Fluoride Removal from Water using Chitosan Coated Activated Carbon and Cuttle Bone Ash in Combination with Alumina

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Abstract

Fluoride contamination of ground water is an important health concern globally. Presence of high level of fluoride in drinking water can lead to issues of skeletal and dental fluorosis. A combination of chitosan coated activated carbon (CCAC) and chitosan coated cuttle bone ash (CCBA) along with alumina was used for the removal of fluoride from drinking water. The sorbents were characterized by SEM and FTIR. Combination of 2.5% CCAC and 1% alumina resulted a fluoride removal efficiency of 85.4%, while a 2% CCBA and 2% alumina combination resulted removal of 96.6%, also the fluoride removal efficiency increased along with increase of contact time (p<0.01). At higher initial fluoride concentrations, CCBA was more effective in fluoride removal than CCAC in combination with alumina. This information can help in modeling and designing of filtration devices with these adsorbents for effectively managing fluoride - contaminated ground water.

Key words: Fluoride, chitosan, adsorbents, activated carbon, cuttle bone ash, alumina

Introduction

Contamination of ground water by fluoride is a serious and common threat in many parts of the world. In India 90% of rural population depend on ground water for their domestic purposes (Godboley et al., 2013). Natural geologic and volcanic activities as well as manmade inputs from industries and power plants may contribute towards ground water contamination. As per the UNICEF (1999) report in India, 66 million people are directly affected by groundwater fluoride contamination. Fluorine is the most electronegative of all elements and is very active physiologically with wide spread occurrence in the form of fluoride salts such as fluorapatite ($Ca_5F(PO_4)_3$), fluorspar (CaF_2), cryolite ($NaAlF_6$), topaz ($Al_2F_2SiO_4$) and apophylite ($KFCa_4(Si_8O_{20})$ $8H_2O$) etc.

High fluoride concentrations (>1.5-2.0 mg L^{-1}) in daily drinking water can lead to dental fluorosis with blackening and mottling of teeth. Human consumption above 3 mg L^{-1} leads to skeletal fluorosis resulting in severe pain, stiffness of backbone and joints, and bone deformation (Mjengera & Mkongo, 2002; Kaseva, 2006). India is identified globally as a nation with fluorosis distress due to contaminated drinking water (Susheela & Majumdar, 1992). In India 12 out of 85 million tons of fluoride deposits on the earth's crust are found (UNICEF, 1999). The most seriously affected states include Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh. Fluoride content above the permissible limit of 1.5 mg L^{-1} (WHO, 2006; Manik & Biswapati, 2009) is reported and Susheela (2003) reported fluoride content in the range of 0.5 to 48 mg L^{-1} in worst affected areas.

A widely accepted technique to remove fluoride from water is adsorption because of ease of operation and cost - effectiveness. The adsorbents used for removal of fluoride include natural, synthetic and biomass. Many sorbents have been tested for efficient removal of fluoride including alumina, calcium, ferrous-modified clays etc. But they are reported with slow rate of adsorption. The disadvantage with activated carbon is its high production and treatment cost. Cuttle bone is an internal structure

found in the family of sepiidae and consists of aragonite, crystalline form of $CaCO_3$. Usually cuttle fish bones are in the size range of 10 - 20 cm. Treatment of industrial wastewater using squid bones (cuttlebone) as a carbonate mineral for removal of heavy metal ions is previously reported by Farghaly et al. (2015), where powdered cuttle bone was used. Cuttle bone powder was also reported as a bio adsorbent for removal of copper (Cu II) from aqueous solutions (Vibhatabandhu & Srithongouthai, 2016). Here the feasibility of cuttle bone ash along with chitosan coating for removal of fluoride is investigated. Activated alumina is having good fluoride removal ability, but with low regeneration capacity. The present study investigates the usage of chitosan - coated activated carbon and chitosan - coated cuttle bone ash along with alumina in combination to reduce the content of fluoride in water.

Materials and Methods

Fluoride standard solution of 1000 mg L^{-1} for ion chromatography was procured from Accustandard with NIST Traceability (IC-F-10X-1, 1000 μg ml^{-1}, 100 ml, Lot No. 217105106). Filtered water using Cascada LS water, Lab water technology (Pall Corporation) is used for the batch experiment. Activated carbon and alumina used in the study were procured from Merck.

Chitosan required for the coating purpose was prepared from the shell waste of prawn as per the method of Madhavan & Nair (1974). The degree of deacetylation (DAA %) and viscosity (Cp) of chitosan used in the study were 90.2 and 19.26 respectively. Cuttle bones required for the preparation of cuttle bone carbon were collected from a seafood exporting company at Cochin. The cuttle bones were washed in water and then dried in a hot air oven at 100°C for 2-3 h. After drying, the cuttle bones were broken and fine powdered using a mixer. The powdered cuttle bone carbon was subjected to heating in a muffle furnace at a temperature of 550°C for 6 h. Then the ash was sieved through a 500 μ sieve for making uniform particle size.

Chitosan coated - activated carbon (CCAC) and chitosan coated cuttle bone ash (CCBA) were prepared by modification to the method of Okoya et al. (2016). One gram of chitosan was dissolved in 100 ml of 2% oxalic acid. Activated carbon (AC) and the prepared cuttle bone ash (CBA) were gently

mixed to the chitosan solution for the preparation of CCAC and CCBA respectively. For thorough mixing, it was kept in a water bath cum shaker for 24 h at room temperature and maintained at 150 rpm. The gel coated adsorbent was washed with distilled water and allowed to dry in a hot air oven at 100 ±2°C for 3 h. Again, the process of coating, washing and drying were repeated for a second time. The dried powders were cooled to room temperature and stored in desiccators.

The surface appearance and morphological characters of AC, CCAC, CBA and CCBA were carried out using SEM (XL 30 Philips, Netherlands). Samples were fixed onto SEM stubs with double-sided adhesive carbon tabs, which are coated with gold and evaluated using SEM. AC, CCAC, CBA and CCBA were evaluated using a FT-IR spectrometer (Model Nicolet™ iS ™ 10, Thermo Fisher Scientific, Waltham, MA), by KBr pellet method in the wavelength range of 4000–400 cm^{-1}. OMNIC software (Thermo Fisher Scientific) was used for analysis of FTIR spectra.

Batch adsorption studies were carried out using CCAC and CCBA in combination with alumina to evaluate the efficiency of adsorbent in removal of fluoride from water at lab scale before starting the column experiment. Batch adsorption experiments were carried out in 200 ml beakers containing 100 ml of fluoride solution using adsorbent combination at room temperature. The experiment was carried out at neutral pH. Fluoride removal efficiency was evaluated with changes in dosage of adsorbent combination, contact time and initial concentration.

Adsorption capacity of adsorbent combinations of CCAC and CCBA with alumina was calculated using the fluoride concentration before and after the process of adsorption.

$$\text{Adsorption capacity} = (C_i - C_e) \, V/m$$

Where C_i is the initial concentration in mg L^{-1}, C_e is the equilibrium concentration level in mg L^{-1}, V is the volume of solution in L and m is the weight of adsorbent in grams.

The fluoride removal efficiency is calculated as per

$$\% \text{ removal efficiency} = (C_i - C_e) \, 100/C_i$$

Effect of adsorbent dosage - The effect of dosage of adsorbent combination was evaluated at an initial

fluoride concentration of 5 mg l^{-1}. The adsorbent combinations and dosage used were CCAC or CCBA at 2% along with alumina (0.5, 1 and 2%), CCAC or CCBA at 2.5% with alumina (1%) and CCAC or CCBA at 3% with alumina (0.5%). The adsorbents were added to the fluoride solution and kept in a magnetic stirrer for 60 min which was determined based on previous trial studies. The sorbent was filtered after adsorption using whatman No.1 filter paper. Then the water was further filtered using 0.2 µ filter for further analysis.

Effect of contact time - The variation in contact time was carried out from 15, 30, 60, 90 and 120 min at a dosage level of adsorbent with less content of alumina at 2.5% of CCAC and CCBA along with 1% alumina. The initial fluoride concentration used for the adsorption was 5 mg l^{-1}. Stirred the samples using a magnetic stirrer for the specified time periods, filtered and further analysed the fluoride concentration by instrumental method.

Effect of initial concentration - The fluoride concentration varying from 2, 4, 8 and 10 ppm were subjected to adsorption process at the optimal dosage and contact time.

Fluoride concentration in sample was analysed using Ion chromatography (Dionex ICS 3000, Thermo Fisher Scientific) using chromelon software. AS12A column (RFIC ^{TM}, Ion pac ®, 4×200 mm) was used for fluoride analysis with Na_2CO_3 (2.7 mM) and $NaHCO_3$ (0.3 mM) as eluents. The LOQ and LOD of Ion chromatograph for fluoride is 0.02 and 0.2 mg L^{-1}. Recovery is 103.27% and uncertainty is 3.93.

Filtered samples were injected for analysis after running calibration standards. Before and after running of calibration standards, filtered milli Q water were run as blank at least three times to avoid carryover of standards in the column and to analyse the background fluoride level. The same procedure was followed in case of treated samples also.

Data obtained from the experiment was subjected to One-way analysis of variance (ANOVA) using the SPSS 20 (SPSS Inc., Chicago).

Results and Discussion

The CCAC and CCBA were subjected to evaluation of surface morphology and structure using SEM and FTIR spectroscopy and were compared with that of activated carbon and cuttle bone ash. SEM images of AC, CCAC, CBA and CCBA were given in Fig. 1. In case of AC small minute pores were visible. But in case of CCAC the number of pores was more with enlarged pore size after coating. In the SEM image of cuttle bone ash (CBA) numerous flake like structures were visible. And in case of CCBA more close tight packing of flake like structures with small minute particles were observed after coating. SEM analysis revealed sheat like ultra structures in case of cuttle bone which is found similar to the previous report (Khazri et al., 2014). The microscopic structure of cuttlebone contains narrow layers connected by numerous upright pillars. SEM images of original aragonite as well as apparent original organics are reported (Farghaly et al., 2015). They also described that the "sheet-like" structures
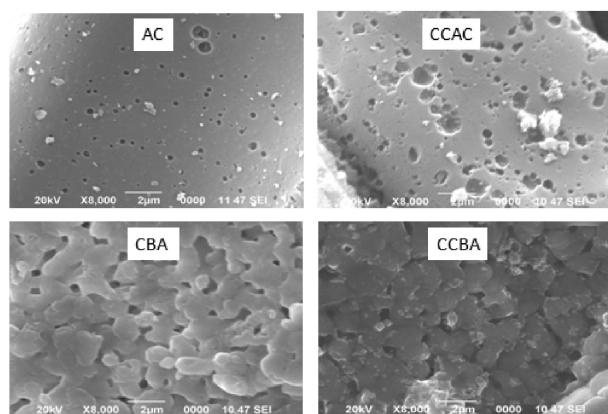

contain high amounts of phosphorous.

Fig. 1. SEM images of activated carbon (AC), chitosan - coated activated carbon (CCAC), cuttle bone ash (CBA) and chitosan - coated cuttle bone ash (CCBA)

FTIR spectra of AC, CCAC, CBA and CCBA are presented given in Fig. 2. Spectra ranging from 4000 to 400 cm^{-1} were recorded and functional groups present in the region were identified. In case of AC a terminal carbon was noticed at 3600 region. Identified the peaks of C=O at 1711, C=C at 1570 and P=O at 1263. While in the case of CCAC, carbonyl stretching (C=O) – amide I and NH binding trans to C=O – amide II was seen at 1600 region (1652-1646). Also peaks of 829 and 710 cm^{-1} were observed in CBA, and peaks of 866 and 708 cm^{-1} were observed in CCBA indicate the presence of $CaCO_3$ polymorphs. The characteristic carbonate v2 band of aragonite is at 858 cm^{-1}; whereas, that of both calcite and vaterite is at 874 cm^{-1}. The characteristic carbonate v4 band of aragonite is at 700 and

713 cm^{-1}; whereas, that of calcite is at 713 cm^{-1} and vaterite at 744 cm^{-1}, respectively (Ni & Ratner, 2008). Periasamy & Mohankumar, (2016) characterized the cuttle bone particles heated at 400°C. They observed aragonite polymorph form of $CaCO_3$ in the cuttle bone particles without heat treatment, while calcite polymorph form of $CaCO_3$ was observed in the heated cuttle bone particles at 400°C by XRD (X-ray powder diffraction) analysis. In the case of CBA, weak shoulders of phosphate group are visible from 1041 to 599 regions. But in CCBA, presence of amide groups was noticed at 1600 region in addition to phosphate groups. The presence of amide I in the region between 1652 – 1646 cm^{-1} and amide II in the region between 1568 and 1585 cm^{-1} corresponding
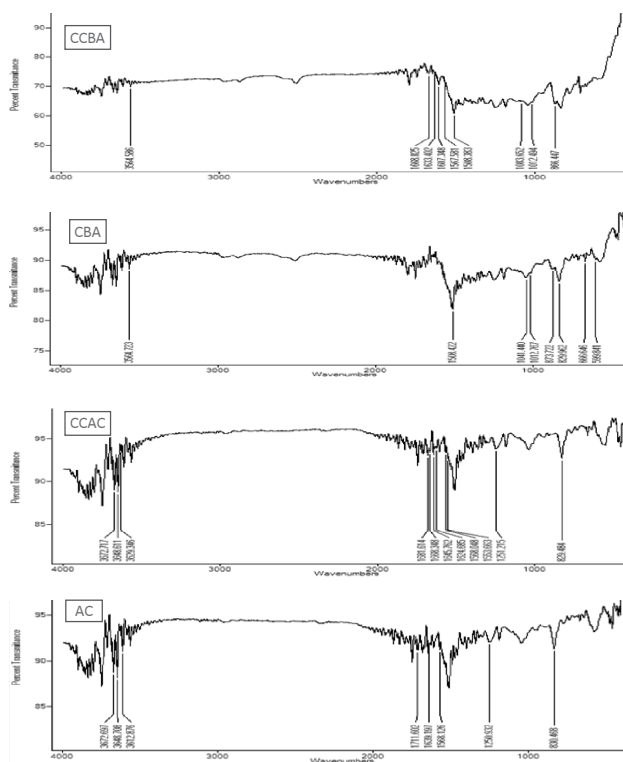
to coated adsorbents indicate the effectiveness of chitosan coating.

Fig. 2. FTIR spectra of AC, CCAC, CBA and CCBA

Efficient removal of fluoride content from water using cost effective biosorbents is extremely important. For evaluating the efficiency of removal of fluoride at various dosage levels of CCAC and CCBA varying from 2, 2.5 and 3% in combination with alumina varying from 0.5 to 1% was studied at an initial fluoride concentration of 4 mg l^{-1} and given in Table 1 and 2. In case of CCAC, the optimal

fluoride removal efficiency of 85.4% was observed at a combination of 2.5 % CCAC and 1% alumina. The higher fluoride removal efficiency of combination with more CCAC content indicate is usefulness in fluoride removal. But a further increase of CCAC to 3% and decrease of alumina to 0.5% resulted in significant decrease of removal efficiency to 53.87%. It is clear that a CCAC level of 2.5% with 1% alumina combination is playing critical role in fluoride removal from water in comparison to other combinations. Removal efficiency of 94% with powdered activated charcoal at an initial concentration of 5 mg l^{-1} and a contact time of 120 min has been reported (Tembhurkar & Dongre, 2006). It is reported that modified form of immobilized activated alumina with good fluoride removal response was shown at higher dosage levels (Rafique et al., 2013).

While in the case of CCBA, a combination of 2% CCBA and 2% alumina was giving optimal fluoride removal efficiency at an initial fluoride concentration of 4 mg l^{-1}. Increase in percentage of alumina in CCBA combination has resulted increase in removal of fluoride than the increase of CCBA. The removal efficiency was observed to be 96.6%. The contact time of treatment was 60 min. Cuttle bone powder was reported for the removal of carbamazépine, an organic pollutant from aqueous solution (Khazri et al., 2014). Although the usage of squid bones for removal of harmful heavy metal ions in waste water treatment is reported (Farghaly et al., 2015), this is the first time the preparation and usage of chitosan coated cuttle bone carbon for fluoride removal from water is being reported. The combination of chitosan coated cuttle bone carbon and alumina can effectively replace the usage of activated carbon for water treatment.

Table 1. Effect of dosage of CCAC and alumina on fluoride removal

Sl. No.	CCAC (%)	Alumina (%)	Contact time (minutes)	% Removal of fluoride
1	2	0.5	60	56.75±2.5[a]
2	2	1	60	67.75±0.5[b]
3	2	2	60	67.875±1.1[b]
4	2.5	1	60	85.375±0.4[c]
5	3	0.5	60	53.875±2.1[a]

Values are means of triplicate analysis with average ± standard deviation (n=3). Values in a column with different superscripts are significantly different (p<0.01)

Table 2. Effect of dosage of CCBA and alumina on fluoride removal

Sl. No.	CCBA (%)	Alumina (%)	Contact time (minutes)	% Removal of fluoride
1	2	0.5	60	53.75 ± 0^a
2	2	1	60	61.5 ± 0.25^b
3	2	2	60	96.63 ± 0.13^c
4	2.5	1	60	66.88 ± 0.88^b
5	3	0.5	60	53.88 ± 0.23^a

Values are means of triplicate analysis with average ± standard deviation (n=3). Values in a column with different superscripts are significantly different (p<0.01)

The effect of combination of CCAC and CCBA at 2.5% with 1% alumina was studied at different contact time ranging from 15, 30, 60, 90 and 120 min and given in Table 3. In the case of CCAC, along with the increase of contact time, the fluoride removal efficiency was increasing (p<0.01). In case of Zirconium (IV), metal loaded chitosan sorbents for fluoride removal from water was reported and 20% metal doped in chitosan was found to be excellent for defluoridation at optimized sorbent dose of 10 g L^{-1} (Dongre et al., 2012).

Even though a combination 2% CCBA with 2% alumina showed maximum fluoride removal efficiency, combination of 2.5% CCBA with 1% alumina was used to study the effect of contact time in order to reduce the usage of alumina in fluoride removal. Along with the increase of contact time, the fluoride removal efficiency of both CCBA and CCAC - alumina combination was increasing (p<0.01). But between 30 and 60 min of contact time, there was no significant increase in fluoride removal efficiency in case of CCBA – alumina combination. At 120th min of contact time, CCBA alumina combination achieved 75.63% in comparison to 94.58% in case of CCAC - alumina combination.

The effect of initial fluoride concentration on fluoride removal efficiency using CCAC and CCBA - alumina combination was evaluated at various concentrations of fluoride ranging from 2, 4, 8 and 10 mg l^{-1} at a contact time of 30 minutes and is given in Table 4. In case of CCAC - alumina combination, the fluoride removal efficiency was decreasing (p<0.01) with increase of initial fluoride concentration. At initial fluoride concentration of 10 mg l^{-1}, the removal efficiency got decreased to 57.48%.

Table 3. Effect of CCAC and CCBA alumina combination on contact time

Contact time (minutes)	CCAC 2.5% and 1% alumina	CCBA 2.5% and 1% alumina
15	80.63 ± 0.88^a	63.63 ± 0.13^a
30	85.38 ± 0.38^b	67.00 ± 1.3^b
60	90.63 ± 0.38^c	66.88 ± 0.88^b
90	93.32 ± 1.5^d	73.25 ± 0^c
120	94.58 ± 0.03^d	75.63 ± 0.13^d

Values are means of triplicate analysis with average ± standard deviation (n=3). Values in a column with different superscripts are significantly different (p<0.01)

Table 4. Effect of CCAC and CCBA - alumina combination on initial fluoride concentration

Initial fluoride concentration (mg l^{-1})	CCAC 2.5% and 1% alumina	CCBA 2.5% and 1% alumina
2	88.45 ± 0.4^d	68.39 ± 1.7^a
4	85.38 ± 0.4^c	73.25 ± 0^b
8	49.38 ± 3^a	75.13 ± 0.3^c
10	57.48 ± 0.54^b	75.04 ± 0.5^c

Values are means of triplicate analysis with average ± standard deviation (n=3). Values in a column with different superscripts are significantly different (p<0.01)

While in the case of CCBA - alumina combination, a significant increase (p<0.01) in fluoride removal efficiency was observed and is highly efficient in removing high fluoride concentrations. At an initial fluoride concentration of 10 mg l^{-1}, fluoride removal efficiency of CCBA – alumina combination was 75.0% in comparison to 57.5% in case of CCAC – alumina combination. There was no significant difference in removal of fluoride between initial concentration of 8 and 10 mg l^{-1}. Alum impregnated activated alumina removed 92% fluoride at a contact time of 3 h from initial fluoride concentration of 25 mg l^{-1} (Tripathy et al., 2005). A maximum removal of 46% from an initial fluoride concentration of 25 mg l^{-1} using nut shell activated carbon has been reported (Ravancic & Habuda-Stanic, 2015).

Chitosan coated activated carbon and cuttle bone carbon was used in combination with alumina for removal of fluoride from water. The characteristics of CCAC and CCBA were evaluated using SEM and FTIR spectroscopy. Batch adsorption experiments

were carried out to evaluate fluoride removal efficiency at different dosages of adsorbent combination, contact time and initial fluoride concentration. Optimal fluoride removal efficiency of 85.38% was observed at a combination of 2.5% CCAC and 1% alumina and in case of CCBA, a combination of 2% CCBA and 2% alumina was giving optimal fluoride removal efficiency of 96.63%. Both in the case of CCAC and CCBA alumina combination fluoride removal efficiency was increasing along with increase of contact time. While at higher levels of initial fluoride concentration, CCBA – alumina combination is highly efficient in removing fluoride. As these adsorbent combinations are effective in fluoride removal, water filtration devices using these filtration materials can be designed and evaluated.

Acknowledgements

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