Copolymerization of Cellulosa-*Glycidyle Methacrylate* (GMA) Using Prairradiation Method and Sulfonate as a Functional Group For Lead Metal Ion Adsorption

Shafira Muzdalifah, Asep Saefumillah, Meri Suhartini
Universitas Indonesia

Abstract

Currently the most water pollution problems are caused by the heavy metals. Therefore, an adsorbent to reduce the problem of heavy metal pollution is needed. In this research, an adsorbent metal ion based on cellulose made with sulfonate functional group. First of all, the cellulose is being irradiated using the electron beam with a variation of irradiated dose 20, 30 and 40 kGy then being grafted using a pre-irradiation method to *Glycidyl Methacrylate* monomer (GMA) with a variation of the concentration 1%, 2,5% and 5%. The cellulose-grafted GMA is modified using a sulfonate functional group in optimum conditions to be applied as a lead metal ion adsorbent. The result of copolymer synthesis of cellulose-GMA-sulfonate was charactherized with FTIR, DSC and AAS.The percent yield of efficient cellulose-GMA irradiated with 40 kGy radiation doses and GMA monomer concentration was 107.62%.The optimum conditionof cellulose-GMA-sulfonate synthesis is at 80°C with 1N concentration. The present adsorption capacity of lead metal ion solution equal to 8,476 mg/g, the required solution is needed to be at pH 7, 150 minutes contact time and with 20 ppm concentration of lead metal ions. An appropriate adsorption isotherm represented for cellulose-GMA-sulfonate adsorbent is Langmuir isotherm model with a regression value at 0.974. The adsorbent kinetics of cellulose-GMA-sulfonate adsorbents is obtained following the first order reaction. Based on the results, the modified cellulose GMA Sulphonate cellulose copolymer can increase the absorption of lead metal ions.

Keywords*: Adsorption, Cellulose, Grafted Copolimer, Glisidil metakrilat, Sulphonate functional groups.*

Introduction

One of the most dominant pollutants for the environmental today is heavy metals released by industrials. To overcome that environmental problem mainly heavy metals pollution, various methods have been used such as coagulation, solvent extraction, ultra filtration, ion exchange and adsorption (Gurgel *et al*, 2008). Adsorption is efficient method for removal heavy metals from the environmental. Adsorbents can be prepared from natural materials or from waste that essentially have a high absorption capacity, low cost and available in nature (Babel and kurniawan, 2003).

Nowadays, cellulose material has a gain attention to be modified as adsorbent. Many researchers are currently working to modify cellulose as heavy metal adsorbent. Modified cellulose has reported to have higher adsorption capacity than unmodified ones (Hokkanen et al, 2016). Rice straw has a high enough cellulose content that can be used as an adsorbent. Rice straw is also biodegradable and renewable so it has other advantages. Therefore this study used cellulose derived from rice straw.

Grafting is a technique for combining cellulose as a matrix with synthetic polymers with specific functional groups. The advantage of the technique is that cellulose can be functionalized based on properties possessed by covalently bonded monomers without affecting the basic structure of cellulose. The hydroxyl group of cellulose is used to modify cellulose by introducing a specific functional group on cellulose through grafting technique. Glycidyl Methacrylate (GMA) is one of the most preferred monomers for cellulosic grafting techniques because of the presence of vinyl group which can be initiated with free radical which will be grafted with cellulose and acts as a parent polymer and the presence of epoxy group can bind to other functional groups.

The epoxy ring will open and form a new functional group for chelate formation with the metal (Chauhan et al., 2005). In this study, the prairadiation method is used. This method has the advantage of producing fewer homopolymers (Bhattacharya and Misra, 2004). In this method, the addition of functional groups to cellulose can increase adsorption ability in metal uptake. The addition of functional groups such as carboxylates (COOH), amines (NH_2) and sulfonates (SO_3H) may also be ion-exchange (Basuki, Fatmuanis, 2005). In this study sulfonates derived from ammonium sulphate $(NH_4)_2SO_4$ were added to the product of copolymerization of cellulosic grafted with GMA monomer for the absorption of lead metal ions.

Experimental

1) Grafting GMA monomer to cellulose with pre-irradiation method

Cellulose sample was irradiated using electron beams with varying radiation doses of 20, 30 and 40 kGy using 2 meV of electron beam machine (PAIR BATAN) to obtain the optimum dose. Optimization of grafting of GMA monomer onto cellulose was prepared by immersing irradiated cellulose into the

GMA solution with water solvent which added TWEEN20 5% for variation of 1% concentration; 2.5%; 5% at 60 °C for 6 hours under nitrogen gas flows. The GMA-grafted cellulose was washed with a mixture of hot aqueous and 5% methanol solution to dissolve the remaining GMA homopolymers and monomers. The cellulose-GMA was rinsed with aquades to a colorless filtrate. Afterwards, cellulose-GMA is dried in the oven and weighed until it reaches a constant weight. The percentage of grafting is calculated using the following general formula:

$$\%G = \frac{w - w_0}{w_0} \, x \, 100\% \quad (1)$$

Note :

%G	= grafting percentage
W	= cellulose weight bounded
W_0	= initial cellulose weight

2) Optimization of cellulose-GMA modification with sulfonat

Cellulose-GMA was immersed in various ammonium sulphate solution and then stirred and heated at different temperatures. Afterwards, the yield was washed using aquades and dried at 60^{o}C until a constant weight was obtained.

3) Expansion degree

0.04 grams of cellulose and cellulose-GMA samples with varying percent of the transplants soaked in 20 mL of aquades for 1, 5, 10, 15, 20, 30, 40, 60, 90 and 120 min were then removed from the solution then weighed.

4) Adsorption of metal ion

The adsorption of Pb metal ion was performed by varying concentrations of Pb's solution, contact time and solution of pH. 60 mg of cellulose-GMA-sulphonate adsorbent was immersed in the 15 ppm of Pb's solution in an erlenmeyer. The erlenmeyer was stirred on a shaker at 100 rpm for 150 min with the various pH namely 3, 4, 5, 6 and 7. Afterwards, the sample was filtered using filter paper until the filtrate was obtained. The filtrate was analyzed by AAS instrument to determine the final concentration of Pb ion in the solution. The adsorption has been carried out for various times namely 60, 90, 120, 150 and 180 min and various concentration of Pb ion solution namely 1, 3, 5, 7, 10, 15 and 20 ppm

Result and Discussion

1. Result of grafting GMA onto cellulose

The higher the radiation dose used, the more radicals were obtained which then lead increasing the products. The radiation doses used in this work namely 20, 30 and 40 KGy with 2.5% concentration of monomer. This work was conducted at 25^{o}C for 6 hours.

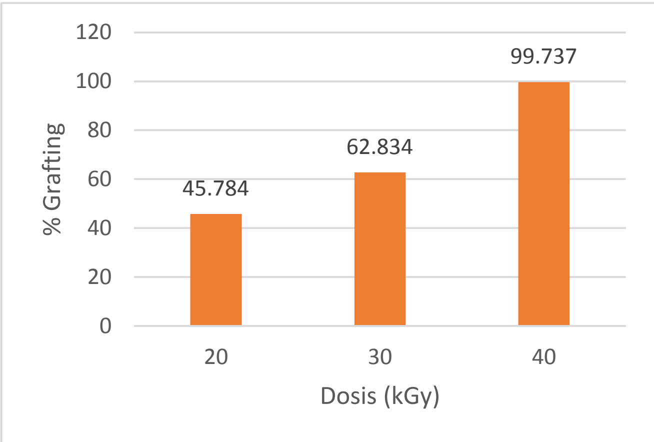


Figure 4. 1 Effect of Radiation Dosage on Graft Process

Figure 4.1. Showed that percentage of grafting increased with increasing of radiation doses. The ionizing radiation energy was used as an initial energy to initiate the polymerization reaction. The increase of radiation dose has lead increasing free radical. Thus, probability of polymerization reaction will be higher (Swantomo, Deni, 2008).

In addition to study the affect of solvent, this work also study the correlation between GMA with percentage of grafting products to obtain the optimum product. This reaction is performed at 60^{o}C for 6 hours. This temperature is chosen since at this condition the opening of epoxy rings can be prevented so it expected that the vinyl group that only reacted with the cellulose (C.E, Janrizka Betta., 2016). This grafting time is also used since the longer the grafting period, the more GMA bindes to cellulose.

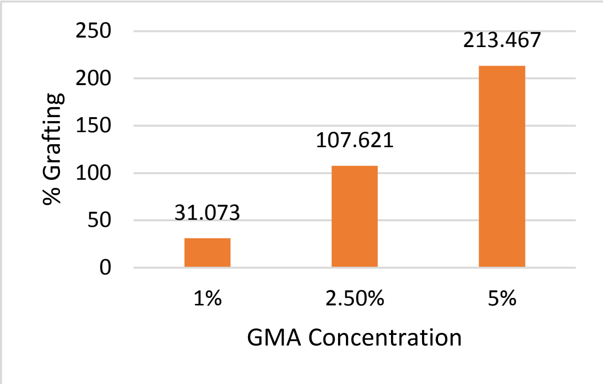


Figure 4. 2 Effect of GMA Concentration on grafting process

As shown by the Figure 4.2, the increase of GMA concentration lead to the increase of grafting percentage. The highest percentage of grafting was obtained at a 5% GMA concentration of 213%. This was because at the high concentrations of GMA, many monomers reacted with cellulose so that more products was obtained.

2. Degree of Expansion

Degree of expansion is a measure of the number of entered water molecules to the sample. The adsorption of water may be affected by the functional group presented in the sample such as hydroxil groups.

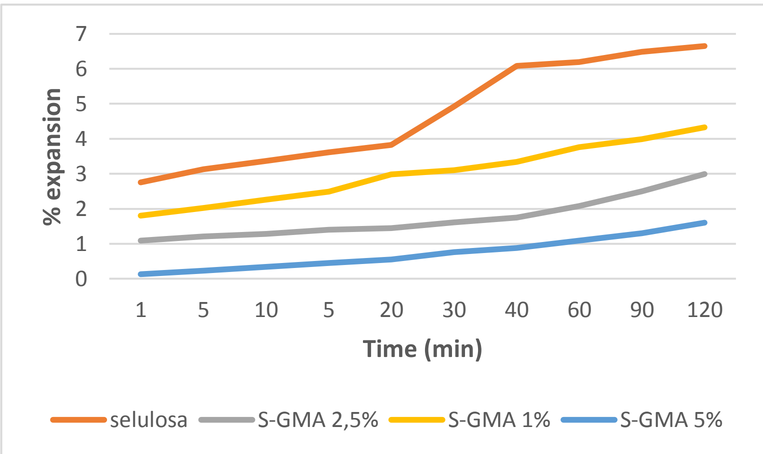


Figure 4. 3 Degree of expansion

Based on Figure 4.3 a pure cellulose obtained the highest expansion degree because of the interaction the hydroxyl groups with the water solvent. On the GMA-modified cellulose, there was a decrease in the degree of expansion on the higher GMA concentration. This is because of the higher the concentration of GMA, the hydroxyl groups will be decreased, since the GMA was attached to the C-6 of hydroxyl groups, so that the adsorption of water by the GMA-modified cellulose will be decreased.

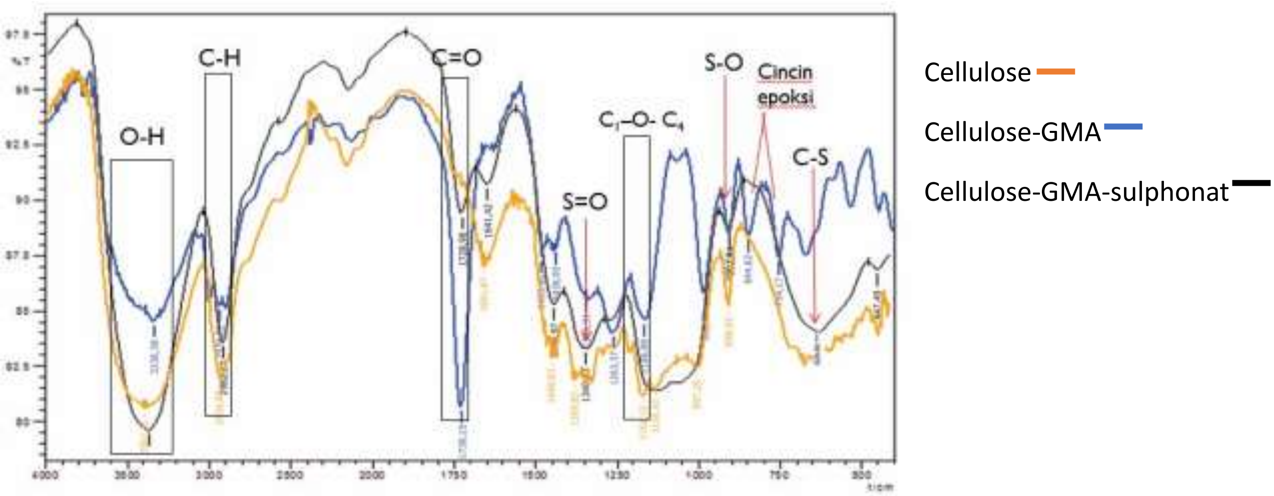
3. Modification of cellulose-GMA Copolymer with ammonium sulphate

The highest of ammonium sulphate concentration on the modification of cellulose grafted GMA was 1 N as shown Figure 4.4 (a). This is due to low concentration, the epoxy ring bonded with the sulphonate group has not been too much. While at relatively high concentrations, the epoxy group undergoes diffusion process because ammonium sulfate is complex so that the sulphonate functional group that has been attached undergoes to discharge. So in this work has obtained optimum concentration of sulfonate group of 1 N with percent conversion of 455%.

In Figure 4.4 (b), it is found that as the temperature increases, the percentage of conversion increases. This indicates that the amount of sulphonate that reacts with the epoxy ring in GMA increases as the reaction temperature increases. It is seen that at 80 ° C, the highest percentage conversion is 335%. The higher temperatures cause the intermolecular collisions to accelerate so that the possibility of the epoxy ring react with the sulphonate will be even greater. At 90°C the value of percent conversion has decreased insignificantly due to the possibility of homopolymer starting.

4. Characterization

Characterizing material using FTIR was conducted to investigate the finger print of functional groups grafted on the cellulose and sulphonate modification yield. DSC characterization was conducted to investigate the changes of material charateristic after grafting process and modification of themal transitions of the polymer.



Picture 4. 4 Spectrum of cellulose-GMA-Sulphonate

Based on Figure 4.5, there was decreasing of -OH at 3367 cm^{-1} of pure cellulose compared to GMA-grafted cellulose which indicated an interaction berween GMA with free radical formed from the –OH of cellulose. The spectra of 1161 cm^{-1} dan 1165 cm^{-1} indicated the bonding of B-1,4-glikosida (C1-O-C4) on cellulose. The presence of functional group of esther (C=O) at 1730 cm^{-1} and epoxy ether at 754 cm^{-1} and 844cm^{-1} showed that GMA have successfully grafted. The appearance of characteristic absorbtions of C-S at 628 cm^{-1} (Rao, C.N.R *et al*., 1963; Hampton, Carissa. 2010), S-O at 902 cm^{-1}, S=O at 1340 cm^{-1} and disappearance of epoxy ether have indicated that sulphonate vahe succesfully added.

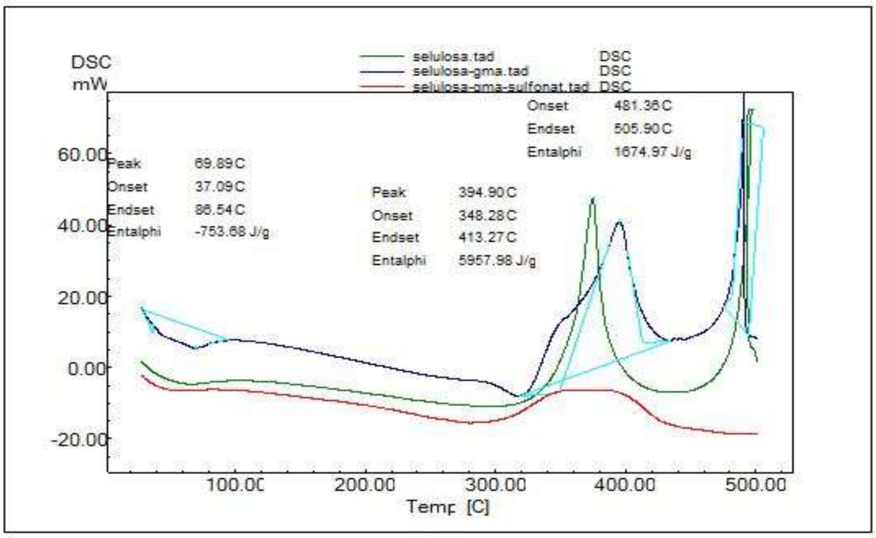


Figure 4. 5 Thermogram analysis of pure cellulose and cellulose-GMA and GMA grafted-GMA

Based on Figure 4.10, two exotermic peaks appearing at 394.90 °C dan 481.38 °C showed existence of pure cellulose. The observed cellulose peaks in the temperature range 400-600 ^{o}C since it indicate the degradation temperature (Suhartini, Meri., 2015). Intensity of degradation temperature of pure cellulose is at 481,38 °C and the GMA-cellulose is in the same temperature. Thus, it estimated both of them have the same degradation temperature. The intensity of exotermic peak at the temperature of 400-600 °C was not seen in the addition of sulphonate on GMA-cellulose. The addition of sulphonate functional groups to GMA cellulose causes the intensity of the exothermic peaks to be lost so that it can be concluded that there is no degradation and result in good and undamaged heat stability. At the peak exotherm of a pure cellulose at 394.90 °C, there is a widening of graphs of pure cellulose by grafting of GMA and sulphonate modification, thus possibly leading to the addition of large side chains and increased molecular weight (Rahmawati, 2013).

5. Adsorption of Pb ions

The adsorption process of metal ion by an adsorbent was influenced by several factors. Factors affecting an adsorption process include the type of adsorbent, the type of substance absorbed, the surface area of the adsorbent, the concentration of solute, the temperature, the pH and the contact time. The filtrate was analyzed using AAS to calculate the concentration of Pb ions in solution. The calculation is done by regression equation of calibration curve that is y = 0.0012x + 0.001 with regression price obtained R2 = 0.9955. In Figure 4.6 (a), it is found that the pH at pH 7 has an adsorption capacity of 10.993 mg / g At a low pH the capacity of Pb adsorption is relatively small, where in acidic conditions, the excess of H^+ ion may interfere with the sulphonate. As more pH binds the H^+ ion it becomes positively charged, so the sulphonate is increasingly difficult to bind to the Pb metal ion. As the pH above 7, the adsorption of metal ions does not occur due to the hydrolysis reaction which produces hydroxide, wherein most of the metal hydroxide is insoluble in water or settling (Zakaria, A., 2011).

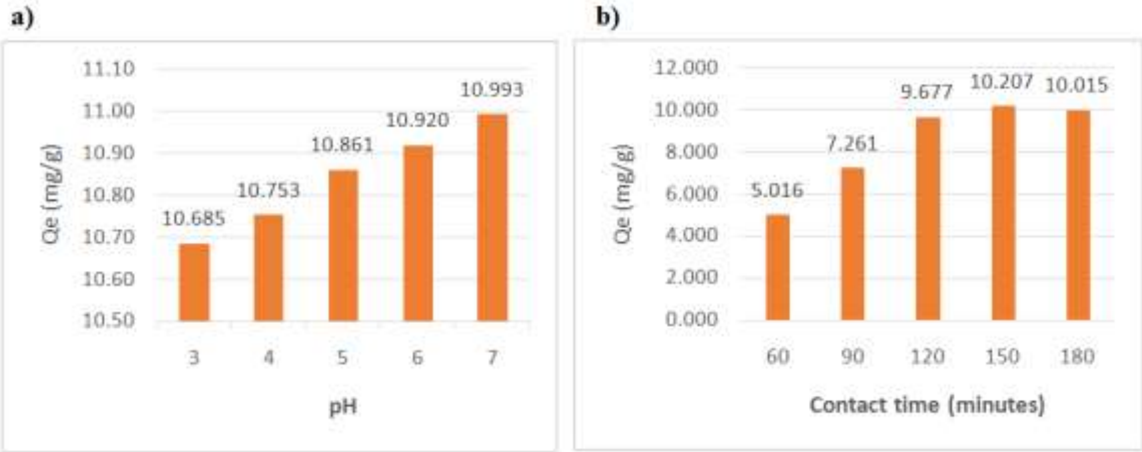


Figure 4. 6 (a) influence of pH to adsorption capacity and (b) Influence of contact time to adsorption capacity

Based on Figure 4.7 (b), it is found that the contact time has an effect on the amount of Pb metal ions absorbed. The adsorption of Pb metal ions by cellulose-GMA-sulphonate adsorbents increases with increasing contact time. This is due to the increasing of contact time, the probability of metal ion interaction with the adsorbent increases also, so that the amount of metal ion absorbed will be more and more. (C.E, Janrizka Betta., 2016). At relatively shorter contact times, the metal ion interaction with the adsorbent tends to be less so that its absorption capacity on the adsorbent active side is reduced. However, during longer contact time there is also a decrease in capacity because the adsorbent's active side is full to absorb metal ions so they begin to saturate and eventually diffuse. The results of this study indicate that the adsorption capacity of Pb metal ions by the cellulose-GMA-sulphonate adsorbent at 150 min contact time is 10,207 mg / g.

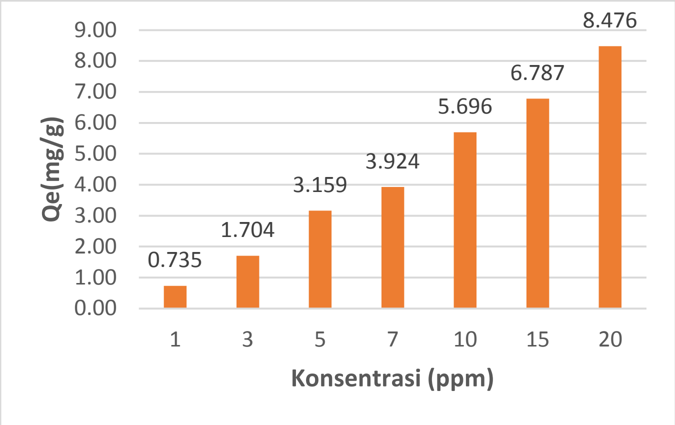
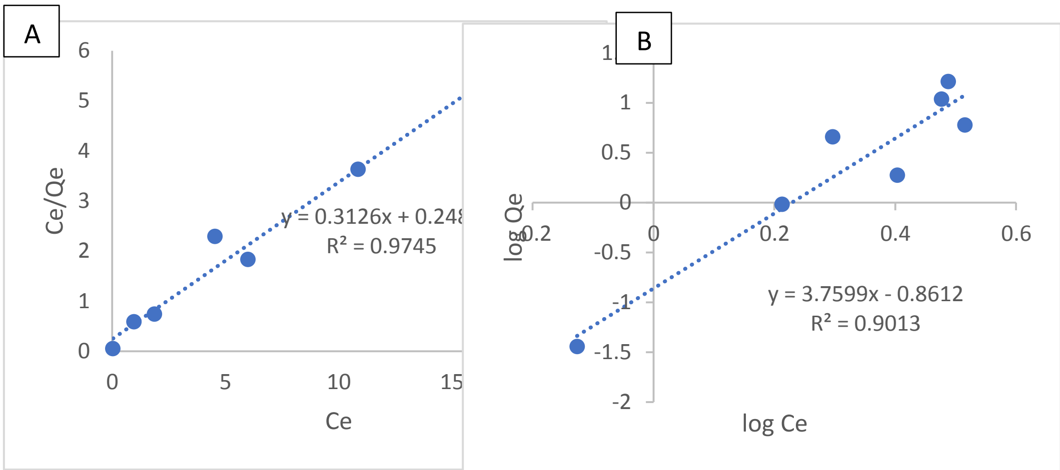


Figure 4. 7 The effect of Pb ions concentration to adsorption capacity

Figure 4.13 showed the increasing concentration of metal ions leading to higher adsorption capacity of cellulose-GMA-sulphonate adsorbents. This is due to at high concentrations; the number of metal ions in the solution is increasing so that more metal ions interact with the adsorbent. Increasing the concentration of reactants will lead the total number of collisions to adsorbent so that the more products are formed. The adsorption capacity of Pb metal ion occurs at concentration 20 ppm that is equal to 8,476 mg / g.

6. Adsorption isotherm

The regression results as shown in Fig. 16 (a) and (b) for the langmuir isotherm equation are 0.9745 and 0.9013 for Freundlich isotherms. The Freundlich isotherm model is used to explain the adsorption of Pb metal ions on heterogeneous surfaces and on multilayer adsorption. While the Langmuir adsorption isotherm model assumes that the adsorption process occurs only on certain homogeneous sites in the adsorbent and each site can only bind the adsorbat molecule (monolayer) (Simanjuntak, Magdalena S., 2016).



Gambar 4. 8 (a) Isoterm Adsorpsi Langmuir dan (b) Isoterm Adsorpsi Freundlich

The regression results obtained for the Langmuir isotherm equation is close to one so it can be concluded that the distribution of Pb metal ions on the cellulose-GMA-sulphonate adsorbent follows the Langmuir isotherm model. Dari hasil meningkatnya variasi konsentrasi seiring dengan menaiknya kapasitas adsorpsi dengan peningkatan konsentrasi awal yang dapat dijelaskan berdasarkan rapatan partikelnya. As the concentration increases, the particle density becomes larger and the interaction between Pb molecules becomes multilayer. The law in the Langmuir isotherms states that the metal binding potential of the metal ion by cellulose-GMA-sulphonate adsorbents is the same on each active side. Here is Langmuir's isotherm linear equation:

$$\frac{Ce}{Qe} = \frac{1}{qmax\ k1} + \frac{Ce}{qmax}\ Ce$$

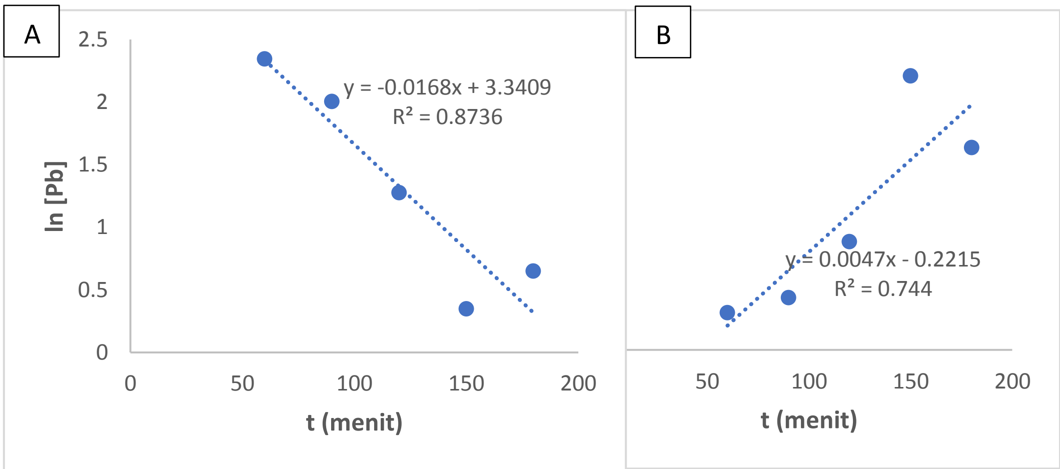
The result of calculation was obtained that the value of y namely 0.3126x + 0.2487, thus the k1 value was 0,9999 and qmax was 3.1990 mg / g. The Pb metal ion forms a monolayer layer on the homogeneous surface of cellulose-GMA-sulphonate adsorbent. Based on the calculation, the adsorption capacity of Pb metal ions by cellulose-GMA-sulfonate adsorbent was 3.1990 mg / g.

7. Kinetics Adsorpstion

Based on Figure 4.10, the linear equation for first order is y = -0.0168x + 3.3409, with a R value of 0.8736. The linear equation is obtained by plotting ln [Pb] to t (min). Using the first order equation:

$$\ln[Pb] = -kt + \ln[Pb_{\circ}]$$

From the above equation can be obtained k value (rate constant) is 0.0168 minute^{-1}. [Pb] is the concentration at the certain time, [Pb_o] is the initial concentration and



Gambar 4. 9 (a) Orde Reaksi Satu dan (b) Orde Reaksi dua

t is the time in minutes.

While the results of the equation for second order is y = 0.0047x - 0.2215 with regression value 0.744. The linear equation is obtained by plotting 1 / [Pb] on t (min). By using a second-order equation:

$$\frac{1}{[Pb]} = kt \frac{1}{[Pb_{\circ}]}$$

The value of k (rate constant) obtained is 0.0047 menit^{-1}.

From these two equations, it can be seen that the first order adsorption kinetics have higher regression value, so that the rate of adsorption kinetics of Pb metal ions follows the first order with the constant rate of 0.0168 min^{-1}, the regression value of 0.8736 and the adsorption rate for 15 ppm was:

$$V = k\,[Pb]$$

ISBN: 978-602-73192-1-9

$$V = 0.0168 \text{ minutes}^{-1} \times 15 \text{ ppm}$$

$$V = 0{,}252 \text{ ppm minutes}^{-1}$$

Conclusion

The synthesis of GMA-grafted cellulose and their modification by using sulfonate functional groups has been successfully performed. Adsorption of Pb metal ion with synthesized adsorbent under PH 7, for 150 min and with concentration of Pb solution 20 ppm followed isotherm of langmuir. The adsorption rate of Pb metal ion followed the first reaction order with the rate constant (k) 0.0168 min^{-1}.

References

Anirudhan, T.S *et al,.Adsorption of Chromium(VI) From Aqueous Solutions by Glycidylmethacrylate-grafted-densified Cellulose With Quaternary Ammonium Groups*. Applied Surface Science, volume 279, Pages 441-449.

Anirudhan, T.S., Senan, Priya. 2011. *Adsorptive potential of sulfonated poly(glycidylmethacrylate)-grafted cellulose for separation of lysozyme from aqueous phase: Mass transfer analysis, kinetic and equilibrium profiles*. Colloids and Surfaces A: Physicochemical. Eng. Aspects 377, 156-166

Babel S, Kurniawan TA 2003. *Low-cost Adsorbents For Heavy Metals Uptake From Contamined Water: A review*. Journal of Hazardous Material, B97, 219-243.

Barsbay, Murat., Olgun Güven., Yasko Kodama. 2016. *Amine functionalization of cellulose surface grafted with glycidyl methacrylare by γ-initiated RAFT polymerization*. Radiation Physics and Chemistry 124: 140-144

Basset, J. 1994. *Buku Ajar Vogel Kimia Analisa Kuantitatif Anorganik* . Jakarta: EGC.

Basuki, Fatmuanis., Asijati, Endang., Sabarinah, Yanti. 2005. Sintesis dan *Karakterisasi Kopolimer Iradiasi Cangkok Asam Akrilat, Akrilamida dan Campurannya pada Serat Rayon Sebagai Penukar Ion*. Departemen kimia, Fmipa UI. P3TIR; Batan. No. I Vol 6.

Bhattacharya, A., Misra, B.N., 2004. *Grafting: A Versatile Means To Modify Polymers. Techniques, Factors and Applications*. Prog. Polym. Sci. 29, 767-814.

Bondar Yu.V. 2004. *Production of sorption-active polypropylene fiber by radiation-induce grafting of glycidyl methacrylate as a precursor* *monomer*. Proceeding of the Third Eurasian Conference "Nuclear Science and its Application"

C.E, Janrizka Betta. 2016. *Sintesis Kopolimer Cangkok Selulosa dan Glycidyl Methacrylate (GMA) Dengan Metode Prairadiasi Menggunakan Etilendiamin Sebagai Gugus Fungsional Untuk Adsorpsi Ion Logam Timbal (Pb)* (Skripsi). Depok: Universitas Indonesia.

Chauhan, G. S., Singh, B., and Kamar, S. 2005. *Synthesis and Characteristics of N-Vinyl Pyrrelidine and Cellulose based Functional Graft Copolymer for Use as Metal ion and Iodine Sorbent*. Journal of applied Polymer Science 98, 373-383.

Dong, Cuihua *et al*,. 2016. *Efficient and Selective Adsorption of Multi-metal Ions Using Sulfonated Cellulose as Adsorbent*. Carbohydrate Polymers, volume 151, Pages 230-236.

Fadilla, Nur Ikfa. 2016. *Sintesis Kopolimer Cangkok Selulosa dan Monomer Asam Akrilat Menggunakan Trimethallyl Isocyanurate (TMAIC) Sebagai Pengikat Silang dengan Mtode Pra-iradiasi Untuk Aplikasi Ion Logam Timbal (Pb)* (Skripsi). Depok: FMIPA UI

Gurgel, L. V. A., Karnitz Júnior, O., Gil, R. P. F., & Gil, L. F. 2008. *Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by cellulose and mercerized cellulose chemically modified with succinic anhydride*. Bioresource Techno344R34logy, 99(8), 3077–3083

Hampton, Carissa. 2010. *Vibrational Spectroscopy Tutorial: Sulfur and Phosphorus.* Fall 2010 Organic Spectroscopy. Missouri State University, USA.

Heinonen, Aki. 2012. *Adsorption of Hydrogen Sulfide by Modified Cellulose Nano/Microcrystals*. Lappeenrannan Teknillinen Yliopisto, Faculty of Technology, Environmental Engineering.

Hokkanen, Sanna. 2016. *A rieview on modification methods to cellulose-based adsorbents to improve adsorption capacity*. Water research(91) page 156-173.

Indriani, Ririn. 2016. *Uji Adsorpsi dan Regenerasi Kopolimer Selulosa-g-Glisidil Metakrilat (GMA) Sebagai Adsorben Ion Logam*. Jakarta: Universitas Pancasila.

Kang, Hongliang *et al*. 2015. *Graft modification of cellulose: methods, properties and applications.* Polymer 70, A1-A16

Kumar, A and Gupta, R.K. (1998). *Fundamentals of Polymers.* International Edition. McGraww Hill, Singapore.

Kumar, P. Senthil. Kirthika, K. 2009. *Equilibrium kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder*. Jurnal of Engineering Science and Technology Vol. 4, No. 4 351-363.

Rahmawati. 2013. *Kopolimerisasi Cangkok Asam Akrilat Pada Selulosa Jerami Padi Dengan Teksik Pra-iradiasi dan Aplikasinya Sebagai Penukar Ion* (Tesis). Depok: FMIPA UI.

Rao, C.N.R *et al*. 1963. *Contribution to the infrared spectra of organosulphur compounds.* Departement of Organic Chemistry, Indian Institute of Science, Bangalore-12, India

Simanjuntak, Septianty Magdalena. 2016. *Studi Adsorpsi Ion Lathanium dan Eribium Menggunakan Pektin dari Kulit Pisang* (Skripsi). Depok: FMIPA UI.

Suhartini, Meri. 2015. *Pencangkokkan secara radiasi asam akrilat pada selulosa dengan keberadaan meril metakrilat*. Pusat Aplikasi Isotop Radiasi, BATAN.

Swantomo, Deni. Megasari, Kartini. Saptaaji, Rany. 2008. *Pembuatan Komposit Polimer Superadsorben Dengan Mesin Berkas Elektron*. Seminar Nasional IV, SDM Teknologi Nuklir, Yogyakarta, 25-26 Agustus 2008. ISSN 1978-0176.

Zakaria, A. 2011. *Adsorpsi Cu(II) Menggunakan Zeolit Sintesis dari Abu Terbang Batubara*. Bogor:Program Pascasarjana Institut Pertanian Bogor..