WATER FILTRATION PERFORMANCE COMPARISON OF SAYONG BALL CLAY MEMBRANE PRODUCED BY GEL CASTING AND SPARK PLASMA SINTERING METHODS

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ABSTRACT

Some membranes are made of ceramic material due to their excellent properties that can withstand almost any feed conditions and possess natural adsorption agents for heavy metal removal. However, due to depleting of membrane resources and the high cost of raw material such as alumina, searching for alternative materials from natural resources attract researchers' attention. Natural Sayong ball clay is abundantly available in Malaysia and has great potential applications such as ceramic membrane but their properties and characteristics are scarcely reported in the literature. This study aimed to evaluate the effect of monomers ratios of Methacrylamide and N, N'-Methylenebisacrylamide (6:1-14:1) and sintering temperatures (550-1050°C) on the ceramic membrane properties. Gel casting and spark plasma sintering were used to fabricate the membrane and control their pore size. The investigation started with the raw powder characterizations by field emission scanning electron microscope (FESEM), x-ray diffraction (XRD), x-ray fluorescence (XRF), and particle size analyzer before being used to fabricate the membranes. After the fabricated membranes have been characterized and tested physically and mechanically, the performance of membranes was then tested with water filtration and quality analysis. It was found that the microstructures and properties of the ceramic membrane were influenced not only by the ratio of monomers during the gel casting process but also was found to be dependent on the spark plasma sintering temperatures. Membranes fabricated by gel casting showed that microstructures of the sintered membranes were highly porous (30-46%) which could not provide enough modulus of rupture (MOR) (20-36 MPa) but vice-versa in the case of membranes fabricated by spark plasma sintering method which achieved maximum MOR of 96 MPa with zero % of porosity. The gel casting membrane with the highest ratio of monomers of 14:1 gave the highest copper ions removal efficiency of 87%, color removal percentage of 99.3%, hardness reduction percentage of 90.5%, and nickel ions removal percentage of 59% while the spark plasma sintering membrane with the lowest sintering temperature at 650ºC gave the highest copper ions removal efficiency of 83%, colour pigment removal percentage of 99.5%, water hardness reduction percentage of 91.2%, and nickel ion removal percentage of 18.2%. It was found that the ball clay membrane was best fabricated with gel casting with a 14:1 ratio of monomers in terms of water qualities.

ABSTRAK

Setengah membran diperbuat daripada bahan seramik disebabkan sifatnya yang sangat baik yang dapat digunakan dalam hampir apa jua keadaan bendalir dan sebagai ejen penjerap semulajadi untuk menyingkir logam berat. Namun, disebabkan pengurangan sumber membran dan harga bahan mentah yang mahal seperti alumina, pencarian bahan alternatif dari sumber semulajadi telah menarik perhatian para penyelidik. Tanah liat semulajadi bebola Sayong banyak terdapat di Malaysia dan mempunyai potensi aplikasi yang besar seperti membran seramik tetapi sifat dan ciri-cirinya jarang dilaporkan di dalam literatur. Kajian ini bertujuan untuk menyelidik kesan nisbah antara monomer iaitu *Methacrylamide* dan *N, N'-Methylenebisacrylamide* (6:1-14:1), dan suhu pensinteran (550-1050°C) ke atas sifat membran seramik. Tuangan gel dan pensinteran percikan plasma telah digunakan untuk menghasilkan membran dan mengawal saiz keliangan membran masing-masing. Penyelidikan dimulakan dengan pencirian serbuk mentah dengan mikroskop imbasan elektron pancaran medan (FESEM), pembelauan sinar-x (XRD), pendarkilau sinar-x (XRF), dan penganalisis saiz zarah sebelum digunakan untuk membuat membran. Setelah membran dicirikan dan diuji secara fizikal dan mekanikal, prestasi membran kemudian diuji dengan ujian penapisan dan analisis kualiti air. Didapati bahawa struktur mikro dan sifat membran seramik tidak hanya dipengaruhi oleh nisbah monomer semasa proses tuangan gel tetapi ia juga bergantung kepada suhu pensinteran percikan plasma. Membran hasil dari tuangan gel menunjukkan bahawa struktur mikro yang disinter sangat berliang tinggi (30-46%) yang mana tidak dapat memberikan nilai modulus rekahan (MOR) (20-36 MPa) yang mencukupi tetapi sebaliknya membran yang dihasilkan dari kaedah pensinteran percikan plasma mempunyai MOR maksimum iaitu pada 96 MPa dengan peratus keliangan sifar. Membran tuangan gel dengan nisbah monomer tertinggi, 14:1, memberikan penyingkiran ion kuprum tertinggi pada 87%, peratusan penyingkiran pigmen warna pada 99.3%, peratusan pengurangan kekerasan air pada 90.5%, dan peratusan penyingkiran ion nikel pada 59% sementara membran pensinteran percikan plasma dengan suhu pensinteran terendah pada 650ºC memberikan kecekapan penyingkiran tertinggi ion kuprum pada 83%, peratusan penyingkiran warna pada 99.5%, peratusan pengurangan kekerasan air pada 91.2%, dan peratusan penyingkiran ion nikel pada 18.2%. Didapati bahawa membran tanah liat bebola terbaik diperbuat dengan kaedah tuangan gel dengan nisbah monomer-monomer 14: 1 berdasarkan faktor kualiti air.

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LIST OF ABBREVIATIONS AND SYMBOLS

°C	-	Degree Celsius
SEM	-	Scanning Electron Microscopy
ρ	-	Density
mL	-	Milliliter
MAM	-	Methacrylamide
MAD	-	N,N'-Methylenebisacrylamide
TEMED	-	Tetramethylethylenediamine
APS	-	Ammonium Peroxodisulfate
IUPAC	-	The International Union of Pure and Applied Chemistry
Dp	-	Pore diameter
GC	-	Gel Casting
SPS	-	Spark Plasma Sintering
ROM	-	Ratio of monomers
CM	-	Ceramic membrane

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Water shortage and more stringent legislation regarding reclaimed water especially effluent from the industry that its activity demands about 25% of the world's total water usage (Judd et al.,2005). Agriculture is the main user of reclaimed water (70%), followed by industry (20%), and domestic uses (10%). Under the circumstance of wastewater in our country, a kind of wastewater treatment should be implemented, which purifies the wastewater to a level of the required safety for releasing and reusing the water.

For this purpose, an effective membranes should be implemented to filter the wastewater. Recently, polymeric membranes are conquering on the membrane market for wastewater filtration and inorganic membranes like ceramic membranes are mainly used in special cases where the polymeric membranes cannot be applied. In the inorganic membrane markets, ceramic

membrane materials are dominant, especially alumina membrane even though it is very expensive.

The ceramic membrane is very stable chemically, thermally, and mechanically, biologically inert, controllable microstructure and little pollution to our environment. Even though they have a high weight and substantial production costs, they are ecologically friendly, cheap and have a long working life. *Sayong* ball clay is material of a ceramic membrane and this clay is abundant in nature so we will be able to fabricate an inexpensive membranes.

By studying various aspects of current casting technology, it was determined that a new system would have to be developed to accomplish the goals of this study. The focus was on developing a membrane with high performance are desired to be fabricated with low cost, from the viewpoints of the economic benefit as well as the popular usefulness.

In this thesis, a brief discussion on the fabrication of microfiltration of the ceramic membrane by using two methods with attention to *Sayong* ball clay as a membrane material was a feature. This process aims to fabricate a complex, homogeneous pore sintered membrane by control the pore sizes by varying the ratio of monomers (ROM) between Methacrylamide and N,N Methylenebisacrylamide from 6:1 to 14:1 during the gel casting process and varying sintering temperature from 550 to 1050°C during the spark plasma sintering process.

In pursuit of this objective, gel casting (GC) and spark plasma sintering (SPS) processing techniques were used to fabricate and examined

the membrane as they are methods that have great potential for further development. Different properties especially mechanical properties of the final product were characterized and finally, the sintered products for both methods were tested for their filtration efficiency before compared to other membranes.

1.2 Problem Statement

Malaysia's environment has been regarded as one of the least polluted ones in Asia as reported by the World Wildlife Fund. But recent industrial and economic development has begun to increase environmental problems and degradation of surroundings. Population growth, urbanization, industrialization and the expansion of irrigated agriculture are imposing rapidly growing demands and pressures on the water resources, besides contributing to the increase in water pollution. Cities and farming residents are mainly responsible as polluters of the aquatic environment. These pollution problems will increase in the maintenance cost to overcome the problems and health problems (caused by heavy metal) that can cause harm to users.

Although water reuse within industrial shows reduction to statistic of water usage but it is tough to get the final output water that near the properties of freshwater as contaminants eventually be in the reclaimed water (Miranda et al.,2009) and worst freshwater intake is always needed to compensate losses in any case (Ordonez et al.,2011). Despite its great

application potential, the market for reclaimed water is nowadays still awaiting wider exploitation.

It is crucial to apply wastewater treatment to overcome the problems as the main factors limiting the use of reclaimed water are meeting quality standards and the cost of membrane material (Toze et al., 2006;Jimenez et al., 2008). As reported by Belibi et al., (2015), removal efficiency is the main problem in conventional methods of water filtration as pore sizes not sufficient enough to filter heavy metals that are smaller than the pore size of the membrane. For the sake of microfiltration that is a cheaper process, less fouled, and more controllable pore sizes, an added value mechanism is a must. Thus, to reduce the problem, along the microfiltration process, the adsorption mechanism of phases also applied to enhance the efficiency of filtration by reducing the heavy metal percentage.

Fabrication of membrane depends on the main crucial factor that is its pores sizes. Thus to fabricates a membrane with controllable pores, chosen the right method is significant. Lots of researches have prepared homogeneous pore sizes through the commonly-used spark plasma sintering method due to excellent homogeneity in the matrix of particle distribution as the conventional way would create a nonhomogeneous pore size problem that undesired for membrane application. This implementation process is restricted to some uncomplicated shape as it is difficult to obtain uniform structure through a complex molds. On the other hand, gel casting is a method to fabricating ceramic products related on a mechanism that combined from traditional clay and polymer- based. This method cheaper than SPS but its pore less controllable compared to SPS. However, the microstructure gel casting membrane-less effected to temperature. This gives benefits to certain phases that are required for the adsorption mechanism.

Recently, no microfiltration or membrane from ball clay-based material has yet been fabricated by those methods for heavy metal removal applications. This means it is an excellent choice to produce a new and cheap type of ceramic material as most ceramic material used Alumina-based that is expensive and limited. Therefore, natural and abundant clay would be a great choice.

1.3 Objectives of Research

The objectives of this study were:

1. To determine the optimum gel casting process parameter and the best ratio of monomers for the gel casting membranes in term of water assessments and related to its membrane characterization.
2. To determine the best sintering temperature for spark plasma sintering membranes in term of water assessments and related to its membrane characterization.
3. To compare the two methods in term of characterizations, water filtration performances, and water quality analysis.

1.4 Scopes of Research

i. Preliminary testing for gel casting was conducted based on slurry/ surrounding temperature, mixing parameters (speed and period), drying period at room (28ºC) and high temperature (35ºC), and sintering parameters (temperature, soaking time, heating and cooling rate)

ii. Preparation of ceramic membrane with different ratio of monomers (6:1 to 14:1) by using gel casting method and preparation of ceramic membrane with different sintering temperatures (550°C-1050°C) by using SPS method.

iii. To relate the physical characteristics (shrinkage, bulk density, apparent porosity, and open porosity) with the microstructure evaluation for various ceramic membrane sintered by SPS and gel casting method.

iv. For gel casting membranes, effects ratio of monomers (ROM) were related to the physical characteristics, microstructure evaluation, pore size distribution, water absorption, modulus of rupture (MOR), water filtration performances (flux and flow rate), and water quality analysis (copper, nickel, hardness, and color analysis) of ceramic membrane.

v. For SPS membranes, effects of sintering parameter were related to the phase transformation, physical characteristics, microstructure evaluation, pore size distribution, water absorption), MOR and hardness, water filtration performances (flux and flow rate), and water quality analysis (copper, nickel, hardness, and color analysis) of ceramic membrane.

vi. The best gel casting and SPS ceramic membrane in terms of filtration assessments were identified then compared with other membranes for the sake of enhancement and novelty.

1.5 Significances of Research

In this project, fabrication of *Sayong* Ball Clay as a ceramic membrane material for a medium of filtration by using two different methods to get an enhanced pore structure. The idea comes to use the cheap material *Sayong* ball clay and to study the efficiency of these membranes as a microfiltration filter and then be compared to other membranes as it is a local product and contributing to a green environment.

Besides that, the efficiency of these membranes in term of water filtration performances and water quality analysis were significant to fabricate a new membrane-type from a local source that can overcome the problems associated with water pollution caused by the human being. This pollution hazard from heavy metal was toxic to humans neither consume orally nor become a contact to skin literally (A.Djukic et al., 2013).

On top of that, the results obtained from this study can be used as guidelines in fabrication of microfiltration membrane made from clay based materials. The results may be useful to other researchers to improve the performance of the filtration ceramic membrane.

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Appendix A List of Publications

A) ARTICLE JURNAL

1. **Nurhanna M Z**, Norhayati Ahmad, Y Nakamura, Muazu Abubakar (2021). Sayong ball clay membrane for copper and nickel removal from effluent. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*.81.

2. Ahmad, N., **Mohd Zaidan,N.** (2013).Effect of Sintering Temperature on Membrane Properties of Sayong Ball Clay. *Advanced Mechanics and Materials*. 315, 349-353.

3. Ahmad, N., **Mohd Zaidan, N**. and Mohd Bazin, M**.** (2013). Fabrication and Characterization of ceramic membrane by Gel Cast technique for water filtration. *Advanced Materials Research*. 686, 280-284.

4. Mohamed Bazin, M., Ahmat, M.A., **Zaidan, N**.,Ismail, A.F. and Ahmad, N. (2014). Effect of Starch Addition on the Microstructure and Strength of the Ball Clay Membranes. *Jurnal Teknologi (Sciences & Engineering)*. 69:9, 117–120.

B) CONFERENCE PROCEEDING

1. B.I. Anis Farhana, Yuzo Nakamura, B.M. Maisarah Bazin, **B.M. Nurhanna Zaidan** and Norhayati Ahmad. Sintering Behavior of Shirasu Balloons in Spark Plasma Sintering. *The Society of Material Science, Japan Conference*.

2. **N. M. Zaidan**, M. Bazin, N. Ahmad and Y. Nakamura. Fabrication of Porous Ceramic Materials for the Filtration of Waste Water**.** *Conference of Japan Society of Mechanical Engineering.*

3. Mohamed Bazin, M., Ahmat, **M.A., Zaidan**, N.,Ismail, A.F. and Ahmad, N. Effect of Starch Addition on the Microstructure and Strength of the Ball Clay Membranes. *11th International Conference on Membrane Science & Technology.*

4. Ahmad, N., **Mohd Zaidan, N**. and Mohd Bazin, M**.** Fabrication and Characterization of ceramic membrane by Gel Cast technique for water filtration. *8th International Materials Technology Conference and Exhibition (IMTCE 2012).*

B) CONFERENCES

1. Mohamed Bazin, M., Ahmat, **M.A., Zaidan**, N.,Ismail, A.F. and Ahmad, N. Effect of Starch Addition on the Microstructure and Strength of the Ball Clay Membranes. *11th International Conference on Membrane Science & Technology*, 27-29 Aug 2013, Kuala Lumpur.

2. Ahmad, N., **Mohd Zaidan, N**. and Mohd Bazin, M. Fabrication and Characterization of Ceramic Membrane by Gel Cast Technique for Water filtration. *8th International Materials Technology Conference and Exhibition (IMTCE 2012)*, 9-12 July 2012, Selangor, Malaysia.

3. Ahmad, N., **Mohd Zaidan, N**. Effect of Sintering Temperature on Membrane Properties of Sayong Ball Clay. *3rd International Conference on Mechanical And Manufacturing Engineering (ICME 2012),* 20-21 Nov 2012,UTHM Batu Pahat, Malaysia.