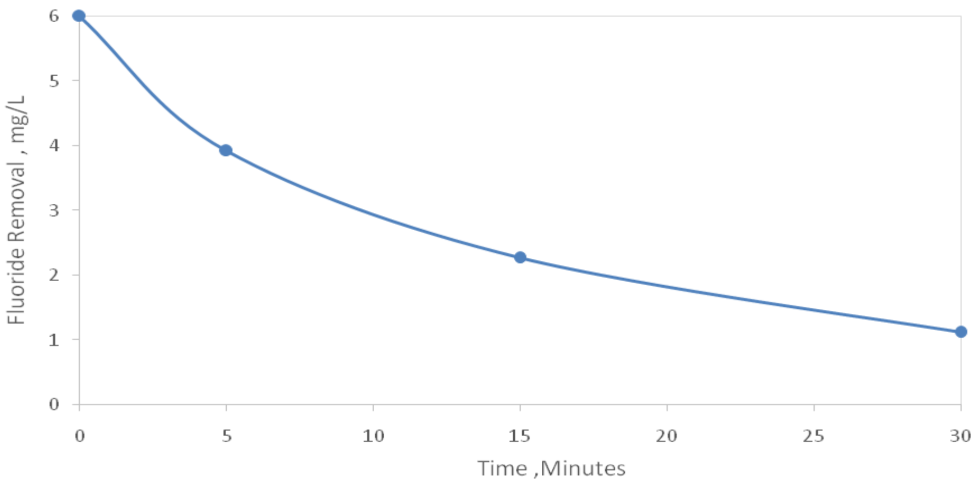

Fig. 3.1: Fluoride Removal with Contact Time

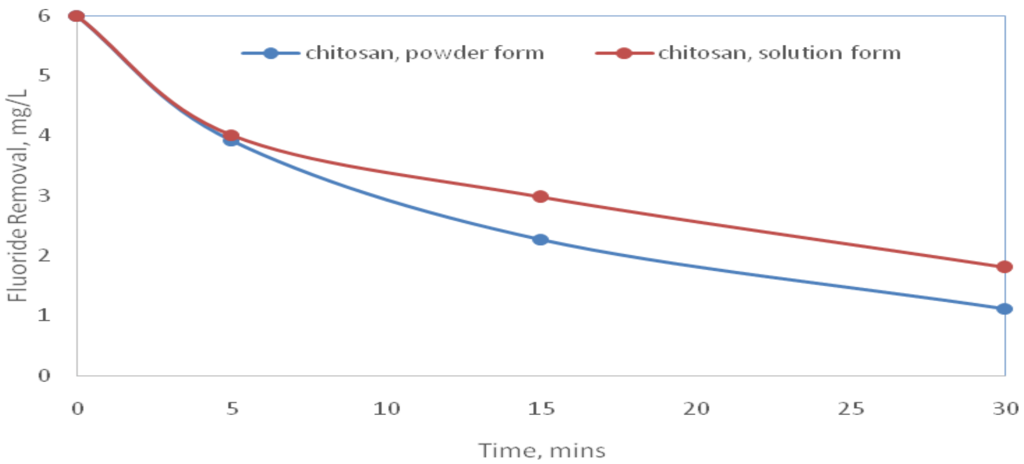

Fig. 3.2: Chitosan used as both powder and solution form for fluoride removal

3.3 Experiments at optimized conditions using Chitosan powder and solution form

Based on experiments carried out, the optimized condition for fluoride removal from initial concentration of 6 mg/L at 60 rpm agitation speed using Chitosan dosage (powder form)of 2.5 g. It was found that the fluoride removal efficiency was 71.17 %. During the contact period, the Chitosan powder was thoroughly mixed with the water to achieve intimate contact and thus yielded better removal efficiencies. According to the results obtained, the optimized conditions for Chitosan as solution form, for fluoride removal, from initial concentration of 6 mg/L at 60 rpm rotation speed were carried out and fluoride removal efficiency of 66-70% .

3.4 Comparison of Powder and Solution form of Chitosan

Table 3.1 and Table 3.2 shows the efficiency of fluoride removal from synthetic water sample using Chitosan powder and solution form. By comparing the results obtained for powder and solution form, it is clear that at initial fluoride concentration, powder form yield better results than solution form. Chitosan in the bead form has been chemically modified by simple protonation and employed as a most promising defluoridating medium. Protonated Chitosan beads (PCB) showed a maximum defluoridation capacity (DC) of 1664mgF^-/kg whereas raw Chitosan beads (CB) possess only 52mg F^-/kg. (Viswanathan. N et.al, 2009).Research work were carried out for removal of fluoride from water using lanthanum impregnated Chitosan as an adsorbent. The optimal condition for synthesis of LCF includes 20w%, stirring time 6h, temperature 75°C for 2 h with maximum adsorption capacity of 1.27 mg/g (Jagtap et.al, 2011).

3.5 Characterization of the Adsorbent

The scanning electron microscope (SEM) analysis was used to examine the structure of the sorbent which indicates different crystallinity and surface morphology. Figure 3.3 shows the SEM image of Chitosan before and after adsorption process to compare their surface texture. The surface of the Chitosan is uniform with Nano-sized crystals before the process. It can be seen from the figure that the surface of the adsorbent is found to be rough with a number of pores in it after adsorption process. These pores provide suitable binding sites for fluoride ions. From these figures, particle size of the adsorbent can also be found out which range between 5-13 µm. Apart from modified surface area of adsorbent small particles of the precipitate adhering on the surface was also seen.

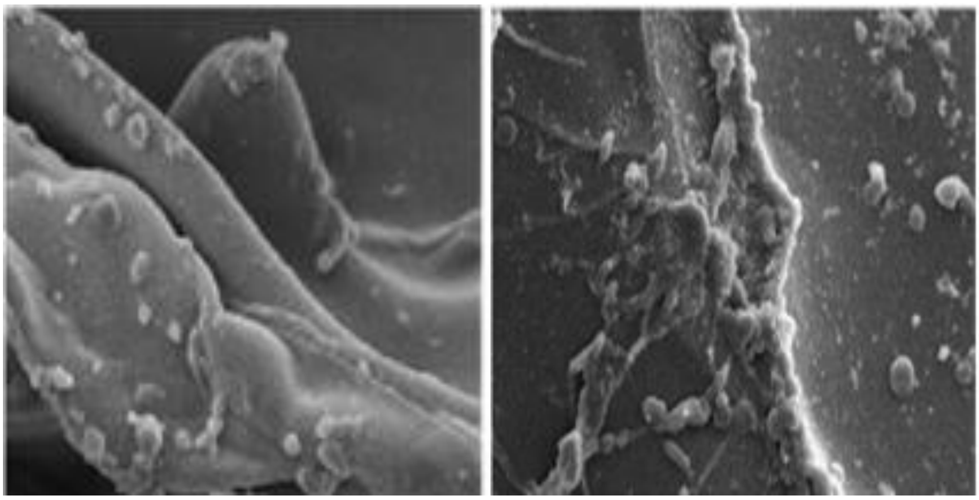

Fig. 3.3: Scanning Electron Micrograph of Chitosan flake before and after treatment (Magnification 600)

3.6 Adsorption Kinetics

The isotherm data is important for predicting the adsorption capacity of the sorbent, one of the main parameters required for design of an adsorption system. In the present study, equilibrium data of adsorption of fluoride from synthetic water using Chitosan as adsorbent in the form of powder has been used for adsorption kinetics. Isotherms from solution may exhibit non-ideality, not only because of lateral interactions between adsorbed molecules but also because of non-ideality in the solution (Castilla, 2004). The linearized form of Langmuir and Freundlich isotherm are studied. Figure 3.4, 3.5 and 3.6 indicate fluoride adsorption using Chitosan as adsorbent in its powder form. The amount of adsorbent taken up per gram of adsorbent, $\ln q_e$ (mg/g), to the equilibrium solution concentration, $\ln c_e$ (mg/L) at different concentration of fluorides are plotted. Accordingly, Freundlich constants (K_F and n) were calculated and recorded in Table 3.3.

With equilibrium data obtained for both Chitosan used as powder and solution form the isotherm models were studied. The high contents of amino and hydroxyl functional groups of Chitosan shows significant adsorption potential for the removal of various aquatic pollutants was efficient by adsorption process (Bhatnagar et al, 2011). The isotherm parameters for adsorption of fluoride from synthetic water by Chitosan in powder form matched well with Freundlich isotherm and are tabulated in table 3.3 and 3.4. Langmuir and Freundlich isotherm adsorption models were studied for defluoridation from synthetic water by using pure Chitosan and 20% Zr (IV) doped in Chitosan skeleton. Experimental defluoridation data fits Freundlich model with efficiency K_f =3.27 mg/g and adsorption coefficient of n = 0.939. 20% zirconium (IV) doped chitosan proved to be a better adsorbent for defluoridation of water with adsorption capacity about 90% (Dongre et.al, 2012).

q_e and q_t are the amounts of MB adsorbed (mg/g) at equilibrium and at time t (min) respectively, k_1 - Rate constant adsorption (h^{-1}), k_2 (g/mg min) - rates constant of second-order adsorption. The linear plots of t/q versus t gives the value of k_2.Figure 3.5 shows pseudo- first order kinetics for the adsorption of fluoride from synthetic water sample. The values of k_1 and q_e are presented in Table 3.4. Figure 3.6 shows pseudo- second order kinetics for the adsorption of total hardness from synthetic water sample. The values of k_2 and q_e for both pseudo first order and second order are tabulated in Table 3.4.

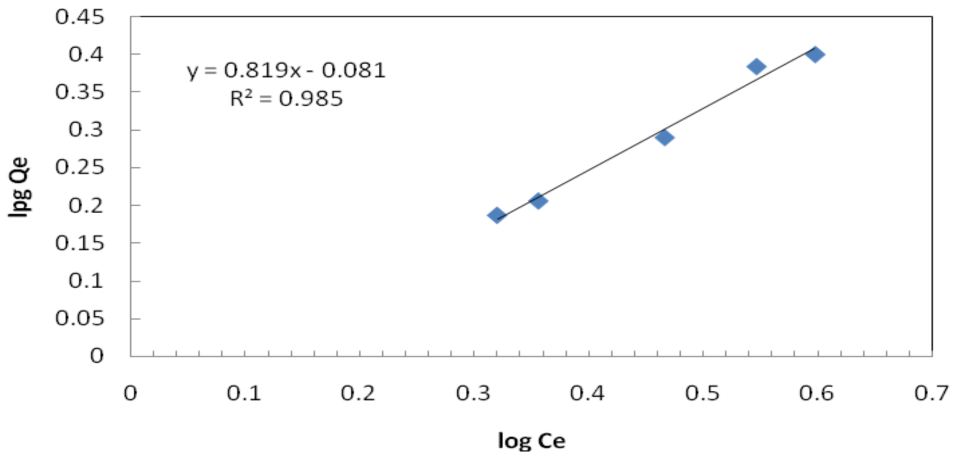

Fig. 3.4: Freundlich isotherm of the adsorption of fluoride from synthetic water on to Chitosan powder

Table 3.3: Freundlich Isotherm parameters for adsorption of fluoride from synthetic and groundwater samples by Chitosan powder

Parameters (mg/L)	Parameters	Values
Fluoride	K_F [(mg/g)(1/mg)$^{1/n}$]	1.205
	1/n	0.819
	R^2	0.985

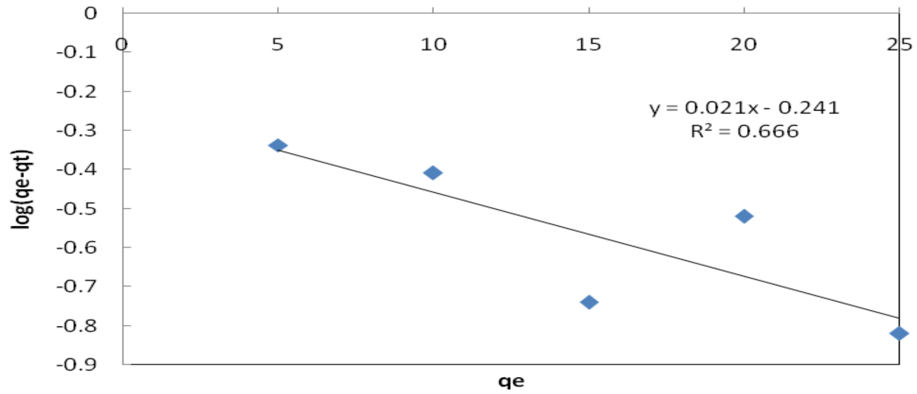

Fig. 3.5: Pseudo – first order kinetics for adsorption of fluoride on Chitosan

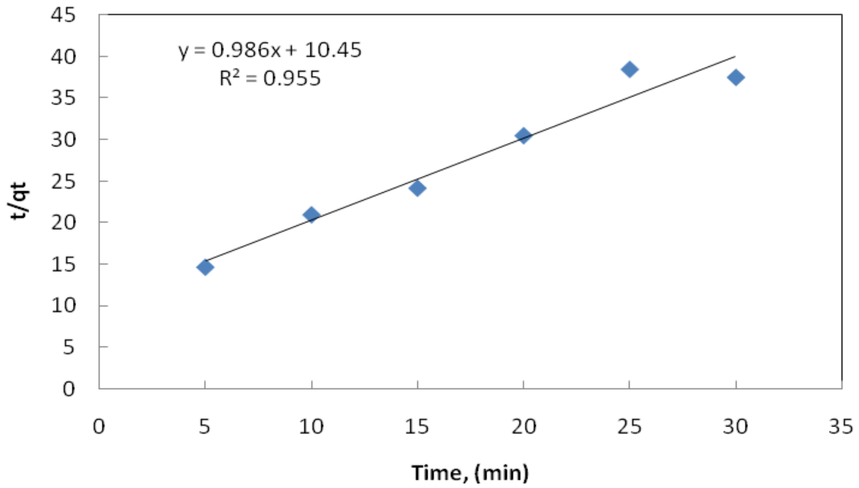

Fig. 3.6: Pseudo – second order kinetics for adsorption of fluoride on Chitosan

Table 3.4: Comparison of pseudo first order and pseudo second order adsorption rate constants, calculated and experimental q_e values for fluoride removal using Chitosan

Parameters	$q_{e,exp}$ mg/g	First order kinetics			Second order kinetics		
		k_1(1/h)	$q_{e,cal}$ (mg/g)	R^2	k_2[g (1/mg h)]	$q_{e,cal}$ (mg/g)	R^2
Fluoride	0.8	0.021	0.574	0.666	0.093	1.014	0.955

From the Table 3.4, for fluoride, the values of correlation coefficient were very high and the theoretical $q_{e,cal}$ values were closer to the experimental $q_{e,exp}$ values. Hence, it can be concluded that fluoride follows pseudo-second order kinetic model.

IV. Conclusions

- Among the different forms and varying dosages of Chitosan used in batch study for the removal of fluorides, the optimized operating condition was found to be of 2.5 g of Chitosan in powder form at 60 rpm mixing speed which nearly reduced fluoride up to 71.17%.Of different dosages of Chitosan in solution form, 15 ml of 0.1 g Chitosan solution proved to be the optimum dosage which was found to be exceptionally good disinfectant achieving a disinfection efficiency of 66-70%.
- Chitosan in its powder and solution form was effective for the removal of fluoride from synthetic water. Of these two different forms of Chitosan, powder form is comparatively more viable than the solution form. From the experimental data, the adsorption for fluoride on to Chitosan fit well with Freundlich adsorption isotherm and fluoride follows pseudo-second order kinetic model.
- Chitosan a versatile sorbent andis a modified natural carbohydrate can be effectively used as an adsorbent for the treatment water due to high contents of amino and hydroxyl functional groups which show significant adsorption potential for the removal of various aquatic pollutants. It is low cost natural polymer and environmentally friendly compared to other adsorbents.

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Vishishtta Nagaraj "Removal Of Fluoride From Synthetic Water Using Chatoyant As An Adsorbent." IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT) 12.4 (2018): 43-48.