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Application of An Organic Plant-Derived Binder in the Fabrication of Diatomaceous Earth Waste-Based Membranes for Water Purification Systems

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ABSTRACT

This work reports on the use of diatomaceous earth (DE) waste and organic binder derived from Corchorus olitorius, locally known as "Mrenda" in the design of an efficient water filtration membranes. Charcoal powder was incorporated to enhance the porosity of the membrane. The firing was done at temperatures varying from 700.0 °C to 1150.0 °C. The DE waste samples comprised 79.0% silica (by mass) and 11.0% total flux content compared to porter's clay that had 50.0% silica, 28.8% AL_2O_3 and 7.0% total flux content. On the other hand, the "Mrenda" binder contained 6.5% total organic matter. The use of the plant-derived binder enhanced the mechanical strength of the greenware by 52.7% and the fired membranes by 152.2%. The fabricated DE waste-based membranes were 15.0% stronger than clay-based ceramic membranes prepared under similar conditions. A sintering temperature of 900.0 °C was optimal in producing porous membranes for filtering of 4.1 liters of water per hour. The pore diameter of the membranes fabricated from DE waste only ranged between 2.0 nm – 99.0 nm. On micro-organisms filtering efficacy, the DE waste-based membranes and those fabricated with 5.0% charcoal were 99.9% and 88.4% effective in the removal of E. coli and Rotavirus respectively.

INTRODUCTION

Diatomaceous earth (DE) is made of fossils of diatoms which are planktonic single-cell aquatic organisms (1). When diatoms die, they get deposited on the shores of a water body and accumulate over a period of time (2). During volcanic eruptions, such water bodies die off leaving behind deposits of DE. Diatoms are made of natural silica (silicon dioxide) (3). In Kenya, freshwater DE is mined from the Great Rift valley (4). The capability of DE to purify water was discovered by engineer Wilhelm Berkefeld who developed a candle filter from DE that was used successfully in 1892 to handle the cholera epidemic in Hamburg (5). Since then, DE has found applicability in wine (6), and fruit juice (7) processing because of its filtering abilities. Despite the existing technologies in water purification, communities with low incomes, and not connected to piped water are more prone to water-borne diseases. On their own, these communities cannot afford the expensive methods of water purification. In this work, we revisit this ancient water purification technique using DE waste. DE waste has not found direct application in the filtration industry. In this work, a cheaper, effective but hardy water filter is developed. The work investigates the effect of the use of a plant-derived organic binder on the strength of DE waste-based filters.

MATERIALS AND METHODS

The white diatomaceous earth waste was sourced from the disposal site of African Diatom Industries Limited (ADIL) in Kariandusi, Kenya, and then ball-milled for 30.0 minutes to micro-and nano- fine powder. For comparison purposes, the red porter's clay sourced from western Kenya was also used in this study. And in order to form the membranes, the DE waste and the porter's clay powders were kneaded with the organic binder ("*Mrenda*" binder was prepared as described by Njogu et al (8)). In order to vary the strength of ceramic membranes, the binder was diluted with distilled water to various concentrations (0.0 % to 100.0%). To form the membranes, the porter's clay and DE waste powders were separately mixed with the binder in the ratio of 2:1 by mass, kneaded and left for 48.0 – 72.0 hours at room temperature. In order to vary the porosity of the membranes, the charcoal powder was added to the DE waste powders in varying proportions. The greenware was then uniaxially pressed at 2.0 MPa in a hydraulic press to form discs of 2.5 cm (diameter) by 0.3 cm (thickness). Test samples for strength measurements (modulus of rupture, MOR) were prepared by extrusion into cylindrical rolls measuring 15.0 cm (length) by 2.5 cm (diameter). All samples were left to dry for 72.0 hours in ambient air to release the moisture and thereafter heated in the furnace at 110.0 °C for 30.0 minutes. Selected samples were then fired to various maximum temperatures of 700.0 ˚C to 1150.0 ˚C at a 3.2 °C/min heating rate as this was the minimal heating rate that produced membranes without visible cracks. The discs and rolls were soaked at the firing temperature for 2.0 hours. Thereafter, they were left to cool at room temperature for 48.0 hours. The MOR was carried out in a Universal Testing Machine in a 3-point bend test by loading the samples until failure. The distance between the supports was 8.4 cm and the loading rate was 4.2 mm/min. The MOR was then calculated using Equation (1).

$$\sigma = \frac{8LD}{\pi d} \qquad (1)$$

where L is the fracture load (pascal) and D is the distance between supporting rolls (meters) and d is the sample diameter (meters). The physical properties of the membranes were analyzed in terms of linear firing shrinkage, percentage water absorption (%WA) and bulk density. The open porosity of the samples was determined using Archimedes' immersion technique (9).

The chemical analysis of the as-received powders and undiluted binder were carried out using the X-ray Fluorescence Spectroscopy method while the protein was found by the Kjeldahl procedure and the carbohydrate content were found by Benedict test with the aid of a Shimadzu VIS/UV Mini 1240 spectrophotometer. The energy-dispersive x-ray fluorescence spectrometer (ED XRF CG Spectrometer Rigaku) was used for elemental characterization while the crystal structure of powders and membranes was analyzed by Empyrean, PANalytical–X-ray diffractometer with a Cu target Kα = 0.15406 nm radiation. The degree of crystallinity in the XRD pattern was determined by Equation (2) (10).

$$\%C = \frac{I_c - I_a}{I_c} \tag{2}$$

where *%C* is the percentage of crystallinity, I_a is the minimum intensity of the major peak that corresponds to the amorphous content of the sample and I_c is the height of the highest peak that corresponds to the amount of crystalline material. The microstructure of the fired membranes was analyzed using a high-resolution Carl Zeiss Gemini SEM500 Electron microscope at Botswana Institute for Technology Research and Innovation (BITRI) and the Thermoscientific Apreo instrument housed at Rowan University.

Prior to the *E. Coli,* the MacConkey Broth Purple w/BCP solution was prepared by dissolving 40.0 grams into 1000.0 ml of distilled water then boiled to dissolve to a purple solution. The solution was distributed in inverted Durham's tubes according to the Most Probable Number procedure of testing micro-organisms in water (11) . The samples were classified as either double or single strength. At the same time, the *E. Coli* was incubated at 37 ˚C for 18 - 24 hours under Cystine-Lactose-Electrolyte-Deficient Agar (CLED agar). Several yellow colonies of *E. coli* were then taken from the culture and emulsified in sterile distilled water to obtain a suspension of 10^6 concentration of colony-forming unit, CFU/ml. The suspension was then passed through the membranes. The filtrate was collected in sterile tubes. Five milliliters (5.0 ml) of each filtrate was added to the MacConkey solution and left at room temperature to monitor the growth of *E. coli*. The *E.coli* in the filtrate was quantified by Enzyme-linked immune sorbent assay ELISA. The membranes that passed the *E. Coli* test were taken for the Rotavirus test which was again done by ELISA. One liter of sterile water was contaminated with 5.0 ml of attenuated Rotavirus. Later, the contaminated water was filtered by the fabricated membranes.

DISCUSSIONS

Characteristics of Raw Materials

Table I shows the percentage composition of elements present in DE waste. It is observed that the DE waste had a very high silicon content of 79.0% and calcium at 3.7% which caused the whitish color of the DE powder (13–15), unlike the porter's clay that was characterized with the reddish color caused by the iron oxides (16). The porter's clay, on the other hand, had a lower content of SiO_2 (50.81%) and calcium (1.2%) but had high aluminum content (28.8%) and iron

(15.3%). This may explain why the porter's clay particles formed better compact green wares compared to DE samples. Aluminum aids in plasticizing the greenware because of its plate-like structures. The silicate tetrahedral sheet and aluminum octahedral sheet are held together with an O-H-O bond which allows water or binder to attach to (OH) bond (17) of clay and DE waste. The penetration of water or binder in these sheets results in increased capillary forces that manifest in plasticizing characteristics. Both aluminum and iron oxides that were found in the porter's clay can be traced to weathered clay minerals. DE waste had a high content of sodium than porter's clay at 5.5% which is attributed to the calcination process that entails adding sodium chloride salt in the mining process (18). Potassium, on the other hand, was higher in the porter's clay than in DE waste because potassium is needed for plant growth (19). The other oxides were in traces and their differences were insignificant in the fabricated ceramic. A similar elemental composition of DE was found in the pure samples in the literature (18,20).

Table I: The elemental composition of porter's clay and diatomaceous earth waste

ELEMENTAL OXIDES	Percentage content by mass	
	Clay	DE Waste
SiO_2	50.8	79.0
Al_2O_3	28.8	7.7
FeO_3	15.3	2.8
CaO	1.2	3.7
MgO	0.1	0.2
K_2O	3.5	0.9
Na_2O	2.3	5. 6
P_2O_5	0.1	0.1
TiO_2	-	0.5
MnO	-	0.1

Figure 1 shows the results of the elemental analysis of the *"Mrenda"* binder. The binder had a high content of soil minerals (silicon and aluminum) characterized by binding abilities. Potassium and calcium ions volatilize during the fabrication process encouraging particle interaction in the material. Similar results were found in the literature (8,21,22).

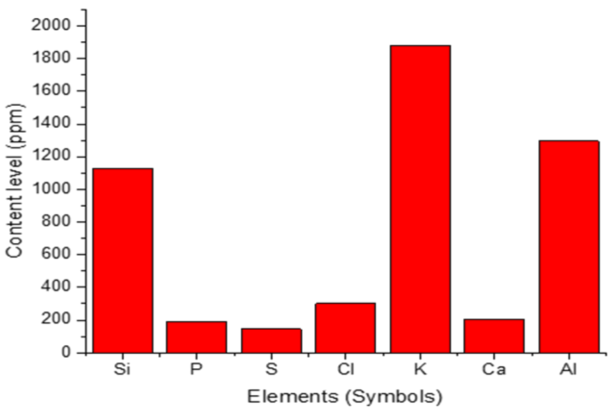

Figure 1. Chemical composition of *Corchorus olitorius*

The results of organic matter in the *"Mrenda"* binder are shown in Table II. It was found that in terms of organic matter, proteins were highest in *"Mrenda"* and fats were least. The high content of carbohydrates and proteins was responsible for the polymeric behavior of the binder (23,24).

Table II. Organic matter in the *"Corchorus olitorius"* binder

Organic matter	% Content
Ash	1.2
Carbohydrates	3.1
Fats	0.1
Flux content	1.2
Proteins	2.1
Total Organic compounds	6.5

The X-ray diffraction pattern of the DE waste powder is displayed in Figure 2. The result showed that DE is a polycrystalline material with regular arrangements. The main peak of cristobalite was identified at 21.9° just as it was found in the literature (25,26). The crystallinity was calculated according to Equation (2) and was found to be 94.13%. It was also found that DE waste is majorly made of cristobalite and traces of hematite, quartz, and wollastonite.

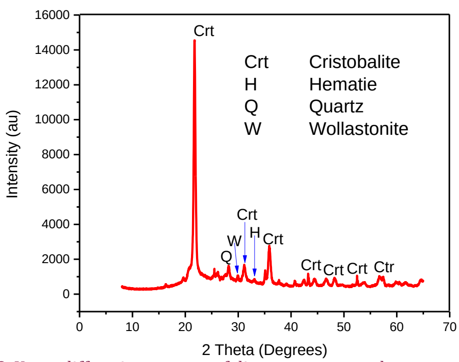

Figure 2. X-ray diffraction pattern of diatomaceous earth waste powder

Physical and Mechanical Properties of membranes

Figure 3 shows the XRD spectra of DE waste membranes fired at, 750.0 °C, 800.0 °C, 900.0 °C, 950.0 °C, 1000.0 °C, and 1150.0 °C. The intensity of the peaks, particularly of cristobalite and quartz decreases with an increase in firing temperature due to the changes in the phases of quartz to form amorphous cristobalite at 900.0 °C (25) characterized with a broad peak. The spectra also showed an increase in crystallinity as the firing temperatures increased. This indicates that high firing temperatures resulted in increased densification, which manifested as increased intensity of peaks. The densification in the ceramic material closes pores and reduces porosity (27). Thus, it is not recommended to fire the DE waste filter membranes beyond 950.0 °C.

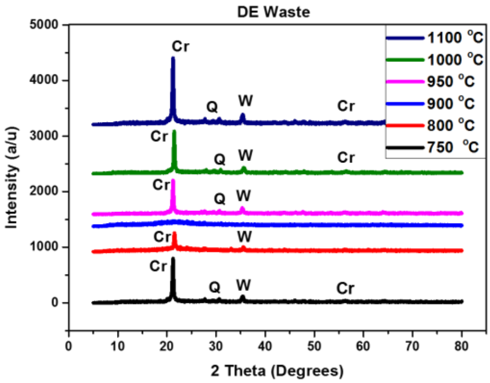

Figure 3. X-ray characteristic spectra of membranes of diatomaceous earth waste fired at (a) 750 .0°C, 800.0 ° 950.0 °C, 900.0 °C, 1000.0 °C, and 1150.0 °C

Figure 4 (a) shows the variation of linear firing shrinkage (LFS) as a function of binder concentration for samples fired at 900.0 °C. It is observed that LFS increased with an increase in binder concentration up to 50.0% followed by a decrease. The particle-particle interactions increased resulting in increased LFS when the concentration of binder was less than 50.0%. Beyond 50.0% binder concentration, the LFS decreased as a result of increased volatilized organic matter present in the highly concentrated binder (21). Figure 4(b) shows the result of porosity and bulk density against the percentage concentration of the binder. Porosity was found to decrease with an increase in the percentage concentration of the binder up to 50.0%. This can equally be attributed to increased particle-particle interaction during firing. The inverse proportion relationship in porosity and percentage binder concentration can also be attributed to the increase in the polymer chain as the percentage of the binder increases up to an optimum of 50.0%. However, beyond 50.0% binder concentration, a further increase in binder concentration increases porosity and bulk density decreases. This is because pores created outweigh the solid-solid and solid-liquid interface formation and enhance

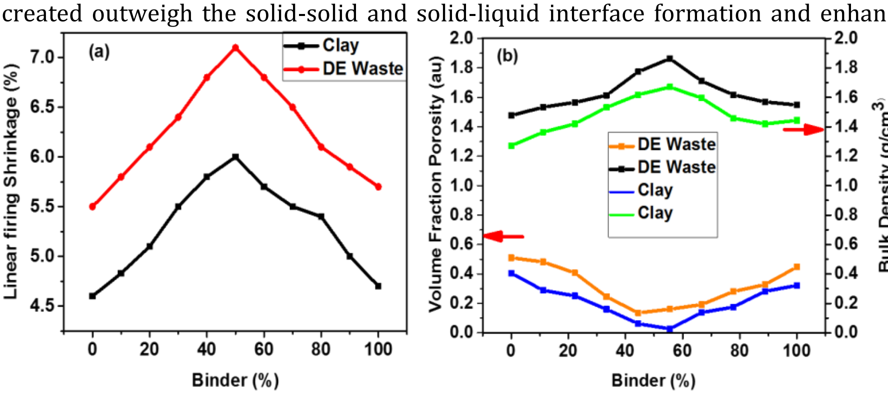

Figure 4. The effect of variation of binder on linear firing shrinkage (a), and (b) volume fraction porosity and bulk density for diatomaceous earth waste membranes fired at 900.0 °C

solid-vapor interface formation (28,29). The porosity in DE waste membranes was 31.2% higher than clay-based membranes. This can be attributed to the presence of micro- and nano-sized pores in the diatomite particles present in DE waste.

Figure 5 (a) shows the plot of the modulus of rupture (MOR) against the percentage of binder concentration used in fabricating membranes fired at 900.0 °C. There was initially an increase in MOR up to 50.0% binder concentration, followed by a gradual decrease in MOR up to 100.0%. Below 50.0% binder, the proteins' polar phases and the key-lock behavior between them and silica enhance particle interaction leading to improved MOR (30). At 900.0 °C firing temperature, the *"Mrenda"* binder was able to improve the MOR of DE waste by 152.2% in comparison to membrane plasticized with distilled water. The membranes made from DE waste were 15.0% stronger than membranes made from the porter's clay. Beyond 50.0% binder, the increased amount of the volatilized organic matter created excess pores that lowered the MOR and the entire mechanical strength of the membranes (28). Figure 5 (b) shows the micrograph of the same membrane. Some of the particles melted bringing the other particles together, at the same time, closing up some pores. This vitrification was responsible for the reduced porosity and improved MOR. Figure 5 (c) shows the plot of modulus rupture against the firing temperature. As the firing temperature increased, the MOR increased due to thermal energy that increased particle-particle interaction. Figure 5 (d) shows the SEM image of the membrane fired at 1000.0 °C. This firing temperature initiated the

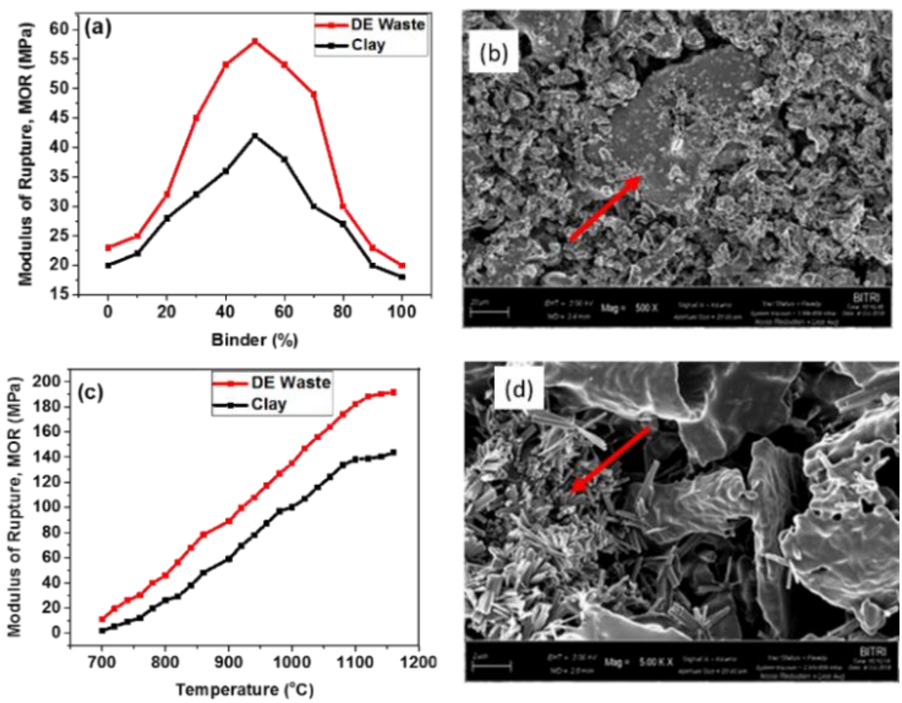

Figure 5. The plot of modulus of rapture (MOR) against binder concentration for diatomaceous earth waste fired at 900.0 °C (a) and its micrograph (b). The arrow on the micrograph show the vitrification process that took place during firing. (c) shows how the MOR varied with firing temperature and (d) shows the micrograph of the diatomaceous earth waste membrane fired at 1000.0°C. The arrows on the micrograph show the growing crystals of wollastonite

growth of the needle-like wollastonite crystals in DE waste as confirmed by the XRD results. The presence of crystals, however, reduced porosity and this was undesirable for the water filter membranes. Higher firing temperatures (> 1000.0°C) caused the onset of the formation of closed pores. Thus, the result confirms that the firing temperature for DE waste membranes for water filtration should not go beyond 900.0 °C.

Figure 6 (a) shows the plot of MOR and volume fraction porosity against the mass of charcoal. The amount of charcoal used to fabricate the membrane was found to have a positive correlation with porosity but a negative correlation with MOR. Charcoal served as a burn-out material that increased the number of pores in the fired membranes. During firing especially above 700.0 °C the charcoal burned to ashes leaving only the DE waste and the porter's clay particles. The voids were then created in the fired membranes as shown in Figure 6 (b) which was a micrograph of the DE waste membrane fabricated with 10.0% charcoal. The image showed pores ranging from 1.2 μm to 3.9 μm. Such pores can allow most water-borne pathogens to seep through them during filtration (31). The membranes with 5.0% charcoal had pores ranging between 12.0 nm to 1.3 μm. Again, membranes from DE waste materials showed higher MOR and porosity than the porter's clay. Higher porosity in DE waste was attributed to the diatomaceous pores shown in the micrograph (Figures 6 (c) and (d)) of DE waste membranes fabricated without charcoal and fired at 900.0 °C. It was shown that DE waste had traces of diatomite evidenced by

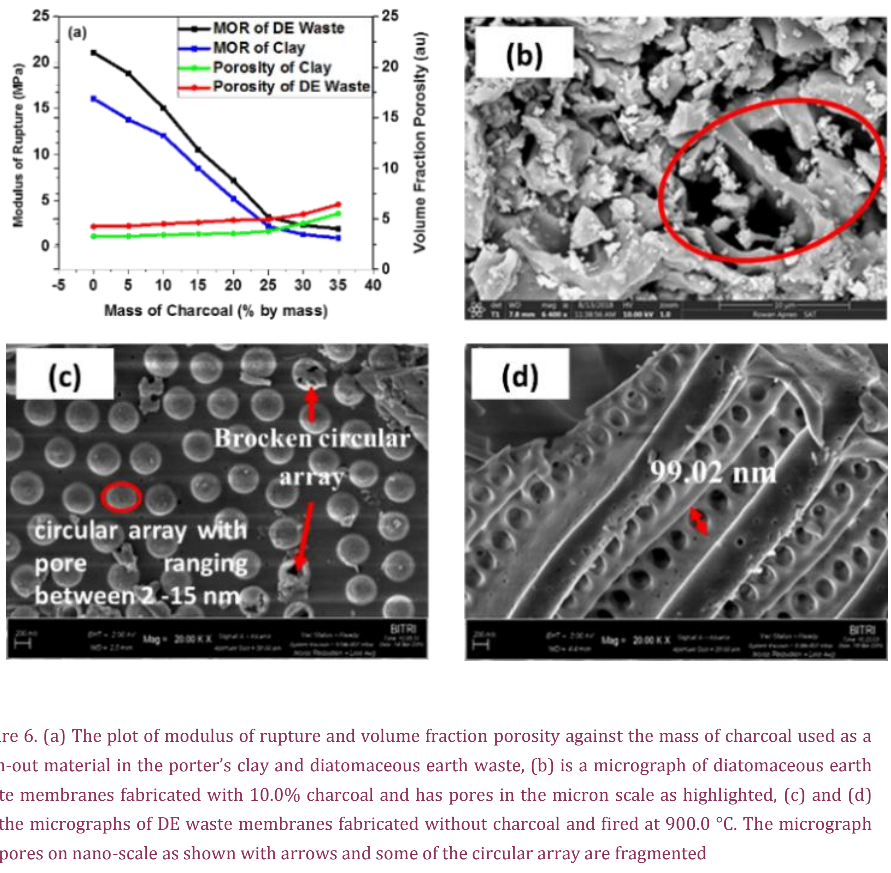

Figure 6. (a) The plot of modulus of rupture and volume fraction porosity against the mass of charcoal used as a burn-out material in the porter's clay and diatomaceous earth waste, (b) is a micrograph of diatomaceous earth waste membranes fabricated with 10.0% charcoal and has pores in the micron scale as highlighted, (c) and (d) are the micrographs of DE waste membranes fabricated without charcoal and fired at 900.0 °C. The micrograph has pores on nano-scale as shown with arrows and some of the circular array are fragmented

the circular array in the membranes. There were numerous pores on the circular array. Some of the pores were hollow (Figure 6 (d)) with pore size around 99.0 nm, while others were closed with perforations of pore size 2.0 nm to 15.0 nm (Figure 6 (c)). some of the circular arrays were broken, owing to wear and tear over time. A similar diatomaceous array was found in pure DE membranes (20,32).

Escherichia - Coli and Rotavirus Tests

Figure7 shows the percentage of pathogens filtered by the fabricated membranes. Membranes made from DE waste only were more effective in filtering *E.coli* than Rotavirus due to the sizes of the pathogen; E.coli measures 0.5 μm (width) by 2.0 μm (length) (33) and Rotavirus is less than 100.0 nm (34). Similar results were replicated in all membranes despite the variation of charcoal. Membranes fabricated with more than 15.0% failed to filter most of the pathogens particularly Rotavirus due to the increased number of pores and pore-size. There was no significant difference in the effectiveness of pathogen filtration between DE waste and porter's clay. The DE waste-based, clay-based and all those membranes fabricated with 5.0% charcoal were at least 99.9% and 88.4% effective in removal of *E. coli* and Rotavirus respectively.

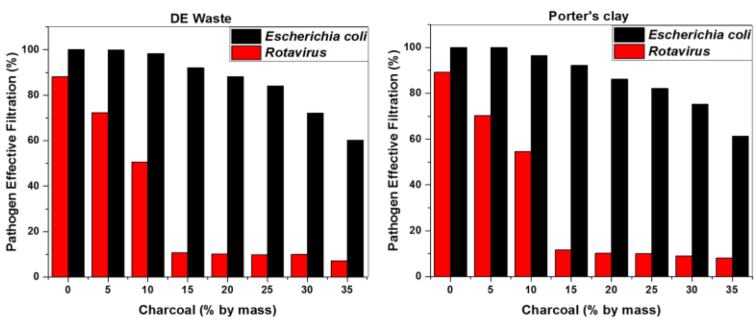

Figure 7: The percentage of pathogen filtered from water against the mass of charcoal used to fabricate the filter

CONCLUSION

In this work, it has been found that DE waste is made up of diatoms and has a similar composition as pure DE making it suitable for fabricating filtering materials. The binder from "*Mrenda"* improved the strength of fired membranes by 152.2%. However, high "*Mrenda*" content is detrimental to the strength of the membranes. The addition of 5.0% charcoal improved porosity by 2.54% in fired membranes without compromising the efficiency of the membranes. The optimal firing temperature was found to be 900.0 °C. The most effective membranes with maximum *E. coli* tests were obtained with 5.0% charcoal content and 50.0% binder content. These were 99.9% efficient in removing *E. Coli* and 88.4% Rotavirus. DE waste-based membranes were 15.0% stronger than those fabricated using porter's clay.

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