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## CLAY COMPOSITE WATER FILTERS: THE CASE OF FLUORIDE, NITRITE AND *Escherichia coli* REMOVAL

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### Abstract

Inorganic ceramic materials is receiving more attention in recent times due to their unique characteristics which include different pore structures, hydrophilic surfaces, high chemical, thermal and mechanical stabilities that offer avenues for application in water treatment. In the present work, cost-effective clay ceramic water filters of different designs were developed from clay (50, 60, and 70) %, sawdust (15, 20, 25, and 35) %, grog (5, 10 and 15)% ratios plus 5% bone char by volume and sintered at temperature of 950°C for 6 hrs. For the flow rate, fluoride and nitrite tests synthetic waters were used, while for *Escherichia coli* removal efficiency test of the filter diluted wastewater sample collected by purposive sampling methods from Modjo River was used. The analysis of the optimal performing sintered filter by X-ray diffraction revealed the existence of mixed phases such as quartz, mulite and ilite. The surface functional group analysis by infrared spectroscopy showed the presence of strong bands at 3696 cm<sup>-1</sup>, 3622 cm<sup>-1</sup>, 3450 cm<sup>-1</sup> of hydroxyl linkages. Field emission scanning electron microscopy of fractured filter surfaces with better performance showed the formation of interconnected porous microstructure materials. The ceramic water filter developed from 50% clay, 15% grog, 35% sawdust, and 5% bone char, (C950-50-35-15), characterized with total porosity 36.33±0.05%, displayed flow rate 1.91±0.55L/h and *E. coli*, nitrite, and fluoride removal efficiencies of 99.91±0.09%, 76.00±0.22%, and 96.8±0.41% respectively.

**Keywords:** ceramic filter, grog, microstructure, porosity, sintering

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### 1. Introduction

Contaminated water causes different diseases which may lead to millions death (Clasen et al., 2004; WHO, 2009). Therefore, lack of clean water is great distress. Contamination of drinking water supply is a concern for millions of people and long-term exposure to some water pollutants can have serious health implications. Fluorine is a chemical contaminant of water and causes dental and skeletal fluorosis (WHO, 2011). Technologies like chemical precipitation (Matlock et al., 2002), adsorption (Ali and Gupta, 2006), ion exchange (Rengaraj et al., 2001), membrane filtration (Zularisam et al., 2006), electrochemical (Vasudevan and Oturan, 2014), phytoremediation (Rezania et al., 2015), and others

(Upadhyay et al., 2014) have been widely studied to purify contaminated water. Of these water treatments, membrane filtration, especially based on clay ceramic water filters have the ability to remove materials that affect color, bad taste and remove contaminants that cause disease and illness from water at large-scale (Sobsey et al., 2008). Ceramic filter, made of clay soil and rice bran, could remove arsenic from actually contaminated groundwater with a concentration of about 200µg/L to levels below the Bangladesh standard level (Hasan et al., 2012; Shafiquzzaman et al., 2011a). A low-cost membrane bioreactor clay ceramic filter was developed and used for Synthetic greywater (prepared by shampoo, dish cleaner, and laundry detergent) treatment (Hasan et al., 2015). A ceramic filter developed with 50%-50% ratio of Igbara

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odo clay to sawdust was the most effective and optimum mix in terms of a flow rate (1.9 L/hour, removal efficiencies of 80% and 100% for coliform and *E. coli* bacteria respectively) (Ajibade et al., 2019). A low-cost ceramic disc membrane made from Cameroonian clay and sawdust fired at 1100°C for 2 h showed turbidity removal efficiency up to 97% (Belibi et al., 2015). According to the study of Zereffa and Bekalo (2017), the ceramic filter manufactured from 15% sawdust, 80% clay and 5% grog, fired at 950°C, with 49% total porosity showed relative better removal efficiencies in total coliform (94%), *E. coli* (96%), turbidity (88%), magnesium (63%), calcium (52%), iron (79%), nitrite (74%). In fact, it is encouraged to use a ceramic filter for household effective water treatment systems of drinking water (Brown and Sobsey, 2010; Du Preez et al., 2008).

The practice of using metal oxides and ceramic membranes for purification has developed because of their efficiencies in the inactivation of bacteria and spore cells (Colombo and Bernardo, 2003; Lyckfildt and Ferreira, 1998; Maximous et al., 2009; Schmidt et al., 2001; Stoimenov et al., 2002; Yang et al., 2006), adsorption of heavy metals (Ponder et al., 2000; Sharma et al., 2009), removal of fluoride, radio nuclides, halogenated hydrocarbons and organic compounds (Darab et al., 2007; Huang et al., 2011; Malay and Salim, 2011). Amongst these membranes, clays containing aluminum and iron oxide and chemically modified clays have been shown to adsorb higher amounts of fluoride by an exchange of OH<sup>-</sup> ions with F<sup>-</sup> ions (Kofa et al., 2017). Similarly, high fluoride adsorption efficiencies by fired clay soil and fired clay soil pillared with tea leave ash have also been reported (Hauge et al., 1994; Mugs et al., 1996). Membrane filters are porous ceramic media which can also filter microbes or other pathogens from water, which can be easily regenerated after fouling because the ceramics can withstand harsh chemical and thermal cleaning methods (Benito et al., 2007; Cohen, 2001; Faibish and Cohen, 2001).

Such filter is prepared by mixing clay with pore formers, shaped into a filter, in a press and fired in a furnace at elevated temperatures. The pore-formers leave small pores of different sizes, which can filter out the majority of harmful microbes (Bogdanichikova et al., 1992; Bottino et al., 2001; Doek et al., 2007; Galdiero et al., 2011; Mwabi et al., 2012; Rob et al., 2003; Yang and Tsai, 2008; van Halem, 2006). A clay water filter has many advantages due to its light weight, portable, low-cost, requires no chemicals and is simple to use; it can be produced locally, using naturally available clay and other materials. The pore size and surface charge of a ceramic water filter determine its ability to remove particles and pathogens from water (Naddafi et al., 2005). The pathogenic microorganisms are ordered by size (Fig. 1), and the screening mechanism of the ceramic filter also depends on pore size diameter. The ceramic filter has been attractive to researchers in the last decade due to their superior thermal and chemical resistance, superior mechanical strength, and good defouling

properties (Jedidi et al., 2009). The successful application of ceramic filters for wastewater treatment is found in the chemical industry, metal industry, textile industry, food and beverage industry (Fang et al., 2011). The use of clay and fly ash as the raw materials for crack-free ceramic membrane filtration have showed good performance in the removal of heavy metals in the treatment of textile wastewater (Subriyer, 2013; Palacio et al., 2009) and ceramic membranes made from clays and phosphates were suggested for use as a previous clarification step in textile water treatment (Campbell, 2005). In another study, it has been shown that simple ceramic filters manufactured from clay soil and rice can be applied to remove more than 95% of iron through oxidation, co-precipitation, and filtration (Shafiquzzaman et al., 2011b). The ceramic filter surface can be regenerated through periodic scrubbing to reduce surface deposits that slow down filtration rates (Bielefeldt et al., 2010).

The effort of this research was to develop a clay composite ceramic water filter from locally available materials such as clay, sawdust, grog and bone char for household water treatment and study the efficiency of the prepared filters in removing microorganisms (*E. coli*), and chemical contaminants: fluoride, and nitrite from the water.

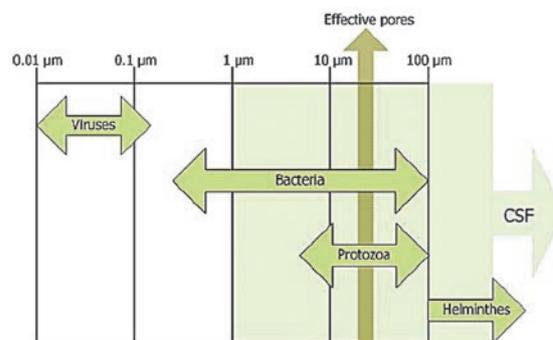


Fig.1. The order of magnitude of pathogenic microorganisms (van Halem, 2006)

## 2. Methodology

### 2.1. Materials and chemical analysis of clay

The raw materials used for the preparation of the filters, clay, water, grog and burnout materials (i.e., hardwood sawdust) and bone char (charred at 400°C) were collected from local sources. Each of the basic materials was subjected to various physical treatments before uses. The treatments included sun drying, crushing, grinding with mortar and pestle, and sieving. The raw materials passed through 75 μm sieve size to obtain fine homogeneous particle size. The grog (fired clay without burnout material) was prepared from fresh dried sieved clay fired at 800°C for 6 hrs.

The gravimetric method was used to determine silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>), whereas ferric oxide (Fe<sub>2</sub>O<sub>3</sub>), calcium oxide (CaO), and magnesium oxide (MgO) were estimated volumetrically of the clay raw material. Alkalies were determined by flame

photometry and the loss on ignition (LOI) was determined by heating the sample in a muffle furnace at 1000°C for 60 min followed by cooling to room temperature and recording the weight loss. The results showed that the major components of the clay were SiO<sub>2</sub> (47.32%), Al<sub>2</sub>O<sub>3</sub> (21.88%), Fe<sub>2</sub>O<sub>3</sub> (11.6%), and minor oxides were CaO (0.44%), MgO (<0.01%), Na<sub>2</sub>O (4.18%) and K<sub>2</sub>O (1.48%). This indicated the filter material is composed of high siliceous clay. The summary of the chemical composition of the clay is shown in Table 1.

### 2.2. Preparation of filters

The preparation of filters with the different design was based on the procedure developed by (Hagan et al., 2009). In a typical process, of the filters, requisite proportions of sieved clay powder, grog, bone char, and combustible matter were dry mixed thoroughly for more than 1h followed by the gradual addition of water under mixing till the first signs of uniform consistency. The different wet compositions were further mixed by wedging and rolling to obtain homogenous uniform mixtures. The mix was then divided into pre-weighed blocks. The clay mixture blocks were molded into frustum shape of dimension 20 cm top diameter, 15 cm height, 10 cm bottom diameter and 1.10 cm wall thickness using a 2-ton car jack. The shaped filters were allowed to sun drying for 2 weeks.

Once dried, they were sintered in a muffle furnace at 950°C for 6 hrs. This temperature was attained at a heating rate of 5°C per minute with an intermediate stay time of 1hr at 500°C to enable the removal of combustible matter and then continuing heating to the final sintering temperature with same heating ramp. After sintering, the filters were left to cool gradually until the temperature reached room temperature. The ceramic filters were removed from the muffle furnace, allowed to soak in distilled water for 24 hrs and tested for their clean water flux. All the filters prepared for this work were washed with distilled water, dried in an oven at the temperature of 100°C for 24 h, cooled, packed in plastic bags to protect from contamination prior to subjecting to different tests. A typical filter prepared is shown in Fig. 2.

### 2.3. Flow rate

Flow rate testing is an important quality assurance step which indicates the rate at which water passes through the filter element. It was measured from the water source with the same turbidity or 58 NTU ( Nephelo Turbidity Unit) as the input for the filtration with the developed ceramic filters. All the prepared filters were fully immersed in distilled water and soaked for 24 hours to ensure complete saturation at the start of the test and ensuring standardized results.

**Table 1.** The chemical composition of raw clay

Oxide	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	H <sub>2</sub> O	LOI
%	47.32	21.88	11.6	0.44	<0.01	4.18	1.48	<0.01	0.07	0.31	2.20	11.55

**Table2.** Percentage composition and sintering temperature of filters

No	Filter Code	Clay(v/v)	Grog(vv)	Sawdust(v/v)	Bone Char	Sintering Temperature(°C)
1	C950-50-15-35	50	15	35	5	950
2	C950-60-15-25	60	15	25	5	950
3	C950-70-15-15	70	15	15	5	950
4	C950-70-10-20	70	10	20	5	950
5	C950-70-5-25	70	5	25	5	950



**Fig. 2.** Some of the filters prepared

Once soaked, the filters were transferred onto a flow test rack designed to drain excess water away and most importantly, to prevent overflow of water from dripping into the measuring cylinders placed below each filter. Each of the filters was filled to the top with water and a timer started to point flow for an hour. The water level in each filter was maintained at brim throughout the duration of the test. After an hour of continuous flow, the filters were removed from the rack and the flow rate of each filter was evaluated by measuring the amount of water collected in the measuring cylinders. The flow rate of each filter was tested three times and the values averaged.

#### 2.4. Turbidity test

The turbidity removal efficiency of the ceramic filters was evaluated for the same water source that used for the flow rate test using the instrument CL52 D NEPHELOMETER (provided turbidity measurement in Nephelometric Turbidity units in a range of 0.1 to 400 NTU) (ASTM International, 2003). The measurement was made before and after filtration of the collected water sample using clay composite ceramic water to evaluate the removal efficiency of the prepared filter. Before measurement the turbidity meter was calibrated regularly using different calibration standards, bottled water (0.18 NTU) was used. The samples were transferred into special covet and placed in the turbidity meter. Finally, the turbidity removal efficiency (1), can be calculated using the Eq. (1):

$$\eta = 100 \left( 1 - \frac{r_F}{r_B} \right) \quad (1)$$

where:  $r_B$  - is the turbidity before filtration and  $r_F$  - turbidity after filtration.

#### 2.5. Total porosity

The porosity of the ceramic filter was determined in accordance with using the water absorption test (direct) method (D'ujanda, 2001). Oven dry filters were weighed in air and then saturated in distilled water at room temperature for 24 hrs. The wet filters were then immersed in boiling distilled water for 2 hrs and then allowed to cool to room temperature while being immersed for another 24 hrs. This was done to ensure that any entrapped air in the open pores of the filters was replaced by water. The water-saturated filters were weighed while immersed in distilled water and then removed. The surfaces were wiped gently with tissue paper and the weights in air recorded.

The weights of the suspending wires used for immersion were subtracted from the values recorded while determining the weights of the filters in water. Apparent porosity was then calculated using the Eq. (2):

$$P = 100[(Ws - Wd)/(Ws - Wu)] \quad (2)$$

where:  $Ws$  is the weight of the filter when saturated with water,  $Wd$  is the weight of the dry filter and  $Wu$  is the weight of the filter immersed underwater. The porosity of each filter was determined in triplicate and values averaged.

#### 2.6. Isoelectric point or Zero Point Charge ( $pH_{zpc}$ )

Zero point charge ( $pH_{zpc}$ ) of the selected filter, C950-50-15-35, was determined by using the method described by (Duran-Valle, 2012). 0.1 M of 10 NaCl solutions having the initial pH values ranging from 1 to 12 was prepared in duplicate using 0.1M HCl and 0.1M NaOH, and the final pH values of the solutions were then measured, and the calculation of  $\Delta pH$  was made by subtracting the initial pH values from final pH values.

#### 2.7. *Escherichia coli* removal

The water used for the bacterial test was collected from Modjo River which is contaminated with pathogenic bacteria by purposive sampling technique (Ilker and Rukayya, 2016). Modjo River is located 75 km East of Addis Ababa, the capital city of Ethiopia, which is geographically situated in between  $39^{\circ} 05' E - 39^{\circ} 4'E$  longitudes and  $8^{\circ} 34' - 9^{\circ} N$  latitudes.

The diluted influent water samples were prepared by taking 1 mL of the river water and diluted with 999 mL sterilized water. The *E. coli* concentration of the influent water and effluent water were determined in triplicate and expressed as CFU/100mL. *E. coli* filtration experiments were performed on all filters with contaminated water which had 250 CFU (*Colony Forming Unit*) *E. coli* bacteria detected in 100 mL. The filtrate was incubated on agar for 24 h at  $37^{\circ}C$ , and the removal efficiency was calculated using Eq(1) and converted to 100% (Bulta and Micheal, 2019) (Eq. 3):

$$\%R.E, \eta = 100 \left( 1 - \frac{NF}{NB} \right) \% \quad (3)$$

where,  $NB$ , is the number of *E. coli* before in 100 mL of raw water and  $NF$ , is the number of *E. coli* in 100 mL of water after filtration.

#### 2.8. Fluoride removal efficiency

The fluoride removal efficiency of the filters was determined using an ion-selective electrode (Expandable Ion Analyzer, Model Orion EA940, Orion Research Inc., Laboratory Products Group, USA). It was used to determine the fluoride removal efficiency of the filters from synthetic water samples prepared by dissolving 10mg of sodium fluoride (NaF) to obtain solutions with different fluoride concentrations: 1 mg/L , 2 mg/L , 3 mg/L , 4 mg/L , and 5 mg/L for calibration of the fluoride selective electrode from the stock solution by dilution with distilled water. In order to determine the extent of

adsorbed fluoride, the calibration and determination were carried out by the addition of TISAB buffer. For the preparation of TISAB 500 mL distilled water was taken in a 1L beaker to which 7 g tri sodium citrate, 56 g sodium chloride, and 2 g ethylene diamine tetra acetic acid were added under stirring till dissolution. To this solution, 57 mL glacial acetic acid was added followed by 5M sodium hydroxide to pH 5.3 which was then transferred to a 1L volumetric flask and diluted with distilled water to the calibration mark. To 20mL each of the prepared fluoride solutions of different concentration: 1 mg/L , 2 mg/L , 3 mg/L , 4 mg/L , and 5 mg/L , 2 mL TISAB buffer was added for the calibration of the electrode.

In each of the triplicate filtration tests, a solution having 10 mg/L of fluoride ion concentration was filtered through each filter and the filtrate analyzed for residual fluoride concentration. The potential reading of each concentration was taken and the graph of potential (E in mv) versus the logarithm of concentration (Log C in mg/L ) was drawn and the slope of the graph and  $r^2$  were calculated to check the accuracy of the measurements.

### 2.9. Nitrite removal efficiency

The removal efficiency of each filter was determined in accordance with the APHA (2012), for reporting wastewater and drinking water analyses by filtering synthetic sodium nitrite solution of strength 10.98 mg/L . The performance of each individual filter was evaluated in triplicate by comparing the concentration of nitrite before and after filtration without any surface modification of the filters by acid. A stock solution of sodium nitrite (1000 mg/L ) in deionized water was used to prepare a 50.0 mg/L working standard in a 100 mL volumetric flask. From this working solution, a series of calibration standards of 0.2 mg/L , 0.4 mg/L , 0.6 mg/L , 0.8 mg/L and 1.0 mg/L sodium nitrite in deionized water were prepared in 100 mL volumetric flasks.

A solution of p-nitro-aniline and 1-naphthol were prepared separately. Nitrite ions in the filtrates under acidic conditions underwent diazotization with p-nitro-aniline and formed a violet colored complex with 1-naphthol. The concentrations of nitrite after filtration were calculated from a calibration plot prepared from the standard sodium nitrite solutions.

## 3. Results and discussion

### 3.1. Removal of *E. coli*

The diluted Modjo river water used for filtration had 250 cfu *E. coli* bacteria detected in 100 mL. From Table 3, it is observed that the number of *E. coli* bacteria colonies after filtration, expressed in terms of percentage reduction of *E. coli* bacteria, ranged from 91.9±3.87 % to 99.91±0.09 %. The filter C950-70-10-20 with 91.9±3.87 % removal efficiency is termed as a high-risk filter according to the WHO water risks categories. While ceramic filter design

C950-50-15-35 with its 99.91 removal efficiency is in the risk free group.

Thus, ceramic water filters with interconnected pores and average pore diameter less than the size of bacteria are more efficient in removing microbial colonies from contaminated water sources (Clasen et al., 2007; Vasanth et al., 2011). The obtained results pointed out the increase of the microbial removal efficiency of the filters with the decrease in the total clay (raw clay plus grog) and an increase in the percentage composition of sawdust. This is attributed the formation of uniform pores during sintering in the ceramic body as confirmed by the microstructure image of the filter C950-50-15-35 design in section 3.8. A ceramic filter developed with 50%-50% ratio of Igbara odo clay to sawdust was the most effective and optimum mix in terms of a flow rate and *E. coli* bacteria removal efficiency (1.9 L/h, and 100%) respectively according to the report of (Ajibade et al., 2019).

### 3.2 Removal of nitrite

From Table 3, it is observed that all the ceramic filters prepared were able to remove a sufficient amount of nitrite from water solutions. The filter design, C950-50-15-35, incorporated 35% burnout materials removed about 76% nitrite without surface modification with acid. The surface modification of the clay composite filter with the ash obtained from sawdust improved nitrite adsorption on the surface of the clay composite adsorbents (Sowmya and Meenakshi, 2013).

### 3.3 Removal of fluoride ions

The removal efficacies of the filters are shown in Table 3. The prepared filters contain three potential defluoridation materials: fired clay, activated bone char, and thermally treated leftover sawdust or activated carbon in their ceramic structures. The main methods used in defluoridation from aqueous solutions are ion exchange and adsorption techniques (Fan et al., 2003).

On average, the filters reduced the initial fluoride concentration of 10 mg/L in the untreated water samples to a residual 0.68 mg/L in the filtered water which is greater than 95% removal efficiency. The high fluoride removal efficacies of the filters sintered at 950°C might be due to the exchangeable hydroxyl ions from clay, bone char, and activated carbon in the ceramic bodies.

### 3.4. Turbidity removal efficiency of the filters

Table 3 signify the results in turbidity removal efficacies of the five ceramic filters. The turbidity of the source water used for analysis was the same throughout the filtration, 58 NTU (Nephelo Turbidity Unit). The turbidity removal efficiency of the filters developed was varied from 84.4% to 99.6%.

**Table 3.** Summary of flow rate, *E. coli*, fluoride, nitrite and turbidity removal efficiency of the filters

<i>N<sub>Q</sub></i>	Filter Code	<i>E. coli</i> (%)	Flow Rate (L/h)	[NO <sub>2</sub> ] <sup>-</sup> mg/L effluent	(%)NO <sub>2</sub> <sup>-</sup> Removal	[F] <sup>-</sup> mg/L effluent	Turbidity after filtration	(%) [F] <sup>-</sup> Removal
1	C950-70-15-15	96.67±2.88	1.20±0.15	3.22	70.69±0.26	0.36	0.25NTU	96.4±0.31
2	C950-60-15-25	98.09±1.90	1.56±0.25	2.86	73.99±0.23	0.62	5.1 NTU	93.8±0.21
3	C950-50-15-35	99.91±0.09	1.91±0.55	2.635	76.00±0.22	0.32	3.65NTU	96.8±0.41
4	C950-70-10-20	91.9±3.87	1.63±0.31	3.138	71.42±0.32	0.14	2.81NTU	98.6±0.20
5	C950-70-5-25	95.94±3.61	2.50±0.27	3.045	72.77±0.22	0.30	9.00NTU	97±0.01

The European standards for turbidity state must be not more than 4 NTU. The WHO established that the turbidity of drinking water should not be more than 5 NTU, and should ideally below 1 NTU. Filters with designs C950-70-15-15, C950-50-15-35 and C950-70-10-20 are in the recommended limit of 5 NTU of the WHO. The ceramic pot manufactured by pottery for peace (PFP) has the potential to reduce turbidity, 30% to 100% as reported by (Lantagne et al., 2009). The ceramic disc membrane developed by ((Belibi et al., 2015) also reduced 97% turbidity.

### 3.5 Porosity

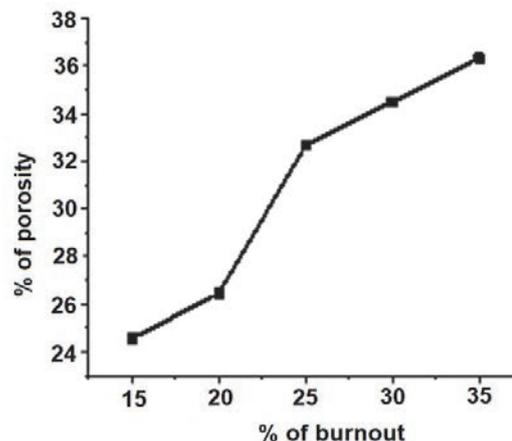
The total porosity of the filters as a function of the percentage of burnout material content is shown in Fig. 3. The Figure indicated that the porosity was proportional to the initial additive content of the pore-forming agent. The porosity of the developed filters increased with an increase in the percentage of burnout material incorporated in the compositions of the filters. This is evident from the total porosity of the filter C950-50-15-35 having the highest ratio of sawdust (35%), with the porosity of (36.33±0.05 %), and flow rate (1.91±0.55 L/h) which is in the WHO standard. But, filter with (25%) sawdust ratio, C950-70-5-25, sintered at the same firing temperature for the same staying time has low porosity (25.43±0.06 %). According to (van Halem, 2006), ceramic filters with total porosity range of 30-38% are free from the fracture.

### 3.6. Zero point charge ( $pH_{zpc}$ )

The isoelectric point,  $pH_{PZC}$ , of the filter design, C950-50-15-35, (Table 4) indicated that the surface of the filter is neutral at ( $pH_{PZC}$  = 8.5). This indicates the adsorption affinity of many negatively charged species including fluoride ions would be feasible in the WHO recommended range (6.5-8.5) for drinking water (Doke et al., 2013). The pH of the filtered water using the developed ceramic filters revealed that the filter was resistant to both acid and base (Bottino et al., 2001).

**Table 4.** The pH change results of filter C950-50-15-35 for Zero point charge determination

Initial (pH)	Final (pH)	$\Delta pH$	Initial (pH)	Final (pH)	$\Delta pH$	Initial (pH)	Final (pH)	$\Delta pH$
1	7.19	6.19	5	7.5	2.5	9	7.4	-1.6
2	6.99	4.99	6	8.0	2.0	10	7.3	-2.7
3	6.79	3.79	7	7.66	0.66	11	6.9	-4.1
4	6.66	2.66	8	7.8	0.2	12	6.7	-5.3

**Fig.3.** The porosity of filters against the ratio of sawdust

### 3.7 X-Ray Diffraction and Energy Dispersive X-Ray Analysis

The XRD pattern of raw clay and filter design, C950-50-15-35, was shown in Fig.4. The major peaks of the fired filter are associated with quartz (Q)  $2\theta = 20.76, 27.08, 49.97$ , mulite (M) ( $2\theta = 32$ ), illite (I) ( $2\theta = 23, 25, 35$ ) and Hematite (H) ( $2\theta = 36, 62$ ). The peaks of the raw clay are related to kaolinite (K) ( $2\theta = 12.47$  and  $24.32$ ). The kaolinite phase of raw clay was transformed into metakaolinite, which is an amorphous material and, consequently, displays no XRD peaks in the fired clay (Carty and Senapati, 1998). The energy dispersive spectrometry (EDS) analysis (Fig.5) revealed that the major elements in the filter were like calcium (Ca), aluminum (Al), silicon (Si), oxygen (O), iron (Fe), carbon (C) and phosphorous (P).

The presence of other elements like copper (Cu) and tin (Sn) may be due to the adsorption of other ions on the surfaces of the filter from the contaminated water during filtration. Trace toxic heavy metals like Pb, Cd, Hg, and As which could have negative impacts on human health are not found in the sintered ceramic filter.

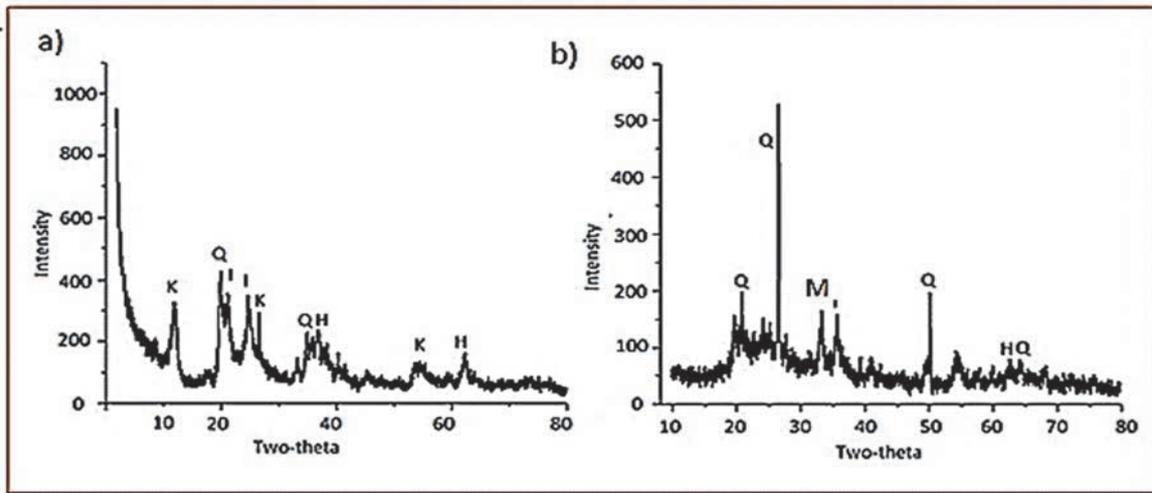


Fig. 4. XRD patterns of a) raw clay and b) filter C950-50-15-35

### 3.8. The microstructure of the filters

The flow rate and microbial removal efficiency of sintered filters are influenced by the formation of defects created in the bulk body of the ceramic filter during the sintering process. The microstructures of the filters investigated by Field Emission scanning electron microscopy are shown in Fig. 6 (a-e). From the figures, it is observed that the differences in structures of the filters are a direct consequence of the variations of the ratios of clay to sawdust.

The filter C950-60-15-25 microfilter (Fig. 6a) showed the presence of uniform porous structures, filter C950-50-15-35 micrograph, (Fig.6b) showed the presence of a fine and interconnected uniform porous microstructure and filter C950-70-5-25 micrograph (Fig. 6c) proved the presence of cracks in the microstructure, which affected both the flow rate and *E. coli* removal efficiency. The connectivity, types of pores, and distribution of pores are observed on C950-70-15-15 micrograph (Fig. 6d), filter micrograph. The SEM micrograph of C950-70-15-15 filter clearly revealed the pore size in the sintered filtered, both

at the external and the fractured inner surface, are nearly similar. Fig. 6c, at higher magnification (50,000) times revealed the presence of homogeneous, interconnected, and smaller pore sizes in the C950-50-15-35 filter microstructure.

### 3.9. FT-IR Analysis

FTIR spectra of filter, C900-60-25-15, before and after filtration of NaF solution are shown in Fig. 7 (a and b). The presences of coupled vibrations are appreciable due to the availability of various groups. Most of the bands such as  $3696\text{ cm}^{-1}$ ,  $3622\text{ cm}^{-1}$ ,  $3450\text{ cm}^{-1}$ ,  $1033\text{ cm}^{-1}$ ,  $917\text{ cm}^{-1}$ ,  $795\text{ cm}^{-1}$ ,  $692\text{ cm}^{-1}$ ,  $533\text{ cm}^{-1}$  and  $466\text{ cm}^{-1}$  showed the presence of kaolinite.

As seen in the spectra of the filter prior to NaF filtration (Fig. 7a), the vibration observed at  $\sim 917\text{ cm}^{-1}$  is attributed to the possibility of the presence of hematite (Farmer, 1974) whereas, the vibrations at  $3622\text{ cm}^{-1}$ ,  $1631\text{ cm}^{-1}$  and  $1033\text{ cm}^{-1}$  are attributed to the presence of gypsum and that of  $693\text{ cm}^{-1}$  is probably attributed to the presence of calcite.

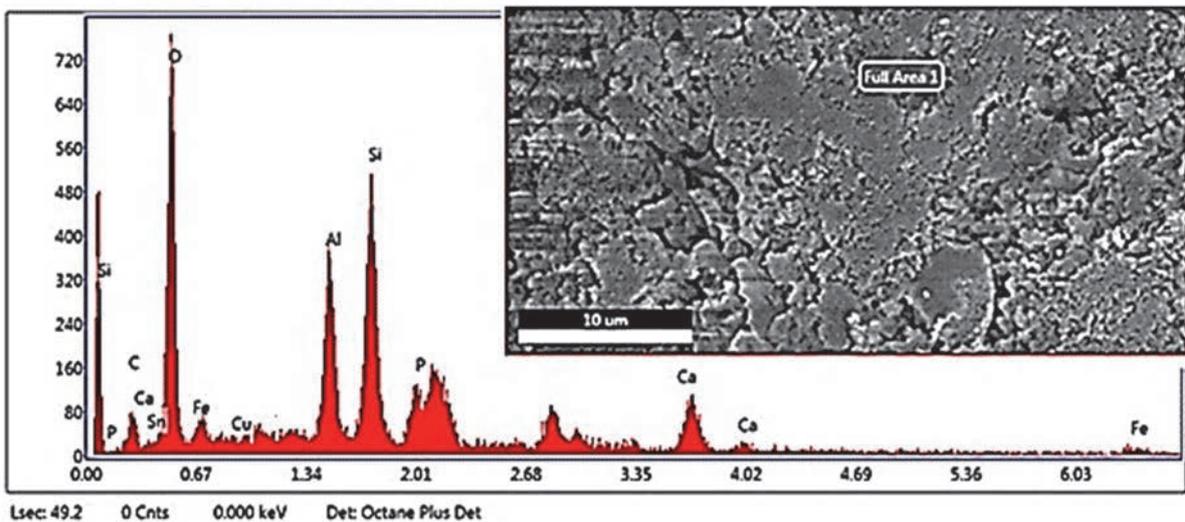
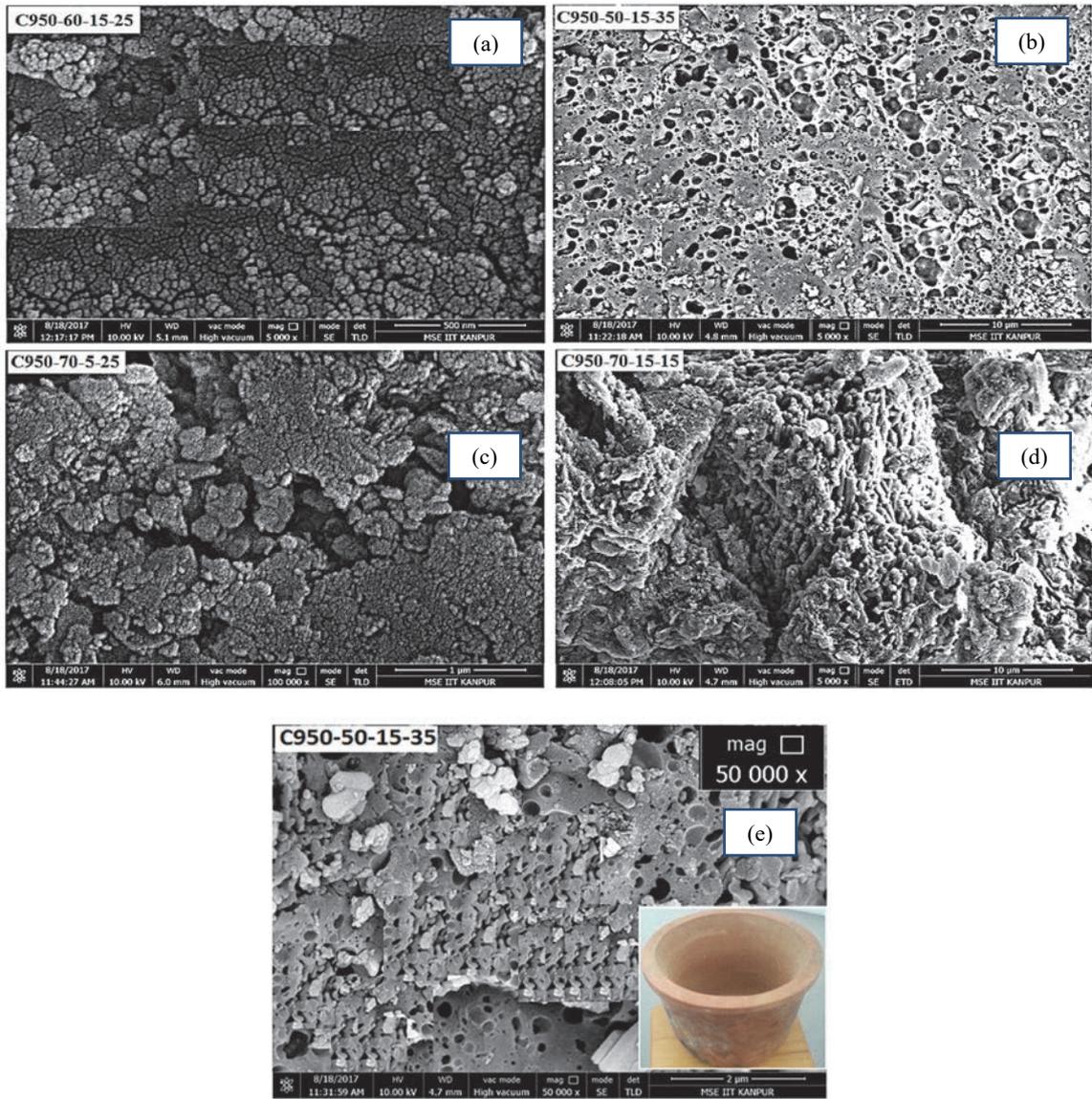
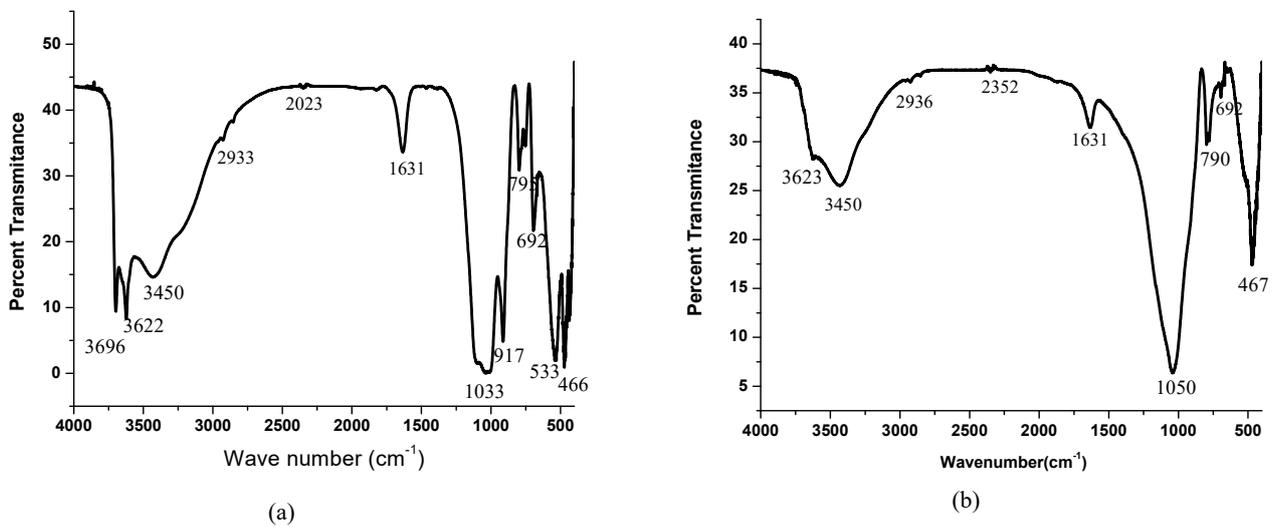


Fig. 5. EDS spectrum of filter C950-50-15-35



**Fig. 6.** Microstructures of the sintered filters by FESEM: (a) represent filter C950-60-15-25 at the magnification of 5000x, (b) C950-50-15-35 filter at 5000x, (c) C950-70-15-15 at 100,000x (d) C950-70-15-15 at 5000x (e) C950-50-15-35 with magnification 50, 000x



**Fig.7.** FT-IR spectrum of filter C900-60-25-15 (a) before, and (b) after filtration of NaF (10mg/L ) solutions

The strong triplet peaks at 3696 cm<sup>-1</sup>, 3622 cm<sup>-1</sup> and 3450 cm<sup>-1</sup> are associated with hydroxyl groups. However, the broadband at 3450 cm<sup>-1</sup> and the band at 1633 cm<sup>-1</sup> are suggestive of the water of hydration in the filter.

The FT-IR spectra also revealed the differences between the functional groups in the filter before and after filtration of the NaF solution. It was observed that the hydroxyl groups present on the filter surface were mainly involved in the sorption of fluoride. Anion exchange and electrostatic interaction were suggested as the main mechanisms involved in the sorption of fluoride on the filter. The changes in the stretching frequency of fluoride-treated filter material compared to untreated filter material confirm the chemical modification.

#### 4. Conclusions

In this work, five ceramic composite water filters were prepared by varying the ratios of clay, grog, sawdust, with 5% bone chare, sintered at 950 °C. The efficiency of the filters for water purification was evaluated by determining their efficacies to remove *E. coli*, nitrite and fluoride ions from synthetic and contaminated river water samples.

It is clearly evidenced that the performance levels of the filters are an influence of their compositional variations with respect to the ratios of clay, grog, and sawdust. The filter design C950-50-15-35 showed better overall performance, able to remove *E. coli* 99.81±0.09 % and possessing a good flow rate 1.91±0.55 L/h.

It is also concluded from the microstructures of the developed filters, flow rates and *E. coli* removal efficacies, it is possible to enhance the performance of the ceramic water filter by fine-tuning the interplay of the ratio of clay to grog to sawdust.

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