



Original paper

Characterization and optimization of calcium and phosphate based material for mitigation of fluoride in ground water

Kuljit Kaur¹, Vipin Kumar Sohpal^{2,*}¹Department of CHE, Beant College of Engineering & Technology Gurdaspur, Punjab India.²Department of Chemical Engg Beant College of Engg & Tech Gurdaspur, Punjab India.

ARTICLE INFO

Article history:

Received 15 March 2016

Received in revised form 28 April 2016

Accepted 11 May 2016

Keywords:

Fluoride

Water

Characterization

Kinetics and Hydroxyapatite

ABSTRACT

Water is essential part of life and quality of ground water control the adjudged that water is suitable for human consumption. The quality of ground water is mainly lower, virtue of reaction between alkaline elements with natural resources. Fluoride is one of the major alkaline elements that to lowered the water quality. So defluoridation of drinking water is the only possible option to overcome the problem of excessive fluoride in drinking water. Therefore, in this paper, we focused on synthesize a low cost eco- friendly technique for removal of fluoride in the ground water. The present study describes the synthesis of calcium and phosphate based material for removal of fluoride from groundwater. Characterization of the synthesize material performs with ICP (OES), XRD, FTIR shows that crystalline material of Hydroxyapatite. Kinetics study of fluoride removal from drinking water analysis is performed through jar test apparatus as a function of coagulant dose, pH of the solution, contact time, initial fluoride concentration and temperature. The highest percentage of removal of fluoride was 96 % observed when at initial dosing concentration 4mg/L, contact time 1hr and pH equal to 7.

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1. Introduction

Sustenance of life is reliant on the accessibility of sufficient quantity and quality of water. Apart from being an essential element of life, demand for usable water is increasing for several anthropogenic activities like industrial and agricultural activities. Out of entire quantum of water accessible on the planet, only 0.6 % is appearance of groundwater which serves as a major source of water particularly in the developing countries. The high dependence of groundwater is essentially credited to slow down treatment requirements as compared to surface water. Groundwater serves 80 % of drinking water requirements and 50% of the agricultural requirements in India. As more than half of the global population depends on the groundwater, the supply, and availability of water for drinking and other purposes has been a key apprehension for worldwide. This high dependence on groundwater in developing countries has emerged the exploration of deeper aquifers (Kasset et al. 2005; Aminaet al. 2004; Oren et al. 2004; Yaqout et al. 2003; Cano-Rodríguez et al. 2013; Liyonget et al. 2016) However, the quality of groundwater is relying on the geological factors as well as industrial activities. The confined aquifers may get contaminated by different dissolved alkaline and other heavy metals. The high rate of withdrawal of groundwater alters the water balance and disturbs the equilibrium resulting in leaching of these contaminants in water. The existence of various harmful contaminants like fluoride, arsenic, nitrate, sulfate, pesticides, other heavy metals, etc. in groundwater has been reported from different parts of India (Liu et al. 2005; Charles et al. 2005). Due to which the water sources have been furnish life-threatening not only for human consumption but also for other activities such as irrigation and industrial purpose. Therefore, now there is a necessity to focus greater attention on the future impact of water resources planning and development taking into consideration all the related issues. Contamination of ground water in India is largely attributed to geogenic inorganic pollutants such as fluoride and arsenic;

while arsenic problem exists in 3136 habitations; fluoride is endemic in 36,988 habitations (Ayoob et al. 2006).

Fluoride is a physically occurring element in both mineral deposits and geochemical deposits and enters food cycle through the water. Fluoride is unconfined into sub-soil water sources by the slow degradation of fluorine in rocks. These are important and are largely used in industries for the production of fertilizer, high grade of graphite, semi-conductors, electrolysis of alumina, and in nuclear applications (Lee et al. 2005). Fluorine compounds make up about 0.08 % of the earth's crust and concentration of fluoride in groundwater lies between 0.5 to 48 ppm habitations (Ayoob et al. 2006).

Many communities and localities are faced the fluoride contamination of groundwater supplies at levels higher than the permissible limit specified by the national and international authoritarian. The chemical nature of water is one of the nearly all criterions that determine its usefulness for a specific need and as such, all the waters are not fit for drinking. Hence, the problem of scarcity of drinking water arises (Rao et al. 2003). As per Indian standards, the desirable concentration of fluorine as fluoride ions in drinking water is <1 mg/L and the permissible limit is 1.5 mg/L. India is one among the 25 nations where biological problems arise due to the consumption of fluoride-contaminated water. Thus, contamination of fluoride in drinking water has acknowledged substantial attention due to its detrimental effects on health (Sharma et al. 2003; Fawell et al. 2006). World Health Organization guidelines (WHO) depict the fluoride concentration in drinking water not exceed 1.5 mg/lit (Murray. 1973). Various health problems observed with a changable concentration of fluoride from long-term use of fluoride-contaminated drinking water. Fluoride in drinking water has a profound effect on degradation of teeth and bones. 60 % of fluoride requirement for the human body is fulfilling by the utilization of drinking water. The occurrence of fluorosis in teeth and bones is enhanced by calcium lack and malnutrition due to be deficient in of nutrients like vitamin A or vitamin D and also low protein energy diet (Teotia et al.1994). Lower concentration range (1–1.5 mg/L) of

Corresponding author Email: vipan752002@gmail.com

fluoride enhance strengthens of tooth enamel, but on another hand/other hands higher concentration range 1.5–4 mg/L of fluoride ion, dental fluorosis occurs. With prolonged exposure to still higher fluoride concentrations (4–10 mg/L), dental fluorosis progresses to skeletal fluorosis (Fawell et al. 2006). Fluoride from water or wastewater can be impassive by an ion exchange/ adsorption process, coagulation or by precipitation processes. Most of the accessible materials for defluoridation are costly and technically non-feasible. The effectiveness of defluoridation using these techniques is reported to be 90% approximately (Mohapatra et al. 2009).

On the basis of published literature, the objective of study to optimize the low cost coagulant dose for Chemo-defluoridation unit. In addition to that evaluation and feasibility of fluoride exclusion using various process parameters such as initial fluoride concentration, coagulants dose, pH, and time and temperature coagulants in Jar test were also studied.

2. Materials and methods

AR grade chemicals were employed in this particular study of waste water. CaCl_2 has purity more than 98 % and di-sodium hydrogen orthophosphate having purity 97 % using for experiment purpose.

Batch experiments were performed at room temperature using the Jar test assembly (Phipps & Bird Stirrer Model-7790-402). Calcium chloride dehydrates ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was added along with di-sodium hydrogen orthophosphate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$) in spiked water with an initial fluoride concentration of 4 mg/L. Experiments were carried out in 1-L glass beakers, with a Jar test apparatus (Phipps & Birds Stirrer 7790-402). Jar test apparatus is equipped with the rotating stirring device consisting of paddles fitted with 77x25x2 mm size plate at the bottom of the shaft. The required quantity of Calcium and phosphate salts was added, and the solution was stirred at 100 rpm for 1min followed by stirring at 20 rpm for 20 min. After stirring flocs were allowed to settle for 20-30 min and treated water was analyzed for fluoride.

Solid Characterization: Solid Sample is prepared through mixing calcium chloride di-hydrate and di-sodium hydrogen orthophosphate di-hydrate in distilled water. Both salts are rapidly mix in one liter distilled water and jar test performed for 1min at 100rpm and then slow stirring at 20rpm for 20 min. The Ca/P salts were mixed in molar ratio 1.38 and 1.24. After settling of sludge for 1 hr sample is filtered by using 0.45 μm filter paper. Sludge is dried at 50 °C for overnight for further processing. The supernatant liquid was processed for residual calcium and phosphate in all the samples. The sample was analyzed for calcium, chloride, phosphate and sodium.

The chemical study of dried solids was performed for calcium and phosphorous content. The solid was accurately weighed and transferred to the beaker and concentrated nitric acid is added to the beaker, and heated to evaporate to 2-3 ml. After ensuring complete digestion, the volume was completed up with distilled water. The concentration of Calcium and Phosphorous was detected using ICP-OES (Thermo Fisher, iCAP 6300 DUO), with detection for Ca at 422.6 nm and phosphorous at 177.x nm. Fourier transform infrared spectroscopy (FTIR) and X-ray diffractometry (XRD) methods are used to determine raw materials, the structure of synthesized and heated powder, phase composition and functional groups.

2.1. Analysis

Fluoride The measurement of a concentration of fluoride ion in the sample was determined by using specific ion meter with fluoride ion selective electrode (ISE). Three-point calibration technique applied for initial calibration of the electrode using 0.1, 1.0 and 10.0 mg/L fluoride

standard solutions. The custom calibration of the electrode was carried out using commercially available 0.1mg/L, 1 mg/L and 10 mg/L fluoride standards. An aliquot of 1 mg/L fluoride standard solution, equal volume of commercially existing TISAB (whose pH was adjusted to 5.5) was added for maintaining pH. This avoiding any interference of complex ions such as Fe^{3+} , Al^{3+} , etc. and the electrode was dipped in this solution to record mV reading. The calibration of the instrument was carried out from time to time during the measurements and slope remains constant. In this study, the concentrations of the samples were calculated and read directly in mg/L range.

Calcium analysis: It is circumscribed by the EDTA method in an alkaline state, EDTA and its sodium salts form a soluble chelated complex including some metal ions. Calcium and Magnesium ions produce wine red color with Eriochrome black T in aqueous solution at pH 10.0 \pm 0.1. When EDTA is computed as a titrant, Calcium and Magnesium divalent ions get shared in the sharp change from wine red to blue which indicates end-point of the titration.

Phosphate analysis: It is included in acidic condition, by reacting orthophosphate with ammonium molybdate to form molybd-ortho phosphoric acid. It is further reduced to molybdenum blue by adding stannous chloride as a reducing agent. The blue color generates after addition of ammonium molybdate is measured at 690 within 10-12 minutes after the development of color by using blank. The concentration of the blue colored complex is measured which is directly proportional to the concentration of phosphate available in the sample. Sodium is determined by flame emission photometry at the wavelength of 589 nm. The sample is sprayed into a gas flame, and excitation is carried out cautiously controlled and reproducible conditions. The preferred spectral line is isolated by the use of interference filters or by an appropriate slit arrangement in light-dispersing devices such as prisms or gratings. The intensity of light is measured by a photo-tube potentiometer or another appropriate circuit/other appropriate circuits. The calibration curve is linear but has a tendency to levels off at higher concentrations. The calibration curve is prepared starting with the highest calibration standard and to work toward the most dilute, measure emission at 589 nm and concentration of sodium in a sample is determined from the calibration curve.

3. Results and discussion

3.1. Solid characterization

The digested solid samples were analyzed for Calcium and Phosphorous using ICP-OES. Calcium and Phosphorous salt ratio in weight were varied from 1 to 3.5 to understand effects on sludge formation in calcium salt-limiting condition. Solids formed during the reaction was weighed, digested and analyzed for Calcium and Phosphorous using ICP-OES. Table 1, lists the weight of solids digested for varying calcium and phosphorous weight ratios. The average Ca/P ratio is 2.15. Each mole of hydroxyapatite contains 5 moles of calcium and three moles of phosphate resulting in a Ca / P molar ratio of 1.667 and Ca/P weight ratio of 2.16. Under the Phosphate limiting conditions the residual calcium in the supernatant liquid was observed to increase while the Ca/P ratio remained the same and only decreased the quantity of HA produced. Table1, Indicates the residual concentration of calcium and phosphorous in the filtrate after the sludge/solids have been removed. As the Ca/PO_4 ratio an increase indicating the increase of Ca in the liquid, the residual calcium also increases while phosphate is completely consumed for the formation of solids. The stoichiometric weight ratio of Calcium salt and Phosphate salt for the formation of HA is 1.38. The solids were dried and further characterized using FTIR and XRD.

Table 1. Weight of solids digested for different calcium and phosphorous weight ratios.

Ca / PO_4 Weight Ratio	Wt. of sludge digested	Ca / P weight ratio
1	0.2919	2.17
1.5	0.2362	2.15
2	0.184	2.12
3.2	0.1237	2.23
3.3	0.1207	2.14
1.67	0.0853	2.1

3.2. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the solids obtained after filtration for different initial Ca/PO_4 weight ratio of 1.38, 3 and 3.3 is shown in Fig. 1. The

spectra can be divided into four regions with peaks having wave number around 3600, 1420, 1100 and 600 cm^{-1} . The double peak near 600 cm^{-1} is attributed to the bending of P-O bonds in phosphate group with contribution from $-\text{OH}$ at about 630 cm^{-1} . In the spectra, a band

from 3400–3700 cm^{-1} is observed indicating the occurrence of hydroxyl group attached to the solid. There is no variation in the IR spectra with the rise in the Ca / PO_4 ratio from 1.38 to 3.3 indicating no change in

the IR absorption characteristics of the solids (Arsad et al. 2011; Nedunchezian et al. 2015).

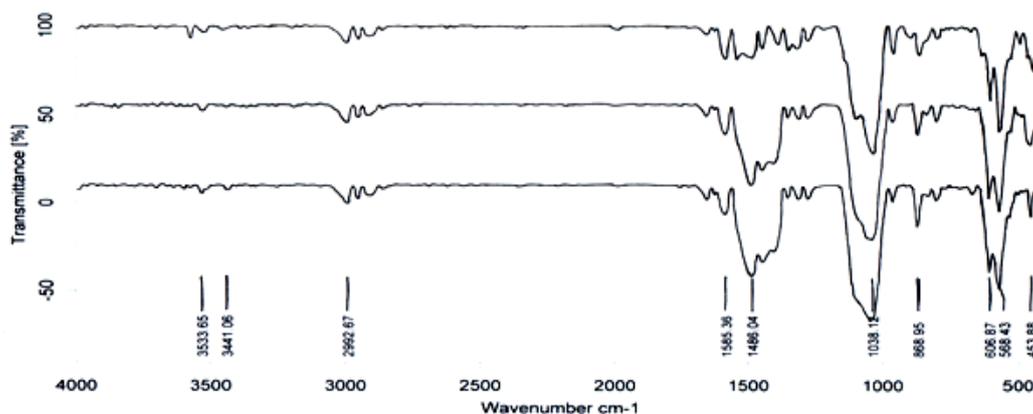


Fig.1. FT-IR spectra for different Ca/PO_4 weight ratio.

3.3. X-Ray diffraction

XRD pattern was recorded using $\text{Cu-K}\alpha$ radiation from 10 – 90 $2\theta^\circ$. Two high-intensity peaks located at around $2\theta = 26^\circ$ and 32° with $\text{Cu-K}\alpha$ radiation are observed. The peak data was compared with the standard JCPDS file and match was obtained for Hydroxylapatite. The XRD diffraction pattern shows excellent accord with the diffractogram of Hydroxylapatite. There was no peak observed with 11 degrees eliminate the existence of Brushite. Results of X-Ray diffractometry for dried solids are shown in Figs. 2 and 3. The solid samples were aged for 60 days, and the XRD phase analysis was performed. Figure 2 shows the comparison of the fresh and the 60 days aged samples.

Diffraction pattern was similar for the fresh and aged samples with same significant peaks at around $2\theta = 26^\circ$ and 32° . The 60 days aged material confirms the presence of HA and no phase change is observed

(Arsad et al. 2011). Fig. 3 represent the diffraction pattern of solids produced by the adding together of different weight ratio of Calcium and Phosphate salt. The XRD spectra of all the samples at room temperature confirm the presence of HA with no deviation in the high-intensity peaks with the change in initial Calcium and Phosphate salt ratio. The relative peak intensity of the entire major and minor peak obtained in all the samples matched with the relative peak intensity of standard HA compared with the standard JCPDS file. Material characterization results indicate the Hydroxylapatite production by incorporation the calcium and phosphate salt. There was no evidence of other material being produced along with HA even with the either of the salt-limiting conditions. There is also no evidence of the presence of other salts like brushite and calcium carbonates which usually are co-precipitated (Adak et al. 2011).

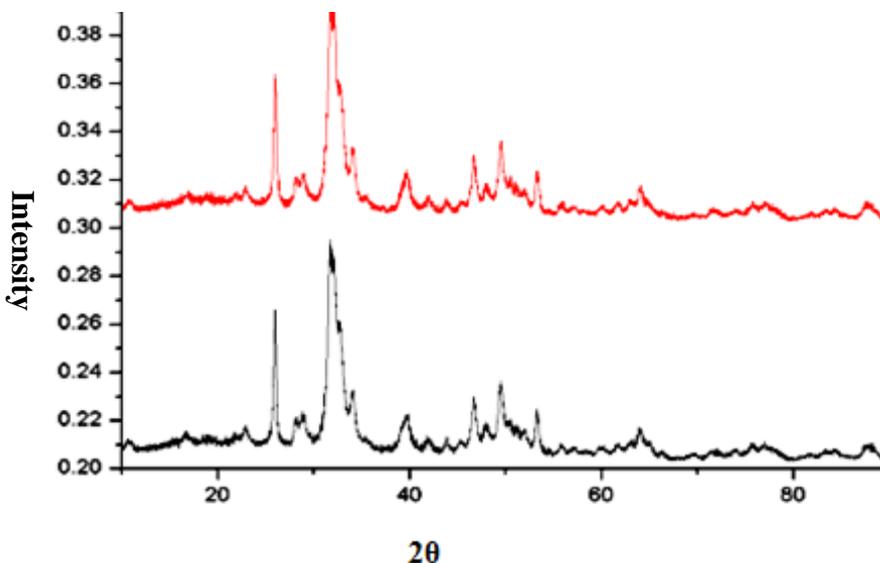


Fig. 2. Comparison of XRD pattern with standard JCPDS with Hydroxylapatite at lower intensity.

3.4. Fluoride uptake

Fig. 4, shows the final fluoride concentration after each batch experiment at increasing Ca/PO_4 weight ratio with an initial fluoride concentration of 4 mg/L . It is observed that the residual fluoride concentration after equilibrium elevates with the increase in the weight ratio. The residual fluoride concentration is constant beyond 6, Ca/PO_4 ratio indicating insufficient solids formation for the fluoride removal. The experiments were conducted for Ca/PO_4 ratio of 1 to 6 and the solid

generation was calculated. Fig. 5 shows the residual fluoride concentration and precipitate formation with respect to varying Ca/PO_4 ratio. It shows the concentration of residual fluoride is inversely proportional to the precipitate formation. Increasing ratio of Ca/PO_4 results in the phosphate limiting conditions in the solution. It results in the diminish of HA formation. Maximum of Ca/PO_4 ratio of 4 can be used in order to reduce the concentration of fluoride from 4 mg/L to less than 1 mg/L (Marriappan P and Vasudevan T. 2002).

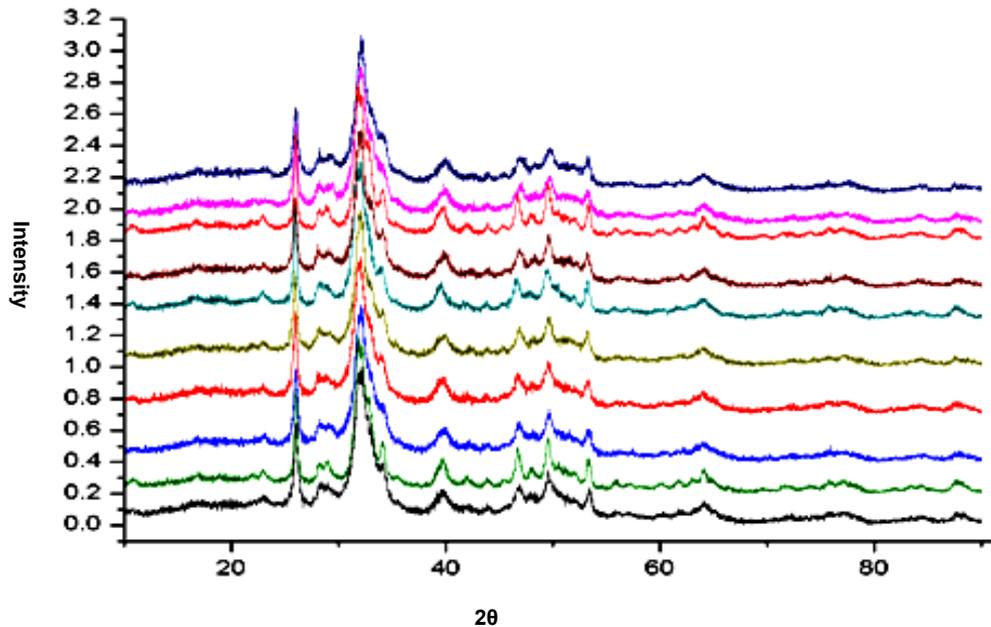


Fig. 3. Comparison of XRD pattern with standard JCPDS with Hydroxyapatite at higher intensity.

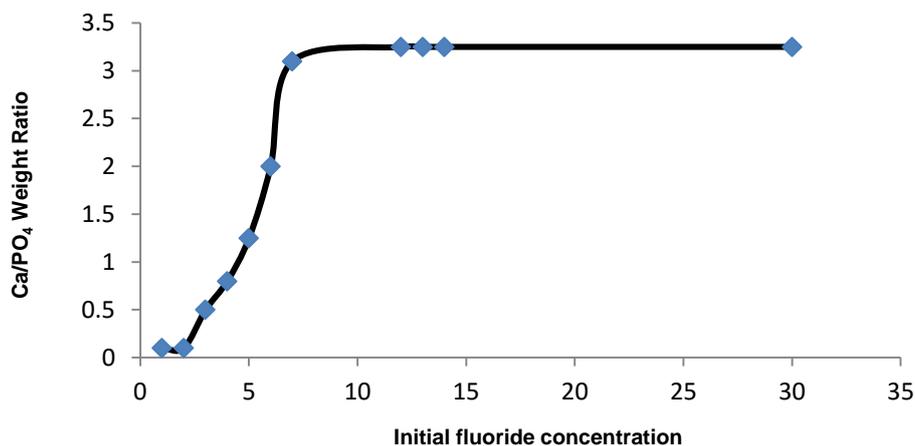


Fig. 4. Ca/PO₄ ratio vs. fluoride concentrations uptake profile.

4. Conclusions

The present study the calcium and phosphate salts are mixed in water for defluoridation and solids formed in the process are characterized by ICP (OES), XRD and FTIR. The Ca / P molar ratio observed in the range of 1.667- 2.16. It indicates the instant formation of Hydroxyapatite in the water after mixing Calcium and Phosphorous.

The comparison of the peak data with the standard JCPDS file confirmed the presence of Hydroxylapatite. It is concluded that optimum Ca/PO₄ weight ratio of 4 that can down the concentration of fluoride from 4 mg/L to less than 1 mg/L. The removal of fluoride below 1 mg/l of permissible limit was achieved with the settling time of 1 hr after rigorous stirring and results confirm the in-situ formation of Hydroxylapatite.

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