Preparation of Ceramic Membranes from Sludge Waste

M. H. Roushdy

Abstract: ***Ceramic tiles industry produces industrial waste wit large amount which become a worldwide problem. Ceramic sludge produced from ceramic tiles wastewater treatment plant is routinely discarded as a useless waste. The aim of this paper is to recycle the ceramic sludge waste to be used as raw material for ceramic membrane production. The ceramic sludge was collected, dried, and characterized by mineralogical composition (XRD), thermal analysis (DTA and TGA), and chemical composition determination (XRF). The support ceramic membrane samples were formed, pressed, dried then fired using temperatures from 1050 to 1200 °C for 1 to 3 hours. Verification parameters were determined. It was found that the firing temperature is the only affecting parameter. The best firing temperature of ceramic membrane is 1150˚C. The prepared ceramic membrane at 1150 oC can be used in both nano-filtration and micro-filtration applications with high separation efficiency.***

Keywords**:** ***ceramic sludge, ceramic wastes, ceramic membranes, nano-filtration, micro-filtration.***

I. INTRODUCTION

The membrane is like a selective barrier which has the ability to separate some components on its surface which called as retentate while the other part pass through it which called as permeate. The main types of membranes are ceramic and polymeric membranes. The ceramic membrane can be fabricated from inorganic materials like titania, zirconia and alumina oxides. The ceramic membranes have disadvantages such as high cost because of the highly cost of the raw materials, the complexity of the fabrication process. The ceramic membranes have many advantages such as long life time, high thermal stability, high mechanical strength, and resistance to chemical solvents. On the other hand, the application of micro–filtration and ultra–filtration for water treatment become an important application nowadays. Nowadays ceramic membrane becomes a favorable method instead of many processes like coagulation, filtration and sedimentation [1].

A lot of researches were done on the use of industrial inorganic waste in the fabrication of ceramic membranes such as the work of Jedidi et al. [2,3] fabricated a ceramic membrane using fly ash waste after being mixed with organic additives and water. They shaped and fired the resulting mix to 1125 °C to obtain a membrane having reasonable mechanical strength. Also, Fang et al. [4] produced a low cost ceramic membrane by using coal fly ash. On the other hand saw dust was used as pore former in a ceramic type membrane devised by Bose and Das [5, 6]. Recently, Tolba et al. [7] fabricated an efficient adsorbent ceramic membrane from amorphous nano–silica particles from rice husk. Recently, Amin el al. [8] prepared a ceramic membrane from roller kiln waste powder. Since water scarcity is a critical concern in many areas worldwide, there is an increasing concern about the problems that arise due to water shortage and the possible solutions available [9].

Revised Manuscript Received on January 05, 2020

M H Roushdy, Chemical Engineering Department, Faculty of Engineering, The British University in Egypt, El-Sherouk City, Egypt.

II. EXPERIMENTAL WORK

A. Raw Materials and Its Analysis

The raw material that was used for production of ceramic membrane is ceramic sludge.

Wavelength Dispersive (WD–XRF) Sequential Spectrometer was used to make the chemical analysis of fine ceramic waste. X–Ray Diffractometer apparatus was used to determine the phase composition. TGA and DTA were used to determine the thermal changes in the waste material. Particle size distribution of fine waste was determined using Laser Particle Size Analyzer according to ASTM B 422 [10]. Powder density was determined by the density bottle method ASTM B 311 [11].

B. Support Membrane Specimens Preparation

The first step that is required to remove the water content from the waste is drying the ceramic tiles sludge at 110 ^{o}C for one day followed by jaw crusher for crushing and finally ball mill for grinding to convert the sludge into a fine waste powder. The fabrication of support membrane specimens was done as follows:

a) A fine waste powder of 10 grams was mixed with water.
b) Cylindrical specimens of diameter 50 mm were formed in molds by pressing under uniaxial pressure = 25 MPa using a laboratory hydraulic press.
c) Membrane samples were dried by dryer. First using a mild drying of 70 °C for 6 hours, then dried using a drastic conditions of 110 °C for additional 6 hours.
d) Laboratory furnace was used to fire the ceramic membrane specimens, at four firing temperatures (1050, 1100, 1150 and 1200 °C), using soaking time from 1 to 3) hours at each temperature. The firing schedule was designed to simulate roller kiln operation as follows:
   i. Fast increasing to the temperature to 600 °C from room temperature.
   ii. Slow temperature increasing from 600 °C to 700 °C to get rid of combined water so as to prevent crack formation.
   iii. Fast temperature increasing from 700 °C to 800 °C.
   iv. Slow temperature increasing from 800 °C to 1000 ° so as to provide suitable time for calcinations of calcium carbonate.

v. Fast temperature increasing from 1000 °C to firing temperature from 1050 to 1200 °C then stop the furnace.

C. Verification Parameters Determination

Apparent and closed porosity, percent water absorption, and bulk density were determined according to ASTM C 373, [12].

D. Filtration Analysis

Experimental work was carried out on the filtration unit fabricated in the lab. This unit as shown in Fig. 1 consists of a ceramic membrane module has openings for feeding, concentrate and permeate. The well water fed to the 50 mm ceramic membrane from a well water feeding tank (5 litres) using a pressure pump having a pressure of 9 bar at 25°C. The test is done onto two steps.

a) The first one include a preliminary work that was done by passing the well water through the ceramic membranes prepared at different firing temperatures of (1050, 1100, 1150 and 1200 °C) using 1 hour soaking time to determine the optimum firing temperature and then the optimum ceramic membrane. The concentration of salts in water in mg/l was determined using a conductivity meter. The conductivity meter was used to determine the conductivity of well water before after treatment to determine the salt separation (SP%) percent using the following relation.

SP%=(concentration of feed water-concentration of treated water)/(Concentration of feed water)*100 (1)

b) The second step include a detailed analysis for well water before and after treatment using the prepared membrane at the optimum firing temperature to determine its application and separation efficiency for each element and finally compared the resulted analysis of treated well water with standards for drinking water.

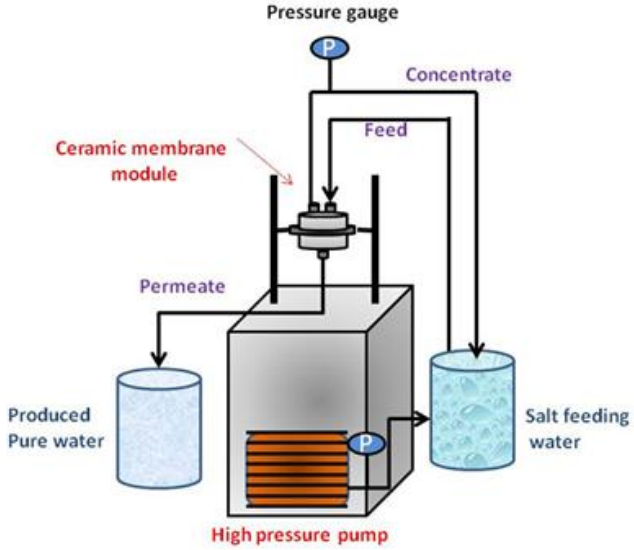

Fig. 1. Ceramic Membrane Testing Unit

E. Characteristics of the Optimum Membrane

The micrographs of the optimum ceramic membranes were obtained using sscanning electron microscope (SEM). Pore size distribution is determined using Hg- Porosimetry method. Specimens were introduced into the sample holder chamber of equipment by micrometric pore size with a type number of 9320 version 2.08. Hg- Porosimetry method is done in a evacuating chamber. The ceramic membrane is subjected to mercury using a hydraulic pressure from 1.81 to 29958.20 psia. the compressive strength was measured using a standard UTM apparatus under the effect of 3 mm/ min^{-1} shear rate.

III. RESULTS AND DISCUSSION

A. Ceramic Waste Chemical Composition

Table (1) shows the chemical analysis of the ceramic waste as determined by XRF

Silica is considered as the main component as shown in Table (1). The loss on ignition (LOI) happened because of the loss of limestone and organic matter from the waste powder.

Table 1 Chemical Composition of Ceramic Waste

Constituents (wt. %)	Waste
SiO_2	54.35
Al_2O_3	21.32
Fe_2O_3	4.67
TiO_2	0.85
MnO	0.12
MgO	0.11
CaO	5.99
Na_2O	2.88
K_2O	1.4
P_2O_5	0.17
Cl	0.05
SO_3	0.12
ZrO_2	<0.01
LOI	7.7

B. Ceramic Waste Mineralogical Analysis

Fig. 2 shows the mineralogical of ceramic waste by XRD method.

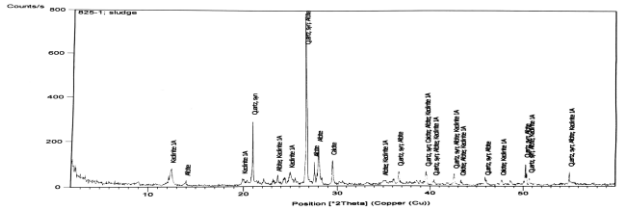

Fig. 2: Ceramic Sludge Waste XRD Pattern

The XRD pattern of ceramic waste proved that the waste powder consist of the following phases: Kaolinite (Al_2 Si_2 $O_5(OH)_4$), Quartz (SiO2), Albite ($Na_{0.98}$ $Ca_{0.02}$) ($Al_{1.02}$ $Si_{2.98}$ O_8), and Calcite ($CaCO_3$). The main phase is quartz.

C. Ceramic Waste Thermal Analysis

Fig. 3 shows DTA – TGA graph for waste powder.

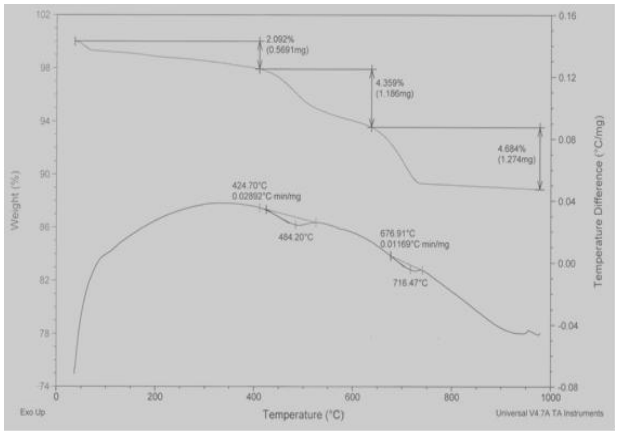

Fig. 3: TGA and DTA Pattern of Ceramic Sludge Waste

The chart gives very important conclusions. The first loss in weight happened due to physical water elimination then the appearance of an exothermic peak ending at about 424.7^{o}C because of the organic impurities oxidation. An endothermic peak follows ending at about 550^{o}C because of clay's lattice loss. An endothermic peak can be observed at about 716.47^{o}C due to the presence of limestone.

D. Ceramic Waste Particle Size Distribution

The particle size distribution of the ceramic powder waste is shown in Fig.4. The minimum particle size is about 0.05 mm while its maximum value is about 1mm.

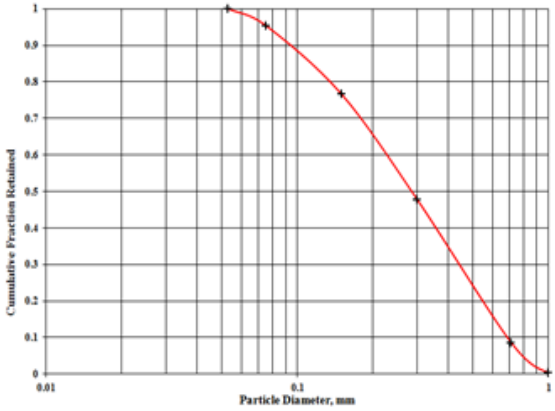

Fig. 4: Ceramic Waste Particle Size Distribution

E. Powder Density

The powder density was found to be 2.72 g/cm^3.

F. Water Absorption

The effect of firing temperature and soaking time on the percent boiling water absorption was investigated. The firing firing temperature is the only effective parameter and there is no effect due to soaking time change. Fig. 5 shows the results obtained at soaking time = 1 hour.

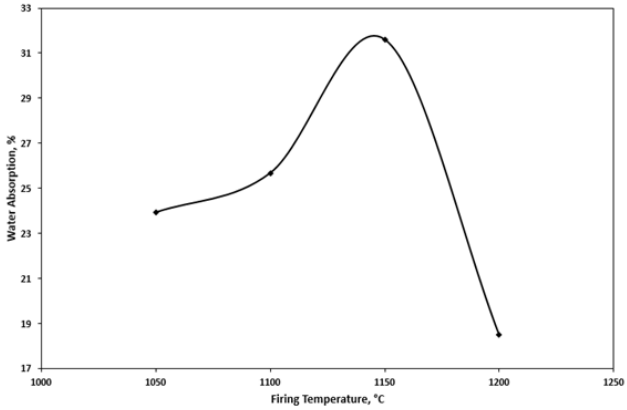

Fig. 5: Percent Water Absorption vs Firing Temperature.

Water absorption increases up to about 1150 °C as dilatation happened to the samples because of the increase in open pore size, then after this temperature there is a decrease in water absorption due to the occurrence of sintering.

G. Apparent Porosity

The behavior apparent porosity is like that of water absorption. The maximum porosity equal 52% was found to be at 1150 °C. The minimum porosity 37% was found to be at 1200 °C. The firing temperature is the only effective parameter and there is no effect due to soaking time change. Fig. 6 shows the results at 1 hour soaking time.

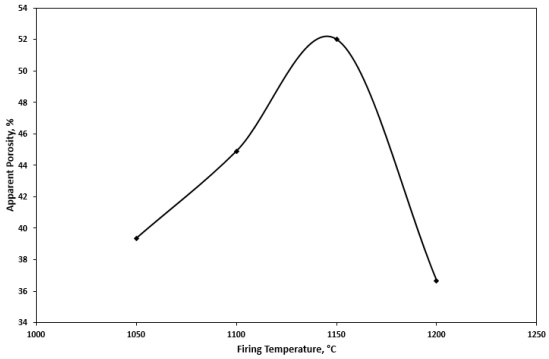

Fig. 6: Percent Apparent Porosity vs Firing Temperature.

H. Bulk Density

The values of bulk density are only influenced by firing temperature. TGA showed that the true powder density remains approximately constant on firing as the losses are very small can can be negelected. The bulk density is inversely proportional to total porosity of the body. bulk density decreases until 1150 °C at which its value equal to 1.31 g/cm^3 and then increases on raising temperature up to 1200 °C at which its value equal to 1.71 g/cm^3. Fig. 7 shows the results obtained on soaking for 1 hour.

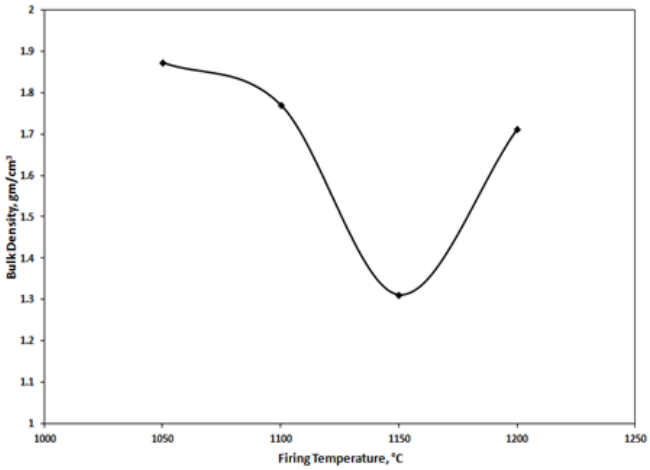

Fig. 7: Bulk Density vs Firing Temperature

I. Closed Porosity

The open porosity was determined at 1150 °C and was found to equal 52% using values of the powder density of the waste which is equal to 2.72 g/cm^3, bulk density which is equal to 1.31 g/cm^3. The total porosity was determined to be 52% so practically approximately there is no closed pores up to firing temperatures 1150 °C.

The open porosity was determined at 1200 °C and was found to equal 37% using values of the powder density of the waste which is equal to 2.72 g/cm^3, bulk density which is equal to 1.71 g/cm^3. The total porosity was determined to be 37.13% so there is very small closed porosity equal to 0.13 %. The previous results that proved that approximately all pores are open pores which are a good prove that the fabricated membrane can be used in filtration applications. The optimum membrane is the membrane prepared and finally fired at temperature of 1150 ^{o}C as increasing the firing temperature results in no change regarding the porosity.

J. Filtration Experimental Work

Preliminary tests were undergone to investigate the viability of the prepared membranes and determination of the optimum ceramic membrane and finally the optimum firing temperature. As shown in Fig. (8) and (9), an experiment was done using well water passed through the membrane. The maximum percent salt rejection was 80 % at firing temperature 1150 °C and soaking time 1 hour; the permeate flux was quite low due to the small pore size; this indicates that this ceramic membrane support can provide a promising separation performance.

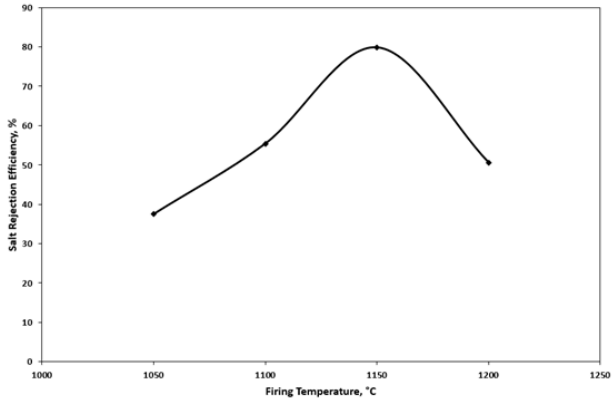

Fig. 8: Salt Rejection for Support Ceramic Membranes

Detailed salt and turbidity separation from well water sample was studied using ceramic membrane prepared at the optimum temperature equals 1150 ^{o}C. The removal of mono, di , and trivalent ions was determined using the prepared ceramic membrane as shown in Tables 2, 3, and 4 that represents the analysis of well water before and after treatment using the membrane. The following tables show that the prepared membrane can be used in nano-filtartion applications and micro-filtration applications It can be used in the separation or removal of water turbidity, mono-valent like sodium ions, potassium ions and chlorine ions, and di-valent ions as sulphates, magnesium and calcium ions. The resulted water after treatment with the prepared membrane has results compatible with the standard limit for drinking water (Ministry of Health and Population. Decree No. 458/2007).

Table 2 Physical Parameters Well Water Analysis before and after Using the Ceramic Membrane

Element to be Analyzed	Results before treatment	Results after treatment	Percent removal	Units	Accepted limits (acc. to 458/2007)
- Colour	Colorless	Colorless	-	mg/l Pt Co	Colorless
- Turbidity	3	0.2	93.3	N.T.U	< 1
- Odour	Odourless	Odourless	-	Odourless	Odourless

Table 3 Physicochemical Parameters Well Water Analysis before and after Using the Ceramic Membrane

Element to be Analyzed	Results before treatment	Results after treatment	Percent removal	Units	Accepted limits (acc. to 458/2007)
- pH	7.55	7.35	-		6.5-8.5
- Conductivity	6670	1100	83.5	µS/cm	< 1200
- Total hardness as ($CaCO_3$)	1700	290	82.9	mg/l	< 500
- Calcium (Ca^{++})	420	73	82.6	mg/l	< 140
- Magnesium (Mg^{++})	190	30.4	84	mg/l	< 36
- Bicarbonate (HCO_3^-)	225	29	87.1	mg/l	–
- Total alkalinity as ($Ca\ CO_3$)	184	25.6	86.1	mg/l	< 120
- Bicarbonate alkalinity as ($Ca\ CO_3$)	184	25.6	86.1	mg/l	–
- Sodium [Na^+]	2190	335	84.7	mg/l	< 200
- Potassium [K^+]	72	10.97	84.8	mg/l	< 10
- Chloride [Cl^-]	1852	280	84.9	mg/l	< 250
- Sulphate [SO_4^{--}]	1200	165	86.3	mg/l	< 250
- Total dissolved solids [TDS]	4308	684	84.1	mg/l	<1000

Table 4 Undesirable Substances Well Water Analysis before and after Using the Ceramic Membrane

Element to be Analyzed	Results before treatment	Results after treatment	Percent removal	Units	Accepted limits (acc. to 458/2007)
- Ammonium [NH_4^+]	0.17	0.13	23.5	mg/l	< 0.50
- Nitrates [NO_3^-]	12.53	4.18	66.6	mg/l	< 45
- Nitrite [N]	0.050	0.015	70	mg/l	< 0.060
- Phosphate [PO_4]	0.36	0.25	30.6	mg/l	< 0.40
- Silica [SiO_2]	16.28	9.21	43.4	mg/l	–
- Iron [Fe^{++}]	0.11	0.003	97.3	mg/l	< 0.30
- Manganese [Mn^{++}]	0.08	0.002	96.3	mg/l	< 0.40
- Copper [Cu^{++}]	0.05	0.003	94	mg/l	< 2.0
- Zinc [Zn^{++}]	0.34	0.03	91.2	mg/l	< 3.0
- Total chlorine	< 0.02	< 0.02	-	mg/l	–
- Free chlorine	< 0.02	< 0.02	-	mg/l	–
- Combined chlorine	< 0.02	< 0.02	-	mg/l	–
- Cyanide [CN^-]	< 0.001	< 0.001	-	mg/l	< 0.05

K. SEM Micrographs

The following SEM micrographs show the difference between two samples (Fig 9.), the first fired at 1150°C and the second at 1200°C using a zooming scales 1000×. These micrographs show that a glassy phase is present in both samples but its amount is larger in case of the sample fired at 1200°C so the separation efficiency at 1150°C is higher than that at 1200°C. The micrographs proved the sample fired to 1200°C have pores which are less numerous and smaller in size than that of the samples fired at 1150°C.

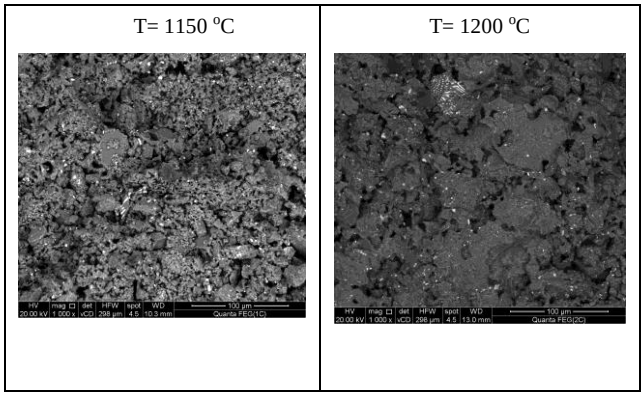

Fig. 9: SEM Micrographs (1000x).

L. Pore size Distribution

The ceramic membrane samples prepared at 1150 ^{o}C has the pore size distribution shown in Fig. 10. It shows the relation between pore diameter (µm) on x-axis and (dV/dD) differential intrusion (ml/g .µm) on Y-axis. The following figure shows that the optimum membrane can be used in Ultra-filtration and Nano-filtration applications. Pore size in range of 0.005 to 0.01 µm is used for Nano-filtration applications while pore size in range of 0.01 to 0.1 µm is used for Ultra-filtration applications.

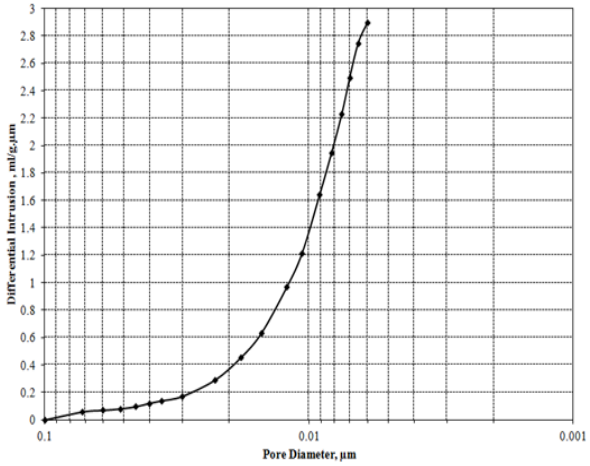

Fig. 10 Pore Size Distribution

M. Membrane Compressive Strength

Tested Specimen fired at 1150 °C was subjected to compression loading. It was found that it can withstand 25 MPa as a maximum stress without failure which means it can safely use in water treatment.

IV. CONCLUSION

This paper investigates the possibility of using the ceramic sludge waste for ceramic membranes preparation that can be used in the desalination of water. Samples were fired at different firing temperatures starting from 1050 up to 1200 °C and soaking time starting from 1 up to 3 hours. Results showed that the sintering parameters (percent water absorption, apparent porosity and bulk density) were unaffected by soaking time. The maximum porosity was resulted at 1150 °C. The percent closed porosity was negligible.

It was found that the firing temperature is the only affecting parameter on the produced ceramic membrane. The best firing temperature of ceramic membrane is equal to 1150˚C. It was proved that the prepared ceramic membrane at 1150 ^{o}C can be used in both nano-filtration and micro-filtration applications with high separation efficiency.

ACKNOWLEDGMENT

The authors would like to acknowledge the British University in Egypt (BUE) for funding this research through young investment research grand (YIRG) and also Ceramica Venus Company for providing facilities required to perform this work. The author would like to thank Prof. Magdi F. Abadir from Cairo university. The author is proud to be his student.

REFERENCES

1. Gaulinger S. , (2007) "Coagulation pre–treatment for microfiltration with ceramic membranes", TECHNEAU. An Integrated Project Funded by the European Commission under the Sustainable Development, Global Change and Ecosystems Thematic Priority Area.
2. Jedidi I., Khemakhem S., Larbot A., Amar R. , (2009) “Elaboration and characterization of fly ash based mineral supports for microfiltration and ultra–filtration membranes”, Ceramics International, 35, 2747–2753.
3. Jedidi I., Khemakhem S., Saïdi S., Larbot A., Elloumi–Ammar N., Fourati A., Charfi A., Ben Salah A., Amar R. , (2011) “Preparation of a new ceramic micro–filtration membrane from mineral coal fly ash: Application to the treatment of the textile dying effluents”, Powder Technology, 208, 427–432.
4. Fang J., Qin G., Wei W., Zhao X., Jiang L, (2013) “Elaboration of new ceramic membrane from spherical fly ash for micro–filtration of rigid particle suspension and oil–in–water emulsion”, Desalination, 311, 113–126.
5. Bose S., Das C., (2013), “Preparation and characterization of low cost tubular ceramic support membranes using sawdust as a pore–former”, Materials Letters, 110, 152–155.
6. Bose S., Das C., (2015) “Sawdust: from wood waste to pore–former in the fabrication of ceramic membrane”, Ceramics International, 41 (3A), 4070–4079.
7. Tolba G., Bastaweesy A., Ashour E., Abdelmoez W., Khalil K., Barakat N., (2015) “Effective and highly recyclable ceramic membrane based on amorphous nano–silica for dye removal from the aqueous solutions”, Arabian Journal of C.
8. Amin Sh.K., Roushdy M.H., El–Sherbiny S.A., Abdallah H.A.M., Abadir M.F., (2016) "Preparation of nano–size ceramic membrane from industrial waste", International Journal of Applied Engineering Research (IJAER), 11 (10), 7176–7181.
9. Hanjra M., Qureshi M. , (2010) “Global water crisis and future food security in an era of climate change”, Food Policy, 35, 365–377.
10. ASTM D 422 / 1963 (Reapproved 2007), “Method for particle–size analysis of soils”, ASTM Annual book, U.S.A., 4 (8).
11. ASTM B 311 / 2017, “Standard test method for density of powder metallurgy (pm) materials containing less than two percent porosity”, ASTM Annual book, U.S.A., 2 (5).
12. ASTM C 373 / 2017, “Standard test methods for determination of water absorption and associated properties by vacuum method for pressed ceramic tiles and glass tiles and boil method for extruded ceramic tiles and non-tile fired ceramic white-ware products”, ASTM Annual book, U.S.A., 15 (2).
13. Ministry of Health and Population. Decree No. 458/2007. [Cited 2009 March, 10th]. Available from http://www.mohp.gov.eg/environment/ laws/report458.doc.

AUTHOR PROFILE

Mai received her B.Sc. in Chemical Engineering at 2009 from Faculty of Engineering, Cairo University with a very good and hounored degree . She received her M.Sc. in January 2013. Mai published eight papers and three books and attended many conferences. She works as lecturer at Chemical Engineering Department in the British University starting from September 2017 till now.