Pervaporation Ethanol-Water Mixture using Membrane Nanocomposite Chitosan-Nature Zeolite Sarulla

Ridwanto1,2 Basuki Wirjosentono2 Thamrin2 Eddiyanto3
1. Pharmaceutical Programs, FMIPA, UMN Al-Washliyah, Medan, Indonesia
2. Chemistry Post-graduate Programs, University of North Sumatra, Medan, Indonesia
3. Department of Chemistry, State University of Medan, Medan, Indonesia

Abstract
The study is aimed to synthesis chitosan membrane and modification of membrane by adding natural nanozeolite Sarulla by varying the composition of nanozeolite toward the membrane performance. The membrane obtained is determined Flux and selectivity on the separation of ethanol-water mixture by pervaporation. The chitosan used has a degree of deacetylation of 84.7% and Natural Nanozeolite Sarulla (@ZAS) used has a @ZAS activated at 400°C for 4 hours and data XRD data showed that the zeolite which used to resemble modernit. The result of SEM showed that the membrane surface is relatively smooth, homogeneous and fine pores evenly dispersed, while the Ch-@NNS membrane surface looks uneven, heterogeneous and rough surface due the zeolite dispersed. These results are supported by IR data which showed the occurrence of mixing physical and chemical interactions between chitosan and @ZAS. The performance (flux and selectivity) of membrane (flux and selectivity) generally increases with the addition of @ZAS composition to the chitosan matrix. The optimum composition membrane obtained addition of 0.30 g @ZAS (membrane Ch-@ZAS 4). The laboratoriru scala tests showed that the nano composite membrane chitosan natural nanozeolite Sarulla, which is synthesized at optimum composition, with the feed ethanol at composition of 98% w/w and 65°C, has the highest fermentation flux of water and totality were 0.98 Kg/m² hour and 1.05 Kg/m² hour respectively, while the highest selectivity was 1168. This study has also able to increase the concentration of ethanol to 99.22% (w/w).

Keywords: Pervaporation, ethanol-water, nanocomposite membrane, chitosan, natural zeolite Sarulla.

1. Introduction
Today research membrane technology continues to evolve rapidly, as this technology has the utility associated with the process of separation, purification and concentration. In general, a thin layer semi-permeable membrane that serves to separate a mixture of several components based on the physical properties and chemical properties. Pass through the membrane separation process is due to the propulsive force such as pressure, temperature, electrical potential and chemical potential.

Pervaporation is one method separation with membranes (permeation) followed by evaporation. Pervaporation process applications in the chemical field including: (1) the dehydration process the alcohol-water mixture, the organic-water and water systems and chlorinated hydrocarbons; (2) separation organic compounds from water; (3) separation from organic mixtures; (4) separation products are susceptible to heat. Another important application is for the separation of the mixture with boiling point adjacent and azeotrope mixture. According Pangarkar & Pal (2009) the excess process pervaporation compared to the conventional separation, such as distillation and extraction is the investment and operation costs low, can separate a mixture azeotropic, does not require the additive (entrainer) so that there is no contamination, energy consumption is relatively lower, so more economical, environmentally friendly because it does not generate waste and easy to operate.

In a membrane system, the principal species rejected by the membrane are called retentate or solute, while the membrane through which the species is usually called permeate or solvent. Pervaporation involving feed and permeate. Feed in the form pure components and a homogeneous mixture at atmospheric pressure has a liquid phase, while permeate is the form the components to be separated in the form of steam as a result very low pressure on the permeate side. The feed to be separated is brought into contact with the surface of the membrane, while permeate is removed in vapor form on the opposite side to the vacuum and then cooled (Kujawski, 2000). So that the pervaporation process of this happening terpermeasi phase change component of the liquid phase to vapor phase.

Ethanol a chemical that very important because it has the benefit a very broad, and in their utilization, ethanol often required with high purity, which can be obtained by distillation process, with a purity of up to 95.6% as it formed an azeotrope. One technique that can be done to produce ethanol with a purity of 100% is extractive distillation process (distillation-extraction) with the addition of benzene, so the ethanol produced contains little benzene, which would be very dangerous when ethanol used in medicines and cosmetics industries. Therefore we need other techniques to separate the ethanol-water in order to obtain absolute ethanol.

Zeolite a mineral as hydrated alumina silicate composed of tetrahedral-tetrahedral form three-dimensional framework consisting of alumina (AlO₄³⁻) and silica (SiO₂⁻) that form hollow structures negatively charged and the open/porous. Natural zeolite have potential applications as an adsorbent, ion exchange, molecular filter and...
One way to improve the usability of natural zeolite is by calcination (Setiawan and Handoko, 2003). Zeolite activation process can be done physically by calcining with the aim of evaporating water trapped within the pores of the zeolite crystals, so that the surface area increases. Calcination must be controlled because excessive heating can cause damage zeolite structure (Weitkamp & Puppe, 1999).

Nanocomposite can be considered a solid structure with nanometer-scale dimensions are repeated in the distances between the different forms of constituent structure. Materials with such kind consists inorganic solids composed organic components. In addition, the nanocomposite material can also consist of two or more molecules inorganic/organic in some form combination with a barrier between them at least one molecular or nano-sized particles have characteristics (Abdullah, et al., 2005). Additionally nanoparticles (size between 1-1000 nm) have different characteristics or functions of similar materials in large sizes. These changes are expected to be superior compared to similar particles in large size. According Ayoup, et al., (2009) nanoparticle synthesis can be performed in a solid phase, liquid, or gas, and can take place in physics or chemistry. In general, there are two approaches in the manufacture of nanoparticles, namely the approach top-down and bottom-up approach.

Nanocomposite membrane is a membrane composed blocks homogeneous particles with nanometer size. Nanocomposite material is made by inserting nanoparticles (filler) in a macroscopic sample material (matrix). Nanocomposite resulting from mixing in a number of different phases. Nanocomposite showed new sft properties that are superior to the original material. After adding the nanoparticles into the matrix material, which dhasilkan nanocomposite can show very different properties compared to the previous material properties.

Nanocomposite membrane research which is conducted by Anadao, et al., (2010) that utilize montmorillonite (MMT) as a component in the manufacture of nonokomposit polysulfone membrane, and the addition of MMT can produce a hydrophilic membrane. Liu, et al., (2011) had dehydration isopropanol using chitosan nanocomposite that implanted into the titanate nanotubes. Application of chitosan membrane that very interesting to do, because all this natural ingredient that often used in the manufacture of the membrane is cellulose, while chitosan has a structure similar to cellulose. Chitosan, poly-β(1-4)-2-amino-2-deoxy-Dglucopyranose a derivative chitin and has structure polyamino carbohydrate (Dutta, et al., 2004). Chitosan is widely used because it includes a hydrophilic biopolymer natural, non-toxic, biocompatible, biodegradable and soluble in acetic acid. In this article explained about the making of chitosan membrane (derived from shrimp waste), written by Natural Zeolite Sarulla sized nanoparticles to improve membrane performance. The resulting membrane characterized morphology and determination flux and selectivities the membrane separation process ethanol and water pervaporation.

2. Research Methods
2.1. Material and Equipment Used
The materials needed in the study consisted of chitosan, natural zeolite Sarulla, acetic acid, absolute ethanol, distilled water, liquid nitrogen, and nitrogen gas. The equipment needed in this study consisted a magnetic stirrer, glass plates for the casting process, equipment pervaporation, molecular Siever, refrigeratior. Balance used to weigh chemicals required. The oven used for the drying process, and the desiccator used to store the membrane after the drying process. It is also used glassware commonly used in every phase of the experiment. The instrument used for the analysis IR spectroscopy, XRF, SEM, TEM, and GC.

2.2. Research procedure
2.2.1. Preparation of Natural Nanozeolite
Zeolite used is a natural zeolite from Sarulla North Tapanuli, North Sumatra Province. Preparation is done by destroying the zeolite crushed and done sifting through size 230 mesh, and then used as nano-sized particles. The next stage is done zeolite activation. The resulting zeolite is activated by heating with a furnace at 400°C and a pressure 1 atm. Zeolite Activities conducted with the aim to increase the surface area and adsorption capabilities.

2.2.2 Membrane Making
Manufacture membranes is done by phase inversion method through solvent evaporation technique. The membranes are made is a membrane derived from pure chitosan and chitosan membrane derived from the addition natural nanozeolite. To dissolve the chitosan used acetic acid. Making the chitosan dope is based on research results Nasrun (2012) and Ridwanto (2016). A total 50 mL of 3% chitosan solution was added to the Natural Nanozeolite Sarulla with varying composition (0.15; 0.20; 0.25; 0.30 and 0.35 grams), stirring constantly so that all the dispersed zeolite perfectly into the dope. The formation a thin layer of membrane made by the process of casting and dried at 80°C for 5 hours, soaked with NaOH and rinsed with distilled water until neutral. The procedures for making pure chitosan membrane as chitosan membrane-making procedures nanozeolite nature but without zeolite.

2.2.3 Process Pervaporation
The series of pervaporation system for the separation a mixture of ethanol and water are shown in Figure 1. The
experiments were conducted with varying concentrations ethanol-water feed mixture (75, 85, 90, 96 and 98% w/w ethanol). Bait is made by diluting ethanol p.a from Merck with the determination of concentrations using gas chromatographic analysis. Bait is a mixture of ethanol-water flow through the modules so that the contact between the membranes with the feed. Permeate out the membrane are frozen in a cold trap with liquid nitrogen cooling media. Then permeate weighed in the balance within a certain timeframe.

Figure 1. Schematic network pervaporation system

Caption :
1. Feed tank 7. Crane
2. Thermometer 8. Tubes dewar
3. Hot plate stirrer 9. Cold trap
4. Circulating pump 10. Tubes silica gel
5. Module pervaporation 11. Vacuum pump
6. Vacuum pressure gauge 12. Magnetic stirrer

The performance observed in the process pervaporation flux and selectivity determined by the mechanism mass transfer through the membrane. Pervaporation done using pure chitosan membrane and chitosan nanocomposite membrane Natural zeolite Sarulla in the form a thin layer of non-porous (dense). Pervaporation process is carried out continuously by means a feed is circulated continuously at a constant temperature. The concentration bait used during the process pervaporation are fixed for circulation carried out continuously and the numbers permeate produced relatively few compared bait used. Besides the mass transfer process carried out by the solution diffusion mechanism.

3. Results and Discussion

3.1 Characterization of Chitosan
Chitosan which will be used analyzed using IR spectrophotometer to determine the degree of deacetylation can affect the physical, chemical and biological properties of chitosan, such as acid-base and karakretistik electrostatic, biodegradability, precipitation and absorption properties of chitosan (Hussain, et al., 2013). Determining the degree of deacetylation conducted using baseline formulated by Dom szy & Robert and Baxter, et al., (Khan, et al., 2000), with the formulation as in equation 1 and the absorbance at the numbers wavelength of about 1655 cm\(^{-1}\) is an amide, while the absorbance in the number of wave around 3450 cm\(^{-1}\) is hydroxyl.

\[
DD = 100 - \left( \frac{A_{1655}}{A_{1450}} \right) \times 100 / 1.33
\]

The results of IR spectra are shown in Figure 2. Data IR spectra show an absorption band at 3433 cm\(^{-1}\) wave shows the OH stretching vibration and stretching vibration NH\(_2\) overlap. CH stretching vibration methylene (-CH\(_2\) and -CH\(_3\)) is shown in the wave number 2885 cm\(^{-1}\). Absorption at 1651 cm\(^{-1}\) indicates the presence of N-H bending primary amine. Absorption at 1419cm\(^{-1}\) supports any CH\(_2\) group which is attached to an amide, thus it can be concluded that there is still a chitin into chitosan, and absorption at wave number 1087 cm\(^{-1}\) shows the C-O stretching vibration.
Based on the calculation of the degree of deacetylation (DD) using equation (1) obtained the degree of deacetylation of the chitosan amounted to 84.7%. This value is obtained from the data by comparing the IR spectrum absorption at wave number 1651 cm\(^{-1}\) of the amide group and the uptake of O-H at wave numbers 3433 cm\(^{-1}\) of the hydroxyl group.

### 3.2 Preparation and Characterization Natural Zeolite Sarulla (@ZAS)

Natural zeolite used in this research from the area of the District Sarulla Pahae North Tapanuli. Natural zeolite Sarulla XRD results shown in Figure. 3, and the data showed that the ZAS diffractogram used in this study tended to be crystalline. Results diffractogram of natural zeolite Sarulla has the greatest intensity at an angle 2\(\theta\) at 29.76; 27.67 and 27.92, approaching zeolite types mordenite which has a high intensity on the corner 2\(\theta\) namely 29, 26 and 23 (Suminta, 2005).

Table 1. Content elements in natural nanozeolite Sarulla (@ZAS) before and after activation

<table>
<thead>
<tr>
<th>Element content</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Activation</td>
</tr>
<tr>
<td>Al</td>
<td>18.2 +/- 0.08</td>
</tr>
<tr>
<td>Si</td>
<td>38.8 +/- 0.03</td>
</tr>
<tr>
<td>K</td>
<td>10.3 +/- 0.0095</td>
</tr>
<tr>
<td>Ca</td>
<td>8.85 +/- 0.004</td>
</tr>
<tr>
<td>Ti</td>
<td>1.69 +/- 0.007</td>
</tr>
<tr>
<td>V</td>
<td>0.072 +/- 0.005</td>
</tr>
<tr>
<td>Cr</td>
<td>0.064 +/- 0.003</td>
</tr>
<tr>
<td>Mn</td>
<td>0.21 +/- 0.007</td>
</tr>
<tr>
<td>Fe</td>
<td>19.4 +/- 0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>0.19 +/- 0.002</td>
</tr>
<tr>
<td>Cu</td>
<td>0.26 +/- 0.008</td>
</tr>
<tr>
<td>Zn</td>
<td>0.11 +/- 0.008</td>
</tr>
<tr>
<td>Rb</td>
<td>0.38 +/- 0.02</td>
</tr>
<tr>
<td>Sr</td>
<td>0.55 +/- 0.03</td>
</tr>
<tr>
<td>Ba</td>
<td>0.45 +/- 0.02</td>
</tr>
<tr>
<td>Eu</td>
<td>0.2 +/- 0.02</td>
</tr>
<tr>
<td>Yb</td>
<td>0.03 +/- 0.007</td>
</tr>
</tbody>
</table>

Table 1 shows the ratio of Si/Al before activation was 2.13, whereas after activation at 400\(^\circ\)C is 2.19. These data suggest that the activation process on the particles showed nanozeolite less influence on the increase in the ratio of Si / Al. In general, the activation process by heating at high temperatures is aimed to remove water
molecules and inorganic materials from the pores so that the particle pore volume increases which causes the greater the surface area (Pandey and Shahi, 2013). Particle formation nanozeolite has resulted in the surface area of particle interaction is high and the data showed that the activation process on the particles nanozeolite not reveal the effect the increase in the ratio Si/Al, which also means less affecting the increase in surface area (Shuai, et al., 2013; Tai, et al., 2012; Wang, et al., 2014).

Results data TEM show natural zeolite particle size before and after activation. TEM data for nanozeolite before and after activation is shown in Figure 3. The data show that the particle size before and after activation did not show a significant difference. Prior to the activation of the particle size the zeolite has a diameter about 322 nm, whereas after the activation process at 400°C shows particle size with a diameter of about 305 nm. Data obtained from TEM analysis using XRF in line with the data showing that the activation process not reveal the effect on the structure of nanozeolite (Liu, et al., 2013; Venkata, et al., 2014)

3.3 Character Membrane Morphology

SEM analysis results are shown in Figure 4 which shows the membrane surface Ch-@ZAS with various compositions. SEM data in Figure 4 shows the pure chitosan membrane surface relatively smooth, homogeneous and visible fine pores evenly distributed. As for membrane Ch-@ZAS visible membrane surface uneven, heterogeneous and looks rough surface alleged @ZAS dispersed. In this research, there is still a zeolite which does not dissolve completely, and helped dry out during printing membrane, as shown in the image in the form of the formation white spots caused by the solubility the material in a solvent is limited at certain concentrations and insoluble longer or experiencing burnout (Takeda, et al., 2013). This leads to homogeneity dope be less than perfect.

3.4 Characterization Functional Groups Ch-@ZAS

Characterization functional groups membrane was observed using IR spectroscopy as shown in Figure 5.
In Figure 5. the spectrum of chitosan membrane pure shows local absorption at 3444 cm\(^{-1}\) indicates that the OH groups, local absorption at 1558 cm\(^{-1}\) indicating the bond NH (amide) on the cluster NH\(_2\), regional absorption at 1643 cm\(^{-1}\) indicating the presence of the C=O (carboxyl). These groups are the main groups that exist on chitosan (Osman & Arof, 2003). These results are similar to results obtained Hefian, et al., (2010) and Wu, et al., (2007). While the membrane Ch- @ZAS, showed the same absorption area is 1643 cm\(^{-1}\) indicating the bond C=O (carboxyl). While the area marks the bond NH (amide) at the NH\(_2\) groups and the OH groups shifted into 1544 cm\(^{-1}\) and 3248 cm\(^{-1}\). Natural zeolite Sarulla there are groups OH, CH (Sp\(_3\)), Si-O-Si were successively at wave number 3425 cm\(^{-1}\), 2862 cm\(^{-1}\), 1049 cm\(^{-1}\) and 470 cm\(^{-1}\) (Xu, et al., 2013; Zhang, et al., 2013; Luz, et al., 2012). Once coupled between chitosan and natural zeolite membrane forming Sarulla Ch-NZS shift wave numbers and decrease in intensity. Can be seen at wave number 1049 cm\(^{-1}\) spectral membrane Ch-ZAS decline in intensity, this indicates that there is interaction with chitosan to form Si-Si-O-Si (Seo, et al., 2014).

### 3.5 Flux Membrane Permeation

To assess performance in relation to the membrane permeation flux is performed for each membrane pervaporation process on Keadaa steady-state is achieved after 2 hours of operation, according to research conducted by Nasrun (2012). In experiments pervaporation permeate the mass of data acquired within a certain time interval. Then the data is processed to obtain a permeation flux. Water permeation flux and total permeation flux at various membranes with varying concentrations of bait at a temperature of 65°C plotted in Figure 6.

In Figure 6. (a) shows that the water permeation flux of each membrane tends to increase with the increasing concentration bait. By their nature nanozeolite on chitosan matrix, the permeation flux of water at the same feed composition also increased, although the increase is not in line with the rising levels of nanozeolite. This is in line with research conducted Premakshi, et al., (2015) which states that the higher levels of zeolite NaY were added to the chitosan matrix, the permeation flux increased. The results showed that a higher level nanozeolite were added, then the permeation flux increased to levels 0.30 grams. As for the addition of 0.35 grams of water permeation flux nanozeolite seen to be lower compared with other compositions, even lower than the flux of permeation without nanozeolite (pure chitosan) for a feed concentration of 75% w/w ethanol. The increase in flux...
fermeasi water and Flux total above point azeotropi c ethanol-water mixture resulting thrust force is working on exactly that point is the difference in pressure between the upper (upstream) and the pressure of the bottom (downstream) so that the prisoners suffered smaller when compared with the situation below the azeotropic point, where the driving force working in these conditions is the pressure difference and the temperature difference causes the prisoner to be great. (Rachipudi, et al., 2013; Wu, et al., 2013).

In Figure 6. (b) indicates that in general the total permeation flux increased with increasing levels of nanozeolite in line with the membrane permeation flux water, for a total permeation flux at a level of 0.35 grams nanozeolite also decreased flux to be well below the total permeation flux pure chitosan (without the addition of nanozeolite ) at various concentrations bait. Nawawi & Zamrud (2014) as well as Nawawi, et al., (2013) states that the flux of permeation is affected by the polarity and affinity membranes. Overall it appears that ethanol permeation flux is very much lower than the water permeation flux. This means that the chitosan modified with nanozeolite Sarulla selective nature of water. Sunitha, et al., (2012) conduct research on the phenomenon in the separation ethanol water with phosphorylated chitosan membranes and expressed flux increases with betambahnya water concentration in the feed caused the higher the concentration water in the membrane. Water permeation flux and the highest total permeation flux respectively is 0.98 Kg/m²h 1.05 Kg/m²h obtained in experiments with chitosan membrane modified with natural nanozeolit Sarulla at a level 0.30 grams (membrane Ch-@ZAS4) with a feed concentration of ethanol in the composition of 98% w/w.

3.6 Selectivity of Membrane

In addition to determining the performance the membrane by the membrane permeation flux, it is the determination the performance of the membrane by the membrane selectivity in separating the ethanol-water mixture. The content ethanol-water in the permeate and feed the data obtained by gas chromatography. The data is then analyzed to obtain selectivity of each membrane used to separate the ethanol-water mixture, and plotted in graph form as shown in Figure 7.

Figure 7. Effect of feed concentration (% www ethanol) to the membrane selectivity

Figure 7. shows that the selectivity in each membrane showed an increase with higher concentrations ethanol feed. This means with higher concentration of ethanol in the feed, the selectivity the membrane will be higher. In addition it seems that the higher the nanozeolite compositions were added to the chitosan matrix, the selectivity increases. In the membrane grading 0.35 grams nanozeolite nature, the membrane selectivity decreased compared with the levels of natural nanozeolite 0.30 grams. This is due to the level of 0.35 grams, has a maximum natural nanozeolite that cover the amorphous part of the polymer chitosan function at the membrane separation process that selectivity decreases.

At concentrations of bait under azeotropic composition (96% (w/w) ethanol), the selectivity the membrane to increase slowly as plasticizing effect on the polymer by water and then rose sharply at a concentration above the azeotropic composition (Uragami, et al., 2015). This means that the separation of a mixture of ethanol azeotrope water will be easily separated by pervaporation for their thrust in the form of pressure difference between the upstream and downstream (part of the feed and permeate). Chen, et al., (2011) and Sajian, et al., (2013) suggest that the activation energy of pervaporation process is lower than the activation energy of distillation. Sunitha, et al., (2012) have done research on the activation energy for ethanol dehydration poses the water, and the results showed that for the distillation process requires an activation energy 2.45 kcal per kg ethanol, while for the pervaporation process requires energy 101.09 kcal per kg ethanol, and for the azeotropic distillation process requires energy 0.79 kcal per kg ethanol. The highest selectivity was obtained in 1168 in experiments with chitosan membrane modified with 0.30 grams of natural nanozeolite Sarulla at a feed concentration of ethanol 98% (w/w).
Table 2. Acquisition of Ethanol with Membrane Levels Ch-@ZAS4

<table>
<thead>
<tr>
<th>Feed concentration (% w/w)</th>
<th>Final ethanol concentration (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>78.24</td>
</tr>
<tr>
<td>85</td>
<td>88.61</td>
</tr>
<tr>
<td>90</td>
<td>94.41</td>
</tr>
<tr>
<td>96</td>
<td>97.07</td>
</tr>
<tr>
<td>98</td>
<td>99.22</td>
</tr>
</tbody>
</table>

The research as a whole as shown in Table 2 shows that the nanocomposite membrane separation using natural zeolite Sarulla been able to increase the concentration of ethanol to 99.22% (w/w) ethanol, obtained in the membrane nanozeolite grading 0.30 grams (Membrane Ch-@ZAS4).

4. Conclusions

The results showed that the chitosan-nano membrane Sarulla natural zeolite (Ch-@ZAS) can be used for the separation of ethanol-water mixture by pervaporation. Chitosan used has a degree deacetylation of 84.7%. Nanozeolite nature Sarulla (@ZAS) used is @ZAS that has been activated by heating technique for 4 hours at a temperature of 400°C.

At the same feed concentration, nano-chitosan membrane natural zeolite Sarulla (Ch-@ZAS) has a flux and selectivity performance higher than that of pure chitosan membrane (membrane Ch). Performance the membrane (flux and selectivity) generally will increase in line with the addition natural nanozeolite levels Sarulla the chitosan matrix. The optimum composition the chitosan membrane-nanozeolite Sarulla nature resulting in the addition of 0.30 grams nanozeolite (membrane Ch-@ZAS4). Laboratory scale tests show that the water permeation flux and the highest total permeation flux respectively is 0.98 Kg/m²h and 1.05 kg/m²h, while the highest selectivity the membrane is 1168. This data was obtained with a chitosan membrane modified with natural nanozeolite Sarulla at levels 0.30 gram (membrane Ch-@ZAS4) with a feed concentration ethanol in the composition 98% w/w and temperature 65°C. Besides this research also has been able to increase the ethanol concentration to 99.22% (w/w) ethanol.

References


Nasrun., (2012), Improved Performance Membrane Cellulose Acetate with Addition of Natural Zeolite Ujong Pancu, Aceh Besar On the Separation of Ethanol-Water Mixture By Pervaporation, Dissertation, University of North Sumatra, Medan, Indonesia


Setiawan, D., dan P. Handoko., (2003), The catalyst activity of Cr / zeolite in catalytic conversion reaction of phenol and methyl isobutyl ketone, Basic Sciences Journal, 4 (2), 70-76

Shavandi, M. A., Z. Haddadian, M.H.S. Ismail, N. Abdullah, and Z.Z. Abisin., (2012), *Removal of Fe(III), Mn(II) and Zn(II) from Palm Oil Mill Effluent (POME) by Natural Zeolite*, Department of Chemical and Environmental Engineering, Faculty of Engineering Universiti Putra Malaysia, Malaysia.


