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The Synthesis of Glutaraldehyde-modified Chitosan Utilizing MAOS (Microwave Assisted Organic Synthesis) Method as Adsorbent of Pb(II) Ions Contained in Water Sample of Cikapundung River – Bandung

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ABSTRACT

Indonesia has a vast territory. Approximately 2/3 of Indonesia is water. Indonesia has almost 6% of the world's water resources or approximately 21% of water resources in the Asia Pacific region. Indonesian waters comprise 97.4% seas and 2.6% are rivers, lakes and straits. There are 309 rivers in Indonesia and 49 of them flow through Bandung; one of them is Cikapundung River. Pb(II) ions contained in Cikapundung River has exceeded the quality standard of water river. Therefore, it is necessary to reduce the amount of Pb(II) ions from the river. One of the solutions is by using biodegradable adsorbent, the glutaraldehyde-modified chitosan. Chitosan was obtained from deacetylation of chitin in basic condition. The chitosan was characterized using FTIR showed 85.5% degrees of deacetylation. The other characterization is determination of average molecular mass using Ostwald viscometry method, obtained the average molecular mass of chitosan is 2.7 x 10^6 g/mol. Furthermore, chitosan was modified by reacting with glutaraldehyde using MAOS (Microwave Assisted Organic Synthesis) method at 80°C with irradiation power of 100 W for 60 minutes to form glutaraldehyde-modified chitosan with 79% degree of substitution. The synthesized glutaraldehyde-modified chitosan was characterized by FTIR, SEM, SAA and applied as adsorbent of Pb(II) ions. The results showed that the optimum condition of adsorption for 15 mL of Pb(II) solution was achieved at pH 4 using 0.075 grams of adsorbent and 90 minutes of contact time. The adsorption process of Pb(II) ions follows the Langmuir isotherm model and the pseudo-second order kinetics with percent adsorption of Pb(II) ions from the water sample of Cikapundung river is 84% and 50.2%, for sample collected from middle-stream and downstream of river, respectively.

Keywords: adsorbent, Pb(II) ions, chitosan, glutaraldehyde-modifed chitosan, MAOS (Microwave Assisted Organic Synthesis) method, Cikapundung River, pollutant, Bandung

1. INTRODUCTION

Indonesia is known as a maritime country. Indonesia has six percent of world water resources or 21 percent of Asia Pacific water resources (Kemendagri, 2013). Indonesian's marine consists of 97,4 percent seas and the others are rivers, lakes, and straits. There are 309 rivers existed in Indonesia, and 49 of them flow through Bandung (Kemendagri, 2013). One of the biggest rivers in Bandung is Cikapundung River (Yustiani et al., 2017).

Cikapundung River has 28 kilometers in length (Yustiani et al., 2013).. Its upstream is located in Lembang, West Bandung District, and the downstream is in Dayeuhkolot, Bandung District. This river is used by the community as irrigation, daily water resources, tourism object and also as waste dumping off the vicinity industries.

Based on data of BPLH (Badan Pengelolaan Lingkungan Hidup, or Environmental Management Agency) in Bandung at 2010, Cikapundung river received 2.5 millions liters of wastes every day (Habibi et al., 2014). The wastes were dumped by various industries around Bandung area, such as textile, paper, and automotive industries. Approximately 60 percent of the waste is heavy metals, such as chromium, copper, iron, zinc, cobalt, radium, cadmium, lead, selenium, arsenic, and mercury (Habibi et al., 2014). Almost all of them have concentration exceeded the permitted quality standard of water river. This condition is danger for surrounding community near Bandung vicinity. Therefore, it is necessary to reduce the amount of the heavy metal in the river. The adsorption process of metal ions in the river using biodegradable adsorbent is one of the solutions.

Based on research of Bhavani and Duta, chemical adsorption can be done with polymeric materials based on chitosan (Dutta et al., 2004). Chitosan is natural polymer which isolated from crustaceae's shell. Chitosan is a porous material so that it can act as chemical adsorbent. Chitosan's adsorption capacity can be increased by modification of its structure (Dutta et al., 2004).

In research of Tian, et al. (2003), silica-modified chitosan is used as adsorbent of protein. In research of Baba, et al. (2002), methylthiocarbamoyl-modified chitosan is used as adsorbent of Cu(II) ions and Fe(III) ions(Baba et al., 2002).. In research of Weltrowski, et al. (1996), *N*-benzylsulphonate-modified chitosan sulfonat is used as adsorbent of proton (H^+) (Dutta et al., 2004). In research of Simonescu, et al. (2014), glutaraldehyde-modified chitosan which synthesized with convensional method is used as adsorbent of Pb(II) ions (Simonescu et al., 2014).

In this research, glutaraldehyde-modified chitosan was synthesized utilizing MAOS (Microwave Assisted Organic Synthesis) method. This method applied green chemistry principle in part of energy efficiency. MAOS gives more efficient energy usage than conventional method because the microwave radiation interacts directly to the reacting molecule so that reaction will be faster and the resulting molecule will have more stable structure toward change of pH. Moreover, glutaraldehyde-modified chitosan can be applied as adsorbent of Pb(II) ions from Cikapundung river water sample.

2. METHODS

2.1 Materials

Glutaraldehyde and lead(II) nitrate were commercially purcashed from Merck. Shrimp shells were obtained from *Litopenaues vannamei*. Other chemicals were all of analytical grade.

2.2 Synthesis of chitosan

The method of synthesis chitosan is referred to Zvezdova (Zvezdova., 2010) and Ramadhan, et al. (Suendo et al., 2010). The resulting chitosan was characterized using Alpha Brucker FTIR to determine the degree of deacetylation using the Robert-Domszy baseline method (Eq. (1))(Czechowska et al., 2012) resulting 85.5%, Ostwald Viscometer used to determine the average molecular weight using the Mark-Houwink-Sakurada Equation (Eq. (2)) (Kasaai et al., 2000)(Oberlerchner et al., 2015) resulting 2.7 x 10^6 g mol^{-1}, Scanning Electron Microscope (SEM) to observe the morphology, and BET Surface Area Analyzer (SAA) to determine the surface area.

The selected infrared spectrum of chitin (υ, cm^{-1}, KBr)): 3427 (O-H); 3275 (N-H_{amide}); 2962 (C-H); 1651 (C=O (s)); 1427 (CH_2). Chitosan (υ, cm^{-1}, KBr): 3448 (O-H); 1658 (C=O(sh)); 1448 (CH_2)

$$\text{Degree of deacetylation} = 100 - \left(\frac{loglog\, A_{1655}}{loglog\, A_{3450}} \text{ x } \frac{100}{1.33}\right) \quad (1)$$

$$\text{Molecular weight} = \sqrt[a]{\frac{[\eta]}{k}} \quad (2)$$

Where a= 0.83, k= 1.46 x 10^{-4} and $[\eta]$ is intrinsic viscocity of chitosan.

2.3 Synthesis of glutaraldehyde-modified chitosan

Chitosan was reacted with 25% v/v glutaraldehyde, mol ratio is 1:1, under microwave irradiation (P= 100 W, T= 80°C, t= 60 minutes). The resulting solid was filtered and washed with ethanol. The glutaraldehyde-modified chitosan was characterized using Alpha Brucker FTIR to determine the degree of substitution (α) using the Eq. (3) (Nikolic et al., 2010), Scanning Electron Microscope (SEM), and BET Surface Area Analyzer (SAA).

The selected infrared spectral for glutaraldehyde-modified chitosan (IR (cm^{-1}, KBr)): 3466 (O-H); 3250 (N-H); 2957, 2900 (C-H); 1660 (C=N(s))

$$\alpha = 1 - \left(\frac{A_{N-H,\ t} \cdot A_{C=N,\ 0}}{A_{N-H,\ 0} \cdot A_{C=N,\ t}}\right) \quad (3)$$

2.4 Adsorption of Pb(II) ions

The 15 mL of solution of Pb(II) ions was added with adsorbent glutaraldehyde-modified chitosan. The mixtures were agitated using agitator with stirring speed 120 rpm at 30°C with mass of adsorbent, concentration of Pb(II) ions solution, pH of solution, and time of contact were varied to get the optimal condition of adsorption. The Pb(II) concentration, before and after adsorption, was determined using Absorption Atomic Spectrometer (AAS GBC Avanta). The concentration of the Pb(II) ions remained in the adsorbent phase (q_e, mg g^{-1}) were calculated using the Equation (4)(Sobhanardakani et al., 2014);

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (4)$$

Where C_0 and C_e are the initial and equilibrium Pb(II) concentrations in solution, respectively (ppm), V (L) is the volume of solution and w (g) is the weight of adsorbent.

The kinetic adsorption were analyzed using pseudo-first-order and pseudo-second-order kinetic model. The linear form models are expressed as Equation (5) and Equation (6);

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2{,}303} t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where q_e and q_t are the amount of Pb(II), (mg/g) at equilibrium and time t (min); k_1 is the rate constant of pseudo-first-order (min^{-1}); k_2 is the rate constant of pseudo-second-order (g mg^{-1} min^{-1}) for adsorption.

The isotherm adsorption were analyzed using Langmuir and Freundlich models. The models can be expressed as Equation (7) and Equation (8);

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m.K_L} \quad (7)$$

$$ln\ ln\ q_e = ln\ ln\ K_f + \frac{1}{n} ln\ ln\ C_e \quad (8)$$

where c_e (mg L^{-1}) is the equilibrium concentration of Pb(II) ions in solution, q_e (mg g^{-1}) is the equilibrium adsorption capacity, q_m (mg g−1) is the maximum adsorption capacity for monolayer coverage, K_L (L mg^{-1}) is a constant related to the adsorption free energy, K_f is a constant related to adsorption capacity, and n is an empirical parameter related to adsorption.

2.5 Desorption of Pb(II) ions

The desorption was carried out using nitric acid (HNO_3) with varying concentration., 0.01 M and 0.05 M. 15 mL HNO_3 solution was contacted with adsorbent which used in the first adsorption cycle. The mixtures were agitated using *incubator shaker* 30°C, 120 rpm, with time of contact was varied. The Pb(II) concentration, before and after adsorption, was determined using Absorption Atomic Spectrometer (AAS GBC Avanta).

3. RESULT AND DISCUSSION

3.1 Synthesis of Glutaraldehyde–modified Chitosan

The reaction of chitosan with glutaraldehyde was running using MAOS method. This method is using the microwave as a source of energy (Patel et al., 2011). The principle of converting energy is based on the interaction between molecule and microwave either by collision or by conduction or sometimes by both (Patel et al., 2011). In polar molecule, while irradiating with electromagnetic, the molecule will rotate continuously align with the corresponding fields (Patel et al., 2011). Rotating molecules collide with other molecule distributing energy to adjacent molecules in the material (Patel et al., 2011). The resulting product was characterized using FTIR as shown in **Fig. 1**. Based on the spectrum, there is a sharp peak in 1660 cm^{-1} which can not find in chitosan spectrum. Accordingly, the C=N bonding have been formed. The degree of substitution amine group was determined using Nikolic equation (Eq. 4)(Nikolic et al., 2010) resulting 79%. In previous research which synthesized in 24 hour is resulting 80.8% degree of substitution (Lau et al., 2016).

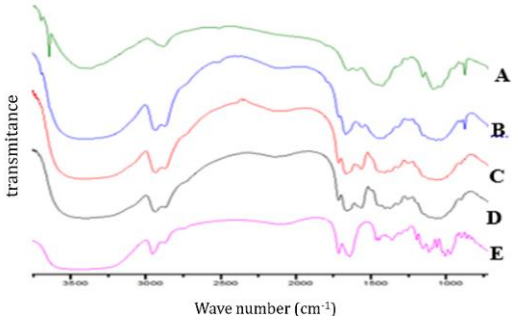
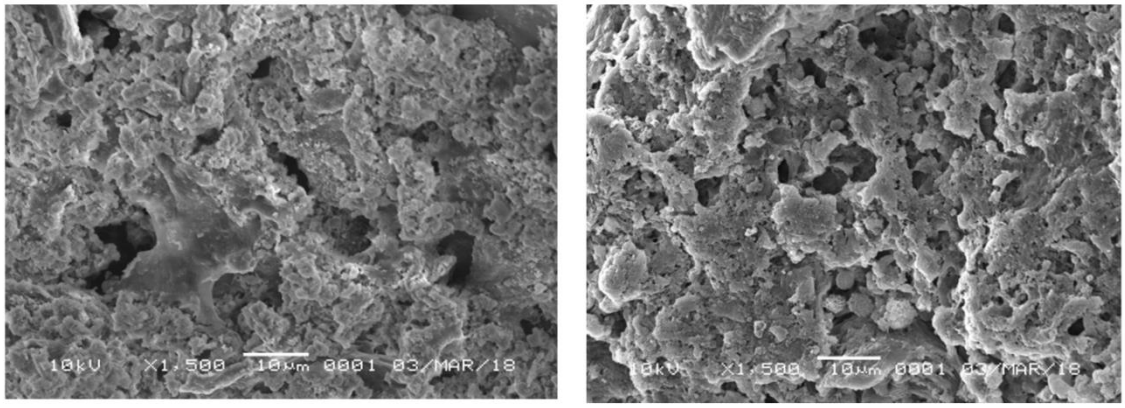


Fig. 1 infrared spectra of chitosan (A), glutaraldehyde-modified chitosan with varied reaction time (B,C,D) and glutaraldehyde (E)

The highest degree of substitution of glutaraldehyde-modified chitosan was hypothesized to have the highest adsorption capacity, because at this condition, the amount of pores were improved, which was proven by morphological images of the surface utilizing Scanning Electron Microscope, as seen in **Fig. 2**.



a b

Fig. 2 Morphological image SEM of chitosan (magnitude 1500 x) **(a)** and glutaraldehyde-modified chitosan (magnitude 1500 x) **(b)**

Table 1 Character of adsorbent's pores

	glutaraldehyde-modified chitosan	kitosan
Surface area ($m^2 g^{-1}$)	78.6	13.9
Pore volume ($cm^3 g^{-1}$)	0.08	0.03
Diameter of pores (Angstrom)	31.12	31.36
Mesopore (%)	100	95
Macropore (%)	-	5

Based on the images, glutaraldehyde-modified chitosan have more pores than chitosan itself. So that, glutaraldehyde-modified chitosan is more potential than chitosan to use as adsorbent. To know its' further potential as adsorbent, glutaraldehyde-modified chitosan was characterized using BET Surface Area Analyzer. The result is shown in **Table 1**.

Based on the data, glutaraldehyde-modified chitosan has larger surface area than chitosan. So that, glutaraldehyde-modified chitosan can adsorb more metal ions.

3.2 Adsorption of Pb(II) ions

Adsorption capacity of Pb(II) ions depends strongly on the morphological surface of adsorbent, adsorbent mass, solution pH and contact time. Based on the data were obtained from surface area analyzer, glutaraldehyde-modified chitosan has a larger surface area than chitosan and the pore volume of glutaraldehyde-modified chitosan is bigger than the chitosan, so that, glutaraldehyde-modified chitosan have more sites to contact with Pb(II) ions. The sites also can be increased by increasing the adsorbent mass. As seen in **Fig. 3**, the optimum adsorption capacity is reached using 0.075 grams of adsorbent mass.

Also the contact time influences the adsorption process. As seen in **Fig. 3**, the optimum contact time is 90 minutes. Increasing contact time will increase the adsorption capacity. This fact is due to increasing contact time will give chance to adsorbent to interact with more Pb(II) ions so that adsorption capacity increase too.

The initial pH of solution also plays key role in the adsorption capacity. As is seen in **Fig. 3**, the optimum adsorption capacity is reached at pH 4. The effect of solution pH on the adsorption process of Pb(II) ions can be explained by competition between H^+ ions and Pb(II) ions to bind in the adsorbent sites. In the low pH solution, the concentration of H^+ ions in solution is too much than the Pb(II) ions. H+ ions which have smaller size than Pb(II) ions will adsorp easily so that the adsorption capacity of Pb(II) ions is low at the low pH. Meanwhile, in the high pH solution, Pb(II) ions form $Pb(OH)_2$ so that the adsorption capacity decreased significantly.

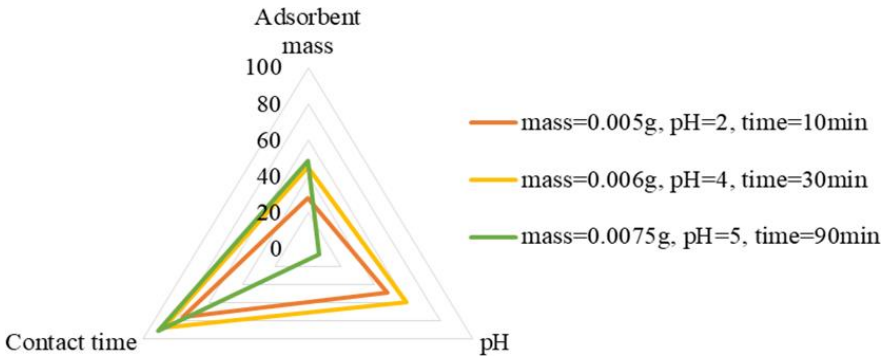


Fig. 3 The effect of adsorbent mass, contact time and solution pH on adsorption capacity of (Pb(II) onto glutaraldehyde-modified chitosan

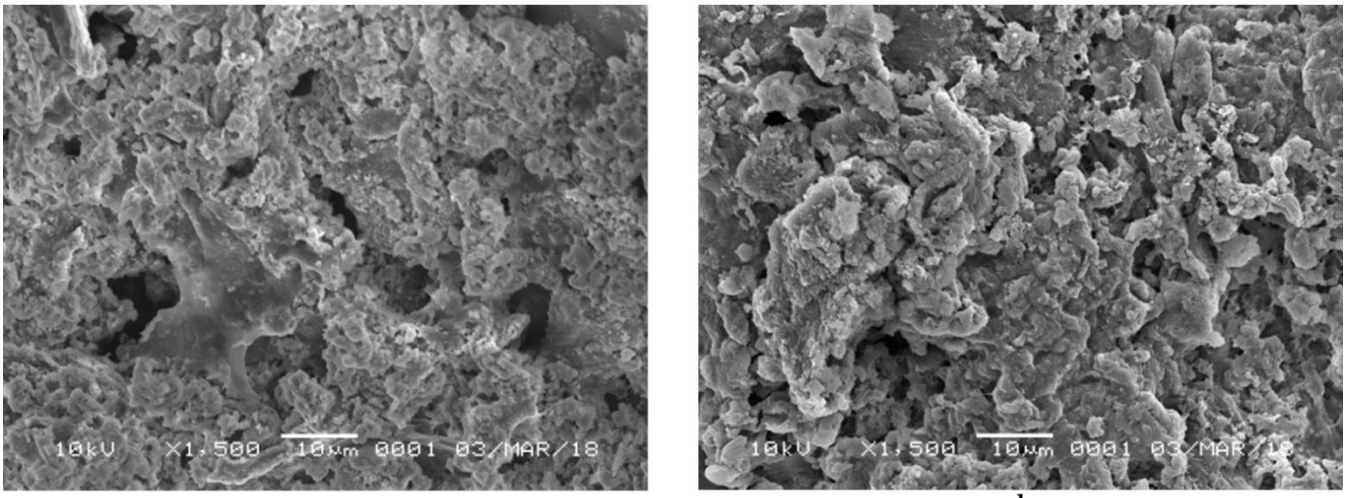


Fig. 4 Morphological image SEM of glutaraldehyde-modified chitosan : **(a)** morphological before adsorption (magnitude 1500x), **(b)** morphological after adsorption (magnitude 1500x)

The kinetic adsorption were analyzed using pseudo-first-order and pseudo-second-order kinetic model. The linear form models are expressed as Equation (5) and Equation (6). As seen in **Table 2** the higher correlation coefficient is shown in pseudo-second-order kinetic model which indicated that the adsorption process of Pb(II) ions onto glutaraldehyde-modified chitosan following pseudo-second-order kinetic model.

The isotherm adsorption processes were analyzed using Langmuir and Freundlich models. As seen in **Fig. 5**, the adsorption process is best fit with Langmuir models which indicated that the adsorption process is chemisorption, forming monolayer and homogeneous distribution of active sites on the surface of glutaraldehyde-modified chitosan (Shan et al., 2013).

Table 2 Pseudo-first order and pseudo-second order kinetic model parameters for the adsorption process of Pb(II) ions onto glutaraldehyde-modified chitosan

Pseudo-first-order kinetic model		**Pseudo-second-order kinetic model**	
K (min^{-1})	**R²**	**K (min^{-1})**	**R²**
-0.0267	0.965	8.9446	0.9998

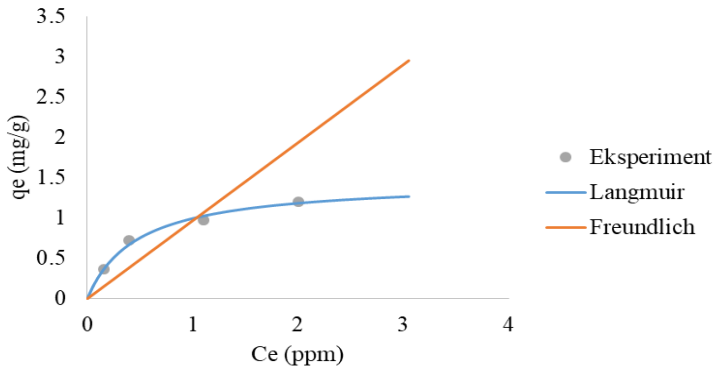


Fig. 5 Langmuir, Freundlich and experimental curve of isotherm adsorption

Table 3 Isotherm parameters of adsorption of Pb(II) ions onto glutaraldehyde-modified chitosan

Langmuir			**Freundlich**		
K_L	**q_m**	**R²**	**K_f**	**n**	**R²**
2.1362	1.4619	0.9952	-0.0709	2.2056	0.9512

To be used as reusable adsorbent, desorption is the one of the most important process. According to the adsorption process is chemisorption, to desorp the ion from the adsorbent need chemicals which can break the bonding between adsorbent and adsorbate. One of the chemical can be used is HNO_3. The existence of H^+ ions which have smaller size and strongly positive charge can enforce Pb(II) ions to leave the sites. As seen in **Fig. 6**, the optimum desorption percent is reached by using 0.05 M HNO_3 with desorption time of 120 minutes.

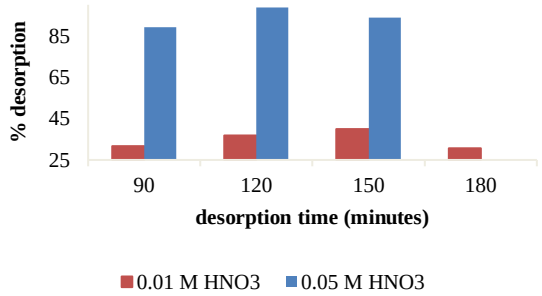


Fig. 6 The effect of concentration of HNO_3 and the time of desorption

3.3 Aplication of glutaraldehyde-modified chitosan as adsorbent of Cikapundung river water sample

The adsorption of river water sample was carried out at optimal adsorption condition and the adsorption percent of middle stream sample is 84% and adsorption percent of down stream sample is 50.2%.

4. CONCLUSION

In summary, glutaraldehyde-modifed chitosan successfully synthesized utilizing MAOS (Microwave Assisted Organic Synthesis) method with optimal condition, 79% of degree of substitution, was achieved at 80 °C, 100 W and 60 minutes time reaction. Glutaraldehyde-modifed chitosan successfully applied as adsorbent of Pb(II) ions with 0.075 gram of adsorbent mass, solution pH 4, and contact time 90 minutes in 15 mL Cikapundung river water sample following the Langmuir isotherm and the pseudo-second order kinetic model with adsorption percent is 84% (for middle stream water sample) and 50,2% (for down stream water sample).

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