



**RESEARCH ARTICLE**

**Batch Adsorption Equilibrium Study on the Fluoride Uptake Capacity of Adsorbent Calcium Alginate Beads**

**Rachna Chhatwani<sup>1</sup>, Anjali Acharya<sup>1</sup> and Ishrat Alim<sup>2</sup>**

<sup>1</sup>Department of Chemistry, Institute of Excellence in Higher Education IEHE, Bhopal (M.P.) India

<sup>2</sup>Quality Assurance Laboratory, Madhya Pradesh Council of Science and Technology Vigyan Bhavan, Nehru Nagar, Bhopal (M.P.), India

Email: [ishrat\\_alim@yahoo.com](mailto:ishrat_alim@yahoo.com)

Received: 1<sup>st</sup> March 2015, Revised: 20<sup>th</sup> March 2015, Accepted: 10<sup>th</sup> April 2015

**ABSTRACT**

Fluoride, as a dissolved constituent of drinking water, is perhaps the only substance producing divergent health effects on the consumer depending upon their relative proportions. Among the various treatment procedures which are effective and can remove fluoride to a suitable level, the adsorption is still widely accepted pollution removal technique. Present study has been undertaken to investigate fluoride uptake capacity of adsorbent and the impact of influencing factors like the effect of solution pH, contact time, quantity of adsorbent or dosage and initial fluoride concentration as tracer and accordingly a series of batch adsorption equilibrium experiments were conducted. Fluoride (*f*-adsorption) investigation was carried out by using aqueous solutions of adsorbate as fluoride-biosorbents system viz., calcium alginate beads (CAB) developed during the study period. In the present study the obtained data revealed that the extent of fluoride (*f*-adsorption) increases with increase in time and attain equilibrium at particular time. The result showed that, the rate of removal percent of fluoride ion was very fast initially. But initially after 80 min the rate of removal percent became very slow and beyond this time, the removal percent showed no increment for the adsorbent CAB. Here we report that with increase in fluoride ion concentration ranging from 1mg/L to 10 mg/L, the percentage removal of fluoride decreases as 78% to 59%. The uptake of the fluoride ion is increased by increasing the initial tracer concentration tending to saturation onto CAB at higher fluoride concentration. From the analysis it is appeared that the removal of fluoride increased from 38% to 70% with the increase of the adsorbent dosage ranging from 0.1 to 0.7 gm/dl followed by the maximum removal achievement (72%) showing adsorbent (CAB) saturation level with the dose of 0.8 to 1.0 gm/dl. Here we also report the extent of adsorption of fluoride ions by the adsorbents as a function of the pH of the system. The adsorption is highly dependent on pH and it is revealed from the analysed data that the maximum adsorption (64%) of fluoride onto the CAB is for pH 4.0 to 6.5. For pH greater than 6.5, fluoride removal decreases sharply from 57% to 39% at pH ranging from 7 to 10.

**Key words:** Calcium alginate beads, Fluoride-biosorbents system, Fluoride uptake, Adsorbent, Adsorbate, Influencing factors.

**INTRODUCTION**

Fluoride a natural constituent of the biosphere in waters is of concern for public health as prolonged intake of high-fluoride water may create problems in the human and also in the animal population. Concerned with the magnitude of health problems due to beyond permissible concentration of fluoride (1.0-1.5 mg F litre<sup>-1</sup>) in drinking water various methods of defluoridation of drinking water have been developed. The ion-exchange, adsorption and precipitation are the usual means of defluoridation. However adsorption method is the most preferred means of defluoridation in which different types of adsorbents are being used by the researchers for defluoridation and found to be highly effective, cheap and eco-friendly (Choi and Kenneth, 1979:

Arulanantham *et al.*, 1989; Killedar and Bhargava, 1993; Hauge *et al.*, 1994; Muthukumaran *et al.*, 1995; Kumar 1995; Karthikeyan *et al.*, 1999; Raghuvanshi *et al.*, 2004).

Recently biosorption is an emerging technique for water treatment utilizing abundantly available biomaterials and chitin, chitosan (Yao *et al.*, 2009) and alginate are attractive adsorbents because of their unique properties like biodegradability, biocompatibility and low cost, in addition to their particular physical and mechanical properties, resulting from the presence of chemical reactive groups in polymer chains. Calcium (Ca)-alginate bio material used for entrapping microbial cells used in the food and beverage industries (Roy *et al.* 1987), pharmaceutical industries (Brachkova *et al.* 2010). Looking to the importance and urgent need to explore the possibility to remove fluoride in water, present problem has been under taken to explore the possibility to develop nanobeads in the form of calcium alginate beads (CAB). Present study has been done with an aim to examine the performance and adsorption capacity of this adsorbent for defluoridation of water at optimum set parameters.

## MATERIAL AND METHODS

Analytical reagent (A.R) grade sodium fluoride as source of fluoride and ethylene diamine tetra acetic acid EDTA (S.D. fine chemicals India) was used without any further purification with Milli-Q water in all the experimental work throughout the study period. The alginate spheres were prepared using 2% (w/v) solution of sodium alginate (Loba Chemie Mumbai, India) as a precursor at 50°C for 3 h until a transparent and viscous solution was observed which was allowed to stand for 24 h. Additionally, 500 ml of 150 mM calcium chloride solution was prepared. For the preparation of the alginate spheres, sodium alginate solution was added drop wise while stirring to allow the spheres to form and left for 24 h. The spheres were separated from the solution and washed with deionised water to produce deprotonated alginate spheres. Finally, the spheres were dried in an oven at 35°C. The calcium alginate beads (CAB) obtained in this procedure was sieved to select particles of approximately 1 mm which were then used in the biosorption (*f*-adsorption) experiments.

The impact of influencing factors like the effect of solution pH, contact time, quantity of adsorbent or dosage and initial fluoride concentration as tracer, a series of batch adsorption equilibrium experiments were conducted. In the present study, a predetermined amount of CAB was mixed with a known concentration of adsorbate and for a given contact period to observe that whether the contact time influences the fluoride (*f*-adsorption) or not. For this study fluoride solution was mixed with the adsorbent and stirred for different period of contact time with a time interval varies as 10, 20, 30....110min for the adsorbent CAB. Similarly determination of optimum dosage of adsorbent was done by adding the different dose 0.1gm to 1.0gm of the adsorbents CAB and accordingly residual and removal percent of fluoride concentration was estimated. The dosage which gives minimum residual concentration has been chosen as optimum dosage. On the other hand determination of optimum pH has also been carried out by adjusting pH ranging from 4.0 to 10.0 followed by calculating the residual fluoride concentration. In the present experiments percentage removal of fluoride and the amount of fluoride adsorbed per unit mass of the adsorbent was calculated as per the equation  $Q_e = v\Delta C / M$  where,  $Q_e$ : adsorbed amount (mg/gm),  $\Delta C$ : difference in fluoride concentration before and after the experiment (mg/L),  $v$ : volume of solution 100 ml and  $M$ : mass of adsorbent.

## RESULTS AND DISCUSSION

### EFFECT OF FLUORIDE INITIAL CONCENTRATION

Present study was done to observe the impact of influencing factors i.e. the initial fluoride ion concentration as tracer, contact time, quantity of adsorbent or dosage and the effect of solution pH, onto the fluoride uptake capacity of adsorbent CAB through a series of batch adsorption

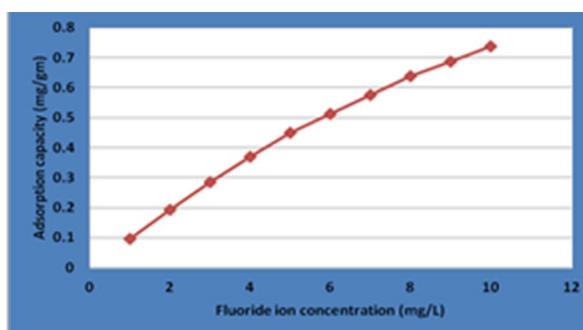
equilibrium experiments (Table 1). From the data obtained for the effect of initial concentration on the percentage removal of fluoride, it is evident that with increase in fluoride ion concentration ranging from 1mg/L to 10 mg/L, the percentage removal of fluoride decreases as 78% to 59% for the adsorbent CAB developed during the study period. The uptake of the fluoride ion is increased by increasing the initial tracer concentration tending to saturation at higher fluoride concentration. From the, it is cleared that the initial fluoride concentration increased from 1-10mg/L the uptake capacity of both adsorbents increased from 0.097mg/gm to 0.737mg/gm for CAB. The results show the loading capacity increases by increasing initial fluoride concentration (Figure 1-2).

**Table 1:** Effect of influencing factors onto the fluoride uptake capacity of CAB

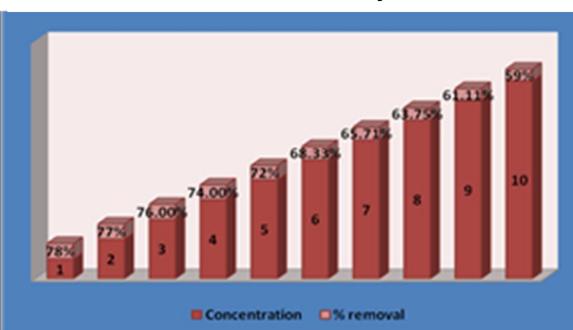
Initial F ion conc. (mg/L)		Contact time (Min.)		Adsorbent dose (gm/dl)		pH		
Conc. (mg/L)	Qe(mg/gm)	Time (Min.)	Qe(mg/gm)	Dose(gm/dl)	Qe (mg/gm)	pH	Qe(mg/gm)	
1	0.097	10	0.32	0.1	1.9	4	0.51	
2	0.192	20	0.45	0.2	1.1	4.5	0.552	
3	0.285	30	0.54	0.3	0.933	5	0.58	
4	0.37	40	0.56	0.4	0.787	5.5	0.6	
5	0.45	50	0.58	0.5	0.68	6	0.62	
6	0.512	60	0.64	0.6	0.575	6.5	0.64	
7	0.575	70	0.66	0.7	0.5	7	0.57	
8	0.637	80	0.68	0.8	0.45	7.5	0.48	
9	0.687	90	0.68	0.9	0.4	8	0.47	
10	0.737	100	0.68	1	0.36	8.5	0.44	
Experimental condition: pH: 6.5 Contact time: 80 Min. adsorbent dose: 0.8 gm/dl		110		0.68		Experimental condition: pH : 6.5 Contact time : 80 min Initial Fluoride ion conc : 5 mg/L		
		Experimental condition: pH: 6.5 initial Fluoride ion conc. : 5 mg/L Adsorbent dose : 0.8 gm/dl				Experimental condition: Adsorbent dose : 0.8gm/dl Contact time: 80 Min. Initial Fluoride ion conc. : 5 mg/L		
						9		0.42
						9.5		0.39
						10		0.39

\*Batch studies data

**Figure 1:** Effect of initial fluoride concentration onto CAB



**Figure 2:** Fluoride concentration effect on the removal efficiency of CAB



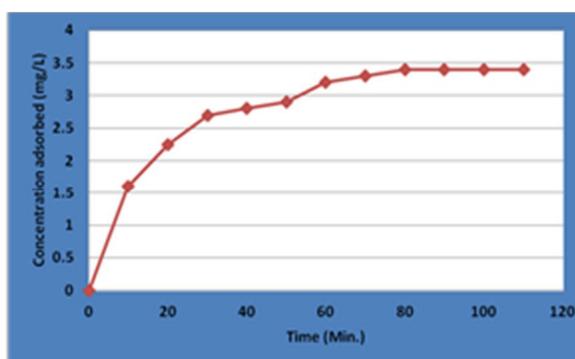
The *f*-adsorption on both adsorbents was found to be very fast where the almost 78% of the total adsorption was completed at the initial value i.e. 0.1mg/L of *f*- concentration. Similarly when the initial concentration is increased from 1-10mg/L the amount of fluoride adsorbed per unit weight of the CAB (mg g<sup>-1</sup>) at equilibrium conditions at room temperature and therefore the adsorption percentage decreases from 78% to 59% (CAB). The analysis data revealed that, when the initial fluoride ions concentration increases the uptake capacity of newly developed adsorbent CAB also increases. From the present findings, it is evident that the fluoride adsorption ability of the adsorbent is higher at higher concentration levels. This extraordinary striking property may be explained by the fact that at higher concentrations the less accessible sites or the vacancies of the

adsorbents are more likely to adsorb fluoride. This is also obvious from the fact that a higher initial fluoride concentration provides an important driving force to overcome all of mass transfer resistance of the fluoride as pollutant between the aqueous and solid phases thus increased the uptake (Aksu, 2005).

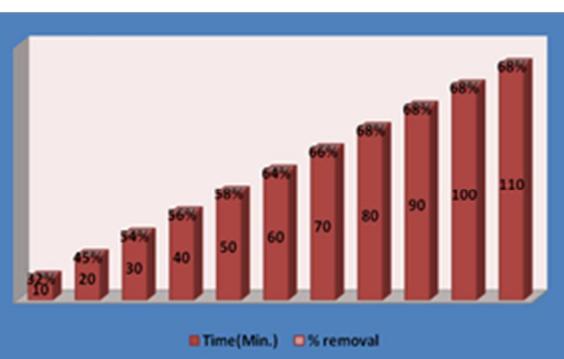
### EFFECT OF CONTACT TIME

The sorption of fluoride ion on the adsorbents has been investigated as a function of contact time in the range of 10–110 minute with 5 mg/L as initial fluoride concentration with the dosage of 0.8gm/dl adsorbent CAB at room temperature. The data revealed that the % removal of fluoride ion increased with time up to about 80 min (CAB) and then the curves became quite level at contact time of 80-110 min for CAB, indicating the attainment of the adsorption equilibrium (Figure 3-4). From the data, it is evident that the extent of fluoride ( $f$ -adsorption) increases with increase in time and attain equilibrium at particular time.

**Figure 3:** Effect of contact time onto CAB



**Figure 4:** Effect of contact time on the removal efficiency of CAB



The result showed that, the rate of removal percent of fluoride ion was very fast initially. But initially after 80 min the rate of removal percent became very slow and beyond this time, the removal percent showed no increment for CAB. The adsorption curves obtained from the data are characterized by sharp rise initial stage and decrease near equilibrium. From the graph after equilibrium further increase in time adsorption is not changing hence the optimum contact time for adsorbent is 80 minutes indicating that longer contact time has a negligible effect on the adsorption. Faster initial removal percent rate is possibly due to the availability of sufficient vacant adsorbing sites in presence of higher fluoride concentration gradient. Afterwards, the fluoride ion removal percent rate decreased significantly due to limited vacant adsorption sites available. Therefore in the present experiment 80 minute for CAB is fixed as minimum contact time for the maximum removal percent of fluoride ion (68%). From the data we find that the capacity of adsorbents in contact with 5 mg/L solution of fluoride in water is 0.68 mg F / 0.8g CAB. The variation of the fluoride concentration in the water adsorbed with time and the amount of fluoride adsorbed increases with time up to certain extent after which equilibrium is attained.

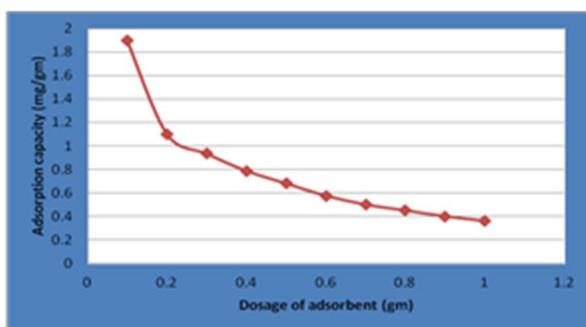
The data revealed that the fluoride adsorption onto CAB process took place in two stages. The first rapid stage in which maximum percentage removal or the adsorption was achieved in 10 minute, and a slower second stage, with equilibrium attained in 1.5 hr for adsorbent CAB developed throughout the study period. It is well documented that the first stage was due to the initial accumulation of fluoride at the adsorbent surface, as the relatively large surface area was utilized. With the increasing occupation of surface binding sites or the vacancies, the adsorption process slowed. The second stage was due to the penetration of fluoride ions to the inner active sites of the adsorbent.

From the data as obtained during the study period are in full agreement which concurs with the observations in similar studies (Sangi *et al.*, 2008; Qaiser *et al.*, 2009). The fluoride adsorption ability of the adsorbent is higher 0.68mg/gm by extending the contact time up to 1.20 hr and this remarkable unique property may be explained by the finding of the present study that at higher the time, less accessible sites of the adsorbents which are more likely to adsorb fluoride. Fast diffusion onto the external surface was followed by fast pore diffusion into the intraparticle matrix to attain rapid equilibrium (Zohre Shahryari *et al.*, 2010).

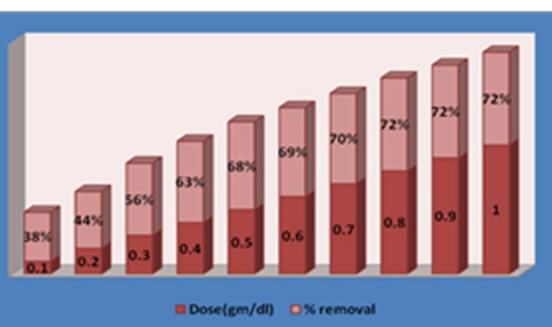
### EFFECT OF ADSORBENT DOSAGE

In the present study it is observed that as the dose of adsorbent increases (0.1gm/dl to 1.0gm/dl) amount of residual fluoride decreases sharply and attains minimum. The point where maximum removal 72% is attained for CAB is taken as optimum dosage i.e. 0.8gm/dl. After this, not much change in adsorption is observed even after increase in the amount of both adsorbents considered for the present study. From the analysis it is appeared that the removal of fluoride increased from 38% to 70% with the increase of the adsorbent dosage ranging from 0.1 to 0.7 gm/dl followed by the maximum removal achievement (72%) showing adsorbent CAB saturation level with the dose of 0.8 to 1.0 gm/dl (Figure 5-6).

**Figure 5:** Effect of dosage and the adsorption capacity of CAB



**Figure 6:** Effect of dosage on the removal efficiency of CAB



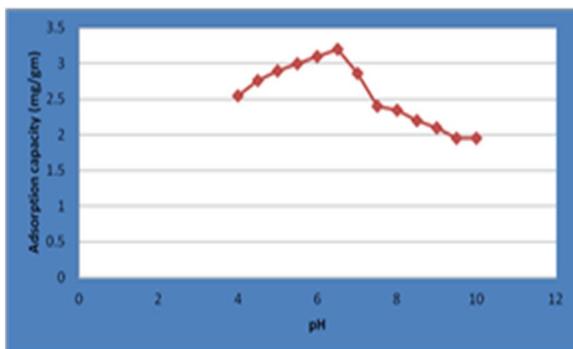
Therefore, dosage of 0.8gm/dl of CAB was considered as the optimum adsorbent dose for batch adsorption experiments. Further addition of the adsorbents did not show a considerable increase of percent of fluoride removal because the overlapping of the active sites at higher concentration of the adsorbent, thus reducing the surface area. Further increase in the adsorbent dosage leads to the decrease of the fluoride adsorption, because there are too many adsorbent doses for the limited amount of fluoride. Here we may explained that fluoride removal is achieved on the basis of adsorption and the extent can be co-related with increasing adsorption sites with increase in the dosage of adsorbents. The percent removal of fluoride seems to be increased with increase in the particular dose of adsorbent. The plateau nature of the plot after 0.8 gm/dl concentration for the adsorbent CAB may be due to the fact based on the exhaustion of the adsorption sites and it might be because of the beads size of the adsorbent fabricated during the study period. From the analysed data we may conclude that for the constant dosage of adsorbent, at higher initial concentration, the available adsorption sites of adsorbent became fewer and hence the removal of fluoride depends upon the initial concentration.

### EFFECT OF pH

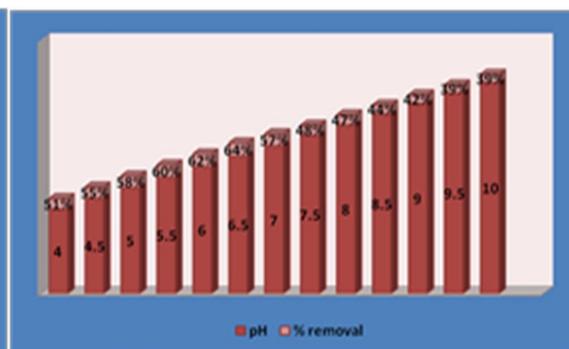
The pH of the medium is one of the most important parameters, which significantly affects the fluoride adsorption. From the data obtained from the analysis values of pH and corresponding fluoride adsorbed, it is evident that the fluoride removal not only depends on surface area, time and dosage but also depends on pH and the pH attains equilibrium at 9.5-10.0 for CAB and therein no

increase after fluoride uptake capacity as 0.39mg/gm takes place. The extent of adsorption of fluoride ions by the adsorbents is a function of the pH of the system. The adsorption is highly dependent on pH and it is revealed that the maximum adsorption (64%) of fluoride onto the CAB is for pH = 4.0 to 6.5. For pH greater than 6.5, fluoride removal decreases sharply from 57% to 39% at pH ranging from 7 to 10 (Figure 7-8).

**Figure 7:** Effect of pH on adsorption capacity of adsorbent for fluoride



**Figure 8:** Effect of pH on the removal efficiency of adsorbent CAB



The maximum adsorption was observed at pH 6.5 for the adsorbent CAB while in acidic and alkaline pH the fluoride removal was observed to decrease as 58% to 46%. The significant decrease of removal percent of fluoride at alkaline pH could be mainly due to electrostatic repulsion of fluoride ion to the negatively charged surface of both the adsorbent. Based on the present findings we may say that the data obtained during the study period are in full agreement with the research emphasised that the adsorption of fluoride ion was found mainly to be influenced by solution pH<sup>1</sup>. It was also observed that defluoridation was observed maximum at pH 6.5 and then steeply decreases as pH increases from the acidic range to alkaline range. In alkaline pH range there is a sharp drop in adsorption which may be attributed to the competition of hydroxyl ions with fluoride for adsorption. In the acidic range the adsorption was slightly decreased and it may be due to the formation of weak hydrofluoric acid (Li *et al.*, 2007; Tang *et al.*, 2009; Sunil *et al.*, 2013).

From the data of the present study, it is cleared that the pH of the aqueous fluoride solution plays an important role in the whole adsorption process, particularly on the adsorption capacity. A consistent increase 0.5mg/gm to 0.64mg/gm (CAB) in adsorption capacity of the adsorbent was noticed as the pH increased from 4-6, whereas in the range 6.5-10, the adsorption amount was only slightly affected by pH. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favour the adsorption of negatively charged fluoride cations due to electrostatic repulsion. In addition, lower adsorption of fluoride at acidic pH might be due to the presence of excess H<sup>+</sup> ions competing with adsorbate cations for the available adsorption sites. Present findings are in full agreement of the findings of the researchers who worked on the methylene blue considered as adsorbate and the authors have reported that methylene blue adsorption usually increases as the pH is increased (Vadivelan and Kumar, 2005; Bestani *et al.*, 2008; Gupta *et al.*, 2004; Singh *et al.*, 2003).

#### ACKNOWLEDGEMENT

Thanks are due to Prof. Pramod K. Verma, Director General Madhya Pradesh Council of Science and Technology Bhopal and Advisor Govt. of M.P. The authors are also thankful to Prof. Meera Pingle, Director Centre of Excellence in Higher Education IEHE, Bhopal, D. K. Soni Incharge Quality Assurance Laboratory for extending support and constant encouragement and to all the staff of QAL offered selfless support and assistance to write this paper.

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