

# Pervaporative Separation of Ethanol-Water Mixtures using Composite Membranes with Hydrophilic Zeolite fillers made from Ghanaian Clay deposits

Emmanuel Godwin Ankudey and Mohammed Nafiu Zainudeen

**Abstract** --- Separation of ethanol-water mixtures by pervaporation was successfully performed using a PVA based composite membrane filled with zeolites made from Ghanaian clay. The substrate for the ultra-thin PVA composite membrane was made of polysulphone. The pervaporation cell was fabricated locally from scrap aluminium and feed concentrations ranging from 60 to 90 volume % ethanol were separated. The clay samples used in the development of the membranes were obtained from Abonku, Anfoega and Teleku-Bokazo and all experiments were carried out at room temperature. For all the feed concentrations, the final retentate concentrations after 10 hours produced relatively higher concentrations of ethanol. For a feed concentration of 87.5 wt %, the mixture was enriched to concentrations more than 95 wt% and a separation factor of more than 85 was obtained.

**Index Terms** – Pervaporation, Ethanol-water mixtures, Ghanaian zeolite-clay, Hydrophilic composite membranes, Flux, Separation factor and Pervaporation separation index.

## 1 INTRODUCTION

It is now accepted that the rate of usage of traditional petrochemical energy resources for meeting the world's chemical and energy needs is expected to lead to global energy shortage in the future [1]. Moreover as nations search for methods to reduce green house gas emissions, there is a renewed focus on alternate production of organic solvents and transportation fuel, such as ethanol, biodiesel, and butanol from biomass and other organic sources. [2]. Alcohols are routinely produced by fermentation and purified mostly by distillation. Distillation is, however, an expensive process especially when the components being separated form azeotropes as is in the case of ethanol-water mixtures. The energy consumption can be reduced drastically using an alternative method of separation such as membrane technology which can also be coupled with the distillation step [3]. The product from the preliminary distillation stage (at a maximum concentration corresponding to the azeotrope) could then serve as feed for the membrane separation unit to further separate the mixture to fuel-grade concentrations of 99.5 wt% or more.

One such membrane process is pervaporation, in which a binary or multi-component liquid mixture is separated by partial vaporization through a dense non-porous membrane [4]. The advantage of pervaporation in separating mixtures apart from its ability to separate azeotropic and close boiling components is the separation of thermally sensitive compound mixtures. Another advantage is that only a fraction of feed is

vaporised.

The challenges in pervaporation have however been the search for suitable membranes with good separating properties in order to minimize concentration polarization. The use of zeolites which have heterogeneous crystal structure, molecular sieving properties, uniform pore size distribution, high thermal resistance, high chemical inertness and high mechanical strength as fillers in membrane forming polymers has been reported [3], [5], [6], [7].

Natural zeolites, such as clinoptilolite, phillipsite and chabazite among others, as well as clays have been found to be suitable adsorbents for the separation of ethanol-water mixtures [8], [9], [10]. However, zeolites can also be formed synthetically with same characteristics as those mentioned above from clay resources [8], [9], [11]. The advantage here is the formation of tailor-made zeolites which are highly replicable and could be used for specific purposes like dehydration of ethanol-water mixtures of any concentration.

In this paper, hydrophilic zeolites were produced from Ghanaian clay resources obtained from three different locations, Anfoega in the Volta region, Abonku in the Central Region and Teleku-Bokazo in the Western Region. The zeolites were used as cross-linkers in polyvinyl alcohol (PVA) based composite membranes with a polysulfone (PSf) support in the separation of ethanol-water mixtures in a locally fabricated cell.

- Dr. Emmanuel G. Ankudey is a lecturer of Chemical Engineering at the Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. E-mail: egankudey@yahoo.com
- Mr. Mohammed Nafiu Zainudeen is a former graduate student of the Department of Chemical Engineering, Kwame Nkrumah University of Science and Technology. Email: zainudeen64@yahoo.ca
- Correspondence email: egankudey@yahoo.com

## 2 METHODOLOGY

### 2.1 Equipment and Materials

Table 1: Required Chemicals

Chemical	Source
Clay	Abonku, Central Region, Ghana
	Anfoega, Volta Region, Ghana
	Teleko-Bokazo, Western Region, Ghana
Dimethylacetamide (DMAc)	Merck Schuchardt, Germany
Ethanol (96.1 v%)	UK Chemicals, UK
NaOH pellets	UK Chemicals, UK
Polysulphone (PSf) (MW=35,000)	Sigma Aldrich, USA
Polyninyl alcohol (98% hydrolyzed) MW 16,000	Acros Organics, USA

### 2.2 Pervaporation cell

The pervaporation cell unit was locally fabricated from scrap aluminium metal that was melted and cast into two semi-spherical shapes of diameter 16 cm forming the two chambers of the cell. In between the two chambers is an indentation for the membrane, its perforated metal support that prevents membrane rupture or collapse and finally a propylene wire mesh that keeps the permeate flow channel opened. A picture of the cell is shown in figure 1.



Fig. 1: PV cell with pressure gauge fitted on the feed chamber.

A limitation of the cell for this study was the possibility of reaction of ethanol with aluminum at elevated temperatures. All experiments were carried out at room temperature.

### 2.3 Hydrophilic Zeolite-A Formation from the raw clay samples

The three different raw clay samples were separately cleaned of any debris and dried in the open for 72 hours. The clay samples were then pulverized and sieved with a 212 microns wire mesh. A modification of the methods of Haden *et al*, [12], Howell *et al*, [13] and Atta *et al*, [8] was used to produce me-

takaolin from the clay samples. The pulverized samples were calcined at a temperature of 700°C in a furnace for two hours. 35g of the metakaolin powder from each of the 3 clay samples were separately mixed with 33.5 cm<sup>3</sup> of 45% NaOH solution. The mixtures were maintained at room temperature, without stirring, for a digestion period of approximately 165 hours (about 6½ days).

The samples were then placed in a water bath at 85°C for another 2 hours in closed containers to ensure complete formation of the polycrystalline aggregate of the required zeolite. This crystalline aggregate was then separated from the mother liquor by filtration and subsequently the residue (crystals) was washed with excess distilled water until the pH of the filtrates were between 9 and 12. The formed aggregated crystals were dried at room temperature for 3 days and further in an oven at 90°C for an hour. The dried aggregated crystals were pulverized and sieved with 212 mesh sieve. The powdered zeolite was then calcined at 180°C for 2 hours and stored in air-tight polypropylene containers.

### 2.4 Composite Membrane Preparation

#### 2.4.1 Polysulfone Support

The microporous support was fabricated by phase inversion from a casting solution containing 16 wt% polysulfone (PSf) [6], [14]. The casting solution was prepared by dissolving 1g of PSf pellets in 5.6cm<sup>3</sup> dimethyl acetamide (DMAc) at 50°C. The PSf solution was then cast onto a paper fabric held on a hard flat plate surface, by pouring it carefully at the upper edge of the paper. With the aid of glass rod and a Gardener's knife that was pre-adjusted to ½ a millimeter thickness the solution was spread evenly on the paper fabric.

The film was allowed to stand for 3 minutes at room temperature after which it was immersed in distilled water at room temperature. The flat plate was then carefully removed. The resulting porous support was removed from the solution and dried in air at room temperature for 24 hours.

The composite solution was prepared by dissolving appropriate amount of the zeolite powder into the membrane forming polymer.

#### 2.4.2 Preparation of PVA Zeolite-Clay Composite Membranes

20 mL of distilled water was added to 1 gram of PVA crystals and stirred while the temperature was increased gradually to 70°C. The mixture was allowed to stand for one hour and the temperature was increased to 95°C to ensure maximum dissolution of PVA. The solution was filtered and 40 mg of the prepared zeolite powder was added and the mixture was stirred at 70°C until the solution became clear. The solution was allowed to cool to room temperature and carefully poured onto the PSf porous support on a flat plate and spread uniformly with the aid of a glass rod. The resulting supported thin composite membranes were hanged vertically to drain all excess polymer solution. The membrane was then dried at room temperature for 15 hours. [15].

## 2.5 Pervaporation of ethanol-water mixtures using PVA zeolite-clay composite membrane

The flow diagram for the pervaporation setup is shown in Fig. 2. Two condenser units were placed on the two flow lines through which the permeate passes.

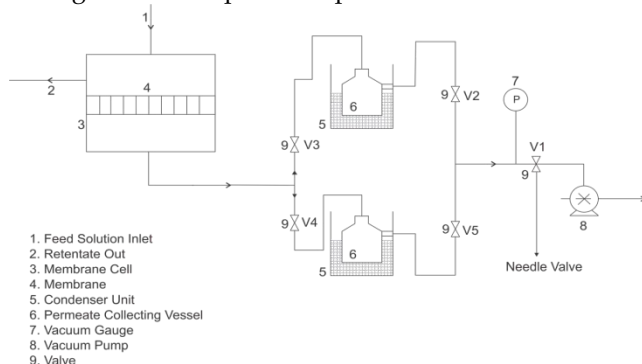


Fig.2: Flow diagram of pervaporation set-up

The feed was introduced into the chamber and allowed to wet the membrane for about 15 minutes. The vacuum pump was switched on while  $V_1$  was opened and then adjusted until the reading of the vacuum pressure was between 0.10 to 0.15 kg/cm<sup>2</sup>.

Then  $V_2$  was opened to create same pressure in the condenser  $W_1$ . When the pressure range was satisfied  $V_3$  was then opened. The pressure was maintained by carefully adjusting the needle valve  $V_1$ . The condensed permeate was collected at predetermined time intervals and analyzed by gas chromatography (GC).

At the appropriate time,  $V_2$  was closed simultaneously as  $V_5$  was opened. For the operation to be pseudo-continuous, valve  $V_3$  was closed simultaneously as  $V_4$  was opened. The resulting retentate for the whole duration was also removed and weighed accordingly. Each sample was subjected to ten hours of continuous pervaporation and the data was recorded in triplicates.

## 3 RESULTS AND DISCUSSION

Feed compositions of 60%, 70%, 80% and 90% ethanol by volume were evaluated in this study. In general, the concentration of ethanol in the permeate increased steadily to a constant value within two to five hours for all the three types of zeolite (clay) filled membranes as shown in figure 3 and figure 4 for two samples..

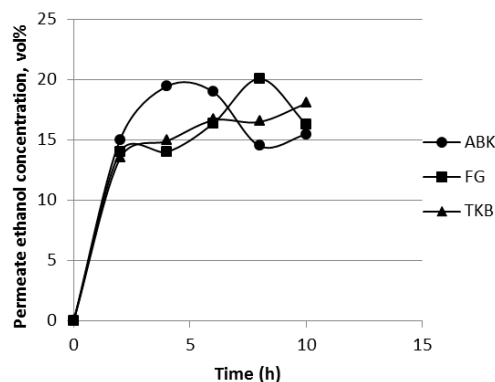


Fig.3: Variation of permeate concentration with time for 70 % (vol) ethanol feed

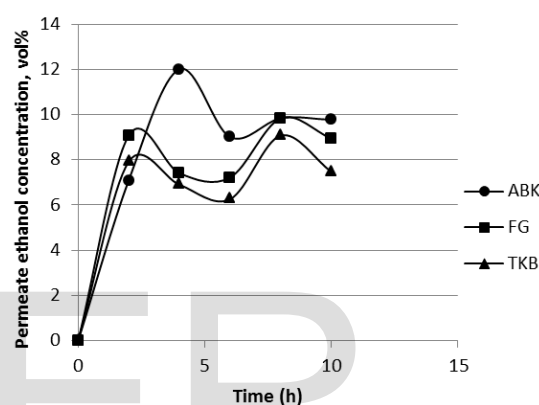


Fig.4: Variation of permeate concentration with time for 90 % (vol) ethanol feed

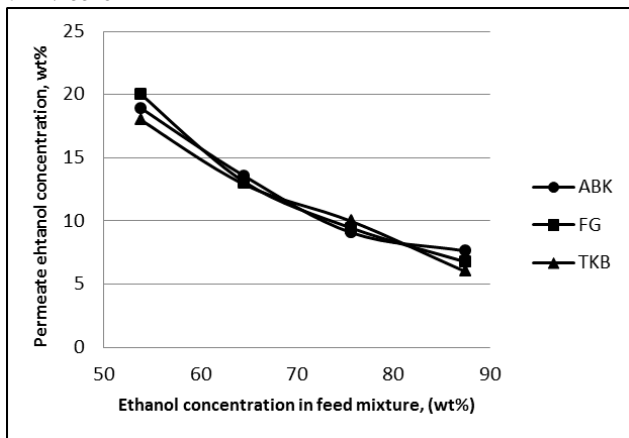
A summary of the effect of concentration of ethanol in the feed on the separation after ten hours is presented in Table 2 and figure 5.

Table 2: Ethanol concentration in all streams after 10 hours

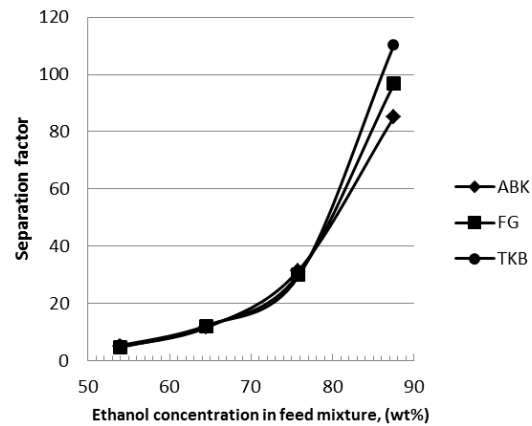
Feed Conc (wt%)	Abonku (ABK)		Anfoega (FG)		Teleku-Bokazo (TBK)	
	Permeate Conc (wt%)	Retentate Conc (wt%)	Permeate Conc (wt%)	Retentate Conc (wt%)	Permeate Conc (wt%)	Retentate Conc (wt%)
53.9	18.9	58.45	20.0	57.27	18.0	57.20
64.6	13.6	70.20	13.1	70.13	13.0	69.59
75.7	9.1	80.84	9.4	81.63	10.0	83.25
87.5	7.6	95.17	6.8	95.89	6.0	96.53

Using the clays from Anfoega (FG) and Teleku-Bokazo (TBK) as fillers, retentate concentrations beyond the azeotropic composition were obtained.

The three membrane samples showed an enhanced separation at higher alcohol concentrations in the feed as also reported by Ling *et al*, [6] for dehydrations of alcohol-water mixtures. In general, at higher concentrations of ethanol in the feed, the sorption capacities of the membranes on the individual components are different which enhances separation [2].



**Fig 5:** Effect of ethanol concentration in feed on permeate concentration



**Fig 6:** Effect of ethanol concentration in feed on separation factor

The current results emphasize the fact that pervaporation with a hydrophilic membrane is more effective when the more permeating component, in this case water molecules, is present at a lower concentration and is also reported by Mulder *et al.*, [3] and Baker, [11]. The efficiency of pervaporation of ethanol-water mixtures is reported to be highest near the azeotropic composition where the concentration of the permeating molecule (water) is less than 5 wt %. [16].

### 3.2 Membrane performance

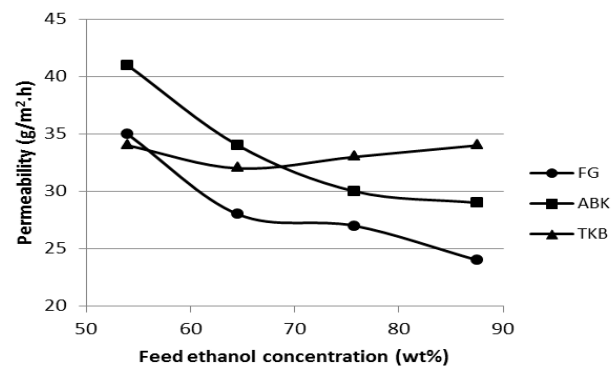
As a measure of the performance of the membrane, the permeability, separation factor, total flux and the pervaporation separation index were evaluated. The characteristics of the sorption depend on the difference between the affinity of the components towards the polymer, the mutual interactions of the components, and the way the interactions with the polymer of each component affects the interactions of the other penetrants with the polymer [17].

Figure 6 shows the effect of ethanol concentration on the selectivity of the three membrane types. An initial gradual increase in the separation factor with increase in feed ethanol concentration was observed up to about 75 wt%, after which there was a sharp increase. As the concentration of the ethanol in the feed liquid increases, the sorption of the feed liquid by the membranes decreases, resulting in a reduction of polymer swelling as predicted and also reported by Praptowidodo [18]. As a result, a sharp increase in selectivity of the composite membranes with respect to water is observed since the hydrophilicity of the PVA-zeolite clay membrane would still attract water molecule into its pores.

At higher ethanol concentrations, it has been suggested that the amorphous regions of the polymer become less swollen and the polymer chains become less flexible, thus increasing the energy required for diffusive transport through the membrane [19]. This therefore reduces the possibility of the permeation of the bulky component molecules through the membrane, hence reduction in permeation rate leading to the high membrane selectivity. It appears the critical or threshold concentration for this change is about 75 wt% ethanol for the three types of membrane formed. Similar results on the general increase in selectivity with increase in ethanol concentration in the feed mixture agrees with the findings of Rhim and Huang [2], Ling *et al.* [6] and Li and Lee [20].

#### 3.2.1 Permeation rate

The flux of material through the membranes was evaluated from the material balance and the effect of ethanol concentration in the feed on the permeability is shown in figure 7.



**Fig. 7:** Effect of ethanol concentration in feed on permeation rate.

A decrease in the permeability with increasing feed concentration was observed for the Anfoega and Abonku clay membranes as expected for hydrophilic membranes, the total flux is expected and reported to have decreased as the feed alcohol concentration increases [2], [6], [20]. As the water concentra-



tion in the feed decreases the possibility of the permeation of the bulky component molecules through the membrane is reduced, hence reduction in permeation rate. The detailed peculiar swelling characteristics of these membranes are being investigated in a separate study.

For the TKB clay membrane, the permeability increased consistently with the feed ethanol concentration. Generally an increase in flux means both components in a binary mixture diffuse through the membrane without much restriction. Little or no restriction implies the membrane is less selective, and results in decrease in separation factor. However in this instance, the selectivity as well as the flux increased with increase in ethanol concentration in the feed. A possible reason could be the relatively higher Si:Al ratio of the Teleku-Bokazo zeolite- clay compared to the Abonku and Anfoega zeolite clays [21]. High Si:Al ratio is an indication of larger pores as well as inclination towards hydrophobicity. When the filler in a hydrophilic membrane has hydrophobic tendencies, it allows both the ethanol and water to permeate through it without much restriction, thereby causing an increase in flux and is also reported by Chan *et al.*, [22].

### 3.2.2 Pervaporation separation index (PSI)

The variation of Pervaporation Separation Index (PSI) with ethanol feed concentration is shown in Figure 8.

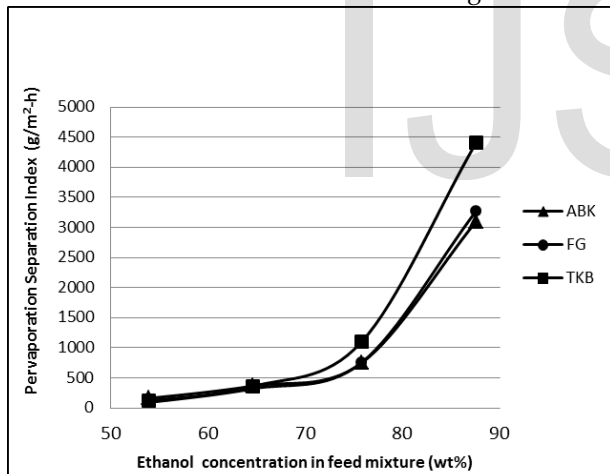


Fig. 8: Variation of Pervaporation Separation Index with feed ethanol concentration.

PSI generally increases with ethanol concentration in the feed and a similar trend to separation factor is displayed. The ideal membrane with a high PSI corresponds to one with a high flux and high separation factor. A high value of PSI could also mean either high flux with low separation factor or low flux with high separation factor. The respective PSI values of the three membranes do not differ much at lower concentrations of ethanol in the feed. This could probably be due to the plasticizing effect of the hydrophilic membrane which gets swollen with increase in water. The Teleku-Bokazo zeolite-clay filled membrane consistently achieved the highest PSI values among the three membranes. As indicated earlier, the high Si:Al ratio of this clay suggests larger pores and a high flux is

expected to contribute to the high PSI. It is also possible that the hydrophilicity of the top separating layer of the composite membrane was influenced by the PSf supporting layer as reported by Sekulic, *et al.* [23]. Water is known to permeate the PSf preferentially in the presence of ethanol [3]. Therefore when this effect of preferential sorption of water in the separating layer is reinforced with the preferential diffusion of water through the support, both the separation factor as well as the flux could increase with increase in ethanol feed concentration.

## 4 CONCLUSIONS

Three different zeolite-clays were prepared from clay deposits at Abonku, Anfoega and Teleku-Bokazu in Ghana and were successfully used as fillers in hydrophilic PVA base composite membranes that were supported on polysulfone substrate for the separation of ethanol-water mixtures. Final alcohol concentrations of more than the azeotropic were obtained. These clay resources have the potential of being developed as specialty support systems for such separations. The effect of excessive swelling of the polymer in this preliminary study appears to occur at an alcohol concentration of about 75 %. The composite membrane with Teleku-Bokazu zeolite-clay filler gave the highest separation factors probably due to its high Si:Al ratio.

## REFERENCES

- [1] G.T. Austin, in: Shreve's Chemical Process Industries. 5<sup>th</sup> ed. McGraw Hill Book Company. New York, ch. 4, 1984.
- [2] J. W. Rhim and R Y. M. Huang, "Pervaporation Separation of Ethanol-Water mixtures using nylon 4 and its Blended Membranes," *Journal of Korean Industrial and Engineering Chemistry*. 4 (4), pp. 791-797, 1993.
- [3] M. H. V. Mulder, J. O. Hendrikman, H. Hegeman and C. A. Smolders, "Ethanol-Water Separation by Pervaporation," *Journal of Membrane Science*. 16, pp. 269-284, 1983.
- [4] W. Kujawski, I. Koter and S. Koter, "Membrane-assisted removal of Hydrocarbons from contaminated soils- laboratory test results," *Elsevier Desalination* 241, pp. 218-226, 2009.
- [5] M. Kazemimoghadem, A. Pak and T. Mohammadi, "Dehydration of Water/ 1-1-dimethyl hydrazine mixtures by Zeolite Membranes," *Elsevier :Microporous and Mesoporous Materials*, 2004.
- [6] L.K. Ling, G.M. Nawawi and A.N. Sadikin, "Pervaporation of ethanol water mixtures using PVA-clay membranes," *Jurnal Teknologi*. 49, pp. 167-177, 2008.
- [7] J.M. Yeh, M.Y. Yu and S. J. Liou, "Dehydration of water-alcohol mixtures by Vapor permeation through PVA/Clay Nanocomposite Membrane," *Journal of Applied Polymer Science*, 89, pp. 3632-3638, 2003.
- [8] A.Y. Atta, O.A. Ajayi and S.S. Adefila, "Synthesis of Faujasite Zeolites from Kankara Kaolin Clay," *Journal of Applied Sciences Research*. 3, pp. 1017-1021, 2007.
- [9] P.K. Igboke, R.O. Okolomike and S.O. Nwokolo, "Zeolite for drying of ethanol-water and methanol-water systems from a Nigerian

- clay resource," *Journal of the University of Chemical Technology and Metallurgy, Bulgaria*. **43**, pp. 109-112, 2008.
- [10] E. Ivanova, D. Dagmaliev, and M. Kostova, "Adsorption separation of ethanol-water liquid mixtures by natural clinoptilolite," *Journal of the University of Chemical Technology and Metallurgy, Bulgaria*. **44**, pp. 267-274, 2009.
- [11] R. W. Baker, "Membrane Technology and Applications," Second edition. John Wiley and Sons Ltd. NJ, USA, pp. 314-355, 2004.
- [12] W.L. Haden, J. Metuchen, and F.J. Dzierzanowski, "Method for making synthetic zeolite Material." US Patent 2,992,068, 1961.
- [13] P.A Howell, "Process for synthetic zeolite A." US Patent 3,114,603, 1963.
- [14] M.G.M. Nawawi, A.N. Sadikin, and T.G. Gi, Pervaporation of Ethanol-Water using Chitosan-Clay composite Membrane. *Journal Teknologi* **49(F)**, pp. 179-188, 2008.
- [15] R.H. Forester, Method of Producing an Ultra-thin Polymer Film Laminate. US Patent 3,551,244, 1970.
- [16] W. Kujawski, "Application of Pervaporation and Vapour Permeation in Environmental Protection." *Polish Journal of Environmental Studies*. **9** (1), pp.13-26. 2000.
- [17] C. C. Bartels, L. E. Tusel and Lichterthaler, "Sorption Isotherms of Alcohols in Zeolite-filled Silicone Rubber and in PVA-composite Membranes," *Journal of Membrane Science*. **70**: pp. 70-75, 1992.
- [18] V. S. Praptowidodo, "Influence of Swelling on Water Transport through PVA -Based Membrane," *Journal of Membrane Science*. **739**, pp. 207-212, 2005.
- [19] V. Dubey, C. Saxena, L. Singh, K.V. Ramana and R.S. Chauham, "Pervaporation of Binary Water-Ethanol Mixtures through Bacterial Cellulose Membrane," *Separation and Purification Technology*, **27**: pp. 163-171, 2001.
- [20] C.L. Li and K. R. Lee, "Dehydration of ethanol/water mixtures by pervaporation using soluble polyamide membranes," *Polymer International*, **55**, pp. 505-512, 2006.
- [21] C. N. K. Kokoroko, "Beneficiation of Ceramic raw materials in Ghana: Composition of samples of clay materials". *Journal of the University of Science and Technology, Kumasi*. Volume 13, (1), pp. 11-15, 2004.
- [22] C. W. Chan, M. G. M. Nawawi and N. S. Aziatul, "Pervaporation of Isopropanol-Water Mixture using Poly(Vinyl) Alcohol-ZSM-5 Membranes," *Jurnal Teknologi*, **49(F)**: pp. 159-166, 2008.
- [23] J. Sekulic, J. E. Elshof and D. H. A. Blank, "Separation Mechanism in Dehydration of Water/Organic Binary Liquids by Pervaporation through Microporous Silica," *Journal of Membrane Science* **254**: pp. 267-274, 2005.