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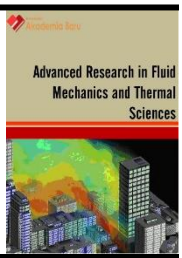

Sayong Ball Clay Membrane for Copper and Nickel Removal from Effluent

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ABSTRACT

An adsorption filtration mechanism using porous ceramic membranes was proposed for the removal of heavy metals from the effluent of the UTM Lake. The effectiveness of the removal depends on kaolinite microparticle which is used as an adsorption agent in ceramic membranes. In this work, Sayong ball clay (SBC) from Malaysia was used in the preparation of the ceramic membrane. Sayong ball clay membranes were fabricated by gel casting (GC) and spark plasma sintering (SPS) methods. The effect of kaolinite and pore size on copper and nickel removal was investigated. X-ray fluorescence (XRF), X-ray diffraction (XRD), mercury porosimetry, and adsorption analysis were used to relate with the adsorption performance. It is found that kaolinite with the 14:1 ratio of monomers in the GC-SBC membrane performed the highest heavy metal removal.

Keywords:
Copper; nickel; removal; heavy metal; clay; adsorption agent; adsorption; gel casting; spark plasma sintering; microfiltration; pore size

1. Introduction

Rapid economic growth and industrial development contribute to continuous heavy metal contamination in the environment. This pollution is common in industries such as electroplating tannery and, mining. There are numerous ways of removing heavy metal through adsorption, reverse osmosis, precipitation, and electrodialysis processes [1,2]. Recently, heavy metals removal in wastewater using membrane-based ceramic has gained tremendous importance as suitable water and wastewater remediation. However, harsh chemicals during the processes tend to change the physical and chemical properties of the inorganic membrane leading to secondary effluent pollution subsequently may suffer higher costs for maintenance or repair. Adsorption and membrane filtration are widely investigated for heavy metal removal due to its advantages such as

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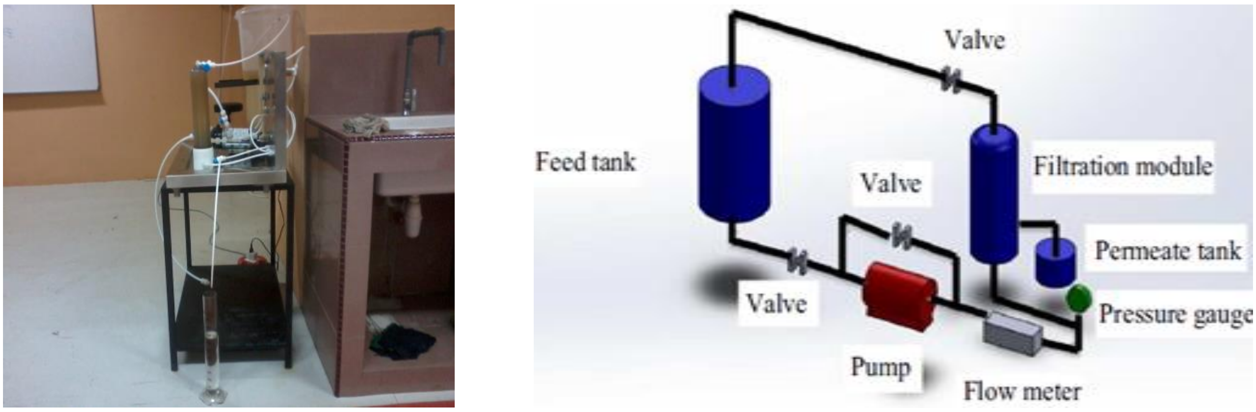
withstand continuous and longer operation period, easy to set up and changed, high performance, low cost, and wider feed conditions [3-6]. Adsorption agents are known in the previous researches for the efficient removal of nickel and copper from effluent [7]. The adsorption mechanism only works in the existence of the adsorption agents on the surface where the heavy metal will accumulate. Previous researches [8-10] reported natural clay-based adsorption agents such as wood and moss are safe to aids the removal of heavy metals from effluents. The use of alternative low-cost and abundant clay for heavy metal removal has been emphasized recently [11,12]. Though there are lots of works on the use of clay as a ceramic membrane for the treatment of wastewater, however, there are few studies on the use of ball clay from Malaysia as a ceramic membrane for the removal of nickel and copper from wastewater. Among common adsorption agents used for the removal of nickel and copper ions is kaolinite from the Phyllosilicates class. A clay-based adsorption agent was used to remove heavy metals from effluent due to its inertness and environmentally friendly. Furthermore, it is also relatively cheaper compared to others such as zeolites, and activated carbon [13-16]. Authors [17,18] revealed that the removal of heavy metals from effluent by using kaolinite is through exchangeable ions. This agent consists of a combined 3D tetrahedral network of SiO_4 and AlO_4. The replacement of Si4+ by Al3+ ions creates a negative charge in the tetrahedron lattice which later will be occupied by nickel and copper ions. On the other hand, membrane technology is considered the most efficient technology for the removal of heavy metals from effluent in combination with the adsorption mechanism. One type of membrane filtration is microfiltration. This type of filtration offers many benefits such as automatic and continuous systems [19], an easy and cheaper process, mild operating conditions [20], and not easily fouling [21]. The pore size of microfiltration has a significant influence on the percentage of heavy metal ions that succeeds to be attracted to a membrane wall or pass through the open pore [22]. Larger pore size will decrease the probability of ions to be attracted onto the membrane wall, therefore easier the ions to pass through. The objective of this study was to use of porous ceramic microfiltration membrane in combination with kaolinite as an adsorption agent for the formation of adsorption assisted filtration process able to operate at cost-efficient while producing significantly filtered effluent with pore sizes and adsorption agent dependable. A low-cost clay, Sayong ball clay from Malaysia will be used due to their chemical and thermally inert ceramic as the membrane may stand very broad indifference conditions without showing structural changes that can affect their operational behavior. The heavy metal adsorption performances were related to XRD, XRF, Mercury Porosimetry, and adsorption analysis.

2. Materials and Methods

Both spark plasma sintering (SPS) and gel casting (GC) membranes were fabricated by using Sayong ball clay powder from Perak, Malaysia. Details of fabrication information over the GC and SPS membranes were found in [23,24] but the different ratio of monomers (ROM) (Methacrylamide and N,N'Methylenebisacrylamide) and sintering temperatures were varied between 6:1 to 14:1 and 650°C to 1050°C, respectively. Chemical composition and phases of the membranes before and after filtration were analyzed using X-ray fluorescence spectroscopy Rigaku 3065 (XRF) and X-Ray Diffraction-XL30 (XRD), respectively. The pore size of the membranes was measured using mercury intrusion porosimetry (Micromeritics AutoPore-iii). The membranes are disc geometry with a diameter of ±30mm and a thickness of ±5mm were fabricated by using the direct forming method. The membrane filtration unit setup is shown in Figure 1. The unit was installed with a back-flushing system. The filtration tests were conducted by using lake contaminated effluent, and the effluents were measured before and after filtration in terms of pH, copper, and nickel contents. The spectrophotometer, DR1900 instrument was used to measure nickel and copper contents in the effluent based on ASTM D1886 and ASTM D1688, respectively.



(a) (b)

Fig. 1. Membrane filtration setup (a) filtration process and (b) its schematic diagram [25]

3. Results and Discussions

Table 1 showed the chemical compositions of Sayong ball clay. It is observed that raw SBC shows a 93% amount of future-to-be kaolinite (combination between silica and alumina). Figure 2 and 3 show the pores size distribution for SPS and GC membranes. The pores size distributions decreased as ROM (6:1 to 14:1) and sintering temperatures (650°C to 1050°C) increases. Authors [26-28] stated, these parameters can be attributed to more consolidation of the membrane powders as the temperature and ROM varied. Thus, affect the pores size distributions. The 6 and 8 ROM membranes presented bimodal to multimodal pore size distribution as compared to 10-14 ROM. SPS membranes presented a narrow peak indicated pores size is homogeneous as shown in Figure 2. This can be explained by the broader channel for diffusion and more available active sites for interaction which could improve adsorption amount [29]. However, SPS membranes were involved with high temperatures during sample preparation, leading to loss of adsorption agent due to the collapse of kaolinite structures that changed to other phases based on Eq. (1)-(3) [30].

Table 1
Chemical compositions by using XRF

	Compositions (mass %)
SiO_2	73.4
Al_2O_3	19.6
Na_2O	2.4
K_2O	1.2
CaO	1.1
MgO	1.1
others	1.2

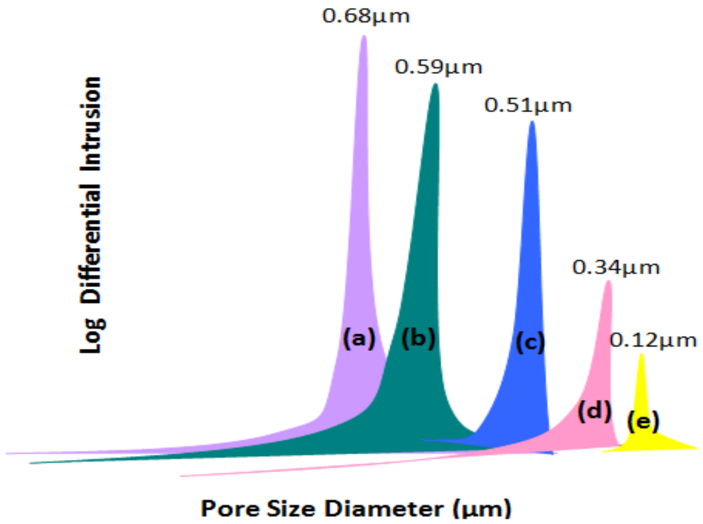


Fig. 2. Pore size distribution of the membranes fabricated using SPS sintered at (a) 650ºC, (b) 725ºC, (c) 800ºC, (d) 900ºC, and (e) 1050ºC, respectively

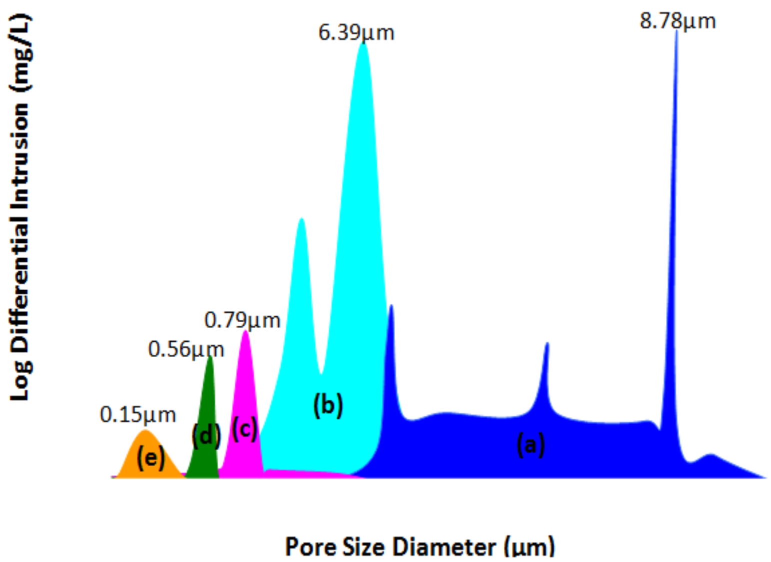


Fig. 3. Pore size distribution of the membranes fabricated using gel casting for ratio of monomers (a) 6, (b) 8, (c) 10, (d) 12, and (e) 14, respectively

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O(Kaolinite) \rightarrow Al_2O_3 \cdot 2SiO_2(Metakaolin) + 2H_2O \quad (1)$$

$$Al_2O_3 \cdot 2SiO_2(Metakaolin) \rightarrow Al_2O_3 \cdot 3SiO_2(spinal) + SiO_2(Quartz) \quad (2)$$

$$Al_2O_3 \cdot 3SiO_2(spinal) \rightarrow SiO_2(Tridymite) + Al_2O_3 \cdot 2SiO_2(Mullite) + Al_2O_3(Corundum) \quad (3)$$

From Table 2, nickel and copper removal percentage showed increment as ROM increased and sintering temperature decreased. These results coincided with the XRD pattern depicted in Figure 4 indicated the decrement of kaolinite for SPS membranes with temperature increasing as based on the intensity of the kaolinite. The results showed that the amount of the adsorption agent significantly affects the success of heavy metal removal in effluent other than the pore size factor. This statement valid with XRD pattern for the membrane fabricated by SPS sintered at 900°C with fairly least removal percentage as copper and nickel elements has found in the membrane after been filtered as shown in Figure 5. For GC membranes, changing in ROM does not affect the phase transformation as no heating is involved. Increasing ROM will yield a smaller pore size up to 0.15 µm and more homogeneous pore size distribution as graphs changed from multimodal to unimodal distributions. A large amount of adsorption agent and smaller pore size contributes much in successful of heavy metal removal based on the adsorption analysis of the membrane fabricated using gel casting with ROM 14. Even though the maximum temperature for both methods was set at a constant value which is 1050 ºC, the mechanism in the spark plasma sintering leads to better particle contact and densification, which affects the transformation of phases in the membrane. The contrast data between nickel and copper adsorption analysis is because of optimum pH factor where current 7.0-7.5 pH of effluent (Table 3) is optimum pH for copper adsorption compared to nickel that required 9-10 pH to adsorb the heavy metal efficiently [31].

Table 2
Pore sizes and adsorption analyses using mercury intrusion porosimetry and spectrophotometer, respectively

	Adsorption (%)		Mean pore sizes(µm)
	Copper	Nickel	
GC-6	68	12	8.78
GC-8	75	23	6.39
GC-10	81	44	0.79
GC-12	84	50	0.56
GC-14	87	59	0.15
SPS-650	83	18	0.68
SPS-700	80	18	0.53
SPS-725	76	18	0.59
SPS-875	65	17	0.18
SPS-900	62	17	0.12

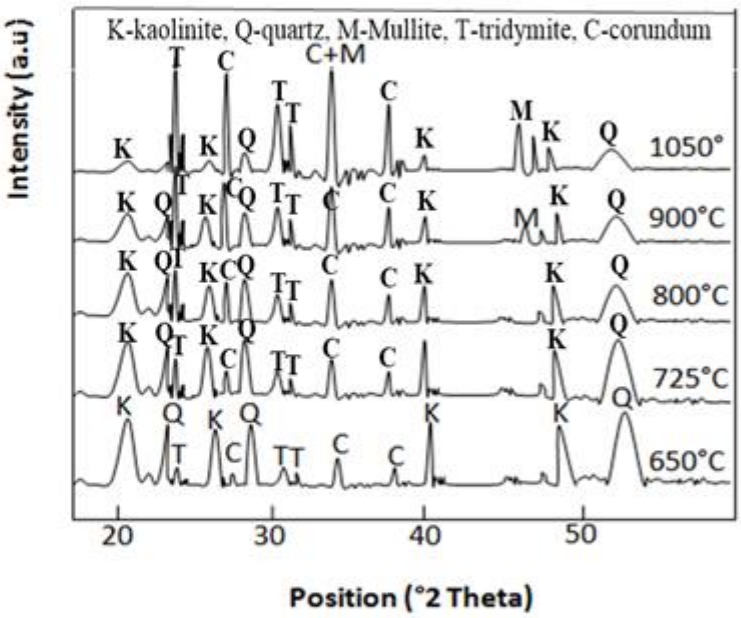


Fig. 4. XRD patterns of sintered membrane fabricated from SPS with various sintering temperatures

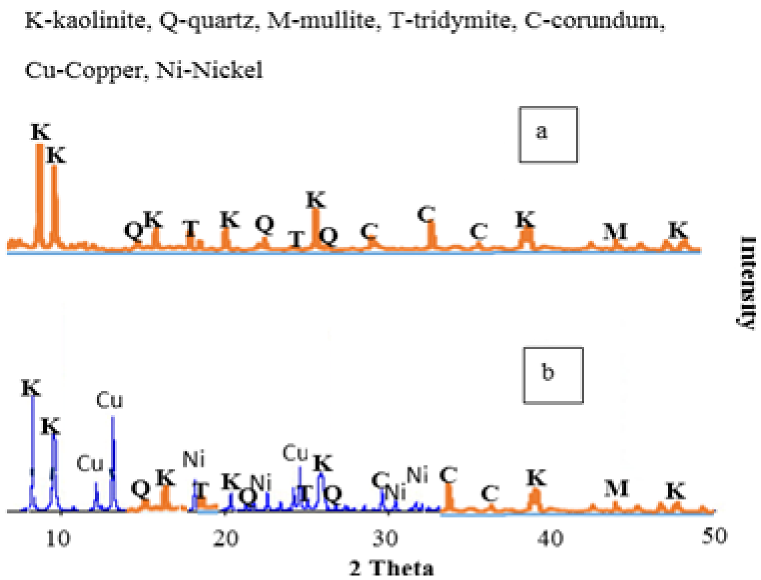


Fig. 5. XRD patterns for Nickel and Copper content in (a) virgin (before filtration) and (b) fouled (after filtration) SPS-900 ball clay membrane

Table 3
Characteristics of wastewater as taken from UTM lake

Parameters	Values
Copper(mg/L)	0.11
Nickel(mg/L)	0.08
pH	7.00-7.50

4. Conclusions

Clay-based kaolinite is suitable to be used as a material for heavy metal removal. This study has shown the effect of kaolinite as an adsorption agent and pore sizes on heavy metal removal by varying ratios of monomers and sintering temperatures using gel casting and spark plasma sintering method, respectively. The membrane fabricated by gel casting with the ratio of monomers 14:1 that possessed optimum pores (0.15µm) and the highest amount of kaolinite as the adsorption agent contributes to maximum removal of nickel and copper ions 59% and 87%, respectively. It was also found that effluent pH plays a significant role in the efficiency of the adsorption agent to adsorb both heavy metals.

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