

Fluoride Removal from Water By Calcium Materials: A State-Of-The-Art Review

Sanghranta S. Waghmare¹, Tanvir Arfin²

Senior Scientist, Dept.of Environmental Materials Division, National Environmental Engineering Research Institute (CSIR), Nehru Marg, Nagpur, India¹

Scientist, Dept.of Environmental Materials Division, National Environmental Engineering Research Institute (CSIR), Nehru Marg, Nagpur, India²

ABSTRACT:The current manuscript reviews show about adequacy of various materials based on calcium for removal regarding fluoride through drinking water and industrial waste water. Fluoride is really a conscientious and non-biodegradable toxin in which aggregates inside the earth, plants, untamed lifestyle and inside people. Like this, understanding regarding it's evacuated, utilizing best strategy together with ideal efficiency is required. For that enlargement regarding attributes, upgrade within the sizes to modify the particular interest regarding reliance for calcium, the primary and fundamental technological improvement are already essential finished through the use of calcium base absorbent for different application inside remedy regarding waste water. On this content, the particular review associated with the latest progress on the modification of calcium based adsorbent to collect in order to enhance the solubility and application. It exhibits the basic factor, for example, type and concentration of initiator, temperature and time are responsible for affecting the calcium based absorbent. The calcium and its subsidiaries have bunches of abilities for the procedure of defloration, so it is likewise anticipated to great hotspot for tossing from water and waste water as too. A recovery strategy was proposed to reuse the adsorbent for better economy of the procedure. In the current review, the different characteristic of calcium based absorbent, for example, preparation, application, kinetic studies impacts have been advanced for further viewing.

KEYWORDS:Calcium; Adsorption; Langmuir; First order reaction; Nano-material.Introduction

I. INTRODUCTION

Water fluoridation is a critical safeguard apportion conveyed in a significant part of the world. It brings about a percentage of the hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ of which human tooth lacquer is made being supplanted by fluoroapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$ -as substance essentially more impervious to rot. In this way to secure the teeth of the populace, water is regularly fluoridated. Fluoride happens normally out in the open water frameworks as a consequence of spillover from weathering of fluoride-containing shakes and soils and filtering from soil into ground water. The vicinity of fluoride and different contaminants has additionally been accounted for from diverse parts of the world where individuals experienced hurtful illnesses because of modern release of fluorides and in this manner the water sources have been risky for human utilization and a watering system and mechanical employments. Numerous strategies for the deduction of fluoride ions from water have been produced to decrease the keenness of their harm to human wellbeing and the ecological dangers that they affect [1-2].

The relief of fluorosis is most fundamental to keep their risky effect on people, creatures and plants. The vast majority of the research works are as yet going ahead to evacuate or decrease the concentration of fluoride to make it fit for drinking reason by different treatment techniques since the option wellspring of drinking water are restricted or not accessible in the vast majorities of the nations. Endeavours have been under taken to review on defluoridation system utilizing adsorption procedure in view of a wide cluster of minimal effort and particular adsorbents to water for utilizing having fluoride in attractive or passable sums recommended by various national and international measures. The recovery and safe transfer of adsorbents have been additionally reviewed in this chapter.

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II. CALCIUM BASED ADSORBENTS

The defluoridation process of aqueous water was carried out by the calcium based adsorbents due to the property such, they have an excellent affinity for fluoride, low cost in nature and biocompatibility with the human body, and they make them to be used in worldwide basis. For discussing about calcium bearing materials used as adsorbent for removal of fluoride in basis of we have divided them as follows.

III. DEFLUORIDATION BY APATITE MATERIALS: HAP

Badillo Almaraz *et al.* (2007) have found that hydroxyapatite (HAP) evidently adsorbed 19 mg of fluoride per 1 g of solid at a pH range between 7.0 and 7.5 [3]. Gao *et al.* (2009) have suggested about the size-dependent defluoridation properties of synthetic hydroxyapatite from aqueous solution. In his study, it was observed that the HAP with smaller size particles possess, the better fluoride removal capacity than bigger size particles. The Langmuir adsorption capacity of different size HAP ranged between 0.295 to 0.489 mg/g. The experimental data from nano-sized HAP was quite suitable with pseudo-second-order kinetics and Freundlich isotherm models and it also found that adsorption process was basically physisorption and endothermic in nature according to the thermodynamic study. The fluoride removal efficiency increases with an increase in the adsorbent dose and contact time, but it decreases with an increase of initial fluoride concentration and pH of solution [4].

Li *et al.* (2010) predominantly used Ca-deficient hydroxyapatite (d-Hap) as adsorbent for defluoridation from wastewater in-presence of Ca^{2+} , Mg^{2+} and Cl^- . The fluoride removal of around 85% was achieved with pH ranging widely between 4 and 7. The adsorption followed Langmuir isotherm and pseudo-second-order reaction model with the maximum adsorption capacity of d-Hap to be as 26.11 mg/g. It was found that the ion-exchange mechanism played significant role in the adsorption process [5].

Jimenez-Reyes and Solache-Rios (2010) have widely explored hydroxyapatite (HAP) as adsorbent for removal of fluoride from water. The adsorption capacity of 4.7 mg/g was obtained using 0.01 g of HAP and 25 ml of solution and noted to be the highest value, whereas 96% of removal took place by using 0.1g of HAP and 25 ml of fluoride solution. The optimal pH range and equilibrium time was 5-7.3 and 16 hours respectively. The pseudo-second-order kinetics and Freundlich isotherm model had outstanding results from adsorption process. The fluoride desorption was carried out by the alkaline solution of pH 10.0 [6].

Liang *et al.* (2011) used sodium calcium borate glass derived hydroxyapatite (G-HAP) prepared by immersion of sodium calcium borate glass in 0.1 M K_2HPO_4 solution in the ratio of 50g/l for 7 days approximately. The maximum adsorption capacity of G-HAP was 17.35 mg/g under optimum condition of dose 5g/l, size <100 μm , pH 6.72 and adsorption time 12h. The fluoride uptake by micro-G-HAP was more in comparison to commercial nano-HAP. The adsorption data were quite suitable for pseudo-second-order kinetic model and Freundlich isotherm model [7].

Wang *et al.* (2011) have studied the effects of low molecular weight organic acids (LMWOAs) on the defluoridation capacity of nanosized hydroxyapatite (nHAP). The higher concentration of LMWOAs enhanced the adsorption capacity of nHAP for the process of defluoridation as LMWOAs on nHAP had more amount of active sites for fluoride adsorption. At low pH, the adsorbed LMWOAs were protonated as positively charge and attract fluoride ions in the maximum amount. The adsorption capacity was found increase with contact time whereas it decreases with an increase of adsorbent dose and pH of the solution. The experimental results fitted predominantly well with Freundlich isotherm and pseudo-second-order kinetics. The adsorption by the LMWOAs adsorbent was spontaneous and endothermic in nature [8].

Poinern *et al.* (2011) have indigenously employed nanostructured hydroxyapatite (n-HAP) manufactured by the combination of ultrasonic and microwave techniques during wet chemical synthesis of hydroxyapatite. The maximum adsorption capacity of 5.5 mg/g was obtained at pH 6.0 and 298K. The experimental data was quite well with both Langmuir and Freundlich isotherm models and followed pseudo-second-order kinetics and the adsorption process was endothermic and spontaneous in nature as well [9].

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Nie *et al.* (2012) revealed that the adsorption capacity of aluminium-modified hydroxyapatite (Al-HAP) was found to be 32.57 mg/g in comparison to unmodified hydroxyapatite of around 16.38 mg/g due to the presence of abundant surface hydroxyl groups on the surface of Al-HAP. The adsorption process followed Langmuir adsorption isotherms and pseudo-second-order kinetic models and the adsorption reaction was spontaneous and endothermic in nature [10].

Garg and Choudhari (2012) have exclusively studied the defluoridation capability of magnesium substitute hydroxyapatite (HAP) from aqueous solution. The result of the study revealed that the data fitted with pseudo-second-order kinetic model and Freundlich isotherm model. The 25.68% of fluoride removal was obtained in first 30 minutes, whereas 47.94% removal occurred within equilibrium time of 24 hours at pH of 6.0 to 5.5 mg/l of initial fluoride concentration. The adsorption capacity of 8.8 mg/g was achieved at pH 6.5 and it was found to decrease by 41% at pH 8.7. The leaching of Ca-Mg was 31.3 mg/l at pH 6.5 which was later decreased by 68.7% at pH 8.7. The presence of co-existing anions have negligible effect on the defluoridation capacity and found to be in the order of sulphate > bicarbonate > nitrate > chloride [11].

Mourabet *et al.* (2012) have investigated the defluoridation capacity of hydroxyapatite (HAP) by using response surface methodology. The 88.86% of fluoride was removed from solution of 20 mg/l of initial fluoride concentration under optimal conditions of pH as 4.16, temperature as 39 °C and adsorbent dose as 0.28 g. The maximum Langmuir adsorption capacity was noted to be as 3.12 mg/g. The experimental data fitted well with Langmuir and Freundlich isotherms models as well as pseudo-second-order kinetic model and the adsorption process by HAP was found to be endothermic in nature as per dynamic study [12].

Yu *et al.* (2013) have investigated about cellulose@hydroxyapatite nanocomposite prepared in NaOH/thiourea/urea/H₂O solution via in-situ hybridization. The adsorption equilibrium reached within 360 minutes and followed the pseudo-second-order kinetic model. The experimental data fitted well for both Langmuir and Freundlich isotherm models. The adsorbent dose of 3 g/l was responsible for bringing down the fluoride concentration within permissible limit as prescribed by W.H.O. for 10 mg/l of initial fluoride concentration [13]. Nath and Dutta (2014) have critically reviewed the defluoridation capabilities of calcium containing materials. The materials for defluoridation through calcium hydroxyapatite (HAP), quick lime, slack lime, calcium chloride, limestone or calcium carbonate, calcium hydroxide, calcium phosphate, calcium nitrate, calcium sulfate, bleaching powder, plaster of Paris, cement paste, hydrated cement, aluminium cement etc. Each and every mentioned above materials have certain advantages and disadvantages [14].

Prabhu *et al.* (2014) prepared cationic surfactant modified hydroxyapatite (HAp) for defluoridation of water in batch mode. The maximum defluoridation capacity of the modified HAp powder was 9.369 mg/g at 50 mg/l dose of adsorbent at room temperature for 10 mg/l of fluoride solution and was found 3 to 4 times higher than bare HAp (2.63mg/g). The adsorption process mainly occurred due to electrostatic attraction and ion-exchange mechanism. The adsorption data were described well by Freundlich, Langmuir and D-R isotherm models. The adsorption followed the pseudo-second-order kinetic and intra-particle diffusion kinetic models. The thermodynamic study revealed that the reaction was spontaneous and endothermic in nature and the modified HAp was tested for field sample also [15].

Melidis (2015) studied the precipitation and adsorption treatment for defluoridation of wastewater generated from aluminium finishing industry. The precipitation was driven out by calcium hydroxide at pH 12.5 to reduce the fluoride content from 74.5±4.6 mg/l to 8.69±1.84 mg/l. Further, the residual fluoride from precipitation was treated by using hydroxyapatite (HAP) as adsorbent to reduce from 8.69±0.16 mg/l to 4.09±0.16 mg/l by 4g/l of adsorbent dose. The precipitation by Ca(OH)₂ removed approximately 88.36% of fluoride whereas HAP further enhanced the fluoride removal of 6.2% to obtain the overall fluoride removal efficiency of nearly 94.5%. The adsorption data fitted well with Freundlich ($r^2=0.992$) and Langmuir ($r^2=0.994$). The Langmuir maximum adsorption capacity of HAP was 12.4 mg/g. The adsorption on HAP was favorable for the mechanism ($R_L=0.62$). To meet the effluent discharge limit of 8 mg/l, the adsorption by HAP was used as a post treatment for removal of fluoride from aluminium finishing industry wastewater [16].

Manzola *et al.* (2015) used dicalcium phosphate dehydrate (DCPD) and lacunae hydroxyapatite (L-HAP) for the defluoridation process from aqueous solution and natural water of Koudoumawa. The fluoride removal capacity of

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DCPD at dose of 0.0174 g and 0.1012g were 26.37 mg/g and 9.81 mg/g respectively whereas defluoridation capacities of L-HAp were 18.96 mg/g and 8.0 mg/g at doses similar to that of DCPD. The DCPD optimum dose of 0.0623g/100ml was responsible for bringing down the fluoride level to 0.38 mg/l at pH 5.10 and contact time of 72 h, whereas L-HAp of 0.1012 g/100ml could bring down fluoride to 1.98 mg/l in the same condition of dose, pH and time. The L-Hap of 0.0527 g/100ml reduces the fluoride level of Koundoumawa natural water to 0.84 mg/l. The DCPD and L-HAp were used to remove fluoride by ion-exchange, adsorption process, dissolution, precipitation and co-precipitation processes [17].

IV. DEFLUORIDATION BY LIMESTONE/ CALCITE MATERIALS

It is mostly believed about the reduction in fluoride levels that occurs via precipitation as fluorite (CaF_2) in the presence of calcite (CaCO_3) [18-24].

Simonsson (1979) has investigated the technique of fluoride removal by a limestone particle in a fixed bed. The shape and size of the limestone particles remain unchanged after the conversion of fluoride to fluorite. The conversion of CaCO_3 to fluorite was dependent on the temperature. The reaction rate was affected by the presence of few cations in the wastewater. The rate of adsorption was initially dependent on the fluoride ion concentration, but at higher concentration of fluoride ion chance to formation of CO_2 may tend to occur which increases the hindering of the diffusion process of fluoride through newly formed CaF_2 layer and the reaction with the untreated lime [25].

Larsen and Pearce (2002) carried out defluoridation of drinking water by boiling with brushite (0.3-0.5 g) and the equivalent weight of calcite in 1 liter of water. The distilled water having a fluoride concentration of 5, 10 and 20 ppm were eventually reduced to 0.06, 0.4 and 5.9 respectively, while the Aarhus tap water with the same concentration were reduced to 1.2, 2.5 and 7.7 ppm respectively, due to the formation of organized crystallized apatite or settling of calcium salts. The runs without calcite gave results similar to that of calcite [26].

Turner *et al.* (2005) have investigated the fluoride removal by crushing limestone of 99% pure calcite by batch studies and surface-sensitive techniques for solution having fluoride concentration ranging from 3 to 2100 mg/l. The adsorption process from the aqueous system was based on combination of surface adsorption and precipitation and it was confirmed with the aids of surface techniques, such as atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) as well as zeta potential measurements. The removal capacity of fluoride was dependent on calcite surface area [27].

Jain and Jayaram (2009) used limestone (LS) and aluminium hydroxide impregnated limestone (AILS) for removal of fluoride in batch mode. The maximum fluoride removal capacity of LS and AILS were found to be 43.10 mg/g and 84.03 mg/g respectively. The optimum pH for maximum removal of fluoride was found to be 8.0. The adsorption results best fitted to Freundlich isotherm model and pseudo-first-order kinetic model for AILS. Fourier transform infrared (FTIR) studies refers that the adsorption of fluoride through AILS was physi-sorption in nature [28].

Gunawan *et al.* (2010) used calcite for removal of phosphate and fluoride from optoelectronic (TFT-LCD manufacturing) wastewater. The maximum phosphate adsorption capacity of 40.65 mg/g of calcite was achieved at pH 6.5. The fluoride removal of 85.2% was obtained by 10 g/l doses of calcite at pH 6.5 and regarded to be suited condition. The main mechanism of fluoride adsorption was precipitation and adsorption onto brushite and HAP [29].

Nath and Dutta (2010) have investigated the defluoridation capability of crushed limestones approximately 3-4 mm diameter for pre-acidified fluoride water by acetic acid (AA) and citric acid (CA) in batch study. The CA (0.05M) and AA (0.033M) reduced the fluoride concentration from 10 to 1.5 mg/l with a contact time of 12 hours without affecting the taste and odor of water having pH between 5.7 to 7.0 [30]. Further, they have studied the limestone defluoridation in a fixed bed reactor for fluoride water pre-acidified with edible organic acids, viz. Acetic acid (AA) and citric acid (CC). The fluoride removal process was enhanced by both the acid treatment such as AA and CC and removed upto 90% from 10mg/l fluoride containing distilled water and ground water. The reactions of fluoride removal involved precipitation as CaF_2 and adsorption on limestone. The presence of co-anions had little influence on the adsorption capacity and their influence was in the order of phosphate > sulphate > bromide > chloride > nitrate [31].

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Husain and Jha (2010) have investigated fluoride removal capacity of marble slurry from aqueous solution. The fluoride removal of 51-58 % was obtained by 15 g dose of adsorbent with 5 mg/l of initial fluoride in the pH range of 6.0 and 8.0 for a minimum contact time of 2 hours. The exhausted adsorbent was used for making construction products such as bricks, tiles, road sub-base, cement and door panels [32].

Turner *et al.* (2010) have studied the influence of phosphate (PO_4^{3-}) for the removal of fluoride by calcite. The fluoride was precipitated by calcite and phosphate in the form of fluorite, fluorapatite and hydroxyapatite. The presence of a small amount of phosphate approximately 17 mg/l could remove 20% of fluoride whereas 500 mg/l of phosphate was responsible for completely holding back the fluoride removal [33].

Bhagat (2011) has investigated the acid enhanced limestone defluoridation (AELD) technique by using citric acid that lowers the concentration of phosphate, nitrate and sulphate present in the ground water, which ultimately led to the benefit for defluoridation. But this technique was capable enough to increase the concentration of calcium from initial value of 0.72 mg/l to the range of 69-115 mg/l that were further beneficial for human health and could fulfill the demands [34].

Lakshminarayan *et al.* (2011) have studied the defluoridation potential of water with brushite-calcite and two bioadsorbent such as dried, ground neem and peepal leaves. A suspension of 0.5g of each brushite-calcite was added to 1 liter of distilled water with 5 ppm of initial fluoride concentration and boiled for 30 seconds. The 5ppm fluoride was reduced down to 1.2 ppm and 1.0 ppm after 90 minutes and 18 hours of contact time, whereas 10 g of bio-adsorbent packed in cloth, suspended in water reduced 5 ppm to 4 and 3.22 ppm after 90 minutes and 18 hours of contact time respectively. Hence, Brushite-calcite was preferred exclusively for defluoridation of water [35].

Nath and Dutta (2012) have studied acid-enhanced limestone defluoridation in column reactor by using oxalic acid (OA). The concentration of 0.1M OA removed upto 95% of fluoride with low residual oxalate and acceptable pH for drinking purpose. The adsorption mechanism involved precipitation of CaF_2 and adsorption on limestone [36].

Murutu *et al.* (2012) used limestone derived apatite (LDA) for removal of fluoride from drinking water in batch mode. The adsorbent was prepared by reacting with orthophosphoric acid. The adsorption reaction was endothermic in nature. The experimental data were quite suitable for Dubinin-Radushkevich and Langmuir isotherms with maximum adsorption capacity of 19.88 and 22.22 mg/g respectively. The effects of co-anions were negligible on adsorption. The kinetic study followed pseudo-second-order model with an activation energy of 225.4 KJmol^{-1} . The chemisorption mechanism governed adsorption process as well [37].

Saxena *et al.* (2013) have used limestone slurry impregnated fly ash (LSFA) catalyst for removal of fluoride in batch mode. The adsorption kinetic data followed pseudo first order rate model and adsorption equilibrium data followed Freundlich and Langmuir isotherm model. The Freundlich and Langmuir regression coefficient for 0.1 gmdm^{-3} of LSFA at 10 mg/l of initial fluoride concentration was 0.9892 and 0.9597 respectively. The impregnated limestone slurry did not leach out during the adsorption process any more [38].

Gandhi *et al.* (2013) have investigated chalk powder as adsorbent for defluoridation of water. The chalk powder simultaneously, mainly contained 86% of CaCO_3 , 43-47% of CaO and 35-37% of CO_2 . The high content of calcium in chalk powder helped in removal of fluoride. The fluoride removal of 83% was obtained at pH 5. The experimental data fitted well with Langmuir and Freundlich isotherm models as well as pseudo first and second order of kinetic models. The adsorption process was spontaneous and exothermic in nature [39].

Mondal *et al.* (2014) have studied the defluoridation of drinking water by calcite in acidic medium. The 0.05 M acetic acid treated with calcite having adsorption capacity of 75.6% as calcium ions dissolved into the solution provided more surface area for adsorption. Calcite of 7 g/l doses without treating with acetic acid removed 65.03% of fluoride and the pH of treated water was observed to be in the range between 6.7 and 7.4 [40].

Fufa *et al.* (2014) have investigated the defluoridation potential of gypsiferous limestone (GLS) from water. The fluoride removal of 59% was achieved from 11.28 mg/l fluoride bearing ground water of Kentiri at an equilibrium time

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of 24 hours without adjusting the pH of water. High fluoride removal of 89% was obtained in an acidic pH range of 3 and 5. The experimental results were captive with pseudo-first-order kinetics and Langmuir adsorption isotherms and the maximum Langmuir adsorption was found to be 1.07 mg/g. The defluoridation capacity of GLS was increased when calcined at 200°C for 4 hours. The regeneration of adsorbent was carried out by using 0.2M NaOH solution respectively[41].

Gogoi *et al.* (2015) studied the defluoridation of water by the addition of dilute phosphoric acid (PA) to the influent water before the limestone treatment. The defluoridation capacity of Pa-enhanced limestone was observed to be 1.10 mg/g when compared to 0.39 mg/g of bare limestone. The regeneration of spent adsorbent was carried out by simple scrubbing and rinsing with lime or NaOH. The adsorption mechanism involved precipitation of CaF_2 and adsorption by limestone [42].

V. DEFLUORIDATION BY CEMENT AND RELATED MATERIALS

Kagne *et al.* (2008) used hydrated cement (HC) for defluoridation of water that did not produce any chemical sludge and worked on a wide range of pH between 3 and 10. The optimum pH and dose of HC was found to be 6.9 and 10g/l. The experimental data fitted well for both Langmuir and Freundlich isotherm models. The Langmuir adsorption capacity was found to be 2.68 mg/g. The defluoridation was effective at acidic range due to the presence of alumina and loses its capacity in the alkaline range due to an exploring competition between OH^- and F^- ions. The chemisorption and precipitation were governed the adsorption process and the carbonate and bicarbonate ions were affected the fluoride adsorption whereas chloride, sulphate and nitrate had no effect on the adsorption capacity [43].

Park *et al.* (2008) have investigated cement paste granules filled column for simultaneous removal of fluoride, phosphate and nitrate in fluoridic acidic wastewater generated from semiconductor fabrication plants. The calcium and calcium phosphate or calcium aluminate phases of cement paste were responsible for the removal of contaminants in the form of fluoride. The removal of fluoride and phosphate was lower in MF column. The removal capacity of mixed fluoridic acid (MF) column was half of that in hydrofluoric acid (HF) column because the rate of calcium wasted in the effluent was twice higher in HF and removal rates were lowered by competition for calcium between fluoride and phosphate. The removal capacity of fluoride and phosphate in MF column was 1.67 $\text{m}_{\text{eq}}/\text{g}$ and 1.96 $\text{m}_{\text{eq}}/\text{g}$ respectively [44].

Ayoob *et al.* (2009) have investigated defluoridation capacity of alumina cement granules (ALC) from synthetic and natural ground water. The 2 g/l doses of ALC reduced the fluoride concentration in water from 8.65 mg/l to below 1.0 mg/l under optimal conditions. The fluoride adsorption capacity of synthetic and natural water was 3.91 mg/g and 0.806 mg/g at an initial fluoride concentration of 8.65 mg/l respectively. The maximum adsorption capacity was found to be 2.27 mg/g at a flow rate of 4ml/min. The adsorption had no significant effect on pH range of 3.0-11.5. The co-anions like sulfate, nitrate, chloride and bicarbonate had no effect on the fluoride adsorption whereas higher concentrations of silicates and phosphates reduced the fluoride uptake by ALC. The adsorption process was spontaneous and endothermic in nature. The chemisorptive ligand exchange reaction was involved between an inner-sphere complexes of F^- with ALC [45].

VI. DEFLUORIDATION BY BONE CHAR AND ALLIED MATERIALS

Bhargava and Killedar (1991) have investigated the defluoridation of water by using Fishbone charcoal in batch study. Bone char was created by crushing and heating bones which removes organic matter from the bone structure and left large internal surface area for adsorption process. The fluoride adsorption was directly dependent on the time and pH of the solution. The equilibrium fluoride concentration decreased with an increase in adsorbent dose. The fluoride adsorption capacity was poorly correlated with Langmuir and Freundlich isotherms [46]. Larsen and Pearce (1993) improved the efficiency of defluoridation by pre-treating the raw material as bone char with brushite and calcium hydroxide [47].

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Bregnhøj *et al.* (1995) studied the modeling of bone char columns for defluoridation of water. The adsorption capacity of bone char in column by the dynamic parameter was 3.5 and 6.6 mg/g for two different bone char materials. The results of modeling revealed that smaller grain sizes of the bone char made the fluoride sorption faster and higher hydraulic retention times or smaller flow velocities made the bone char more effective for the defluoridation [48].

Bhargava (1997) used 45 g Fishbone charcoal column at domestic level for defluoridation method. The adsorption capacity between 0.3 and 1.4 mg/g were achieved. The maximum adsorption occurred at low flow rate and high initial fluoride concentration [49].

Bhargava (2000) again used Fishbone charcoal in batch study for obtaining nomograph. The adsorption capacities between 0.05 and 0.65 mg/g were obtained depending upon the stirring time to bring down the initial fluoride concentration within permissible limit as prescribed by WHO [50].

Jacobsen and Dahi (1997) used bone char based bucket filter defluoridator for removal of fluoride from water in Ngurdoto village, Arusha region, Tanzania. The fluoride adsorption capacity of 1.1 mg/g was achieved by bone char of 10 kg filled in a 20 liter of the plastic bucket. The fluoride concentration of 8.5 mg/l was reduced to 0.37 mg/l approximately 95.6% within a period of two months. Further, the defluoridator reduced the fluoride concentration from 10.5 mg/l to less than 1 mg/l within the periods between 4 and 13 months [51].

Further, they have studied the effect of the addition of a small dose of calcium chloride to fluoride water prior to contact with bone char resulting into enhancement of fluoride removal capacity. The removal capacity of 3 mg/g was obtained by the addition of 100 mg/l of calcium to fluoride water at 2 hours of contact time and with a filtration velocity of 0.07 m/h in comparison to the adsorption capacity of bone char (0.9 mg/g). The regeneration of bone char was carried out by increasing the pH of water to 11 and allowing it to flow for few bed volumes. The useful regeneration capacity was 1.0 mg/g where in contradiction to it fluoride concentration was reduced from 10 to less than 1.5 mg/l [52].

Kaseva (2006) has optimized the regenerated bone char for the defluoridation of drinking water in Tanzania. The optimum regeneration was achieved out at 500°C for 2 hours and the smallest grain size particle of bone char was 0.5-1.0mm which could yield the best fluoride removal. The highest fluoride removal and adsorption capacity were 70.64% and 0.75mg/g, obtained by regenerating bone char at 500°C. The optimum dose and time for regenerated bone char for 0.5-1.0 mm diameter in jar test were 25g and 120 minutes, captive enough to reduce initial fluoride concentration of 21.26 mg/l to 11.26 mg/l at the stirring rate of 52 rpm with fluoride removal capacity of 0.55 mg/g. The column performance of bone char could even remove subsequently the fluoride within permissible limit of WHO [53].

Wei Ma *et al.* (2008) have investigated the fluoride removal capability of bone char (BF) in batch and column modes. The removal of fluoride by bone char was higher than tourmaline and activated alumina as per batch study. The fluoride removal capacity was increased with an increase in fluoride concentration and the adsorption mechanism involved an ion exchange between bone char and fluoride. The column study of bone char revealed that the removal efficiency was affected by factors such as flow rate and bed height. The model results and experimental data have a good consistency where the regeneration of bone char was carried out with 0.5% NaOH [54].

Korir *et al.* (2009) have investigated contact precipitation for defluoridation by dissolving bone char and calcium phosphate pellets. These chemicals were slowly released into the water for fluoride precipitation. The fixed bed laboratory experiments show that the mixture of materials can increase the filter uptake by a factor of 3 or more when compared to single bone char filtration. But small modification has to be done for the full scale community filters for field testing to reduce the phosphate concentration in the treated water [55].

Esayas *et al.* (2009) have studied about the household bone char filter performance developed by the Catholic Diocese of Nakuru (CDN), Kenya in villages of Ethiopia. The fluoride removal efficiency was observed to be satisfactory and below 1.5 mg/l. The lifespan of the bone char filters was limited due to high fluoride concentration in some ground sources which was upto 23 mg/l and hence regeneration of bone char or its replacement was done frequently and in the

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gentle way. To overcome this limitation, CDN and Eawag developed contact precipitation method. CDN had developed pellets containing calcium and phosphate and was added to the bone char to extend the lifespan of bone char filter [56]. Nasr *et al.* (2011) have used cuttlefish bone for removal of fluoride. The fluoride removal of 80% was achieved at pH 7.2 in contact time of 1 hour, 15 g/l adsorbent dose and 5 mg/l initial fluoride concentration. The presence of anions such as Chloride and sulphate had no effect on the adsorption capacity [57].

Gourouza *et al.* (2014) have used charred beef shoulder blade bones for defluoridation of water. The optimum dose of adsorbent was 8 g/l for removal of 60.27% and 10 mg/l of initial fluoride concentration within 180 minutes. The experiment results followed Freundlich isotherm and pseudo-second-order kinetic model. The adsorption process was spontaneous in nature and chemisorption by mechanism [58].

Rugayah *et al.* (2014) used chicken bone waste charcoal for defluoridation of groundwater in Indonesia. The fluoride removal of 67% was obtained by chicken bone charcoal when compared to cattle bone charcoal that had the efficiency of 77%. More bone charcoal was added for 3 ppm of initial fluoride concentration for achieving higher adsorption capacity at 12 hours of contact time [59].

Mutchimadilok *et al.* (2014) reported about Thai bone char for defluoridation of synthetic and ground water and compared it with Indian bone char. The Thai bone char was as effective as the Indian bone char for defluoridation except some social constraints found in Thailand. The Langmuir adsorption capacity of 0.841-1.18 mm size, bone char was 0.243 mg/g with co-efficient value $R^2=0.984$. Langmuir isotherm fitted well in comparison to Freundlich isotherm [60].

Teresaka *et al.* (2014) studied the removal of fluoride and methylene blue (MB) by bone char prepared at different temperature range. The bone char prepared at 400°C contain less char and high hydroxyapatite (HA) and could efficiently remove fluoride less than 1.5 mg/l along with MB. Thus bone char prepared at 400°C was used to remove fluoride and organic contaminants [61].

VII. DEFLUORIDATION BY EGGSHELL AND RELATED MATERIALS

Tantijaronroj (2009) has removed fluoride from water by using egg shell, activated carbon and rice husk ash in column study at 60 cm height of adsorbent for 10 mg/l of initial fluoride concentration. The fluoride removal efficiency of egg shell, activated carbon, rice husk ash and mixed adsorbent were found to be 61.8%, 53.4%, 42.5% and 62% respectively [62].

Bhaumik *et al.* (2012) have used eggshell powder as adsorbent for defluoridation of aqueous solutions and the maximum adsorption was achieved at a pH range between 2.0 and 6.0. The fluoride removal of 94% obtained at optimal conditions such as 5 mg/l of initial fluoride concentration, 2.4 g/100 ml of dose and 120 minutes of time. The experimental data was also fitted with Langmuir isotherm model and pseudo-second-order kinetic model. The chemisorption mechanism involved in adsorption and Intra-particle diffusion did not the sole rate controlling factor [63].

VIII. DEFLUORIDATION BY QUICK LIME, SLACK LIME, CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, CaSO_4 , $\text{Ca}_3(\text{PO}_4)_2$, BLEACHING POWDER AND PLASTER OF PARIS

Macintire and Hammond (1938) have used phosphoric acid, lime and HAP. These are beneficial for removing of fluoride ion. The HAP was also converted into FAP by replacing of F- anions and it was reconverted into Hap through the treatment with NaOH [64].

Huang and Liu (1999) have used CaCl_2 for industrial wastewater purification for reduced fluoride level from 742.3 mg/l to below 10 mg/l through precipitation of CaF_2 , followed by dispersed air floatation method. The amount of residual fluoride was 91.5 and 9.7 mg/l at pH of 2 and 3 or more respectively in these experimentations [65].

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Kassa *et al.* (2006) have used calcium based bentonite, and red clay for defluoridation from aqueous solution. The ion exchange capacity of the calcium-based bentonite and its original bentonite was also found to be 0.275mmol Ca²⁺/g and 0.013 Ca²⁺/g respectively. 80% of fluoride removal was achieved through calcium based bentonite for 5×10⁻³ mol/L of initial fluoride concentration in water while red clay removed 10.5% at the same concentration. The leaching of calcium ions had not taken place from modified bentonite and hence hardness of water had not increased [66].

Islam and Patel (2007) have investigated the activated and ordinary quick lime for removal of fluoride from aqueous solution. The fluoride removal was 80.6% for 50 mg/l of initial fluoride concentration at optimum condition and the Langmuir maximum adsorption capacity was 16.7 mg/g. The adsorption process was followed by first-order kinetics and Langmuir adsorption isotherm model. The chemisorption and precipitation phenomenon were leading to fluoride removal. The pH of treated water was increased and it was found above 12 due to quick lime. The presence of anions was reduced the fluoride adsorption in the following order, phosphate > sulphate > nitrate [67].

Gopal and Elango (2007) have investigated plaster of parish [CaSO₄.1/2H₂O] for removal of fluoride from synthetic water and the optimum dose was 1g/50 ml of fluoride solution. The saturation was achieved within 20 minutes. The removal of fluoride was 83.5% at neutral pH. The experimental data was also fitted to Langmuir isotherm and Freundlich isotherm model and Langmuir adsorption capacity of sorbent was 0.366 mg/g at 30°C. The adsorption reaction was spontaneous and exothermic in nature. The adsorption process was followed first order equation and it was involved three stage mechanisms such as external surface adsorption, intraparticle diffusion and final equilibrium [68].

Kagne *et al.* (2009) have used bleaching powder [Ca(ClO)₂] for defluoridation. 90% fluoride removal was obtained from 5 mg/l of initial fluoride concentration at an adsorbent dose of 100 g/l and pH of 6.7 within 60 minutes of contact time. The mechanism of adsorption was involved precipitation of fluoride [69].

Palishahjee *et al.* (2013) have also used bleaching powder for removal of fluoride from aqueous solution and the maximum fluoride removal was 91.6% at optimal conditions such as pH = 8.0, contact time = 8 hours, and dose = 0.7 g/l [70].

Zhang *et al.* (2011) have used calcium chloride modified natural zeolite for defluoridation of wastewater and removal efficiency of 94.3% as compared to untreated zeolite with 9.6% of removal efficiency at optimum conditions such as an adsorbent dose of 100 g/L, initial fluoride concentration 70 mg/L, contact time 6 h, initial pH = 6.0, temperature 25 °C. The maximum adsorption capacity was found to be 1.766 mg/g at an initial fluoride concentration of 100 mg/l. The kinetics results were best fitted to both pseudo-second-order kinetics and intra-particle diffusion models. The Langmuir and Freundlich isotherm models were suitable for adsorption method. The thermodynamic study revealed that the adsorption reaction was spontaneous and endothermic in nature. The presence of carbonate ions in the water was reduced the defluoridation capacity, whereas chloride and sulphate ions had no effected the fluoride removal efficiency [71].

Yang *et al.* (2012) have investigated fluoride uptake by various calcium phosphate minerals like hydroxyapatite (HA), octacalcium phosphate (OCP) and di-calcium phosphate dehydrate (DCPD) with polymeric additives from aqueous solution. The fluorapatite formation by dissolution and recrystallization have kinetics in the order of DCPD > OCP > HA. The polymeric additive like poly (ethylene imine), poly (acrylic acid) and poly (ethylene glycol) were significantly affected the fluoride uptake and also the fluorapatite formation. Poly (ethylene imine) inhibited the formation of fluorapatite which was overcome by ultrasound [72].

Mourabet *et al.* (2013) have used Apatitic tricalcium phosphate for removal of fluoride from aqueous solution. The maximum fluoride removal of 82.34% was achieved for 60 mg/l of initial fluoride concentration under the optimum condition such as 29 g of adsorbent dose, pH of 4.0 and temperature of 40°C. The experimental data were fitted well for Langmuir and Freundlich isotherms models and pseudo-second-order kinetic model [73].

Lawrance and Dsouza (2013) have used silica and calcium phosphate in 1: 1 and 1:2 ratios for defluoridation from aqueous solution. The combination of silica and calcium phosphate were also removed 100% of fluoride from water,

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chip in coast, not produced any hazardous residue in treated water and high calcium bearing calcium phosphate. The performance of fluoride removal was more than 1:1 from 1:2 combinations. The regression coefficients for Langmuir isotherm were 0.997 and 0.976 for 1:1 and 1:2 combinations respectively. The dose of 300 g was removed to be 80-90% of fluoride and equilibrium was reached in 45 minutes for 1:1 combination [74].

Mondal *et al.* (2013) have used *Aspergillus* and calcium pretreated *Aspergillus* for defluoridation from aqueous solution in batch study. The maximum fluoride removal was 65.06% and 91.96% for *Aspergillus* biomass (at pH 10) and Ca-pretreated *Aspergillus* (at pH 8) respectively. The experimental data were fitted with Freundlich isotherm and pseudo-second-order equation and the adsorption process was exothermic and it was spontaneous for both adsorbents [75].

Sivasankari and Arulanantham (2014) have investigated fluoride removal by powder and polymer-agglomerated granular tri-calcium phosphate (GTCP) from aqueous solution in batch study and the maximum fluoride was obtained at a pH range between 3.0 and 8.0. The equilibrium adsorption capacity of GTCP was 4.55 mg/g. The efficiency of fluoride removal was also increased with increase in adsorbent dose and contact time. The experimental data were fitted with Langmuir, Freundlich isotherms models and pseudo-second-order kinetics model. The optimal fluoride removal capacity was 2.1005 mg/g. The regeneration was achieved with 0.5% aluminium sulphate solution for 8 cycles without loss of efficiency. The presence of existing co-anions were decreased the fluoride removal in the order of following phosphate > bicarbonate > sulphate > chloride [76].

Mourabet *et al.* (2014) have removed fluoride by brushite from aqueous solution. The maximum fluoride removal was 88.78% under optimal conditions such as Initial fluoride concentration = 49.06 mg/l, pH = 5.36, adsorbent dose = 0.15 g and temperature = 31.96°C. The experimental data were fitted with Langmuir isotherm model and pseudo-second-order reaction and the Langmuir adsorption capacity was 36.260 mg/g at 313 K [77].

IX. CONCLUSIONS AND FUTURE PERSPECTIVES

Studies for the removal of fluoride fluoride from drinking waters for local utilization in the rustic territories where high concentration of fluoride in drinking water prompts various sick wellbeing impacts, utilizing a few adsorbents have been summarized briefly in this review. The adequacy of every adsorbent has been inspected and examined. The accompanying conclusions have been made on the premise of literature review. The method needed in the territories ought to be basic, simple to work and minimal effort with no or little upkeep separated from being eco-accommodating. This method is convenient and viable for the removal of fluoride from drinking water, simple to be worked by a non-specialized individual. Nano- adsorbents have been pulled in impressive consideration in the later years in fluoride removal and these materials have indicated higher fluoride uptake limit. In this way, the future research ought to be amassed in assessing the adequacy of adsorbents regarding expenses and possibility for removal of fluoride. It is advantageous to mull over the actual suitability involving various chemicals in order to recover the actual used adsorbents.

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BIOGRAPHY



Sanghratna S. Waghmare is working as a senior scientist at Environmental Materials Division, National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur. He has experience in condition assessment of RCC buildings and bridges using NDT and PDT techniques also engaged in development of building materials from wastes, design and development of instant houses and polymer composites from sisal fibers. Currently, he has been involved in defluoridation and carbon dioxide sequestration.



Tanvir Arfin is currently working as the Scientist at Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), India. Dr. Arfin has been actively engaged in research related to various fields of electrochemistry, defluoridation, platinum group materials, polymer science, membrane, hybrid materials, graphite oxides and biomass energy. He has published more than 25 scientific peers reviewed journal papers and 9 book chapters.