Performance Test of Gelcasted Porous Ceramic as Adsorbent of Azo Dyes

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Abstract. Has been done a research about performance test of gelcasted porous ceramic as adsorbent of azo dyes. The method of synthesis porous ceramic used was gelcasting method. The monomers used was acrylamide (AM) with crosslinkers was methylenbisacrylamide (MBAM). The polymer formed acts as a pore template. Variation of AM:MBAM ratio used at 6:1; 12:1; 18:1; 24:1. Characterization of gelcasted porous ceramic carried out were the density, porosity, morphology, and percent adsorption of ceramic to azo dyes. The results showed that the lowest density occurred at ratio 6:1 of 15.82 g/cm³ with the highest porosity of 36.86%. The morphology test indicated the presence of open and closed pores in the ceramic body. The highest adsorption percentage occurred at the ratio 6:1 against to congo red, acid orange, and direct blue with adsorption percentage respectively 39.72%; 48.38%; 32.26%.

1. Introduction
Rapidly growing industrial developments have a positive and negative impact on human life. Positive impacts lead to human needs fulfillment are efficient and effective, while the negative impacts are resulting in the occurrence of environmental pollution caused by industrial waste disposal.

Some examples of emerging industries, such as the paper industry, plastics, food, cosmetics, textiles, etc., use dyes in their production. The output of the industrial waste containing dyes with high concentrations. The dye waste discharged into the river will disrupt the biological activity. Groundwater quality will also be affected due to the leaching process of the dye from the soil [1].

Some conventional waste treatment methods have been widely used, for example by filtration, flocculation, decoloring, adsorption, and microbiological processes. The microbiological process is the easiest way, but it only reduce the biodegradable compounds, whereas non-biodegradable compounds
can not be decomposed by microbiology. One of the non-biodegradable organic waste is textile dyes, especially dyes containing azo groups, such as congo red, acid orange, and direct blue.

Azo dye is the most common compound in textile waste, which is about 60% - 70% [2]. The azo compounds have a general structure of R─N═N─R ', where R and R' are the same or different organic chains. This compound has a ─N═N group called azo structure. Azo compounds may be aromatic or aliphatic compounds. Aromatic compounds are stable and have a bright color.

One of method in handling azo dye waste is adsorption. Adsorbents used can be activated carbon, biomass, membrane, and porous ceramics. In this research, porous ceramic adsorbents are used. Techniques in making porous ceramics such as dry-pressing [3], extrusion [4], and slip casting have been developed. However, the methods have some constraints e.g. requiring considerable pressure, using porous molds, and quite complicated manufacturing methods [5]. Gelcasting is a new method used in developing porous ceramic making process. The gelcasting method has several advantages compared with other methods of making techniques that are fairly easy to do with low cost, high porosity, fewer organic additives, and the molds used can be varied. However, this method is difficult to produce a homogeneous pore size [6].

The basic principle of this method is in situ polymerization in the ceramic body, the polymer formed acts as a pore template when the ceramic is sintered [5]. The gelcasting process can produce non-toxic ceramics using starchy natural ingredients from cassava [7] and gelatin [8]. However, the resulting porosity is very low at only about 30 - 50%. According to [7], high porosity can be produced using pure materials, e.g. using acrylamide (AM) as monomer and methylene-bis-acrylamide (MBAM) as a crosslinker resulting in porosity up to 80% as did [9].

According to Janiszyn [10], one of the pure materials used in the manufacture of porous ceramics by gelcasting is AM which will form a gel in a water solvent. The monomer used in gelcasting must have some properties i.e., it should be soluble in water and have a vinyl bond. In addition to monomers, other ingredients used in the gelcasting method are crosslinkers and initiators. Omatete, Janney, & Nunn [11] suggests that crosslinkers are needed if the organic monomers used have only one double bond which will form a linear polymer when polymerized.

The similar research has been done by Dhara, et.al. [9] and Liu, et.al. [12] made a porous ceramic by gelcasting with alumina and kaolin base materials, AMAM monomers and MBAM crosslinkers initiated by APS with tetramethyl ethylene diamine (TEMED) catalyst with APS : TEMED ratio of 2 : 1. The average pore diameter produced around 1.50 μm. Yu, Wang, & Zhang [13] suggests that the ratio of monomer and crosslinker affects in ceramic porosity, the higher the ratio of monomer and crosslinker then the resulting porosity is increasing. The formation of pores in the ceramic body is based on the loss of the polymer system in the ceramic body when sintered.

The sintering process is based on the analysis using TGA / DTA, the temperature of sintering process is 28°C - 1100°C with a certain treatment of temperature and time. Heating is carried out at a heating rate of 50°C, 200°C, 500°C, and 1100°C [14].

2. Experimental Details

2.1. Sample Preparation

Natural clay is dried then homogenized. The sample finely pulverized in a mortar and sieved with 40-80 mesh-sized sieve. The sample used is the sieved powder. Natural clay then analyzed using XRD and XRF to determine the metal oxide content.

2.2. Synthesis of Porous Ceramic by Gelcasting Method

2.8 g of clay is added into the mixture of AM 40% and MBAM 2% with the mole ratio of AM monomer and MBAM crosslinker is 6:1; 12:1; 18:1; and 24:1. Then 40 μL of APS 10% and 20 μL TEMED 99% are added to the mixture. The dough is put in a cylindrical mold and let until the dough can be removed from the mold. The resulting ceramic sample is dried in the air. The crude gelcasted ceramics further is sintered based on result of TGA/DTA analysis at the temperature of 28 °C - 1500
°C with a certain treatment of temperature and time [14]. Heating is carried out at a heating rate of 50 °C / 15 minutes with 60 minutes detention at the temperature of 100 °C, 200 °C, 500 °C, and 1100 °C. The ceramics before and after sintered were characterized by Scanning Electron Microscope (SEM). The resulting ceramics are then characterized to determine its density, porosity and percent of adsorption to azo dyes. Azo dyes used are congo red, acid orange and direct blue.

2.3. Application of Gelcasted Porous Ceramic as Azo Dyes Adsorbent
Ceramic is stored in filter holder then drop 25 mL of 50 ppm azo dyes solution with each optimum pH. Flow rate of azo dyes solution is 10 drops per minute. The concentration of the residual azo dyes solution was then analyzed using the UV-Vis Spectrophotometer Thermo Scientific Evolution 201 at the maximum wavelength of each azo dyes i.e. 490 nm (congo red), 621.8 nm (direct blue) and 484.4 nm (acid orange). Concentrations of the residual azo dyes were calculated using the Lambert-Beer equation.

3. Results and Discussion
The composition of natural clay minerals as the basic material of porous ceramic synthesis is shown in Table 1.

Table 1. Mineral Component of Natural Clay as a Raw Material

| Minerals        | Amount (%) |
|-----------------|------------|
| Anorthoclase    | 55.0       |
| Ferroaxinite    | 22.1       |
| Paragonite      | 11.6       |
| Diopside        | 6.4        |
| Dellaventuraite | 4.9        |

The main content of mineral clay as a base material is silica alumina. The presence of silica alumina content in natural clay was confirmed by analysis using XRF. The metal oxide content in the natural clay is shown in Table 2.

Table 2. Metal Oxide Component on Natural Clay

| Metal Oxide | Amount (%) |
|-------------|------------|
| Si          | 66.39      |
| Fe          | 13.25      |
| Al          | 10.09      |
| K           | 4.88       |
| Ca          | 2.19       |
| Ti          | 1.78       |

The silica content in the natural clay is 66.39% and the aluminum content is 10.09 %. High levels of silica alumina indicate that natural clay can be used as the basic material of ceramic synthesis.

Porous ceramics are synthesized by gelcasting method. The monomer used is acrylamide (AM). The AM structure is shown in figure 1 (a). AM monomer has only one double bond so it needs a crosslinker to produce polymer with a bulk phase. The crosslinker used was methylene-bis-acrylamide (MBAM) and the structure is shown in figure 1 (b).
In addition to monomers and crosslinkers are also used initiators which act to initiate the formation of radicals. The polymerization process underway in polyacrylamide is an anionic polymerization consisting of initiation, propagation, and termination steps. The initiator APS is used in this study because AM monomer contains amide group (\(\text{C} = \text{NH}_2\)). This is based on Cowie & Arrighi [15] who suggests that the type of monomers containing substituents -CN, -COOR, -CONH\(_2\) losing of electrons in double bonds will occur with the help of anionic species. Homolytic termination of the APS initiator results in an SO\(_4\)\(^{-}\) anionic radical. The formed polymer acts as a pore template that will escape from the ceramic body in the sintering process. The morphology of the gelcasted porous ceramic body before and after sintering are shown in Figure 2.

**Figure 1.** Structure of (a) monomer AM and (b) crosslinker MBAM

**Figure 2.** Morphology of gelcasted porous ceramic body (a) before sintering (b) after sintering

Based on figure 2, it is showed that ceramic pores are formed after sintering. The morphology test indicated the presence of open and closed pores in the ceramic body. The process that occurs in the sintering process is the release of the polymer system. Thus in this study we examined the ratio of monomer and crosslinker, i.e. AM : MBAM of 6:1; 12:1; 18:1; and 24:1. In addition to the release of the polymer system, the pores are also predicted to be formed due to the oxidation of Fe\(_2\)O\(_3\) metal oxides, as shown in Table 3. The content of Fe\(_2\)O\(_3\) metal oxide decreases from 15.06 % to 12.73% after the ceramic was sintered.

The gelcasted porous ceramics then characterized to determine its density, porosity, and percent adsorption of azo dyes. The porous ceramic density for each variation of the comparison of AM monomers and the MBAM crosslinker is shown in Figure 3.

**Table 3.** The content of metal oxide before and after sintering

| Metal oxides | Before sintering (%) | After sintering (%) |
|--------------|----------------------|---------------------|
| SiO\(_2\)    | 64.61                | 67.12               |
| Fe\(_2\)O\(_3\) | 15.06               | 12.73               |
| Al\(_2\)O\(_3\) | 9.54                | 9.12                |
| K\(_2\)O     | 4.01                 | 4.86                |
Metal oxides | Before sintering (%) | After sintering (%) |
---|---|---|
CaO | 3.12 | 2.64 |

**Figure 3.** Density character of gelcasted porous ceramic for each variation of AM: MBAM ratio

The lowest ceramic density occurred in the 6: 1 ratio and increased in 18: 1 ratio. This is parallel with the porosity data shown in Figure 4.

**Figure 4.** Character of gelcasted porous ceramic porosity for each variation of AM: MBAM ratio

The highest porosity occurs in a 6: 1 ratio. This is parallel with the ceramic density data, where the lowest ceramic density occurs in a 6: 1 ratio indicating the number of pores present in the ceramic body. This is due to the large amount of bulk phase produced with the increasing in amount of crosslinker added. Thus there are more pore templates produced.

The next characteristic is the adsorption test of the azo dye. Azo substances used are congo red, acid orange, and direct blue. The synthesized ceramic is placed in the ceramic holder shown in figure 5.
Ceramic porous are placed in a ceramic holder. Azo dye solution is placed in an adsorbate container and then flowed with a flow rate of 10 drops per minute. The adsorption capability of porous ceramic gelcasting is shown in Figure 6. The largest adsorption percentage occurs in the AM: MBAM ratio of 6:1 i.e. congo red of 39.72%, acid orange of 48.38%, and direct blue of 32.26%.

The largest adsorption capacity occurs in acid orange adsorption using a porous ceramic with the ratio of AM : MBAM (6 : 1). This is due to the lowest density and the highest porosity of ceramic with the ratio of AM : MBAM (6 : 1). The adsorbed azo dyes most commonly occur in acid orange dyes. It is because the acid orange has only one azo group, its structure is shown in table 4.
Table 4. The Difference of Azo Dyes Structure

| Azo Dyes     | Structure |
|--------------|-----------|
| Congo red    | ![Congo Red Structure](image1) |
| Acid orange  | ![Acid Orange Structure](image2) |
| Direct blue  | ![Direct Blue Structure](image3) |

4. Conclusion
The results showed that the lowest density occurred at ratio 6:1 of 15.82 g/cm³ and the highest porosity of 36.86 %. The morphology test indicated the presence of open and closed pores in the ceramic body. The highest adsorption percentage occurred at the ratio of 6:1 against to congo red, acid orange, and direct blue with adsorption percentage respectively 39.72 %, 48.38 %, 32.26 %.

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References
[1] Namasivayam, C., Muniasamy, N., Gayatri, K., Rani, M., & Ranganathan, K. (1996). Removal of dyes from aqueous solutions by cellulose waste orange peel. *Bioresource Technology*, 57(1), 37-43.
[2] Laksono, E. W. (2009). Kajian Penggunaan Adsorben Sebagai Alternatif Pengolahan Limbah Zat Pewarna Tekstil. *Jurdik Kimia*.
[3] Harefa, F. B. (2009). Pemanfaatan limbah padat pulp grits dan dregs dengan penambahan kaolin sebagai bahan pembuatan keramik konstruksi.
[4] Mongkolkachit, C., Wanakitti, S., & Aungkavattana, P. (2010). Investigation of Extruded Porous Alumina for High Temperature Construction. *Journal of Metals, Materials and Minerals*, 20(3), 123-125.
[5] Meng, G., Wang, H., Zheng, W., & Liu, X. (2000). Preparation of porous ceramics by gelcasting approach. *Materials Letters*, 45(3), 224-227.
[6] Yang, J., Yu, J., & Huang, Y. (2011). Recent developments in gelcasting of ceramics. *Journal of the European Ceramic Society*, 31(14), 2569-2591.
[7] Panyathanmaporn, T., Asira F., Thanawadee L., Piyawan S., dan R. Chummanaklang, 2005. Gelcasting of porous alumina by using cassava starch as binders, National Metal and Materials Technology Center 114 Bangkok, Thailand

[8] Lombardi, M., Naglieri, V., Tulliani, J. M., & Montanaro, L. (2009). Gelcasting of dense and porous ceramics by using a natural gelatine. *Journal of porous materials, 16*(4), 393-400.

[9] Dhara, S., Kamboj, R. K., Pradhan, M., & Bhargava, P. (2002). Shape forming of ceramics via gelcasting of aqueous particulate slurries. *Bulletin of Materials Science, 25*(6), 565-568.

[10] Janiszyn, Z., Dziuba, E., Boruczkowski, T., Chmielewska, J., Kawa-Rygielska, J., & Rosiek, G. (2007). Application of porous ceramic sinter as a support for immobilization of *Saccharomyces cerevisiae* yeast cells. *Polish Journal of Food and Nutrition Sciences, 57*(4)

[11] Omatete, O. O., Janney, M. A., & Nunn, S. D. (1997). Gelcasting: from laboratory development toward industrial production. *Journal of the European Ceramic Society, 17*(2-3), 407-413.

[12] Liu, Y. F., Liu, X. Q., Li, G., & Meng, G. Y. (2001). Low cost porous mullite-corundum ceramics by gelcasting. *Journal of materials science, 36*(15), 3687-3692.

[13] Yu, J., Wang, H., & Zhang, J. (2009). Neural network modeling and analysis of gel casting preparation of porous Si 3 N 4 ceramics. *Ceramics International, 35*(7), 2943-2950.

[14] Putri, S. E., & Pratiwi, D. E. (2016). The Effect of Mole Ratio of Acrylamide (AM) Monomer and Methylene-bis-acrylamide (MBAM) Crosslinker Toward the Hardness of Gelcasting Porous Ceramics. In *Proceeding International Conference on Mathematic, Science, Technology, Education and their Applications*.

[15] Cowie, J. M. G., & Arrighi, V. (2007). *Polymers: chemistry and physics of modern materials*. CRC press.