

Application of Local Adsorbant From Southeast Sulawesi Clay Immobilized *Saccharomyces Cerevisiae* Bread's Yeast Biomass for Adsorption Of Mn(II) Metal Ion

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Abstract. Southeast Sulawesi has a great stock of clay. It is probably to use as a source of adsorbent. The adsorbent capacity of clay can be largered with teratment using bread's yeast as biomass. At this research, study of analysis adsorption of Mn(II) metal ion on clay immobilized *Saccharomyces cerevisiae* bread's yeast biomass adsorbent has been conducted. The aims of this research were to determine the effects of contact time, pH and concentration of Mn(II) metal ion and to determine the adsorption capacity of clay immobilized *S. cerevisiae* biomass for adsorbtion of Mn(II) metal ion. Activated clay was synthesized by reaction of clay with KMnO_4 , H_2SO_4 and HCl . *S. cerevisiae* biomass was result by bread's yeast mashed. Immobilization of *S. cerevisiae* biomass into clay was done by mixing of ratio of *S. cerevisiae* bread's yeast biomass and clay equal to 1:3 (mass of biomassa : mass of clay). The adsorption capacity was determined by using Freundlich and Langmuir adsorption isotherms. The results of FTIR spectrums showed that the functional groups of clay immobilized *S. cerevisiae* biomass were Si-OH (wave number 1643 cm^{-1}), Si-O-Si (wave number 1033 cm^{-1}), N-H (wave number 2337 cm^{-1}), O-H (wave number 3441 cm^{-1}), and C-H (wave number 2931 cm^{-1}). The result of adsorption capacity from Mn(II) metal ion of contact time optimum 120 minutes , pH optimum at 7 and concentration optimum 50 mg/L were 1,816 mg/g; 0,509 mg/g and 2,624mg/g respectively. The adsorption capacity of Mn(II) metal ion with ratio 1:3 (biomass : clay) was 0,1045 mg/g. Type of isothermal adsorption followed the Freunlich adsorption.

1. Introduction

Advances in science and technology followed by a very rapid industrial development give a lot of positive and negative impacts for life. The negative impact is produced pollutants that interfere the environment, particularly the aquatic environment such as the spread of heavy metals into the environment at concentrations above the threshold include manganese. Manganese (Mn) are included in one of the essential micro heavy metals needed by plants in relatively small quantities of up to 50 ppm [1]. Clay is inorganic compound composing soil, containing active sites such as silanol (Si-OH), a siloxane (Si-O-Si), aluminol (Al-OH) and iron oxides which can adsorb harmful metal ions in the environment [2]. Southeast Sulawesi is rich in clay minerals by the number of clays 537,000 million m^3 . Others interesting properties of clay are have a large specific surface area, multi-layered structure, a Bronsted and Lewis acid, have high mechanical and chemical stability [3]. Application this clay for porous ceramics for various applications were also reported previously [4]. The porous ceramic were produced by mixing clay and ash of sago waste from local farmer and processing by using conventional heating as well as microwaves.

Another method which has been developed to reduce the heavy metals in environment, especially in industrial waste is biosorption. Biosorption is most promising technologies in wastewater treatment. The method using living or dead cells biomass to absorb metal. Process of metal absorption by biomass is a combination of passive accumulation processes. The process also does not depend on the biomass



metabolic processes. Biosorption involves chemical and physical adsorption process, ion exchange, coordination interactions, complexation, chelation, and microprecipitation [5].

Biomass from bread's yeast has been widely studied related to its potential as bioaccumulator and biosorbent of heavy metals. Adsorption of Cr^{3+} metal ions have been conducted, using biomass adsorbent of bread's yeast immobilized on montmorillonite clay with maximum absorption capacity 5.025 mg [6]. The use of biomass from bread's yeasts, caused material percentage of cell wall as a source of high metal binding. The cell wall consists primarily of polysaccharides, lipids and proteins which have functional groups such as carboxylic, hydroxyl, and amino which can bind with metal ions [7]. Other materials than clay for ceramics from local biomass such as sago wastes and rice ash husk [8-10] as well as commercial powder such alumina have been also reported in detail previously [11-13].

In this study, biomass of bread's yeast immobilized on clay. The advantage of bread's yeast biomass after immobilized on clay was created of material which not easily to degraded, with a relatively large size so it is more efficient to use as an adsorbent of heavy metal ion.

2. Research Method

2.1 Materials

The materials used in this study include bread's yeast of fermipan brand, clay, standard solution of Mn(II) 1000 ppm (E. Merck), sulfuric acid (H_2SO_4 95%, E. Merck), hydrochloric acid (HCl 37%, E. Merck), nitric acid (HNO_3 56%, E. Merck), solid potassium permanganate (KMnO_4 , E. Merck), pH indicator paper (Macherey-Nagel), Whatman filter paper (cat. No. 42), aquabidest, aquadest, and tissue paper.

2.2 Research Procedure

2.2.1 Adsorbent manufacture from clay, synthesized of clay immobilized by bread's yeast and characterization by FTIR.

Clay samples were sampled from Amesiu village of Pondidaha District of Southeast Sulawesi province at a depth ranging 10-20 cm. Clay has been cleaned of dirt, dried, pulverized and then sieved with a 200 mesh sieve. Subsequently, 200 grams of clay mixed with KMnO_4 0.5M while stirring with a stirrer for 4 hours at temperature of 80°C. The result was filtered and the sediment was washed repeatedly until the washing water reached a neutral pH, then heated in an oven for 12 hours at temperature of 80°C. Clay results of KMnO_4 0.5M treatment then added H_2SO_4 6M while stirring with a stirrer for 4 hours at temperature of 80°C. The results were filtered and the precipitant washed repeatedly until the washing water reached a neutral pH and then heated in an oven for 12 hours at a temperature of 80°C. Furthermore, clay results of KMnO_4 0.5M and H_2SO_4 6M treatment were added HCl 6M while stirring with a stirrer for 3 hours at temperature of 80°C and then washed repeatedly until the washing water reached a neutral pH, then heated in an oven for 12 hours at temperature of 80°C.

Immobilization of bread's yeast biomass on clay made by mixing the clay and bread's yeast that has powdered using variations of ratio 1: 3 (mass of yeast: mass of clay) [14]. Analysis of samples with spectrophotometer fourrier Transform Infra Red (FTIR) [15].

2.2.2 Effect of Contact Time on Manganese Metal Ion Adsorption [6]

A total of 40 mL solution of Mn(II) metal ion with a concentration of 50 ppm were mixed with 0.5 gram of clay adsorbent immobilized by *S. cerevisiae* biomass. The contact time varied successively 5, 10, 30, 60, 90 and 120 minutes. The filtrate separated by filtered using Whatman filter paper and analyzed by Atomic Absorption Spectrophotometer (AAS) to determine the concentration of the Mn(II) metal ion which were not adsorbed.

Immobilisasi biomassa ragi roti pada lempung dilakukan dengan pencampuran antara lempung dan ragi roti yang telah dihaluskan menggunakan variasi perbandingan 1:3 (gram ragi : gram lempung)[7]. Analisis sampel dengan Spektrofotometer *Fourrier Transform Infra Red* (FTIR) [8].

2.2.3 Effect of pH of solution on the Adsorption of Manganese Metal Ion [6]

Solution of Mn(II) 10 ppm put into 6 glasses of erlenmeyer each 40 mL, which was then the pH of the solution in the glasses varied on 3, 4, 5, 6, 7 and 8 with the addition of HCl and NaOH. Furthermore, the Mn(II) metal solution with different pH were contacted with an adsorbent. The filtrate was filtered using Whatman filter paper and then analyzed using Atomic Absorption Spectrophotometer

(AAS) to determine the metal ion were not adsorbed by the adsorbent.

2.2.4 Effect of Mn(II) Metal Ion concentration on Manganese Metal Ion Adsorption [6]

A total of 40 mL solution of Mn(II) metal ion with concentrations of 5, 10, 15, 20, 50 and 75 mg/L were mixed with 0.5 gram of adsorbent clay immobilized by *S. cerevisiae* biomass. The filtrate separated by filtered using Whatman filter paper and analyzed by Atomic Absorption Spectrophotometer (AAS) to determine the concentration of the Mn(II) metal ion which were not adsorbed.

3. Results and Discussion

FTIR analysis were used to identify the main functional groups of biomass of bread's yeast immobilized on clay. Fig. 1 shows the cluster of biomass NH at wave number 2337 cm^{-1} and wave number 3441 cm^{-1} in carboxylic OH group from biomass. In addition, there were also an absorption band of Si-OH group at wave number 1643 cm^{-1} and CH absorption band at wave number 2931 cm^{-1} , while group of Si-O-Si appears at wave number 1033 cm^{-1} . The spectrums shows there has been a hydrogen bond between H atoms in the NH group, CH and OH from biomass with O atoms in Si-OH group and Si-O-Si of clay.

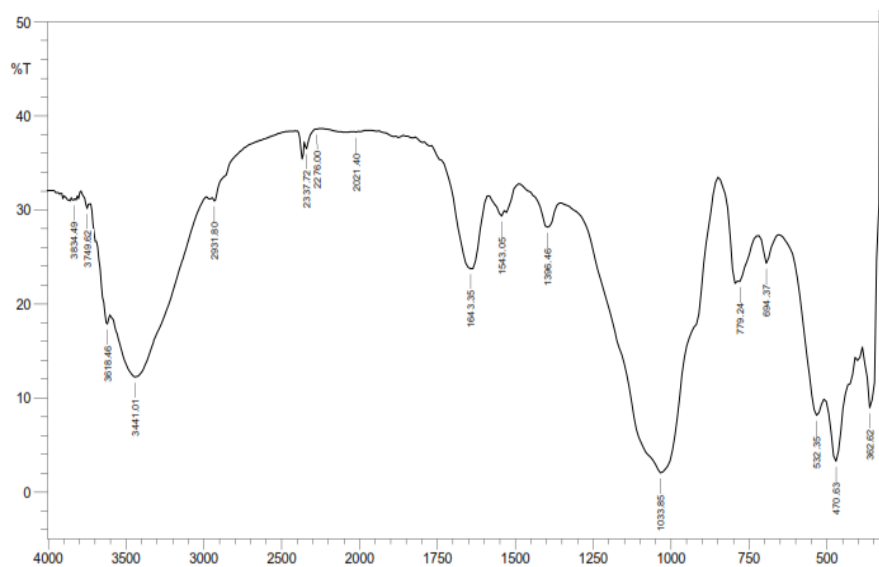


Fig. 1. The spectrum of biomass which immobilized on clay

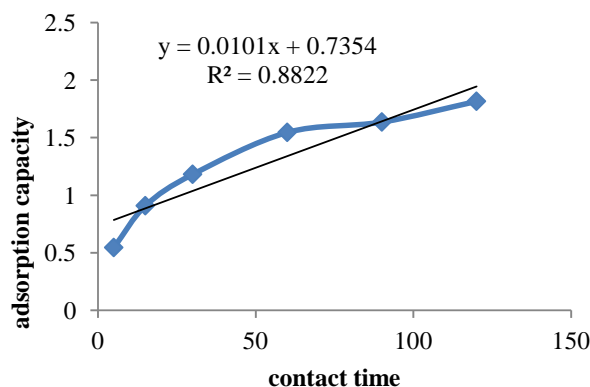


Fig. 2. Graphic of Effect of Contact Time of Mn(II) Metal Solution (mg/L) on Mn(II) Metal Ion Adsorption capacity by Bread's Yeast Biomass immobilized Clay (adsorbent weight = 0.5 gram)

3.1 Effect of Contact Time on Mn(II) Metal Ion Adsorption

Effect of contact time on the adsorption of Mn(II) metal ion by yeast biomass adsorbent immobilized clay are presented in **Fig. 2** and **Table 1**. Based on **Fig. 2** and **Table 1**, increased of Mn(II) metal ion adsorption by adsorbent yeast biomass immobilized by clay with increasing of contact time. At the contact time of 5 minutes the adsorption capacity 0.546 mg/g. By increasing the contact time to 10, 30, 60, 90 and 120 minutes, then the adsorption capacity of the adsorbent for the adsorbate were respectively 0.909; 1,182; 1,546; 1,636 and 1.816 mg/g. The increasing of the adsorption capacity because of the longer time contacting the more likely the process of diffusion and annealing of the Mn(II) metal ion in the adsorbent better.

Table 1. Comparison of Adsorption Capacity on Ssome Contact Time Variations

Contact Time (minute)	Adsorption Capacity mg/gram
5	0,546
15	0,909
30	1,182
60	1,546
90	1,636
120	1,816

3.2 Effect of pH on Mn(II) Metal Ion Adsorption

Effect of pH on the adsorption of Mn(II) metal ion by yeast biomass adsorbent immobilized clay are presented in **Fig. 3** and **Table 2**.

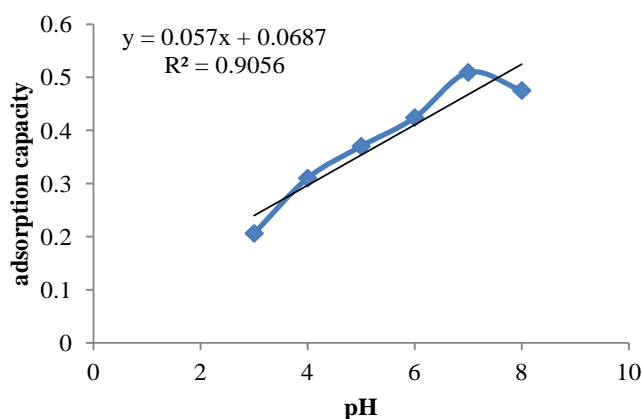


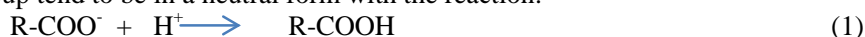
Fig. 3. Graphic of Effect of Mn(II) Metal Ion pH of solution (mg/L) on Adsorption Capacity of Mn(II) Metal Ion by Bread's yeast Biomass Immobilized Clay (adsorbent weight = 0.5 gram)

Table 2. Comparison of Adsorption Capacity on Some pH of Solution Variations

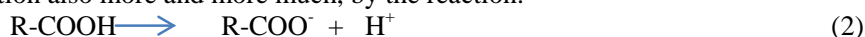
pH of Solution	Adsorption Capacity mg/gram
3	0,206
4	0,310
5	0,370
6	0,424
7	0,509
8	0,475

Based on Fig. 3 and Table 2, an increased in the adsorption capacity along with increasing of pH of solution from pH 3 to 6 by the adsorption capacity successively 0.206; 0.310; 0.370 and 0.424 mg/gram to achieve optimum absorption at pH 7 i.e. 0,509 mg/g. Decrease of adsorption capacity occurs at a pH of 8 i.e. 0.475 mg/g.

The absorption of the Mn(II) metal ion by bread's yeast biomass is strongly influenced by the pH of the solution. Absorption efficiency of Mn(II) metal ion increased from pH 3 to pH 6 to achieve maximum absorption at pH 7. This is because at low pH, the surface of the cell wall of biomass protonated or positively charged, so the adsorption of metal that occurs is very small, because carboxylate group tend to be in a neutral form with the reaction:



At high pH, the surface of the cell wall biomass negatively charged, so the adsorption of metal becomes larger. The higher pH will also make more group R-COO biomass that can act as ligand in complex formation also more and more much, by the reaction:



The presence of negative charge will cause interactions between positively charged metal with active sites on the surface of the negatively charged cell walls. At the same time, the surface ligands will compete with OH⁻ in binding metal cations, that will lead to an increase in metal adsorption by biomass. At pH 8 shows the pattern of absorption of the Mn(II) metal ion decreased. These are because the pH of the number of OH⁻ ions more, so that OH⁻ ions formed tend to bind to the Mn(II) metal ion to form hydroxide Mn(OH)₂.

3.3 Effect of Mn(II) Metal Ion solution Concentration on Mn(II) Metal Ion Adsorption

Effect of concentration on the adsorption of Mn(II) metal ion by biomass yeast immobilized clay are presented in Fig. 4 and Table 3.

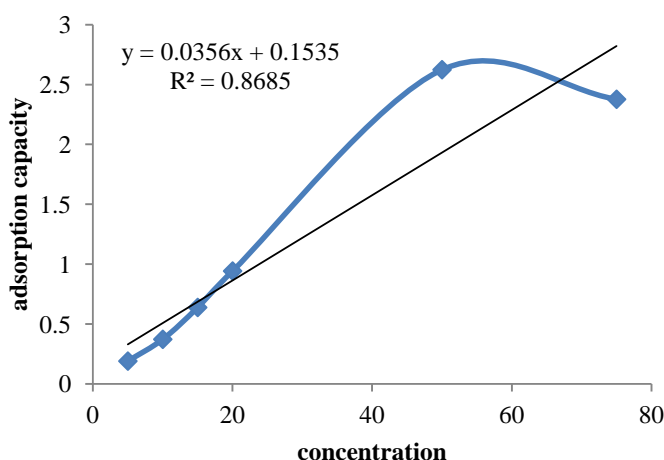


Fig. 4. Graphic of Effect of Mn(II) Metal Solution concentrations (mg/L) on Adsorption capacity of Mn(II) Metal Ion by Bread's yeast biomass Immobilized Clay (adsorbent weight = 0.5 gram)

Table 3. Comparison of Adsorption Capacity on Some Solution Variations

Concentration (mg/L)	Adsorption Capacity mg/gram
5	0,191
10	0,373
15	0,639
20	0,943
50	2,624
75	2,377

Increasing of Adsorption capacity also occurred in several variations of the Mn(II) metal ion concentration. Adsorption starting from a concentration of 5 mg/L with a higher adsorption capacity equal to 0.191 mg/g and continued to increase until the concentration equal to 50 mg/L i.e. 2,624 mg/g and at a concentration of 75 mg/L adsorption capacity descend to 2.377. In Fig. 4 and Table 3, it is clear that the state of the active site of the fourth adsorbent on each addition concentration were not saturated due to continued improvement of the adsorption of Mn(II) metal ion or in other words all of the active sites on the clay is considered not saturated up to a concentration 50 mg/L. However, at a concentration of 75 mg/L occur decreasing of adsorption capacity. This shows that at a concentration of 75 mg/L of active sites on the fourth adsorbent has saturated. On Oscik [16], Langmuir explained that the surface of the adsorbent viz bread's yeast biomass immobilized clay has a number of active sites which proportional to the surface area of the adsorbent. At each active sites is only one molecule can be adsorbed. In the state of active sites which has not been saturated with adsorbate of the Mn(II) metal ion, then increasing the concentration of Mn(II) metal ion which contacted with bread's yeast biomass immobilized clay whose numbers will still produce uptake of Mn(II) metal ion which increases linearly. When the active site has been saturated with adsorbate, then increasing concentrations of Mn(II) metal ion in further will not increase the amount of Mn(II) metal ion which is absorbed.

Freundlich's Isothermal adsorption curve, Mn(II) metal ion by the yeast biomass adsorbent immobilized on clay made by plotting $\log q_e$ to $\log C_e$, where q_e is the amount of adsorbed adsorbate and C_e is the concentration of the adsorbate in the adsorption equilibrium are presented in Fig. 5.

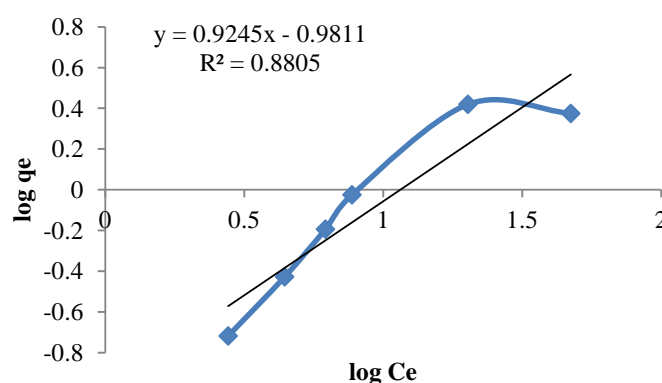


Fig. 5. Graphic of Freundlich adsorption isotherm of Mn(II) Metal Ion by yeast Biomass adsorbent Immobilized on Clay.

Langmuir adsorption isothermal curve Mn(II) metal ion by yeast biomass adsorbent immobilized on clay made by plotting C_e/q_e on C_e where q_e is the amount of adsorbed adsorbate and C_e is the concentration of the adsorbate in the adsorption equilibrium are presented in Fig. 6.

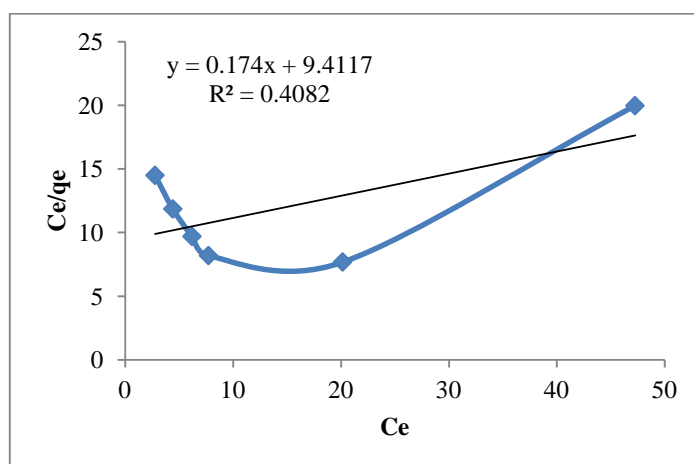


Fig. 6. Graphic of Langmuir Adsorption Isotherm Mn(II) Metal Ion by Yeast Biomass Adsorbent Immobilized on Clay.

Based on Fig. 5 and Fig. 6 above, the linear regression values obtained in Freundlich equation for yeast biomass adsorbent immobilized on clay i.e. 0.8426 while the value of the linear regression of Langmuir equation for the adsorbent obtained 0.5351. Therefore, it can be stated that the type of metal ion adsorption of Mn(II) by the adsorbent tends to follow Freundlich isotherm linearity for linear regression values for Freundlich isotherm is greater than the value of the linear regression on the Langmuir isotherm, thus determining the adsorption capacity used Freundlich equation. Freundlich equation obtained on the adsorption capacity (K_F) for yeast biomass adsorbent immobilized on clay equal to 0.1045 mg/g. In this study, yeast biomass adsorbent immobilized on clay which adsorbed Mn(II) metal ion categorized as physical adsorption [17].

4. Conclusion

The adsorption capacity of the Mn(II) metal ion obtained optimum contact time in 120 minutes, the optimum pH 7 and the concentration of Mn(II) 50 mg/L, the adsorption capacity equal to 2,624 mg/gram. Based on Freundlich adsorption isotherm equation, the known value of the adsorption capacity of yeast biomass immobilized clay equal to 0.1045 mg/gram.

References

1. Lusiana, Muchyar, M. Najib. 2000. Unsur-unsur Hara Esensial. Lambung Mangkurat University, Banjarbaru. [in Indonesian]
2. Tan, 1995, Dasar-Dasar Kimia Tanah, Gadjah Mada University Press, Yogyakarta. [in Indonesian]
3. Bhattacharyya, K.G. and Gupta, S.S., (2008b), Kaolinite and Montmorillonite as Adsorbents for Fe(III), Co(II) and Ni(II) in a Aqueous Medium, Applied Clay Science, 41, pp. 1–9.
4. H. Aripin, S. Mitsudo, I. N. Sudiana, N. Jumsiah, I. Rahmatia, B. Sunendar, L. Nurdiwijayanto, S. Mitsudo, S. Sabchevski, Preparation of Porous Ceramic with Controllable Additive and Firing Temperature, Advanced Materials Research, Vol. 277 (2011) pp. 151-158
5. Herrero, R., B. Cordero, P. Lodeiro, & C. Rey-Castro. 2002. Interactions of Cadmium(II) and protons with dead biomass of marine algae *Fucus* sp. Departamento de Química Física e Engenharia Química I. Coruña, Spanyol.
6. Muslimin, 2010, Pemanfaatan Lempung Montmorillonit Terammobilisasi Biomassa Ragi Roti Untuk Mengadsorpsi Ion Logam Cr(III), Minithesis, Haluoleo University, Kendari. [in Indonesian]
7. Hughes, M.N., and Poole, R.K., 1990, Metal and Microorganism, Chapman and Hall, London.
8. I. N. Sudiana, S. Mitsudo, T. Nishiwaki, P. E. Susilowati, L. Lestari, M. Z. Firihi, H. Aripin, Synthesis and Characterization of Microwave on Sintered Silica Xerogel Produced from Rice Husk Ash, Journal of Physics: Conference Series Vol. 739 No. 1, (2016) 012059
9. Balcu, I., Macarie, C.A., Segneanu, A.E. dan Pop, R.O. 2011. Combined Microwave-Acid Pretreatment of the Biomass. Progress in Biomass and Bioenergy Production.
10. Dehani, F. R., Argo, B. D. dan Yuliningsih, R. 2013. Utilization of Microwave Irradiation to Maximize Pretreatment Process Degradation of Lignin Jeremi Paddy. Jurnal Biopress Komoditas Tropis Vol.1 No. 1, 175-182 [In Indonesia].
11. W. H. Sutton, Microwave processing of Ceramic Materials, Microwave Solutions for Ceramic Engineers, American Ceramic Society, (2005), 35-65.
12. M. Z. Firihi., I. N. Sudiana, S. Mitsudo, Microwaves Enhanced Sintering Mechanisms in Alumina Ceramic Sintering Experiments, Contemporary Engineering Sciences, Vol. 9, 2016, 5, 237 – 247
13. I. N. Sudiana, S. Mitsudo, M. Z. Firihi, Effect of Initial Green Samples on Mechanical Properties of Alumina Ceramic, Contemporary Engineering Sciences, Vol. 9, 2016, no. 12, 595-602.
14. I. N. Sudiana, S. Mitsudo, M. Z. Firihi, H. Aripin, Effect of High-Frequency Microwave on Micro Hardness of Alumina Ceramic, Material Science Forum, Vo. 872, 2016, pp.114-117.
15. Fahmiati, Mashuni, Alimin, dan Amiruddin, 2007, Pengembangan Teknologi Pemisahan Logam Berat dengan Memanfaatkan Biomassa *S. cerevisiae* dari Ragi yang Diimmobilisasi pada Lempung sebagai Adsorben, Report of Compete Grant Research, FMIPA, Haluoleo University, Kendari. [in Indonesian]
16. Darmayani, S. 2010, Karakterisasi Lempung Montmorillonit Immobilized Ragi Roti Menggunakan Analisis BET, FTIR dan SEM, Minithesis, Haluoleo University, Kendari. [in Indonesian].
17. Oscik, K., 1982, Adsorption, John Wiley, New York.
18. Al-Duri. B., 1995, A Review in Equilibrium in Single and Multicomponen Liquid Adsorption System, Review in Chemical Engineering, 11, p.p. 101-143