New Ceramic Nanocomposite Filters for Fluoride Removal using Acacia Waste

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***Abstract*— Present work elaborates the development of energy efficient gravity dependent ceramic water filtration system, capable of removing fluoride (>90%). These new filters are constituted with natural organic waste material (sawdust and Pods of American Babool) with in-house prepared hydroxyapatite and local pond sand. Therefore, a low cost solution has been provided with simple preparation of such filters via precipitation and dissolution procedures using all three components.**

The water filtration occurs through a quasi-static gravity based water filtration system. This paper exemplifies the ceramic materials, prepared using distinct permutations of pond sand and unused organic materials. Acacia waste is an important ingredient, obtained from Prosopis Juliflora or Mesquite or Vilayati Babool in India, which covers the large areas in most of the arid and semi-arid regions of India. The pods have piper dine alkaloid structures with high surface area to adsorb fluoride efficiently. These filters are appropriate for rural and remote areas because of its low cost, easy operation and handling.

Keywords- Fluoride, HAP, Sintered, Removal, Filtration, Cost, Water, Prosopis Juliflora

I. INTRODUCTION

The importance of water for the existence of human society is necessary. Groundwater is the major source of drinking water in both urban and rural India. The quality of available ground surface water in India is not par with the drinking water quality requirements.[1] Water becomes contaminated with geogenic impurities (Table 1). High concentration of fluoride can lead to fluorosis, which is normally found in Asian region. Nine states of India have higher fluoride content in ground water (ranging 1.5-20 ppm) than the permissible limit given by WHO, which affects human health through irrigation.[2] In previous report, we developed a low cost gravity based water filtration system to remove fluoride from ground water, composed of local waste product of acacia (Prosopis juliflora), pond Sand, sesame saw dust, water and calcium hydroxyapatite.[3] This ceramic system was fabricated using distinct permutation of pond sand, calcium hydroxyapatite and organic materials as an alternate of Reverse Osmosis (R.O.). R.O. wastes almost 80-90% of inlet water and uses electricity. Similar efforts were made to develop an efficient and selective route for arsenic sensing and removal.[4]

Table 1 Major chemical contaminants of water in India and its local spread[1]

S. No.	Pollutant	States	District
1	Fluoride	9	37
2	Salinity (inland)	5	12
3	Salinity (coastal)	4	11
4	Nitrate	12	68
5	Chloride	5	17
6	Arsenic	1	4
7	Sulphide	1	3
8	Iron	7	26
9	Zinc	3	6
10	Chromium	1	1

Table 1 shows the number of states and districts affected by various impurities in ground water. Fluoride is second major pollutant after nitrates in ground water, affecting 37 districts of India.

Materials and Methods

Pods and seed of acacia plant (Prosopis Juliflora), Pond Sand, Seasam saw dust and Calcium Hydroxyapatite were used for the fabrication of such ceramic filter filters for fluoride removal.

Prosopis Juliflora

Prosopis Juliflora is commonly known as Mesquite or Vilayati Babool in India, found over large areas in most of the arid and semi-arid regions of India. Its pods have piper dine alkaloids which reduces Total Dissolved Solids (TDS) and its charcoal is of high quality than normal charcoal. Therefore, it acts as a good water purifier.[4,5] In peninsular India, more than 80% felled tree of Prosopis Juliflora is commonly used for charcoal production.[4] The tree provides alternative livelihood security during the severe drought periods, as its pods are the rich source of fragmented sugar. Prosopis

Juliflora seeds are polysaccharides that are known as galactomannan, also called Prosopis Juliflora pods powder (Fig. 1).

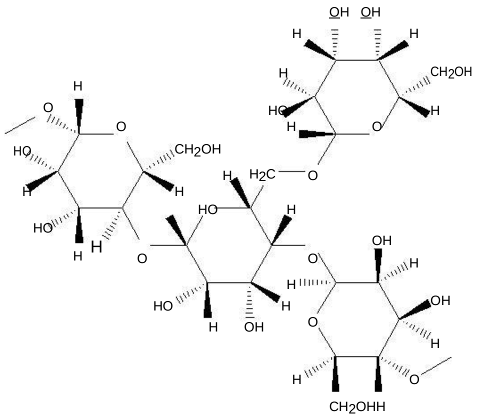

Fig. 1. Structure of Galactomannan from Prosopis Juliflora

Pond Sand

Sand is the main entity for making fluoride removal filter system due to its mild adhesive properties, strength and thermal stability. The controlled addition of water to the composite mixture was required to prepare the mold.[1]

Sesame Saw Dust

Sesame saw dust is used to create pores in the filters to improve water penetration. These pores get filled with charcoal during calcinations to absorb the inorganic impurities from ground water.[5]

Calcium hydroxyapatite

Calcium Hydroxyapatite (CaHAp) is a major inorganic component of bone. Its porous structure offers high binding affinity towards the absorption of fluoride content in drinking water.[6] The chemical reaction to synthesize CaHAp by co-precipitation is given below-

$$10Ca(OH)_2 + 6H_3PO_4 \longrightarrow Ca_{10}(PO4)_6(OH)_2 + 18H_2O$$

$$10Ca^{+2} + 6PO_4^{-3} + 2OH^- = Ca_{10}(PO4)_6(OH)_2$$

$$pH = 10.5 \quad \downarrow\uparrow$$

$$H_3PO_4 + H_2O$$

II. RESULT AND DISCUSSION

X-ray diffraction technique was used to identify the phase composition and crystallinity of the calcium hydroxyapatite compounds. FT-IR spectra were recorded to determine the shifting of peak position after and before fluoride absorption. The surface morphology and element detection in powders have been established from SEM and EDAX data. TGA analysis was performed to measure the percentage weight loss and quality of powder samples.

XRD analysis: The structure aspects of nanocomposites were analyzed by X-ray diffractometer (XRD, Bruker D8 advance, Cu Kα radiation (λ = 1.54056A°) as a X-ray source, operated at 40 mA in the range of 2θ = 10–90°). Crystalline sizes of all materials were measured using Scherrer equation (see Table 2). The XRD patterns of the analyzed samples are shown in Figure 2. Pond sand and calcium hydroxyapatite showed high crystallinity.

Table 2. Variation of crystalline size of raw materials which used for preparation of ceramic filter

S. No.	Material	Crystalline Size (Scherrer)
1.	Pond Sand	388.9 A^{O}
2.	Calcium Hydroxyapatite	311.3 A^{O}
3.	Pods of Prosopis Juliflora	57.3 A^{O}
4.	Seeds of Prosopis Juliflora	35.5 A^{O}

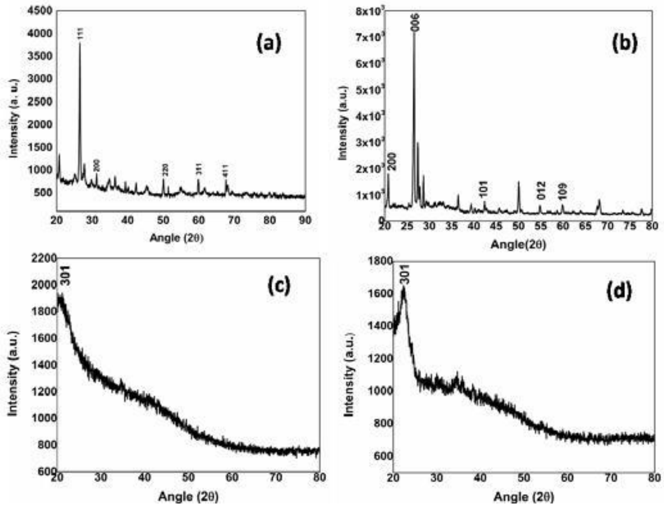

Fig. 2. (a) Pond sand (b) Calcium hydroxyapatite (c) Sesame saw dust (d) Prosopis juliflora

FTIR analysis:

Fourier-transform infrared spectra (FT-IR) of the CaHAp powder were recorded on a Vertex 70v Bruker spectrometer at 400–4000 cm^{-1}, using KBr as a reference (Fig. 3). The measurements were performed in the transmission mode with spectroscopic grade KBr pellets for all the CaHAp powders.

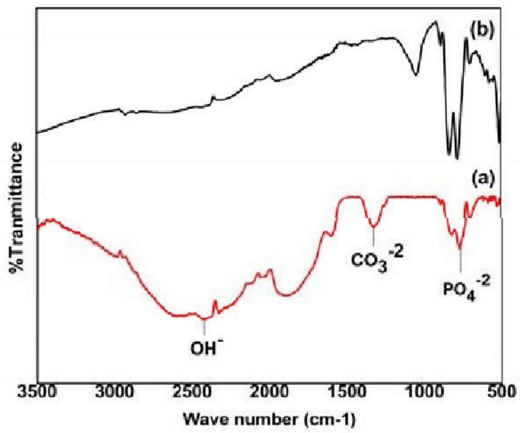

Fig. 3. FTIR spectra of CaHAp (a) before and (b) after fluoride adsorption

FT-IR analysis represents vibration band of different functional groups at 603, 1451 and 2565 cm^{-1} of the $PO4^{-3}$, $CO3^{-2}$ and OH^-, respectively (Table 3). A strong peak at 2565 cm^{-1} was identified to the O-H vibration. After, fluoride treatment of CaHAp, the intensity of O-H peak decreases due to its exchange with fluoride.

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Table 3. Functional group assignments for calcium hydroxyapatite nanoparticles in FT-IR spectra.

S.No.	Polar Functional group	Stretching / bending / vibration mode	Wave number (cm-1)
1.	OH^-	Stretching	2565
2.	CO_3^{2-}	Asymmetric stretching	1451
3.	PO_4^{3-}	Asymmetric bending vibration	603

SEM AND EDAX analysis- Nanocomposites surface morphology was studied using scanning electron microscopy (SEM, EVO18 special edition Carl Zeiss) with an accelerating voltage of 20 kV. The SEM samples were prepared by dispersing the particles in ethanol and applying the resulting suspension on aluminum tape.

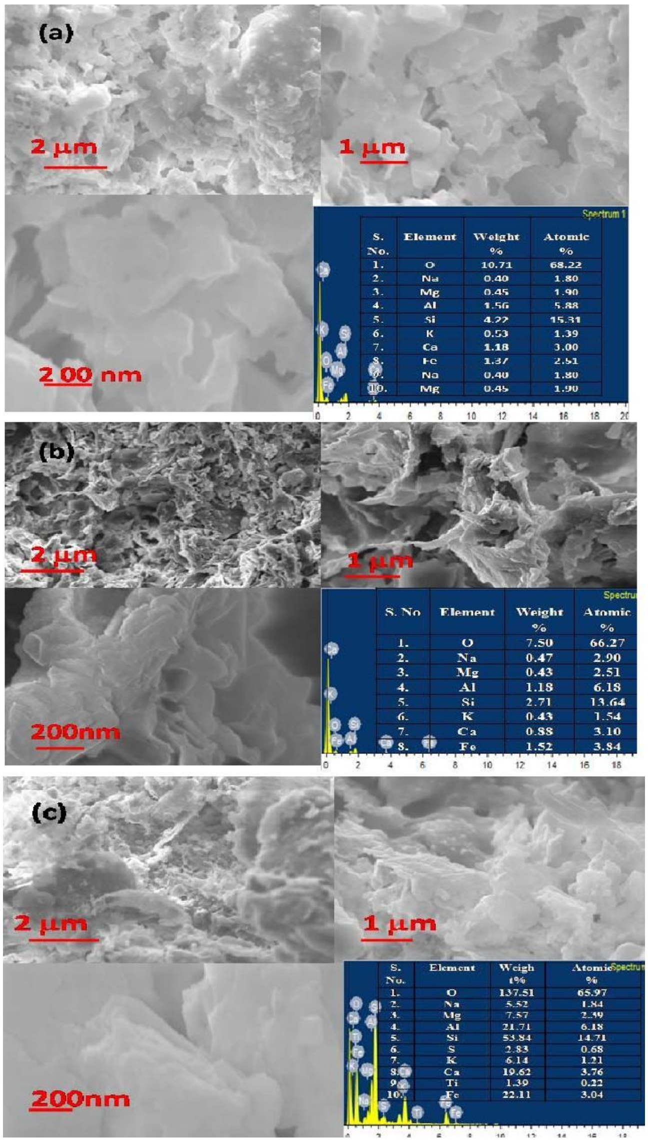

Fig. 4. SEM and EDAX analysis of (a) Pond sand (b) Sesam saw dust (c) Prosopis juliflora (pods) (d) Prosopis juliflora (seed) (e) CaHAp

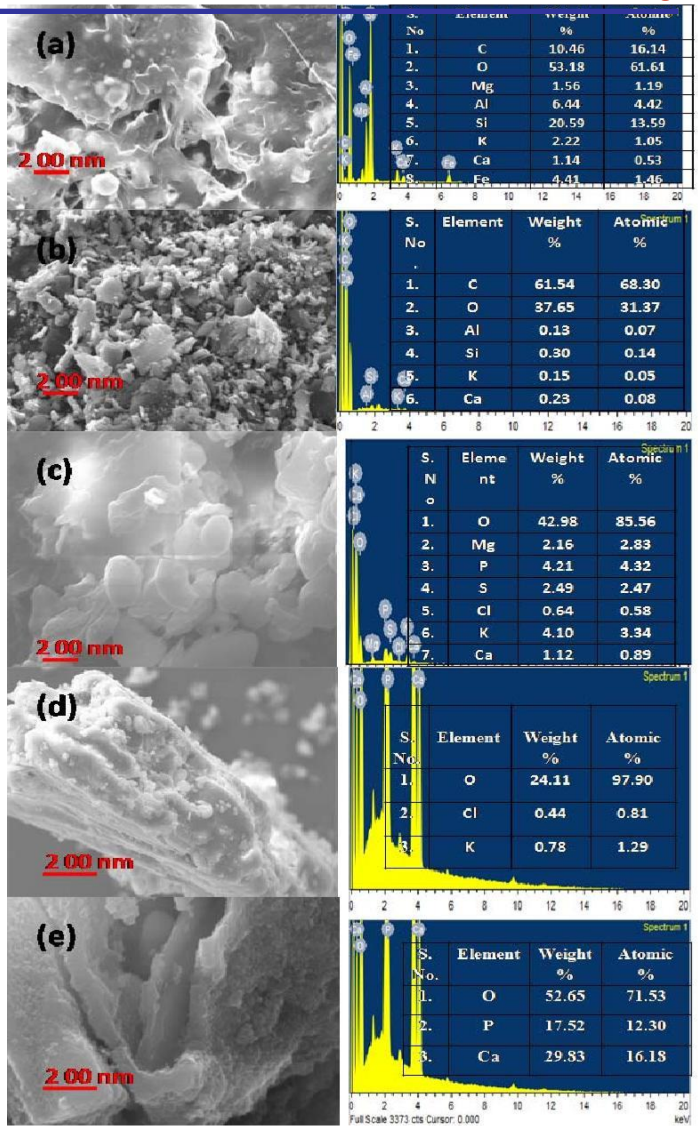

Fig.5. SEM & EDAX analysis of (a) Pot-1 (b) Pot-2 (c) Pot-3

Initially, SEM and EDAX data were recorded for the raw materials (Fig. 4). The surface modifications and change in elemental composition of ceramic filter raw material before and after fluoride sorption were studied at 200 nm magnification (Fig. 5). Similarly, the morphologies and elemental composition in different type of fabricated pots after fluoride absorption were ascertained. The EDAX spectra evidenced for fluoride sorption by the change in elemental compositions of fabricated ceramic filters.[2]

TGA analysis: TGA analyses were performed on a TGA-6000 thermal analyzer (Perkin Elmer) under a nitrogen atmosphere and a heating rate of 10 ºC min^{-1}. TGA analysis was performed to determine the percentage weight loss of different raw material content of ceramic pot filters (Fig. 6). The details are given in Table 4.

In Fig. 10, percentage weight loss was found for CaHAp (10.77%) and CaHAp-F (4.30%). Due to the replacement of volatile water molecules and increase the effective ionic interactions with hydroxyapatite by fluoride, observed less weight loss in fluoride adsorbed CaHAp.[1]

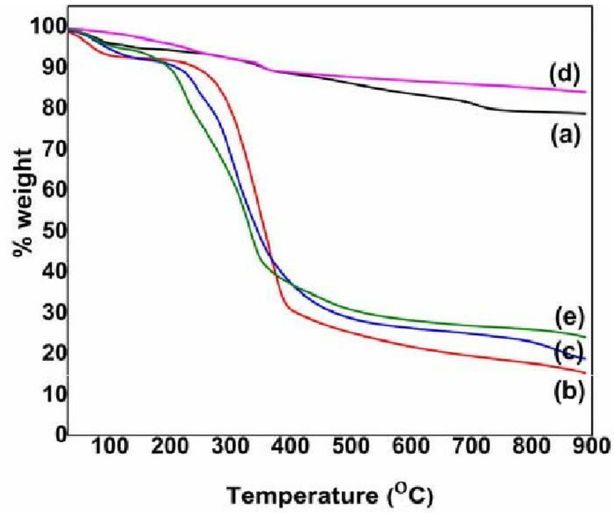

Fig. 6. Thermogravimetric analysis (a) Pond sand (b) Sesame saw dust powder (c) Prosopics juliflora (Pods) (d) CaHAp (e) Prosopis Juliflora (seed)

Table 4. Percentage weight loss in various content of ceramic raw material

S.N0.	Sample	% Weight loss
1	Pond sand	21.19
2	Seasam saw dust	84.77
3	Prosopis Juliflora (pods)	75.94
4	Prosopis Juliflora (Seeds)	81.20
5	Calcium hydroxyapatite	12.52

The reduction in weight loss of ceramic filters could be due to the replacement of volatile water molecules by fluoride and effective ionic interactions (Fig. 7). Comparative percentage weight loss is given in Table 4. Maximum weight loss in raw material of ceramic filters was observed around 30-500 ºC.

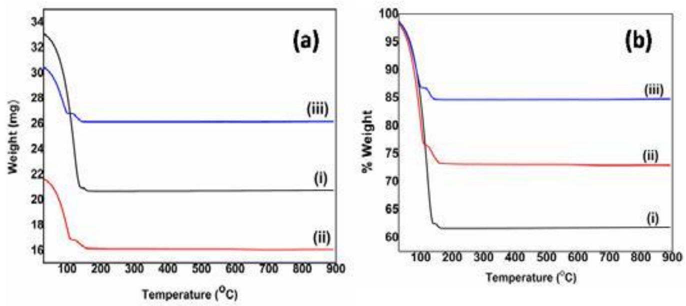

Fig. 7. Thermogravimetric analysis of (a) pot-1 (b) Pot-2 (c) Pot-3

Table 5. Thermogravimetric analysis of percentage weight loss for ceramic pot filter

S.N0.	Sample	% Weight loss
1	Pot-1	38.04
2	Pot-2	26.82
3	Pot-3	15.18

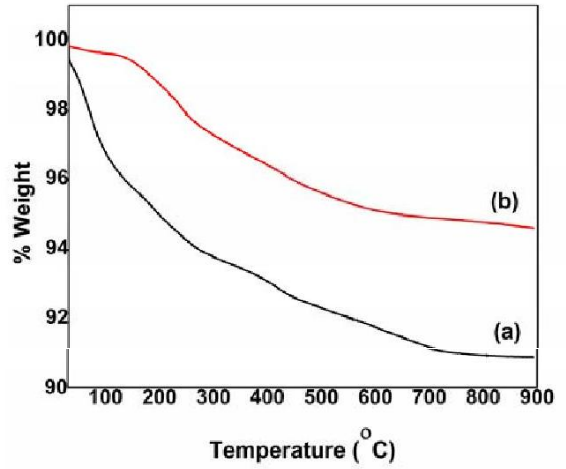

Fig. 8. Thermogravimetric analysis of CaHAp (a) before (b) after fluoride absorption

III. CONCLUSION

In conclusion, new ceramic filters were designed using easily accessible local materials and tested for their fluoride adsorption capacity. The fluoride content of ground water could be reduced upto 98%. Synthesized CaHAp powder was considered as the most efficient absorbent by removing upto 95 % fluoride due to its high affinity towards the fluoride ion.

IV. EXPERIMENTAL SECTION

Calcium hydroxyapatite nanoparticles were synthesized from calcium hydroxide and orthophosphoric acid (Fig. 9). The pH of the reaction mixture was maintained at 10.5 by the drop wise addition of ammonia solution. The mixture was stirred for 48 h at 2000 rpm. A white precipitate of calcium hydroxyapatite was formed, which was separated, dried and washed with ethanol.

Preparation of calcium hydroxyapatite –

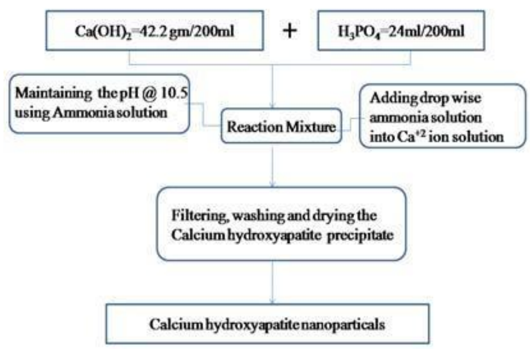

Fig. 9. Flow chart of calcium hydroxyapatite nanoparticals by wet chemical route

Table 6. Percentage composition of raw materials used for fabrication of ceramic pot filter

S.No.	Pond Sand (gm.)	Sesam Saw Dust (gm.)	Powder of pods (gm.)	Powder of seeds (gm.)	CaHAP (gm.)	Water (ml)
1.	276	73	34.98	0	0	240
2.	276	73	0	17.5	17.5	420
3.	276	73	0	34.9	0	340

Preparation of Filters

Pond sand and sesame sawdust were mixed in an optimized 1:1 ratio by volume.[3] In this composition, 10% powdered pods of Prosopis Juliflora were taken. Water was added accordingly to obtain a paste. The resulting paste was taken in male pattern for molding and designing the filters by applying 20 psi pressure with female pattern. Further, sterile plastic sheet is used to remove the mold thus formed during this process. This wet mold is known as the "green ware".[1] For second filter, the composition of materials were same as first but 5 wt% calcium hydroxyapatite and 5 wt% powder of seeds of Prosopis Juliflora were added. The third filter contained 10 wt% powder of seeds of Prosopis Juliflora with no CaHAp.

Fig. 10. Schematic flow process chart for the fabrication of pots by the using of various natural raw materials

The greenwares are air dried under sunlight for 4 h, and heated to 100 °C for 15 minutes to remove water molecules trapped in the greenware mass. A three step sintering process is charted. After this, the greenware were heated at 250 °C for 1.5 h in a box furnace. As the temperature approaches to 400 °C, the greenware turns black in color due to the combustion of organic materials. The rate of heating is 20 °C/min. The temperature is raised to 500 ^{0}C and left for another 1.5 h. Finally, the greenware is heated to approximately 800 °C for 6 h (Fig. 10). The gravity based ceramic composite water filter wares were used for water filtration (Fig. 11). The wares of specific mixture composition were saturated with water by dipping them in a water bath containing purified water for about 12 h. The filtration rate was dependent on the porosity of the filter, which could be increased by adding more the saw dust content during fabrication. The porosity of these filters could be increased from 36% to 47% and pore size varied from 10 nm to 100 nm by taking the sand and saw dust in 3:1 volume ratio.[2]

Drying, Heating and Saturating of Filter

50 mL of water sample having different concentration of fluoride was mixed with 500 mg CaHAP in a conical flask. The mixture was shaken for 30 minutes at 150 rpm and filtered. The fluoride concentration in filtrate was measured by an auto titrator. Calcium hydroxyapatite reduced the fluoride content in water upto 90-95% (Table 7). Calcium hydroxyapatite powder was found to be an efficient fluoride absorbent.

Fig. 11. Images of ceramic pot (a) Green ware (b) After calcinations at 800 °C for 5 h (c) After saturation

Experimental Procedure

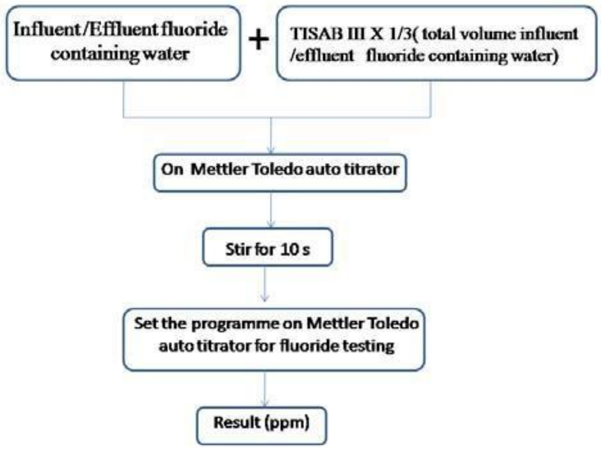

Fig. 12. Experimental setup for estimation of fluoride content in inlet and outlet fluoride contaminated drinking water

Table 7. Percentage fluoride reduction efficiency with Calcium hydroxyapatite

S.No.	NaF (ml)	CaHAp (mg)	Inlet fluoride (ppm)	Outlet fluoride (ppm)	Reduction in fluoride (%)
1.	50	500	9.863	0.938	90.48
2.	50	500	7.214	0.636	91.17
3.	50	500	10.173	0.643	95.30

Systematically parameters such as flow rate, initial concentration of fluoride ion and the amount of the adsorbent required to reduce the fluoride ions from drinking water were measured for different type of pots. The results are shown in Table 8.

Table 8. Fluoride adsorption study with different type of pots

S. No.	Pot description	Inflow Fluoride (ppm)	Effluent Fluoride (ppm)	Percent Fluoride Reduction (%)	Water Filtration Rate (ml/min)
1.	Pot-1	10.70	0.28	97.38	2.1
2.	Pot-2	10.70	0.15	98.50	3.7
3.	Pot-3	10.70	0.39	96.35	4.4

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