Preparation and Characterization of Ceramic Microfiltration Membrane for Water Treatment.

F.T. Owoeye, B.Eng.*; O.S. Olokode, Ph.D.; Prof. P.O. Aiyedun; H.O. Balogun, B.Eng.; and B.U. Anyanwu, B.Eng.

Mechanical Engineering Department, Federal University of Agriculture, Abeokuta (FUNAAB), PMB 2240, Abeokuta, Nigeria.

E-mail: lordphems2008@yahoo.com*

ABSTRACT

Six ceramic disc type microfiltration membranes of diameter 200 mm and thickness of 8 mm each were fabricated by the mold and press method from different percentage compositions of clay, kaolin, sawdust, wood charcoal, and binding agent (sodium carbonate). The fabricated membranes were sintered at 1100^{o}C and characterized by X-Ray Diffractometer as determined by Radicon MD-10, version 2.00 of CuKα radiation at exposure time of 1200/1200 seconds with Lambda: 1.5418 with a Beta filter used for all samples. Scanning Electron Microscopy (SEM) was conducted by optical electro machine. Compressibility tests were determined by Instron Universal Testing Machine with Model Number of 3369. Water absorption, bulk density tests, porosity tests, and filtration tests were measured by Digital Electronic Scale with Model: JCS-A Gallenkomp.

The first and the last membranes out of six that were fabricated have compositions of 95% clay, 0% kaolin, 4.5% sawdust, 0% charcoal with 0.5% sodium carbonate and 40% clay, 45% kaolin, 0% sawdust, 12% charcoal with 3.0% sodium carbonate, respectively. It was observed that increase in the percentage composition of kaolin and decrease percentage composition of clay, the filtration rate decreased from 33.66% to 4.045% and the percentage value of porosity also decreased from 108.8% to 80%. During the firing process, the sawdust burns creating a system of pores within the ceramic, allowing water to flow slowly through the vessel wall. It was also found that bulk density increased with increases in amount of kaolin in the prepared membranes, but reverse was the case in term percentage of water absorption. Body compositions containing higher amounts of kaolin showed lowest water absorption and highest strength due to better densification. SEM showed uniformly distributed pores and no cracks was seen around them. The porosity, percentage of water absorption and mechanical properties depend on the content of kaolin composition which had an effect on the membrane performance.

(Keywords: ceramic membrane, microfiltration, clay, kaolin, clay, ceramic firing)

INTRODUCTION

Archeologists have uncovered human-made ceramics that date back to at least 24,000 BC. These ceramics were made of animal fat and bone mixed with bone ash and a fine claylike material. After forming, the ceramics were fired at temperatures between 500-800°C in domed and horseshoe shaped kilns partially dug into the ground with loss walls. While it is not clear what these ceramics were used for, it is not thought to have been a utilitarian one. The first use of functional pottery vessels is thought to be in 9,000 BC. These vessels were most likely used to hold and store grain and other foods.

The history of ceramics begins with earthenware. Thousands of years ago, humans learned how to make earthenware vessels by kneading, forming, and firing clay. Prior to this discovery, the only other man-made items were stone tools made by chipping rocks. In this sense, earthenware could be called "the root of all industrial products." After the Stone Age, countless advancement was made over the millennia before fine ceramics appeared as we know them today.

A membrane is a semi permeable which can be used in liquid applications for removing colloidal particles, organic molecules or dissolved salts. Development of ceramic membrane for microfiltration application in treatment of waste water is very important. Ceramic membranes have to be resisting with chemical, thermal and mechanically suited environments. Its pore size is in the range of 0.1 micrometer to 20 micrometers which is normally suited for water treatment [1]. Ceramic membranes are thin layers and have a permanent place in microfiltration and ultrafiltration which are used in application involving high temperature, extreme pH values.

The microfiltration of ceramic has the small pore sizes. [2], stated that ceramic membranes are used in the cross flow filtration mode, which allows maintaining a high filtration rate compared with direct flow filtration mode used in convectional filtration process. Thermal, chemical and mechanical properties of ceramic membranes give them significant advantages over polymer ones [3]. Microfiltration refers to filtration processes that use porous membranes to separate suspended particles with diameters between 0.1 and 10µm. Microfiltration (MF) has the largest pore size (0.1-3 µm) of the wide variety of membrane filtration systems. Ultrafiltration (UF) pore sizes range from 0.01 to 0.1 µm.

In terms of pore size, microfiltration fills in the gap between ultrafiltration and granular media filtration. In terms of characteristic particle size, microfiltration range covers the lower portion of the conventional clays and the upper half of the range for humic acids. Microfiltration is also typically used for turbidity reduction, removal of suspended solids, Giardia, and Cryptosporidium.

Ultrafiltration membranes are used to remove viruses, color, odor, and some colloidal natural organic matter [4]. Microfiltration is a membrane separation process with membrane pore sizes between 0.05 and 5µm, operating at pressures up to 0.1MPa. The membrane rejects particles and dissolved macromolecules larger than 0.1µm. Membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. In separation applications, it allows one component of a mixture to permeate the membrane freely, while hindering permeation of other components [5].

Ceramic membranes, a special class of micro porous membranes, are being used in ultrafiltration and microfiltration applications for which solvent resistance and thermal stability are required reverse osmosis, ultrafiltration, microfiltration, and conventional filtration are related processes differing principally in the average pore diameter of the membrane filter.

Technologies have been developed in the recent decades. By improvement of prescriptions, development of new concepts, use of new technologies like nanotechnology and increase of the production of ceramic membrane there is an enormous development. For large scale water treatment, the ceramic microfiltration is very interesting as pre-treatment step in the production of drinking water from surface water [6].Ceramic membrane has been applied in drinking water treatment for approximately 20 years [7].

The objectives of this research work are to develop six different ceramic membranes with different materials compositions in subsequent to water treatment and to characterize the functional properties of membrane such as the morphology, pore network and flux mechanisms.

MATERIALS

The clay sample of 150kg and 80kg of kaolin sample used in this research study were excavated from natural deposit Ajebo, Abeokuta in Ogun State, Nigeria. The sawdust used was also collected from sawmill and the charcoal was also obtained in Abeokuta. The chemical analyses and other characterizations of all raw materials and prepared samples was determined by X-Ray Diffractometer and Scanning Electron Microscopy/Optical were done in Engineering Material Development Institute (EMDI) Akure, Ondo State.

EXPERIMENTAL PROCEDURES

All the samples were sun-dried for seven days. The dried clay and kaolin samples were cleaned thoroughly by removing foreign materials such as stones, dead roots, and dried leaves. Six ceramic disc type microfiltration membranes of diameter 200 mm and thickness of 8 mm each were fabricated by the mold and press method from different percentage compositions of clay, kaolin, sawdust, wood charcoal and binding agent of sodium carbonate, and the steps involved are summarized below:

i. % weighing of clay powder, kaolin and different binders.

ii. Mixing of different weighed compositions.

iii. Addition of distilled water with the mixed materials to form paste.

iv. Molding and pressing of paste on circular disc shapes.

v. Drying to remove water contents

vi. Firing to remove all binders and un-dried water content.

The six prepared membranes composition is shown in Table 1.

In the fabrication process of membranes, a circular plate was inserted into the primary molder; this enabled the disc sample formed to be removed easily from the primary molder with the aid of an Armateur stand. The primary part of the molder was first wrapped with polythene bags and the measured sample paste was inserted into the wrapped molder. The paste was then spread and pressed inside the primary molder by hand for uniformity. The paste was wrapped with polythene bags and was then compacted at 2.25N/m^2 by secondary molder with the aid of a 2-ton bottle jack in order to form desired shape.

The sample membranes prepared were dried at room temperature for seven days after which the circular discs were carefully removed. The fabricated membranes were fired at the temperature of 1100^{O}C in a regulated kiln for a period of ten hours and allowed to cool gradually for over fifteen hours and characterized by X-Ray Diffractometer as determined by Radicon MD-10, version 2.00 of CuKα radiation at exposure time of 1200/1200 seconds with Lambda: 1.5418 and Beta filter was used for all the samples. Scanning Electron Microscopy by optical electro machine was performed. Water absorption, bulk density tests, porosity tests, and filtration tests were also performed.

ANALYTIC METHODS

Bulk Density

The bulk density of the fired membrane samples was determined by displacement of water from beaker using the Archimedes principle. The weights of all membrane samples were measured in air by digital electronic Scale (Model: JCS-A Gallenkomp). The experimental set up measured the weights of the beaker partially filled with water, with and without the cut up samples immersed in water. The difference gave the weight of water displacement, according to the Archimedes principle. The weight of water displaced can be easily related to the volume of water displaced, as the density of water is known as 1000kg/m3. Thus, the bulk density in g/cm3 is given in terms of mass sample measured in air and the volume displaced by the sample.

$$\text{Bulk Density (g/ml)} = \frac{\text{mass in air (g)}}{\text{Volume of water displaced (ml)}}$$

Table 1: Percentage Compositions of Raw Materials used for the Preparation of Six Samples Membranes.

	Main Materials			Binders			Disc Mass
SAMPLES	CLAY %	KAOLIN %	SAWDUST %	CHARCOAL %	Na_2CO_3	WATER (L)	Mass (Kg)
01	95	0	4.5	0	0.5	0.75	3.8
02	80	0	19	0	1.0	1.06	3.9
03	60	10	18.5	0	1.5	0.8	4.2
04	50	20	20	8	2.0	0.75	4.8
05	45	20	22.5	10	2.5	0.7	5.2
06	40	45	0	12	3.0	1.2	5.5

Percentage of Water Absorption

Water absorption measurements were carried out according to BS EN 12808 – 5: (2008), Grouts for Tiles: Determination of Water Absorption. Fired membrane samples were cut up and measured by Digital Electronic Scale with Model: JCS-A Gallenkomp as initial weights of the membrane samples. The measured membrane samples were then soaked in water in a beaker for 24 hours at room temperature in the Mechanical Engineering Laboratory. As the samples were immersed in water, bubbles were observed as the pores in the samples were filled with water. After the lapsed time, the samples were removed from the beaker and allowed to dry by removing the excess water on the surfaces dry napkin prior to weighing as wet weight.

$$\text{Water Adsorption } \% = \frac{\text{wet weight} - \text{wet weight in air (g)}}{\text{weight in air (g)}} \times 100$$

Percentage Apparent Porosity

In calculation for the percentage apparent porosity, all the specimens were been measured to get the initial weight (weight in air). They were suspended in water individually with string and air bubbling was observed. The weight of each suspended specimen was measured. The specimens were also soaked in water for 24 hours after which the weights were measured. The percentage apparent porosity was determined as follows:

$$\text{Apparent Porosity } \% = \frac{\text{soaked weight} - \text{wet weight in air (g)}}{\text{soaked weight} - \text{suspended weight (g)}} \times 100$$

Filtration Rate

The set-up for the filtration rate is shown in Figure1. Each of the membrane samples was placed on bowl and water to be treated was poured inside the membranes. Time was set and the filtrated volume was measured at different time intervals.

Statistical Analyses

The statistical method used in this research work was majorly SPSS for Windows Release 16.0. The T-Test Compare Means was used to test any significant difference in rate of filtration of all membrane samples at the 95% confidence interval.

In statistics, confidence intervals (CI) estimate and represent uncertainty or imprecision associated with estimates of population parameters from sample data. Instead of estimating the parameter by a single value, the parameter is represented by an interval. In that way, confidence intervals indicate the reliability of an estimate. A confidence interval always presents a particular confidence level, usually expressed as a percentage. The end points of the confidence interval are referred to as confidence limits. Increase in the desired confidence level will increase the confidence interval. Ninety-five percent confidence intervals for all the developed relationships were determined.

Figure 1: Filtration Rate set-up.

RESULTS AND DISCUSSION

Chemical Analysis

Table 2 shows the percentage chemical composition of the raw material used for this work. The presence of silica and alumina with percentage compositions of 46.4% and 34.0% respectively showed the high purity of the clay used.

Table 2: Chemical composition of Ajebo Clay

Clay	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI
% composition	46.4	1.69	34.0	2.49	N-D	0.04	0.02	0.03	0.08	0.04	17.7

N-D: Not Detectable

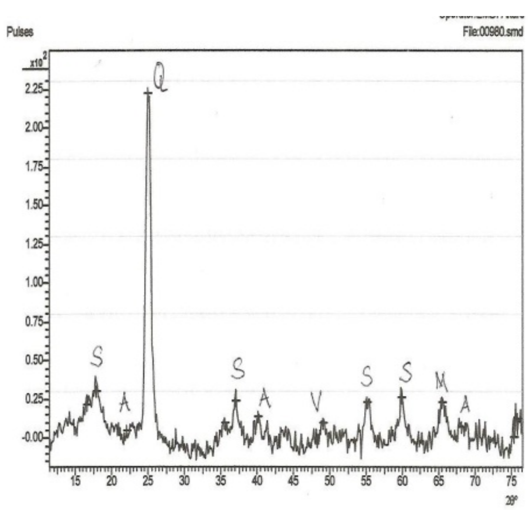
The main minerals identified by X-Ray Diffractometer (XRD) in the kaolin deposits are kaolinite [$Al_2Si_2O_5(OH)_4$], Kaolinite is dominant and the chemical composition of the kaolin is essentially SiO_2 and Al_2O_3 [8].

Percentage Preparation of membranes

Table 1 shows the percentage compositions Different compositions (dry basis) of raw materials used for preparing membranes. The percentage content of clay in the mixture was decreasing from sample 01 to 06 while that of kaolin was increasing from 0% to 45%.

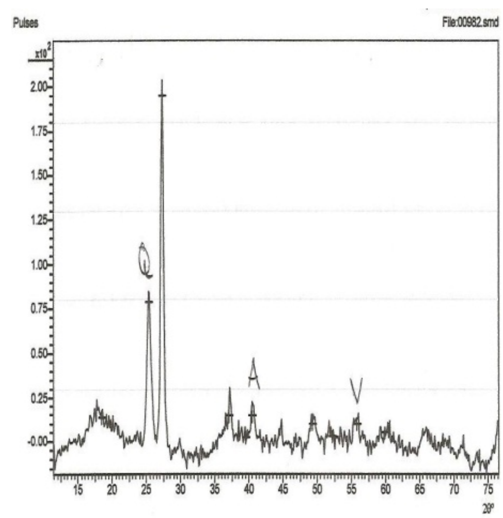
Membranes Characterizations
X-Ray Diffraction Analysis

All the samples membranes were fired at 1100^{O}C and Figures 2-7 show the X-ray diffractometer results of both the raw materials used in preparation and the membranes. There was an observation of reflections of quartz (Q), mullite (M), and nephiline (Na_2O, Al_2O_3, $2SiO_2$) and crystalline form of aluminum oxide (Al_2O_3) with traces of iron, titanium, and chromium [9].



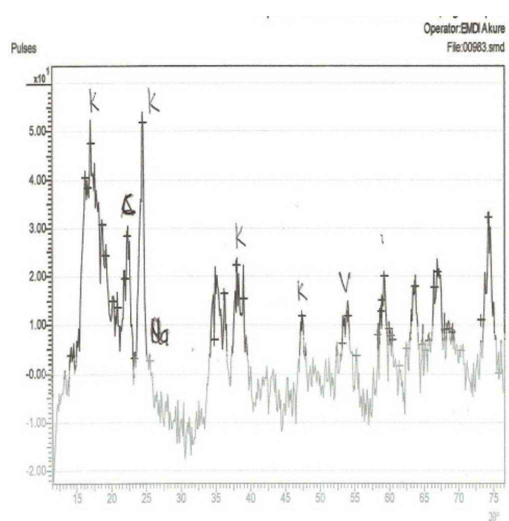
S- Silicate, A-Alumina, Q-Quartz,
V-Vermicullite, M-Montmorillonite

Figure 2: XRD of Sample 01.



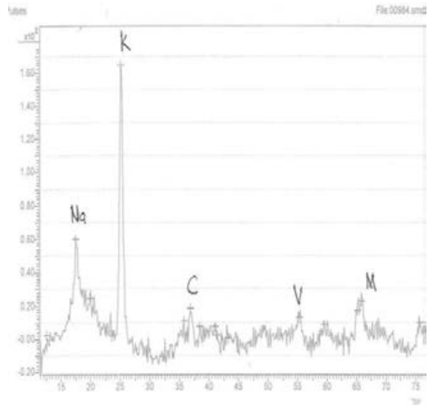
A-Alumina, Q-Quartz, V-Vermicullite

Figure 3: XRD of Sample 02.



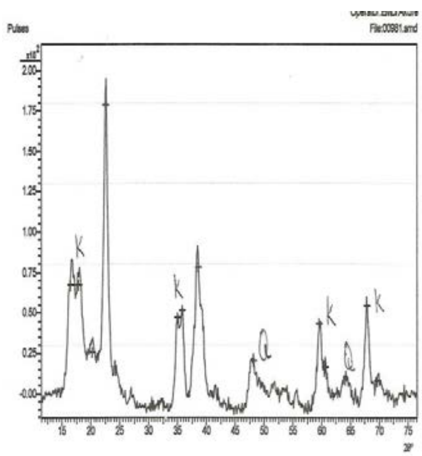
Na-Sodium, K- kaolin , C- Carbon V-Vermicullite

Figure 4: XRD of Sample 03.



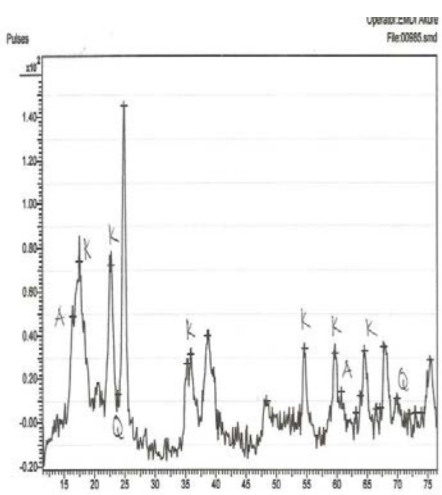
Na-Sodium, K- kaolin , C- Carbon
V-Vermicullite, M-Montmorillonite

Figure 5: XRD of Sample 04.



Q-Quartz, K- Kaolin

Figure 6: XRD of Sample 05.



A-Alumina, K- kaolin ,Q-Quartz

Figure 7: XRD of Sample 06.

Bulk Density

Figure 8 and Table 3 shows the bulk density of the specimens increased from specimens 01 to 06 with a little deviation from specimen 02, the increase in bulk density was as a result of reduction of clay contents in in the specimens with an increase in kaolin [10].

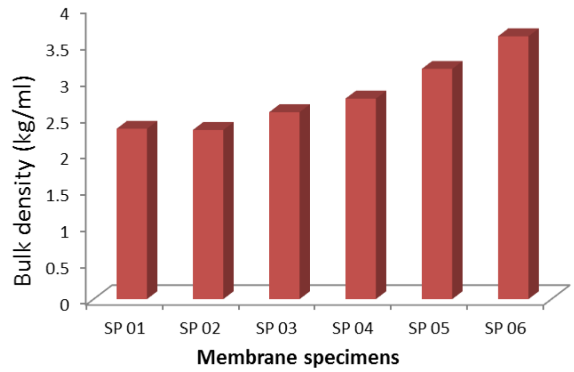


Figure 8: Bulk Density.

Water Absorption (%)

The percentage of water absorption was observed to decrease from specimen 01 to specimen 06. The highest percentage of water absorption was shown in specimen 01 due to highest content of clay in the membrane preparation and the leas percentage in specimen 06 [10 and 11] as shown in Figure 9 and Table 4. The greater the apparent porosity, the greater the water absorption capacity of the clay. The water absorption capacity of the clay has a very strong relationship on its drying behavior [11].

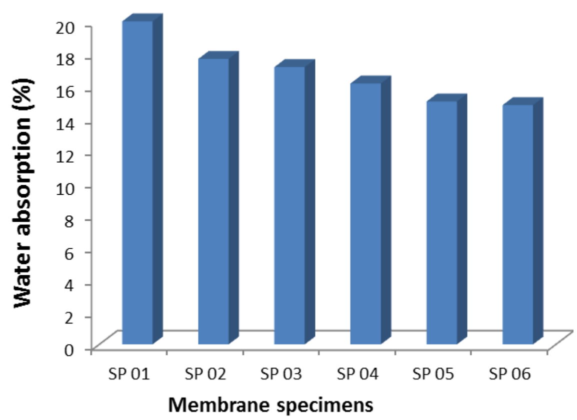


Figure 9: Water Absorption (%)

Table 3: Bulk Density of Samples.

Specimen	Weight in Air (g)	Volume of Water Displaced (ml)	Bulk Density (g/ml)
01	81.7	35	2.334
02	128	55.2	2.319
03	133	51.9	2.563
04	147	53.5	2.748
05	136	43.1	3.156
06	108.1	30	3.603

Table 4: Water Absorption Soaked for 24 Hours.

Specimen	Weight in Air (g)	Wet Weight (g)	Weight Differences (g)	Water Absorption (%)
01	81.7	98.02	16.32	19.976
02	128	150.6	22.6	17.656
03	133	155.81	22.81	17.150
04	147	170.72	23.72	16.136
05	136	156.43	20.43	15.022
06	108.1	124.1	16	14.801

Percentage Apparent Porosity

The percentage of apparent porosity of all the specimens was shown in Figure 10 and Table 5. The highest percentage value of porosity was observed in specimen 01 (SP 01) with 108.8% and the least was on specimen 06. Generally the percentage of apparent porosity decreased from specimen 01 to 06. The least value of percentage apparent porosity in specimen 06 was due the more of Kaolin contents which led to high compact of the membrane and less filtration rate was as well observed.

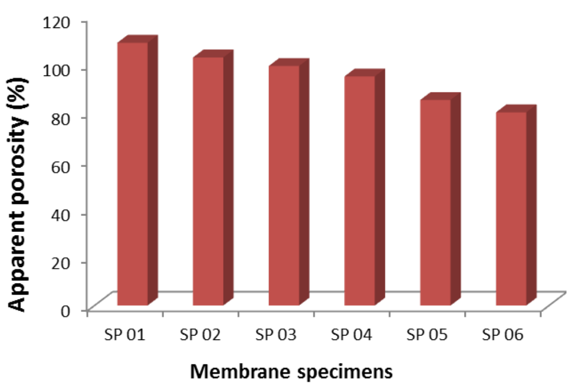


Figure 10: Apparent Porosity (%)

Filtration Rate (ml/hr)

Figure 11 and Table 6 show the comparison of all specimens at different time intervals. The highest filtration was observed on specimen 01 in all the time intervals. The rate of filtration increased with an increase in hour of filtration. The specimen 01 had the highest filtration rate due to the high numbers of porosity of the membrane and specimen 06 with low porosity had the least rate of filtration

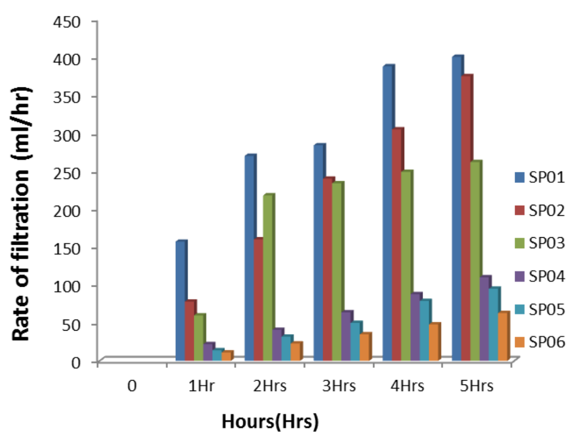


Figure 11: Filtration Rate (ml/hr).

Table 5: Percentage of Apparent Porosity.

Specimen	Weight in Air (g)	Soaked Weight (g)	Suspended Weight (g)	Difference in Soaked Weight & Weight in air (g)	Difference in Soaked Weight & Suspended Weight (g)	% Apparent Porosity (%)
01	81.7	98.02	83.02	16.32	15	108.8
02	128	150.6	128.6	22.6	22	102.727
03	133	155.81	132.81	22.81	23	99.174
04	147	170.72	145.72	23.72	25	94.88
05	136	156.43	132.43	20.43	24	85.125
06	108.1	124.1	104.1	16	20	80

Table 6: Filtration Rate (ml/hr).

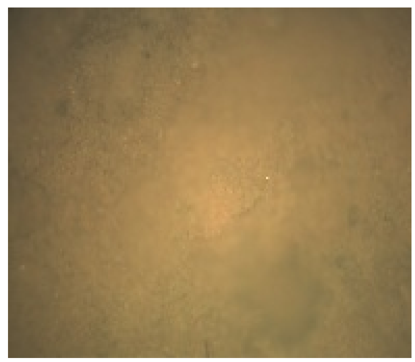
Specimen	1 Hr	2 Hrs	3 Hrs	4 Hrs	5 Hrs
01	157	270	284	388	400.5
02	78	160	240	305	375
03	60	218	234	249	262
04	22	41	64	88	110
05	14	32	50	79	95
06	11	23	35	48	63

Scanning Electron Microscopy of Membranes Specimens (SEM)

The Plates 1 to 6 show the scanning electron microscopy of all the membranes specimens (magnification 100x). It was noticed that no cracks were found in all the membranes specimens. It was seen that with increasing the amount of kaolin in the membrane, the structure was becoming denser. This was due to the fact that finer particles of kaolin were blocking the inter-particle space of clay, thus making the structure more condensed [9] The SEM Plate 5 was observed to have a little rough surface without any cracks.

M: X100

Plate 1: Scanning Electron Microscopy of Sample 01.

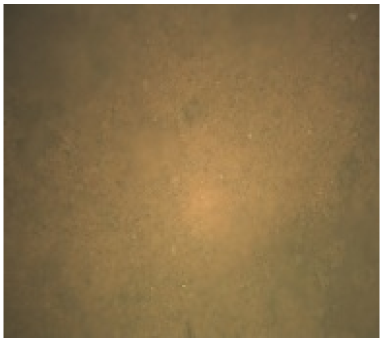


M: X100

Plate 2: Scanning Electron Microscopy of Sample 02.

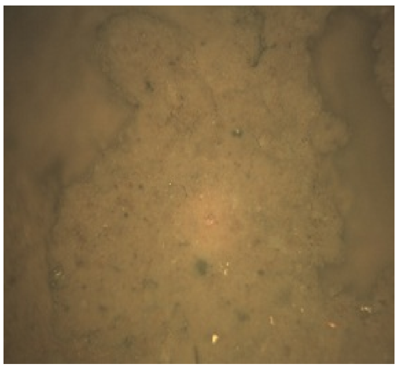
M: X100

Plate 3: Scanning Electron Microscopy of Sample 03.



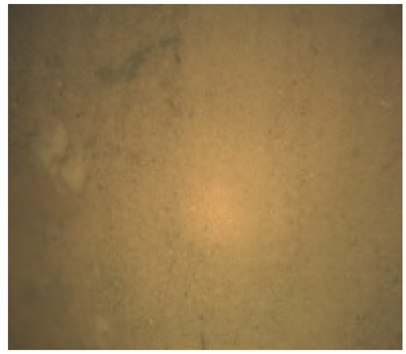
M: X100

Plate 4: Scanning Electron Microscopy of Sample 04.



M: X100

Plate 5: Scanning Electron Microscopy of Sample 05.



M: X100

Plate 6: Scanning Electron Microscopy of Sample 06.

STATISTICAL ANALYSIS

All the membranes samples are significant since they are all greater than 0.0 value with 95% confidence interval of the difference as shown in Table 7.

CONCLUSIONS

From the results obtained in this research study, it can be concluded that all the specimens of micro filtration membranes prepared at different percentages of contents were effective since there was no traces of crack in any of them as shown in all of the Plates, while the most efficient out of them was that of Sample 01 (SP 01). It can also be stated that the Specimen 01 has the highest filtration rate therefore; it has the most economical value.

Table 7: T-Test Analysis of the Filtration Test.

Specimens	t	df	Sig.	(2-tailed)	Mean Difference	Lower Upper
SAP1	6.753	4	.003	299.90	176.5914	423.2086
SAP2	4.427	4	.011	231.60	86.3449	376.8551
SAP3	5.546	4	.005	204.60	102.1736	307.0264
SAP4	4.119	4	.015	65.00	21.1884	108.8116
SAP5	3.638	4	.022	54.00	12.7906	95.2094
SAP6	3.942	4	.017	36.00	10.6445	61.3555

95% Confidence Interval of the Difference

It can be concluded that Membrane Sample 01 has the highest water absorption since the greater the apparent porosity the greater the water absorption capacity of the clay.

It was also found that bulk density increased with increased in amount of kaolin in the prepared membranes, but reverse was the case in term percentage of water absorption. Body compositions containing higher amount of kaolin showed lowest water absorption and highest strength due to better densification. SEM showed uniformly distributed pores and no cracks was seen around them. The porosity, percentage of water absorption and mechanical properties depend on the content of kaolin composition which had an effect on the membrane performance.

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ABOUT THE AUTHORS

Mr. F.T. Owoeye, graduated from the Mechanical Engineering Department of the Federal University of Agriculture, Abeokuta, Nigeria in 2008 with second class honors degree (B. Eng.). He is currently pursuing his Master’s degree in the same Department. His research interests include materials and corrosion engineering.

Dr. Engr. O.S. Olokode, is a Senior Lecturer and Acting Head of Mechanical Engineering Department, Federal University of Agriculture, Abeokuta. He holds Ph.D. degrees from both Imperial College, London and Federal University of Agriculture, Abeokuta.

Prof. P.O. Aiyedun, is a Professor of Mechanical Engineering, Federal University of Agriculture, Abeokuta. He is a registered Engineer and a Fellow of the Nigerian Society of Engineers. He holds a Ph.D. in Metallurgy and Material Engineering. He was a former Dean, College of Engineering, Federal University of Agriculture, Abeokuta-Nigeria. His research interest is in the area of steel production and material Engineering.

Mr. H.O. Balogun, is a staff member of the Ministry of Transportation, Lagos State Government. He earned his Higher National Diploma from Ibadan, Post graduate Diploma from Federal University of Technology, Akure and is presently pursing his Master degree in the Mechanical Engineering Department of the Federal University of Agriculture, Abeokuta, Nigeria. His research interests include materials engineering.

Engr. B.U. Anyanwu, is a Senior Staff in the Federal University of Agriculture, Abeokuta. He is

a registered Member of the Nigerian Society of Engineers.

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