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Local material composite sintered systems for fluoride removal

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ABSTRACT

The article elaborates the development of gravity-based water filtration systems capable of removing fluoride using natural organic material. In this study, the precipitation and dissolution reaction occurring in suspension of hydroxyapatite (HAP) as addition of fluoride were investigated under well-defined condition. This process is set to occur in a quasi-static gravity-based water filter system. This system is a (pond sand, organic material (gaur seed powder, neem, sesame sawdust, and Ayurvedic waste), water, and HAP mixture) composite ceramic. This article illustrates these ceramic material systems manufactured using distinct permutations of pond sand and organic materials. HAP is introduced into the composite mix of pond sand and organic materials to manufacture some of the sintered ceramic filtration material systems tested here. The fluoride removal efficiency of these variant systems is discussed. The energy dispersive X-ray spectroscopy studies of the ceramics provided the mineral content within the system variants. At high temperatures beyond 600°C, the sintered hydroxyapatite is observed to have a microstructural transformation from amorphous to crystalline. The surface properties of these sintered as well as raw materials used in the production of the ceramic composite are also investigated. A mathematical multivariate regression model is derived providing a relationship between the effectiveness of the water filtration systems as a function of the raw material composition and properties. The Ayurvedic waste material was found to be a good substitute for HAP for fluoride removal. The proposed treatment system is appropriate and suitable approach for fluoride removal in rural areas, because of its simplicity and easy operation and handling. Since Ayurvedic and organic waste materials are easily available at low cost, the proposed method is very suitable for the people living in low-income rural areas of developing countries like India.

Keywords: Fluoride; Ayurvedic; HAP; Sintered; Removal; Filtration; Cost; Water

1. Introduction

The water availability, quality, related sanitation problems, and mortality are very high in India. This scenario is appended by lack of piped water and wastewater disposal problems [1]. This elaboration was provided by Hutton et al. in 2007 and is illustrated in Fig. 1 [2]. This also paves way for investing in water in a big way. But as far as price of water to

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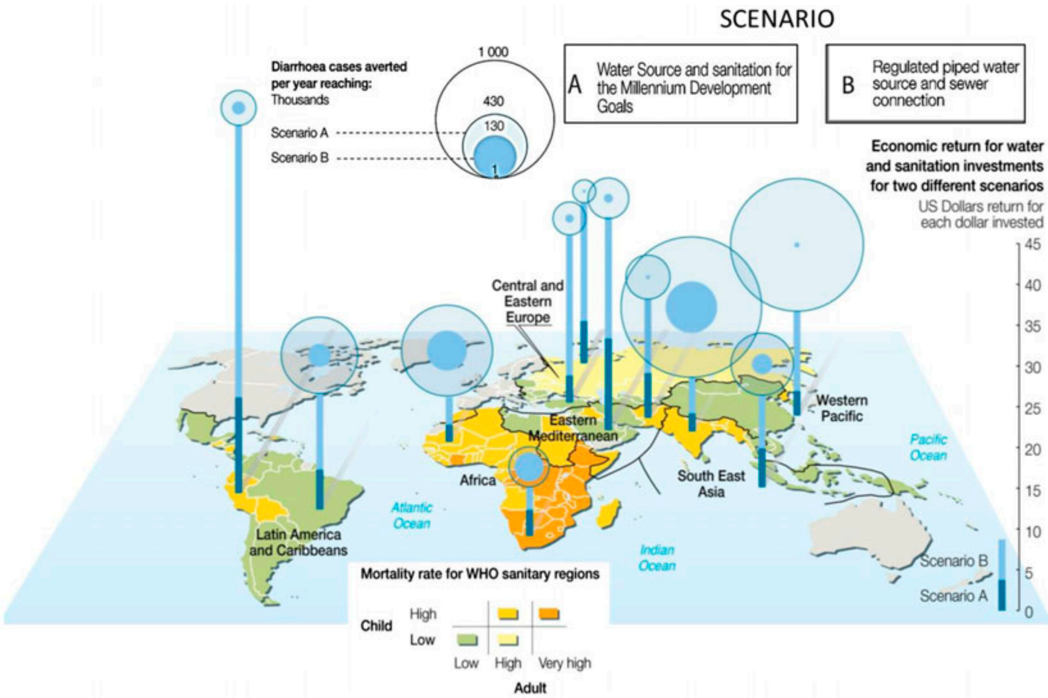

Fig. 1. Economical perspectives of water availability, supply and waste water treatment, and water-related death statistics.
Source: Hutton et al. [1] and UNEP/Grid-Arendal [2].

the society is concerned, India remains water scarce due to high costs of water even in water rich regions in India [3]. Infrastructure and economic stress at per capita levels of India has impeded water resource development [3,4].

The quality of available ground and surface water in India is not at par with drinking water quality requirements. Water gets contaminated with geogenic impurities. Arsenic and fluoride are prominent among them in India [5,6]. Some of the prominent are shown in Table 1 [5].

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

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	Sulfide	1	3
8	Iron	7	26
9	Zinc	3	6
10	Chromium	1	1

Note: [Source: Kalkoti, 2013].

Northeast India is one of the economically water scarce locations of the world due to the above-mentioned pollution in Table 1 [3,4]. If fluoride in water varies from 0.8 to 1.2 mg/L and when consumed, it helps in strengthening the teeth and bones [3–6]. Consumption of fluoride in the range 1.5–10 mg/L of water may cause degradation in human muscles and hemoglobin reduction [3–7]. Fluoride content exceeding 10 mg/L may cause fluorosis [6]. The Environmental Protection Agency guidelines provide the permissible limits of a contaminant in drinking water and for As and F it is elaborated in Table 2 [3,7]. It is observed that a high cost is associated for treating contaminated water sources [3,7].

Clay composites and its modification using organic materials is a low-cost technology applied for remediation of water [3,8,9]. Rural India lacks in centralized treated piped systems for water supply and is dependent on ground water extraction for consumption [3]. This would mean consumption of As and Fl polluted ground water. Piped systems are much costly infrastructure for India [3]. Hence, point of use systems for water purification is sought. Use of waste organic materials and clay or soil can be beneficial in such situation to manufacture low-cost water treatment systems [8].

Recently, two sustainable field options for water treatment were clay-based ceramic filters as well as

Table 2
Permissible maximum contamination level (MCL) values as approved by the EPA and World Health Organization [7]

S. No.	Contaminant	WHO/MCL value	Treatment	Cost/well (US$ rate in 2009)
1	As	10 μg/L–0.01 mg/L	Oxidation/filtration, activated alumina, anion exchange: prior to RO	800–3,000
2	F	4 mg/L	Activated alumina, distillation, electro dialysis: prior to RO	800–3,000

the MIT biosand filter [10]. Here, sustainability was affirmed due to low cost, easily available raw materials clay and organic water materials, scalability and the product turning to be an economic opportunity [10].

According to Table 1, fluoride contamination is the most widespread in India. The development of a low-cost variant of the soil composite-based water pot is the major aim of this work. The work to characterize the flow rate through these clayey soil or pond sand sintered water filters is performed. The flow rate through these filters is modeled as a non-linear function of volume of pond sand and the organic material used in the pot manufacture [8].

"Filtron" is the sustainable clay-based ceramic filter manufactured (by Potters for Peace) using mixture of equal quantity of clay and sawdust and have a flow rate of 1–2 L/h [8]. These clay ceramic pot filters were widely used due to its efficiency to remove microbes [3]. Further, the alkalinity variation with time between input and effluent water was characterized as a function of the electrokinetic parameters and their variations with the transport of water through them [11]. Further reviews on the different clay ceramic filters around the globe is performed and reported elsewhere [3].

Physical properties are another parameter which makes the filter to sustain and influenced by quantity of clay and sawdust [12]. Strength and other physical properties are complicated by the heterogeneous nature of clay and organic additive. Controlled addition of the organic material may result in facture shielding in the clay composite ceramic structures [12]. This also helps in determining the porous structure which helps in restraining microbe during water filtration. The porosity in such materials is a linear function of the organic materials such as sawdust as used in case of clay-sawdust composite ceramics [8]. Strength also relates life of a ceramic water filter in use. The expected structural life of "Filtron" or any clay composite ceramic water filter manufactured around the globe was depended upon various factors on the field such as usage statistics, loading rate, maintenance, region specific clay, local organic material used, water quality, contaminant, water chemistry, and others [12–15].

Since both ceramic water filter and biosand filters are sustainable solutions it is recommended to build on its properties to find newer solutions [12]. In this study, laboratory fluoride removal experiments are illustrated using local soil (Jodhpur, India) materials modified using local materials such as industrial organic plant waste or sawdust. These organic plant wastes are procured from Ayurvedic processing plants in Thiruvananthapuram, Kerala. These wastes are to be disposed and disposal requires space and location far away from human settlements. Using these plant waste materials in the manufacture of water filter also helps in their reuse and remediation.

Further different quantities of hydroxyapatite are also added to the composite in order to assess its fluoride removal capacities [16]. Hydroxyapatite removes fluoride following three major different mechanisms such as fluoro-apatite formation; F-ions substituting OH-ions, and calcium fluoride formation [17,18]. In this article, importance is also given to the microstructural changes that may occur with sintering. The properties of non-sintered and sintered raw materials and pot are critically assessed in the following sections as a function of volumetric ratio as well as by weight of the raw materials used. A multi-parameter regression framework is also developed to analytically support the experimental investigations.

2. Materials and processing

2.1. Pond sand and sesame sawdust

Pond sand and organic matter was mixed in 18 different ways in order to manufacture the composite mixture. Controlled addition of water to the composite mixture helped in preparation of the mold. Water is added to provide enough consistency and plasticity for the greenware or the mold to be manufactured. Before mixture preparation, ISO 565 (TBL 2) 10 μm sieve was used to sieve the sesame sawdust. Energy

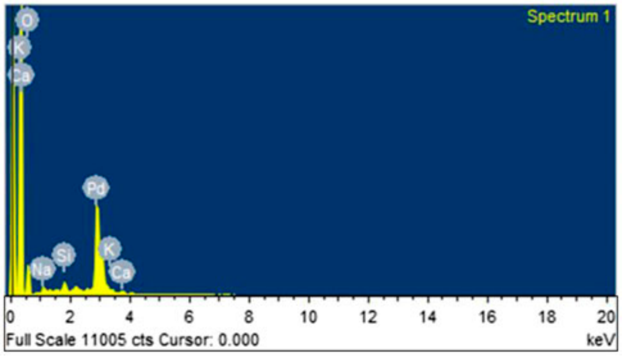

Fig. 2. EDS plot of sesame sawdust.

dispersive X-ray spectroscopy [Model EVO 18 Special, Carl Zeiss, IIT Jodhpur] of the sesame sawdust revealed presence of Ca, K, Pd, Si, Na, and O in elemental form. The energy dispersive X-ray spectroscopy (EDS) plot is illustrated in Fig. 2. The content of Pd is shown in the plot and it is present due to the use of the mini sputter coater in order to charge the sample to get high-resolution imagery.

The EDS plot of the pond sand used is shown in Fig. 3(a). The content of Si, Fe, Ti, Al, Mg, and Ca is found predominant in the pond sand. Fig. 3(b) illustrates the material to be sticky in nature, high holding capacity, and meager infiltration property or porosity. This may indicate that with increase in temperature this may provide a base material of porous nature for the filtration to happen.

2.2. Hydroxyapatite preparation

The hydroxyapatite (C_{10} $(PO_4)_6(OH)_2$) used as an additive in some of the experiments was manufactured in the laboratory. About 24 mL phosphoric acid in 200 mL of water was added to drop by drop for a 3–4 h to 44.2 g of $Ca(OH)_2$ dissolved in 300 mL of water for the preparation of hydroxyl apatite. After its preparation, a high pH of around 10.5 is maintained by addition of ammonium hydroxide solution. Once this pH is attained addition of ammonium hydroxide is stopped and this is kept for 48 h. Precipitate of hydroxyl apatite is separated using vacuum rotary vapor apparatus. Once collected the hydroxyl apatite washed with ethanol and heated to 110℃ for 24 h. Thus, the sample was ready for use. Diffraction analysis of the calcium hydroxyapatite sample is also performed to ascertain its microstructural transformations with temperature. This will help to understand how microstructure can affect sorption efficiency of HAP.

2.3. Extract of Ayurveda medicinal plants

The biomaterial wastes collected after the Kashayam (Traditional Ayurveda Medicines) extraction were collected from the factory of Vasudeva Vilasom™ (www.vasudeva.com). For the ease of our experimentation, the two different waste materials obtained from Vasudeva Vilasom were named samples 1 and 2. The energy dispersive spectroscopy EDS and scanning electron microscopy SEM plots of the samples 1 and 2 are shown in Figs. 4 and 5, respectively.

The SEM image of Ayurvedic sample 1 illustrated in Fig. 4(b). It shows layered cellulosic materials with granular globule structures. This granular globule cellulose may convert directly into carbon nanoparticles when sintered within compressed pond sand composite mix in this case.

A very high-purity natural-layered homogenous cellulosic structure with partial silica dopant is

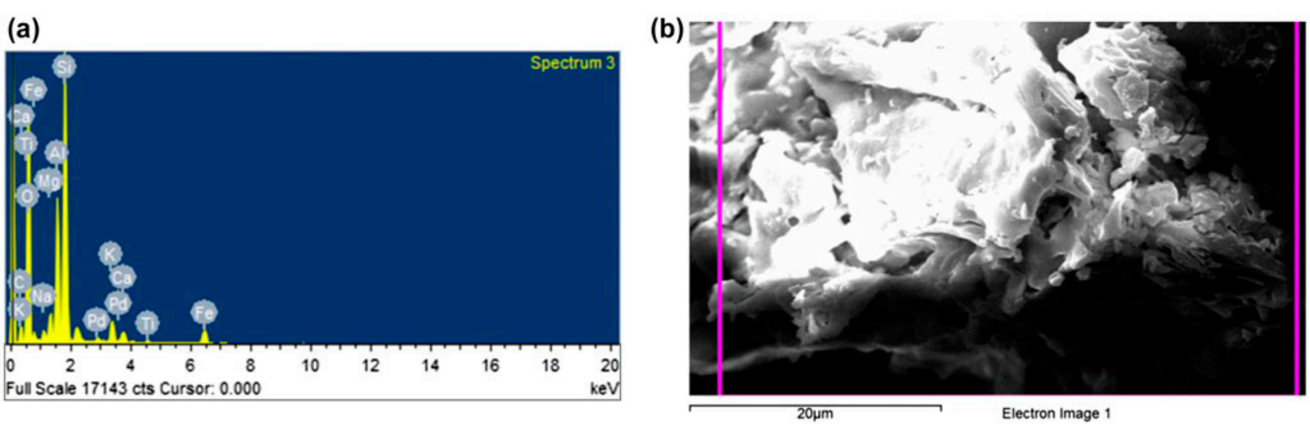

Fig. 3. (a) shows the EDS plot and (b) is the SEM image of the local pond sand sample used in the manufacture of the composite mixture.

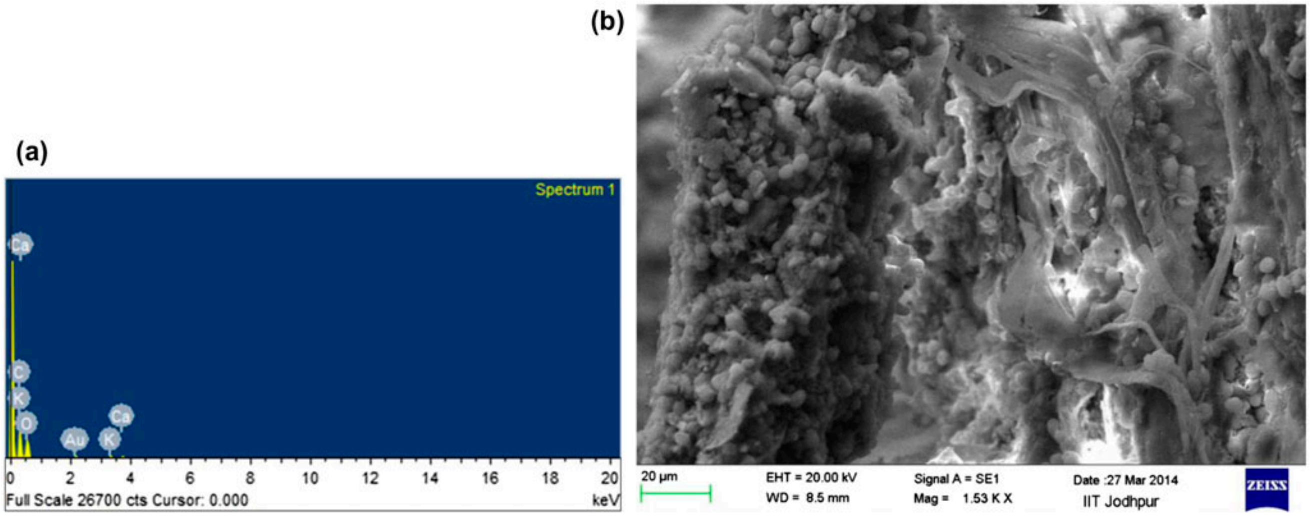

Fig. 4. (a) shows the EDS plot and (b) is the SEM image of the Ayurvedic biowaste materials (sample 1) used in the manufacture of the composite mixture.

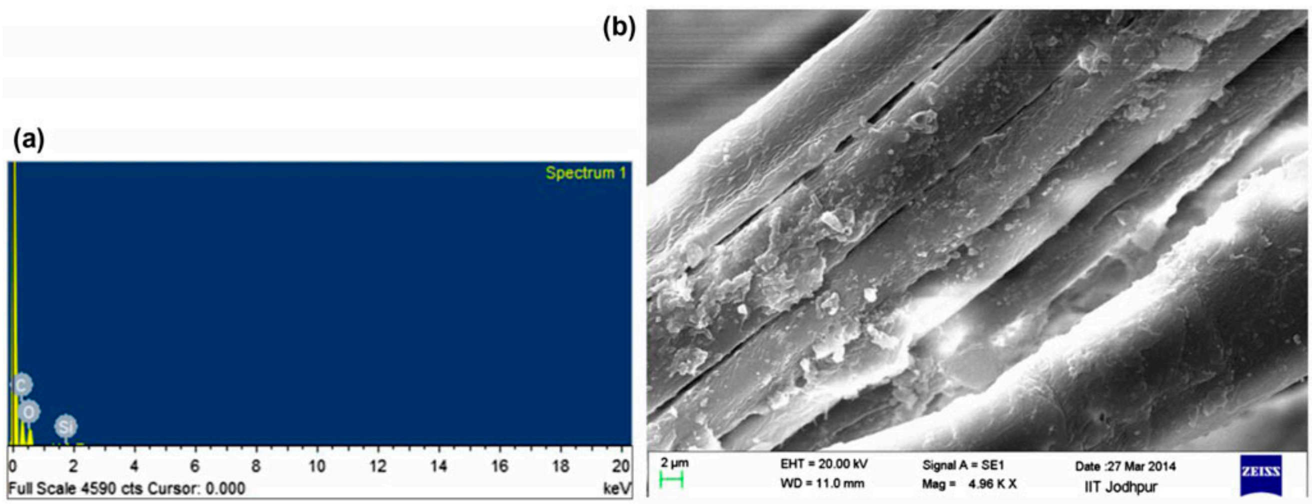

Fig. 5. (a) shows the EDS plot and (b) is the SEM image of the Ayurvedic biowaste materials (sample 2) used in the manufacture of the composite mixture.

enumerated through Fig. 5(b). It is also observed that it contains only carbon and oxygen with very minute amount of Si. This will allow forming high great carbon nanofibers within pond sand layers. So it will behave like a dual filter for the contaminated water.

2.4. Processing

Pond sand and sesame sawdust were mixed in 50:50 ratio by volume in three cases. In each of these cases, hydroxyapatite equivalent to 10% total volume of the mixture is added. This constituted the first set of experiments. Addition of 175 mL of water was performed to manufacture the composite wet mix which is kept into the male pattern for molding. The pattern in illustrated in Fig. 6 and formed by exerting manual pressure of approximately 20 psi using female pattern. Further, sterile plastic sheet is used to remove the mold thus formed during this process. This wet mold is known as the "greenware" [8,11,12].

In the second set of mixture preparations, two different greenware were prepared with the same pond sand to sesame sawdust ratio with addition of 20% by weight of hydroxyapatite. This addition may decrease

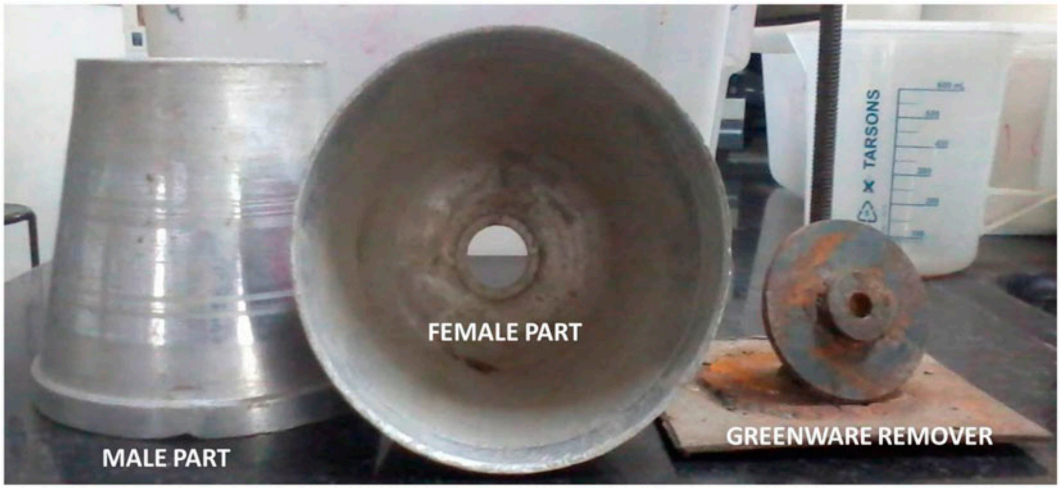

Fig. 6. The male and female pattern for the greenware production.

the flow rate of the filter since higher content of hydroxyapatite may decrease the porosity of the ceramic materials manufactured [17]. Plasticity of this mixture was attained with addition of 175 mL of water.

In another experiment instead of hydroxyapatite addition, 10% by weight of titanium tetra iso-propoxide ($C_{12}H_{28}O_4Ti$) was added. Raw titanium iso-propoxide is amorphous at room temperature but after calcination it may become crystalline. Surface area may drop in this case if sintered to more than 800˚C enhancing photoactivity. Titanium oxides, thus, crystallized and embedded on supporting materials may enhance separation reactions [19]. Here, the production of highly oxidative OH-groups in this process will be used to treat water [20].

Guar gum seed (*Cyamopsis tetragonolobus* (L.)-basically endosperm) has been utilized in powdered form 10% by weight. A greenware was prepared by making a plastic composite with 50:50 ratio by volume of pond sand and sesame sawdust, respectively, mixed with Guar gum powder.

Neem tree bark is substituted instead of hydroxyapatite for mixture preparation. Approximately 10% by weight of the total pond sand and sesame sawdust mixture was added. Two experimental greenware were manufactured. Water used was approximately 175 mL for both, respectively.

Ayurvedic biowaste samples 1 and 2 are substituted instead hydroxyapatite for the mixture preparation. Approximately 3.1% by weight of the total pond sand and sesame sawdust mixture was added. Two experimental greenware were manufactured. Water used was approximately 225 mL for both, respectively.

Two pond sand greenware mixture variants devoid of sawdust were prepared. Additive were Ayurvedic biowaste samples 1 and 2, respectively. Approximately 3.37% by weight of the total pond sand and calcium hydroxyapatite was added to form the mixture. Plasticity was brought to the mixture by addition of 100 mL water only in both cases.

Finally, composite mixture of pond sand, sawdust and hydroxyapatite was prepared with addition of sample 1 (2.69% by weight) and sample 2 (2.69% by weight) individually and also with both samples 1 (2.69% by weight) and 2 (2.69% by weight) mixed together. Thus, three different greenware were produced.

Greenwares were prepared from pond sand with Ayurvedic samples 1 and 2 taken separately each at a time. Thus, two greenwares were prepared with pond sand and one of the Ayurvedic samples taken equally by volume. These pots were devoid of HAP as well as any other organic materials. This was performed to reiterate the hypothesis that Ayurvedic waste samples 1 and 2 were efficient in fluoride removal.

2.5. Sintering procedure

The greenwares are air dried in sun for 2 d. The time for drying varied with variation of mixture compositions [8]. After drying, the individual greenwares were heated to 100˚C for 15 min for removing water molecules trapped in the greenware mass [8]. A three-step sintering process is charted. After moisture removal, the greenware was heated to 250˚C for one and half hour in a box furnace [18]. As the temperature approaches 400˚C, the greenware turns black in

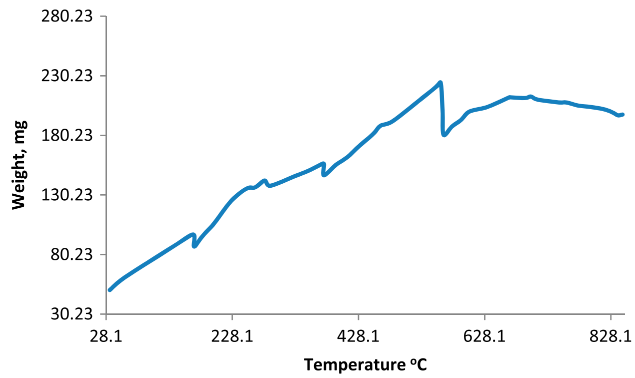

Fig. 7. Thermogravimetric analysis plot of the pond sand.

color. This is due to combustion of organic materials. The rate of heating is 20˚C/min. Secondly, the temperature is raised to 500˚C and left for another 1.5 h. Finally, the greenware is heated to approximately 850˚C [8]. This temperature is sustained for 5 h [8]. All the ceramic composite water filters prepared from different mixture ratio of pond sand, sesame sawdust, hydroxyapatite, Ayurvedic samples 1 and 2, and titanium iso-propoxide are now ready for use [17,18]. The thermogravimetric analysis of the pond sand sample is provided in Fig. 7.

From Fig. 7, it is clear that the heat treatment will provide a sequential weight loss, where crystalline water goes off around 200˚C. This indicates that water molecules are tightly held by pond sand. From 200 to 480˚C, there is a sequential loss of organic molecules. Therefore, there is a zig zag pattern. The most significant characteristic observed at 550˚C when the molecules came closer by losing oxygen significantly.

After 580˚C, the pond sand generates some defects and absorbs partial oxygen and the entire structure rearranges consistently till 850˚C. This enumerates the thermal processing of pond sand after 580˚C. This would mean that actual sintering is already carried out at around 600˚C and further sintering may not incur a major change in structure but will rather densify making the structure more stronger. This result basically supports our premise on the followed sintering technique.

Systematic study of the heat treatment to hydroapatitite revealed that from room temperature to 600˚C, amophous hydroxyapatite did not show much change in its microstructure. In the event of increasing the temperature beyond 600˚C, a transformation to crystalline form is revealed in Fig. 8. This study also supports and reiterates the thermogravimetric analysis studied carried out on pond sand. It can be concluded that 600˚C could be a transition temperature for effective fluoride removal. This microstructural crystalline nature of HAP is clear from the diffraction plot at 800˚C. Crystallinity of the HAP provides the better organized structure which will influence uniform interaction with water as compared with amorphous

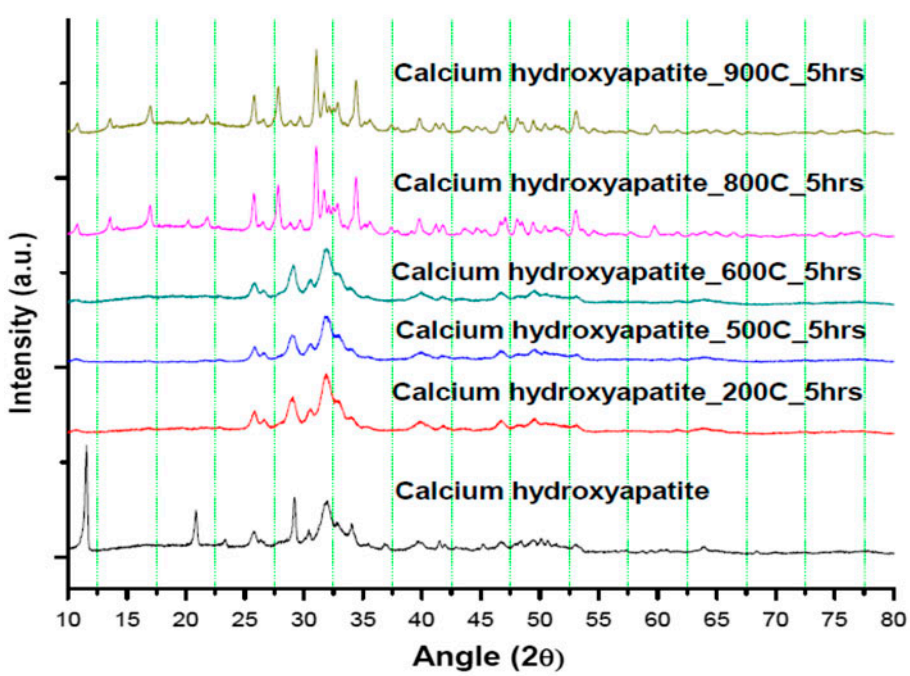

Fig. 8. Diffraction analysis of calcium hydroxyapatite at different temperatures which may occur during sintering.

Table 3
First batch of ceramic water filters with specific composition tested for removal of fluoride from water

S. No.	Pond sand (g)	Sawdust (g)	Hydroxyapatite (% by weight)	Inflow fluoride concentration (ppm)	Effluent fluoride concentration (ppm)	Percent sorption	Water filtration rate (mL/min)
1	276	73	10	118.47	60.047	0.4931	0.9
2	276	74	10	118.47	54.89	0.5366	0.8
3	276	75	20	118.47	6.3	0.9468	0.1
4	276	75	10	118.47	47.148	0.602	0.42
5	276	75	20	118.47	19.07	0.839	0.19

structures. Therefore, crystalline structure may enhance the sorption capacity of the sintered ceramic systems with HAP content.

3. Experimental methodology

Each of the gravity-based ceramic composite water filter ware, thus, manufactured was used for filtering water. Each of the filter ware filled with water. The wares of specific mixture composition were saturated with water by dipping them in a water bath containing purified water (Barnstead/RO, Thermo Scientific Model 7157-40) for about 12 h. This is done to simulate the working condition of ceramic water filter on field. Ware was supported at a specific height such that water percolating could be measured using a small measuring vessel kept below the filter. The volume of water collected in the measuring jar was timed such that flow rate of the filter could be found in mL/min. Inlet water used is a sample solution (100 mL) containing fluoride (80 mg/L), i.e. fluoride standard solution of 80 mg/L was prepared in deionized water. The fluoride was filtered and the captured fluoride was analyzed by titration of the remaining effluent from the filter. The adsorption of fluoride was calculated as follows:

$$\text{Percent sorption} = (C_i - C_f/C_i) \times 100 \quad (1)$$

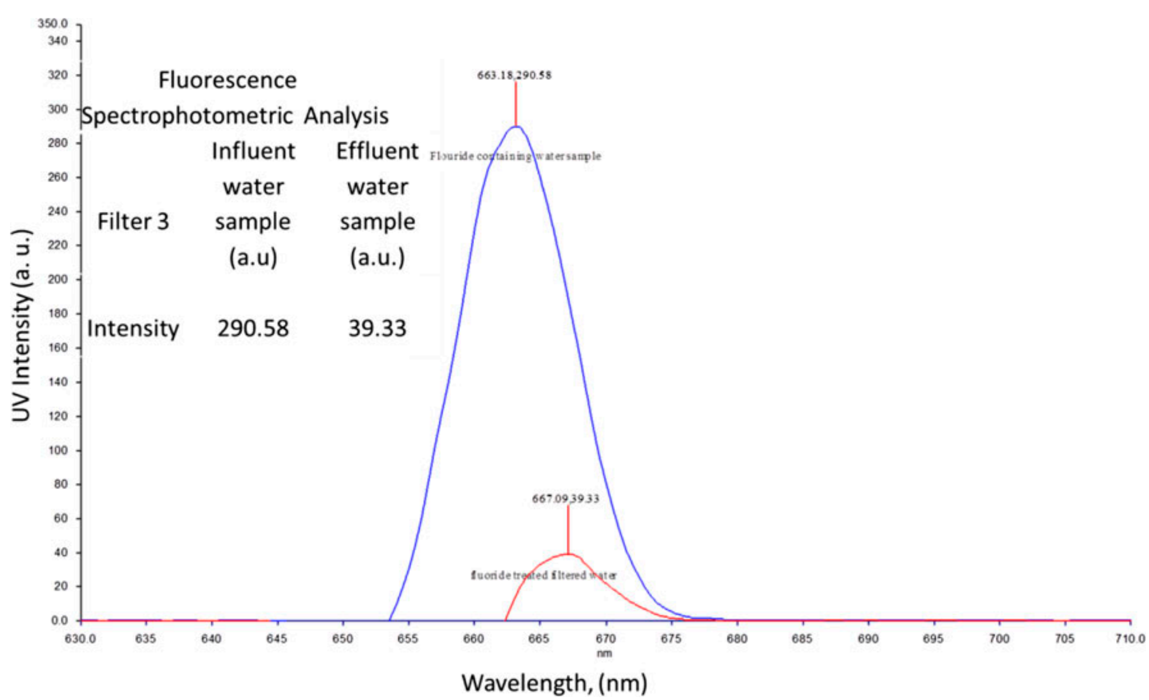

Fig. 9. Fluorescence analysis for the ceramic water filter ware 3 showing extensive reduction in fluoride after being passed through the ware.

where C_i (mg/L) and C_f (mg/L) are initial and final concentration of solution of solution before and after the sorption of fluoride, respectively.

4. Results

The experiments were conducted in batches as discussed above. At first, the ceramic composite water filter manufactured from the basic composite mixture of varying quantities of pond sand, sawdust, and hydroxyapatite was analyzed and contaminated water processed through filters with composition as listed in Table 3. The inflow water was contaminated with 118.47 ppm of fluoride.

It is found that with increase in hydroxyapatite in the mixture; the ceramic wares became less porous thus decreasing the water percolation through them [17]. From Table 3, this phenomenon is confirmed from ceramic water filter ware with number 3 and 5. The fluoride removal was also more than 80% in these pots. This was also affirmed by the results enumerated in Fig. 9 for the UV spectroscopy for influent and effluent from ceramic water filter 3. The influent water sample had a UV intensity of 290.58 a.u. and the effluent sample a UV intensity of 39.33 a.u., respectively. From Fig. 10, it is clear that fluoride removal was maximal from filters with a very minimum filtration rate. This also confirms the results from the first batch of experiments tabulated above.

The next batch of fluoride removal experiments was conducted and results are tabulated in Table 4. Table 4 provides filters manufactured with distinct chemical compositions. Fluoride removal improved comparatively when Guar seed powder was substituted for titanium tetra iso-propoxide but the percolation rate diminished. Performance of neem bark was at par with titanium tetra iso-propoxide.

Ayurvedic sample 2 contributed in removal of impurities but in general, resulted in a comparatively lower flow rate when compared with other material additives listed in Table 4. These results would hint at emulating hydroxyapatite fluoride removal capacity again but also improving flow rate at the same time.

Further experiments on filter wares made of a base mixture of 276 g of pond sand, 75 g of sawdust and 20% by weight of hydroxyapatite modified by controlled addition of other available materials is performed. The results of these experiments are enumerated in Table 5. From the analysis of ceramic water filter ware 14, it can be explained that a combination of Ayurvedic samples 1 and 2 waste materials when added to modify the composite mixture of pond sand, sesame sawdust, and hydroxyapatite (20% by weight) provided a high fluoride removal rate as well as a much better flow rate compared to the base material.

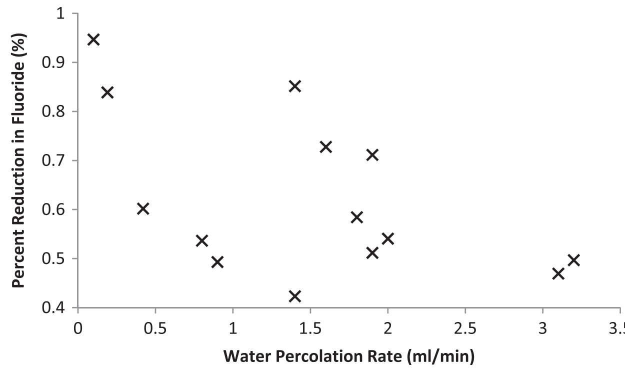

Fig. 10. Variation of fluoride removal is plotted against filtration rate of the individual pond sand ceramic composite water filter wares tested in this paper.

Finally, in order to make sure that ceramic ware composition of 14 in Table 5 is an optimal ware, a regression model is to be developed to enumerate the influence of the individual quantities of additives and flow rate on the fluoride removal capacity of ceramic wares with variable material composition. It should be noted that in the composition 14 listed in Table 5, HAP is also a constituent.

From Fig. 10, non-linearity in removal characteristics is detected with respect to water flow rates through the pond sand ceramic filter wares. The filtrate quality Y_i is a random function of different parameters such as quantity of pond sand (X_1), sesame sawdust (X_2), hydrodyapatite (X_3), filtration rate (X_4), Ayurvedic sample 1 (X_5), and sample 2 (X_6) as well as can be denoted as X_i for i = 0,1,2, …, n. This function can be expressed as [12]:

$$\frac{Y_i}{Y_{i-1}} = X_1^{b_{1i}} \tag{2}$$

and this can be generalized as [12]:

$$\ln Y_i = \ln a + \sum_{i=1}^{k} b_i x_i \tag{3}$$

where X_i = ln X_i. Thus, the Eq. (3) can be utilized as a linear multi-parameter equation.

It should be noted that influences of each of the components in the mixture may influence each other and also the flow rate. This would mean that the X_i's in the Table 5 are correlated. These correlations are enumerated in Table 6.

Table 4
Second batch of distinct ceramic water filter wares with specific composition tested for fluoride removal

S. No.	Pond sand (g)	Sawdust (g)	Material additives (% by weight)	Inflow fluoride concentration (ppm)	Effluent fluoride concentration (ppm)	Percent fluoride reduction	Water filtration rate (mL/min)
6	276	75	$C_{12}H_{28}O_4Ti$ (10)	378.733	200.9	0.4695	3.1
7	276	75	Guar gum seed cover (10)	378.733	157.337	0.5845	1.8
8	276	75	Neem bark (10)	378.733	190.515	0.4969	3.2
9	276	75	Ayurvedic sample 1 (10)	141.568	59.926	0.4123	1.4
10	276	75	Ayurvedic sample 2 (10)	665.05	191.739	0.7229	1.6

Table 5
Third batch of ceramic water filter wares with specific composition tested for removal of fluoride from water

S. No.	Pond sand (g)	Sawdust (g)	HAP (% by weight)	Ayurvedic waste material (10 weight %)	Inflow fluoride concentration (ppm)	Effluent fluoride concentration (ppm)	Fluoride reduction (%)	Water filtration rate (mL/min)
11	276	0	0	Sample 1	665.05	305.366	54.08	2.0
12	276	75	20	Sample 1	665.05	191.739	71.16	1.9
13	276	0	20	Sample 2	665.05	285.512	51.58	1.6
14	276	0	20	Sample 1 + sample 2	141.568	20.993	85.17	1.4

Table 6
The summary of model coefficients a, b_1, b_2, b_3 b_4, b_5, and b_6, coefficient determination R^2 and error S of the fit as illustrated in Eq. (3)

Predictor variables	a	b_1	b_2	b_3	b_4	b_5	b_6	R^2	S
X_1	−0.718	−1.241						23.26	0.232
X_2	−19.3	−69.2	−1.484					38.07	0.220
X_3	−19.5	−70.2	−1.499	−0.0108				38.93	0.217
X_4	−19.3	−68.7	−1.47	−0.0196	−0.1407			70.47	0.167
X_5	−18.35	−66.3	1.409	−0.0273	−0.149	0.0162		72.85	0.165
X_6	−12.08	−44.9	−0.927	0.028	−0.01916	0.04273	0.04184	94.85	0.07

In order to extract the actual influences, X_i's are to be independent to each other mathematically [12]. Multivariate framework is utilized in order to perform this task [12]. Interested researchers are requested to refer to Plappally [12] to know more details about this framework. This framework helps to derive the new model with independent variable V_i's corresponding to quantity of pond sand (X_1), sesame sawdust (X_2), hydroxyapatite (X_3), filtration rate (X_4), Ayurvedic sample 1 (X_5), and sample 2 (X_6), respectively. This may be expressed as:

$$Y = -0.4779 V_1^{-0.0719} V_2^{0.0233} V_3^{0.1142} V_4^{0.168} V_5^{0.3035} V_6^{-6.13} \quad (4)$$

Table 7
Correlations between the variables of quantity of pond sand (X_1), sesame sawdust (X_2), hydrodyapatite (X_3), filtration rate (X_4), Ayurvedic sample 1 (X_5), and sample 2 (X_6) as utilized in Eq. (2)

$\rho x_i x_j$	X_1	X_2	X_3	X_4	X_5	X_6
X_1	1	−0.99	−0.45	0.19	0.63	0.007
X_2	−0.99	1	0.45	−0.19	−0.63	−0.007
X_3	−0.45	0.45	1	−0.41	−0.006	0.17
X_4	0.19	−0.19	−0.41	1	0.188	0.060
X_5	0.63	−0.63	−0.006	0.188	1	−0.188
X_6	0.007	−0.007	0.17	0.060	−0.188	1

Table 8
Fourth batch of ceramic water filter wares tested for removal of fluoride from water

S. No.	Pond sand (g)	Sawdust (g)	Ayurvedic sample (g)	Inflow fluoride concentration (ppm)	Effluent fluoride concentration (ppm)	Percent sorption	Water filtration rate (mL/min)
15	276	74	Sample 1 (20)	80.59	16.43	79.61	12.5
16	276	74	Sample 2 (20)	80.59	17.77	77.95	2.69
17	276	74	Sample 1 (20)	617.30	205.66	66.69	20.5
18	276	74	Sample 2 (20)	617.30	237.62	61.50	5.47

The highest positive coefficient of the independent variable V_5 in Eq. (4) clearly shows that Ayurvedic sample 1 has the maximum positive influence on the removal of fluoride, Y from the effluent. It also confirms the negative yet positive influence of Ayurvedic sample 2 toward the fluoride removal prediction.

For assessing the influence of the Ayurvedic samples 1 and 2 on fluoride removal, a new batch of experiments with filter pots manufactured only Ayurvedic samples, sawdust, and pond sand is performed. Table 7 will enumerate this test for fluoride removal efficiency of this new batch of filters.

From Table 8, it is found that ceramic water filter 15 showed the best removal rates. This supports and reiterates the hypothesis that Ayurvedic sample 1 exerts the most influence on the sorption of fluoride thus, helping in reducing fluoride in the filtrates from the ceramic water filters.

5. Conclusions

New material composite ceramics filters are developed. Mixtures of pond sand, sesame sawdust, and hydroxyapatite are good base materials for sorption to remove fluoride from contaminated water. Increasing the content of hydroxyapatite may increase fluoride removal but in turn reduce flow rate through these pond sand ceramic water filter wares. Crystalline constituents will improve the sorption characteristics of the filter. At temperature more than 600˚C, hydroxyapatite transforms from amorphous to crystalline.

Biowaste from rural Ayurvedic industries can be used beneficially for treating fluoride contaminated waters. These materials when appended with pond sand and sawdust help in the development of fluoride filters as efficient as those containing HAP in crystalline form.

A new multivariable model is also derived which can predict fluoride removal from contaminated water as a function of materials used to manufacture the filter as well as the flow rate through the filter.

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