

# Biosorption of Pb(II) Ion by Crosslinked Pectin-CMC with BADGE (Bisphenol A Diglycidyl Ether) through Reflux Method

B. Hastuti, Mudasir, D. Siswanta, and Triyono

**Abstract**—The aim of this study was to develop a procedure for preparing biosorbent from natural material pectin and chitosan. The method to prepare biosorbent pectin-CMC-BADGE is established by using Reflux method. Pectin-carboxymethyl chitosan crosslinked with BADGE (bisphenol A diglycidyl ether) where BADGE was used as the crosslinking agent and chitosan was grafted with acetate to form carboxymethyl chitosan (CMC). The result of this study was biosorbent Pectin-CMC-BADGE could increase sorption capacity for remove heavy metal ions in waste water by adsorb lead (II) ion. The structure and the morphology of the resulting adsorbent were characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The mass adsorbent adsorb Pb (II) was 15 mg with 94.78% of adsorption and adsorption capacity was 30.29 mg/g. Optimum contact time to adsorb Pb (II) was 60 minutes with 99.13% of adsorption and adsorption capacity was 44.33 mg/g. Optimum pH to adsorb Pb (II) was at pH 5 with 97.73% of adsorption and adsorption capacity was 45.03 mg/g.

**Index Terms**—CMC, pectin, pectin-CMC-BADGE, adsorbent, Pb(II).

## I. INTRODUCTION

The rapid development in industrial sector has led to serious environmental problems, particularly in developing countries, through increasing amount of waste, including hazardous and toxic substances that can harm the environment and human health.

A pollutant is a waste material that produces air, water, or soil pollution which can disturb ecosystem and the balance in the environment. At this time, the pollution of the environment takes place everywhere with very fast rate. Today, the burden of pollution in the environment has been exacerbated by the influx of industrial waste from a variety of chemicals including heavy metals.

The increasing population in world and the development applications of industrial, environmental pollution becomes an important issue. Society produces both liquid and solid waste. Today, a development concentration of heavy metals and other pollutants has increase a level of danger to the

environment in a variety of areas. The presence of toxic heavy metals and pollutants in wastewater, water supply and water mines and their removal has received much attention in recent years. A large number of heavy metals contained in the wastewater industry endanger public health and the environment. Heavy metals are elements that are usually associated with toxicity and natural components of the earth's crust. They can not be damaged or destroyed and can enter our body through food and air [1].

Lead (Pb) is one of the major pollutants that contaminate the environment. It happens because the main source of lead pollution is get from motor vehicle exhaust emissions. In addition there is also a lead in industrial wastewater in the production process to use lead, such as battery manufacturing industry, paint industry, and industrial ceramics. The presence of lead in the environment component of the water, soil, and air pollution allowed the development of the transmission became more widely to a variety of living things, including humans, causing health problems, such as the disruption of the synthesis of red blood, anemia, and decreased intelligence in children [2].

Nowadays heavy metals are the environmental priority pollutants and are becoming one of the most serious environmental problems. So these toxic heavy metals should be removed from the wastewater to protect the people and the environment. Many methods that are being used to remove heavy metal ions include chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc [3]. Adsorption is one of the physicochemical treatment processes which found to be effective in removing heavy metals from aqueous solutions [4]. According to Bailey *et al.* [5], an adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a by-product of waste material from waste industry. Adsorption methods are generally based on the interaction of metal ions with functional groups that exist on the surface of the adsorbent through interaction and complex formation usually occurs on the surface of solids which have rich functional groups such as -OH, -NH, -SH and -COOH [6].

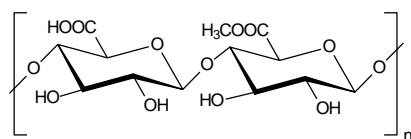
Pectin is one of the compounds found in plant cell walls mainland. Pectin, an anionic plant cell wall polysaccharide based on  $\alpha$ -(1-4) linked D-galacturonic acid, is commercially extracted from pectin-rich sugar-beet pulp, apple pomace, and citrus peels. [7]. All this time, the pectin was widely used in the food industry, pharmaceuticals and cosmetics. At these industries pectin is used primarily as a gelling material [8]. However, when considering that the structure of the pectin component also contains a lot of active groups, the pectin can also be used as a source

Manuscript received March 26, 2014; revised May 21, 2014.

B. Hastuti is with Chemistry Program, Science and Mathematics Education Major, Faculty of Teacher Training and Education, Universitas Sebelas Maret, She with the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Yogyakarta, Indonesia (e-mail: bhastuti.uns@gmail.com).

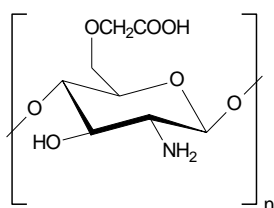
Mudasir, D. Siswanta, and Triyono are with the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Yogyakarta, Indonesia.

biosorbent [9]. The main functional groups of pectin are hydroxyl, carboxyl, amide and methoxyl. These functional groups can be used to bind heavy metals, especially hydroxyl groups.



Scheme 1. Pectin structure.

Chitosan, a cationic copolymer of glucosamine and Nacetylglucosamine, is a partially deacetylated derivative of a natural polysaccharide - chitin, which is one of the most abundant carbohydrates in nature and is mostly derived from the exoskeleton of crustaceans. [10]. Chitosan can be used as an adsorbent because it has amine and hydroxyl groups that can be used as an ion-exchanger, and can act as an adsorbent to adsorb heavy metals. Carboxymethyl chitosan (CMC) is one of the modified chitosan made through esterification process; the product is widely used in the pharmaceutical industry / healthcare and cosmetics. CMC is a water-soluble chitosan derivative forming semi permeable membranes and films [11].



Scheme 2. Structure of carboxymethyl chitosan.

This research conducted between the chitosan and pectin by crosslink. Crosslink is an effective way to improve the stability of the polymer in acidic conditions. Crosslink is prepared by reacting a material with a crosslinker agent a stable polymer, so the physical properties of the material will change and become stable [12]. Crosslink in this study is intended for rearranging a structure of polymeric compounds contained in the adsorbent. In this study chitosan will be crosslink with pectin which has a methoxy and a carboxyl active group using crosslink agent BADGE (Bisphenol A diglycidyl ether). BADGE have been choosing because have a cyclic ester on both of ends so it can be used to bind the-OH group chitosan and pectin through a cross-link mechanism. Besides it, BADGE is rigid (stiff) so it is expected to result in a stable crosslinked product. Initially chitosan will be synthesized into carboxymethyl chitosan (CMC) and then crosslinked with pectin, to enrich the active groups on the chitosan so increases adsorption. Crosslink is also intended to form preorganizer polymer composition, so it will be more accessible metal. It is expected that composite KMK-pectin-BADGE can be applied as a superadsorbent that can be applied in the environmental purposes.

## II. MATERIALS AND METHOD

### A. Materials

The pectin was obtained from local pectin from orange

peels. And chitosan used was obtained from local chitosan from crab shell. BADGE (bisphenol A diglycidyl ether) from Sigma Aldrich.

### B. Method

Before use, a first modified chitosan, carboxymethyl chitosan with the workings of the following: Dissolve 3 g chitosan in 80 ml of isopropanol. Add 28 mL NaOH 40% w/v carefully by drops. Chitosan and isopropanol was stirred for 30 minutes.

Add as much as 7.65 g of chloroacetic acid, then stirred for 12 h. The mixture was filtered and washed with ethanol. Dried sediment filtering results in an oven at 600 C for 3 h. g. Carboxymethyl chitosan derived functional group characterized using Infrared spectrophotometer. Once formed CMC, then combined with the following steps:

1 mmol pectin and CMC were dissolved into 100 ml of HCl pH 6 and were mixed with 2 mmol BADGE in 50 ml of acetone. The mixture was then heated under reflux for 24 h at approximately 50 °C. The reaction mixture was subsequently transferred to glass vessel and further centrifuged 100 rpm for 10 min. The supernatant solution carefully decanted through a Whatman paper filter (no. 5), and the obtained precipitate was finally dried in an oven at 60 °C for 3 h to get a adsorbent powder. Functional groups characterization was later carried out by using IR spectrometry analysis. The sorption capacity of adsorbent to metal ions was determined by adding 10 mg of adsorbent into 10 mL of 50 mg/L Pb ion with the variation of pH, contact time, and adsorbent mass. For each variation, the solutions were filtered and Pb concentrations were measured by atomic absorption spectrophotometry (Hitachi 170-30 atomic absorption spectrophotometer).

## III. RESULT AND DISCUSSION

In this study used the absorbent material of pectin and chitosan, because it can be used as a biomaterial that can absorb the metal. Pectin has an active group of carboxylic and chitosan has amine groups. BADGE has a cyclic ester on both of ends so it can be used to bind the-OH group chitosan and pectin through a cross-link mechanism. Besides it, BADGE is rigid (stiff) so it is expected to result in a stable crosslinked product. Initially chitosan will be synthesized into carboxymethyl chitosan(CMC) to enrich the active groups on the chitosan and then crosslinked with pectin, it will intended to form preorganizer polymer composition so it will be more accessible metal consequently can increase adsorption. Thus Composite CMC- pectin - BADGE can be applied as superadsorbent that can be applied in the environment.

### A. Characterizations

The particle of pectin-CMC-BADGE was prepared using the Reflux method. The FTIR spectra of chitosan (Fig. 1a) show absorption peaks at 3464 cm<sup>-1</sup> assigned to the O-H stretching vibration. Width and shift absorption of wave number on -OH group is caused by the overlap -NH of the amine. Absorption band at 2877.79 cm<sup>-1</sup> is the stretching vibration of C-H group methylene and at 1026.13 cm<sup>-1</sup> is the -C-O group. Another Uptake of chitosan look at wave

numbers  $1651.07\text{ cm}^{-1}$  indicate the presence of amide groups ( $\text{-NHCO}$ ) [10] and [13].

In Fig. 1b, CMC shows absorption of peaks IR spectra at wave numbers  $3464.15\text{ cm}^{-1}$  which is the absorption of the  $\text{-OH}$  stretching vibration that overlap with the  $\text{-NH}$  stretching vibration absorption. Peak absorption of  $\text{CH}$  stretching vibration shifted from  $2877.79\text{ cm}^{-1}$  to  $2924.09\text{ cm}^{-1}$ . Increasing the absorption peak of carbonyl bands (stretching  $\text{C=O}$ ) at  $1740\text{ cm}^{-1}$  indicates the addition of a carboxylic group ( $\text{-COOH}$ ) which means it has been formed CMC. From all these data it can be concluded that it has formed CMC result of synthesise chitosan with chloroacetic acid [10] and [13].

FTIR spectra of pectin in Fig. 1a shows a broad

absorption band at  $33875.00\text{ cm}^{-1}$ , indicates the range of the  $\text{OH}$  group vibrations. Peak at  $1064.71\text{ cm}^{-1}$  is the stretching vibration of the  $\text{-CO}$ . Absorption at  $1627.92\text{ cm}^{-1}$  is a specific absorption for  $\text{-COOH}$  group [14]-[16].

CMC-Pec-BADGE characterization by using FTIR shows that this material has an active force hydroxide ( $\text{-OH}$ ) indicated by the spectra with wave numbers  $3425.58\text{ cm}^{-1}$  and the active carboxylic group ( $\text{-COOH}$ ) at wave number  $1604.77\text{ cm}^{-1}$  and bands related to  $\text{C=O}$  stretching of the ester could be observed at  $1743.65\text{ cm}^{-1}$  [17]-[19]. Peak on  $833.25$  show peak of  $\text{C-H}$  substituted para on the benzene ring, it indicate BADGE have been crosslink into pectin and Chitosan.

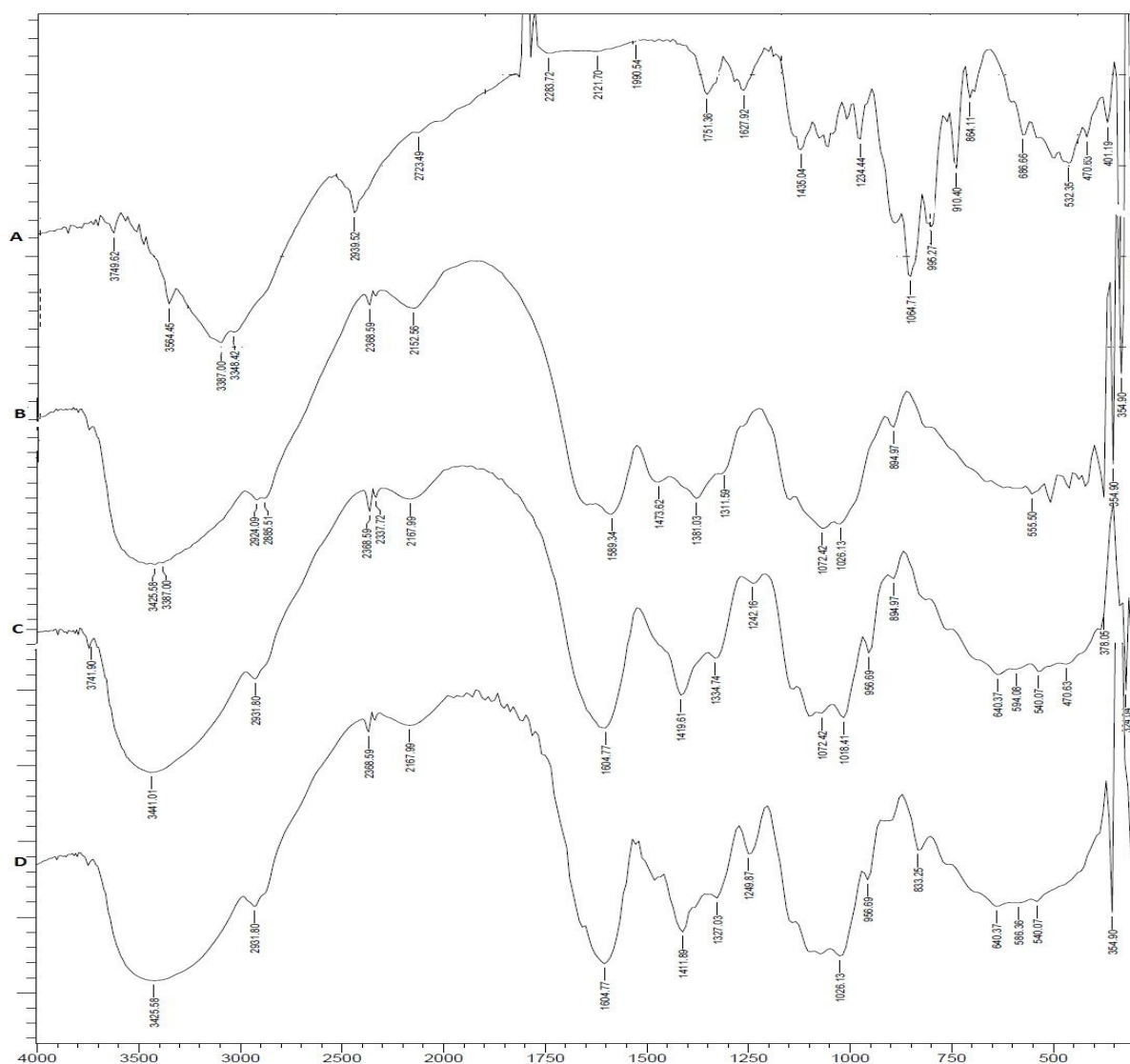


Fig. 1. FTIR spectra of particle pectin-CMC-BADGE: A. Pectin, B. CMC, C. Pektin-CMC, D. Pektin-CMC-BADGE.

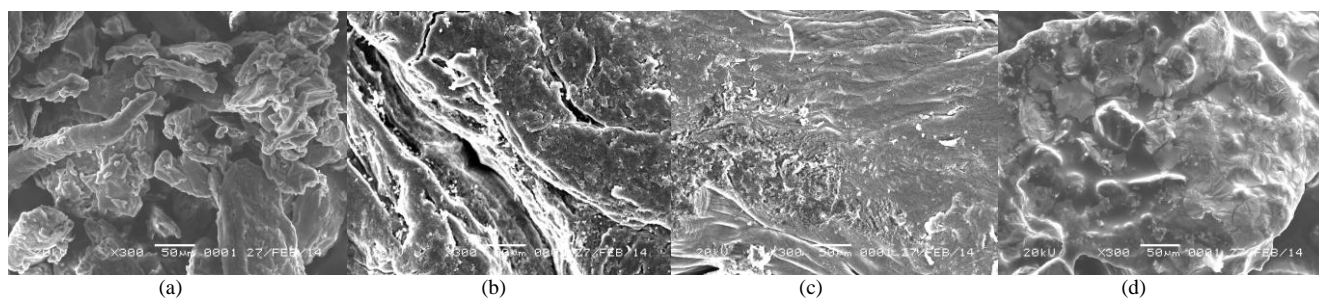


Fig. 2. Scanning electron micrographs of the microparticle surface at 300x: a. Pectin; b. Chitosan; c. CMC; d. Pektin-CMC-BADGE.

The SEM observation of pectin, chitosan, CMC is shown in Fig. 2a, 2b and 2c. has a smooth surface and a slightly porous surface whereas pectin-CMC-BADGE and Fig. 2d the surface is microporous. This result show the morphological that particle have been chemically modified so it potential as a super adsorbent

#### B. Determination of Optimum Adsorbent Mass

The relationship between the adsorbent mass of and adsorption capacity is shown in Fig. 3. It shows at 5-10 mg adsorbent mass absorption levels are increasing due to the growing number of adsorbent process of diffusion and binding of the better adsorbate molecules and adsorbent mass reaches a maximum at 15 mg. At 15-20 mg adsorbent mass absorption levels of Pb (II) adsorbents have decreased due to absorb maximum Pb (II) and the active adsorbent was no longer able to bind Pb (II). From this study, the optimum adsorbent mass obtained was 15 mg with a metal ion concentration of Pb (II) adsorbed at 95% and the adsorption capacity of 30.29 mg/g.

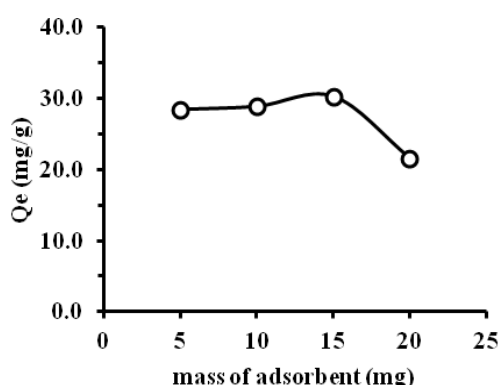


Fig. 3. The relationship between adsorbent mass vs. adsorption capacity.

#### C. Determination of Optimum Contact Time

The graph of the relationship between the contact time of Pb(II) ion with adsorption capacity and % adsorbed of film and is show in Fig. 4

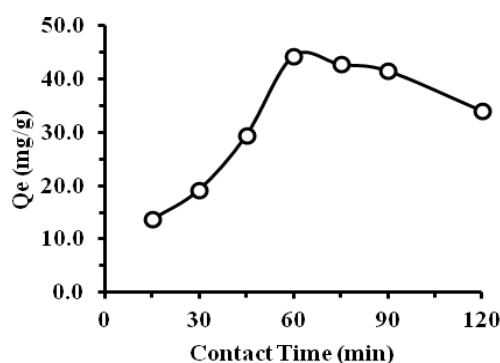


Fig. 4. The relationship between contact time vs adsorption capacity.

Contact time is one important parameter to determine the optimum condition for adsorption process. Optimum contact time allows better mechanism the diffusion process and binding of adsorbate molecules. Variation of contact time was in the range of 15, 30, 45, 60, 75, 90, and 120 min. After 15 min, the adsorbent adsorbs Pb (II) ion with adsorption capacity and % adsorbed are 13.74 mg/g and 31% respectively. The binding process is grow up with the

increasing time and reach the optimum at minute 60 with 99% absorption and 44.33 mg/g adsorption capacity. At this point, a perfect mixing occurs so that the particle CMC-pectin-BADGE can absorb Pb (II) optimally. After 60 min, adsorption of Pb(II) metal ion process tend to decrease, because the pores of adsorbent was saturated by the Pb(II) metal ion

#### D. Determination of Optimum pH

Fig. 5 show the relationship between pH solution vs adsorption capacity of Pb (II) adsorbed.

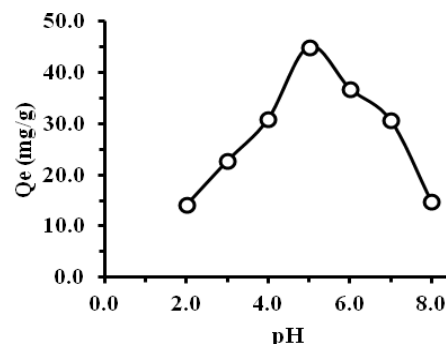
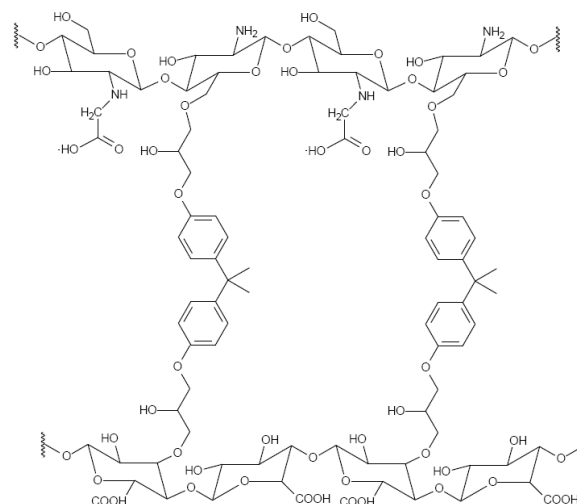


Fig. 5. The relationship between pH of solution vs adsorption capacity.

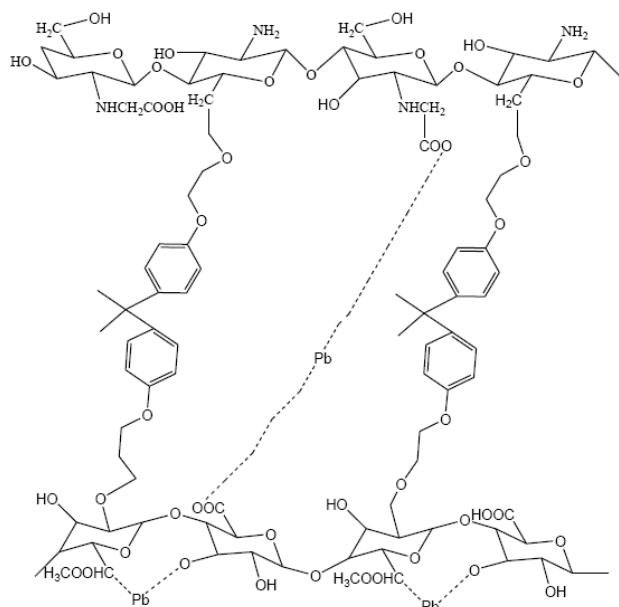
The degree of acidity or pH of the solution is one important factor that determines the performance of a adsorbent in the adsorption process. pH value is too low or too high will make optimum adsorbent unable to work. From Fig. 5 obtained results that on pH 2 adsorption percentage of the particle is 27% with adsorption capacity is 14.17 mg/g. Meanwhile, the percentage of adsorption tends rise on pH 3. The pH 5 is the optimum condition, in which the percentage of Pb (II) absorbed is 98% and the adsorption capacity is 45.03 mg/g. Furthermore at pH 6, the adsorption percentage decreased to 85% and the adsorption capacity is 36.89 mg/g. It is caused of the condition that higher pH, the solution have more  $\text{-OH}$  ions in the solution. The existence of these ions causes Pb (II) ions are hydrolyzed and forms  $\text{Pb(OH)}_3$ . The percentage adsorption decreases sharply when the pH is raised back to 8, in which the obtained percentage adsorption is 38% and adsorption capacity is 14.77 mg/g.

#### E. Pectin-CMC-BADGE as Adsorbent of Pb(II) Metal Ion



Scheme 3. Structure of pectin-CMC-BADGE.

Pectin-CMC-BADGE has potential to be applied as an adsorbent primarily due to the presence of the active group -OH and -COOH. Structure of pectin-CMC-BADGE is shown in Scheme 3. Those groups can interact with components of the adsorbate Pb(II) metal ion. Adsorption of the adsorbent to Pb (II) metal ion occurs by interaction between the -COOH groups of pectin and CMC with Pb (II) metal ions by chelating agent reaction as shown in Scheme 4.



Scheme 4. Structure of pectin-CMC-BADGE bind Pb metal (II) ions.

#### IV. CONCLUSION

Particle of pectin-CMC-BADGE were prepared by reflux method of both polysaccharides crosslinked BADGE as a crosslink agent. Chitosan was grafted with acetate to form a carboxymethyl chitosan (CMC) to increase active group as adsorbent, it was a carboxylic ion. Pectin and CMC each dissolved HCl mixed BADGE through reflux method yield particle pectin-CMC crosslinked BADGE as a super adsorbent to bind Pb (II) metal ions. It was occur by a complexing reaction with adsorption capacity is 45,03 mg/g and percent absorbed 99%. Therefore the adsorbent particles potential as a super adsorbent to remove Pb (II) metal ion in waste water compared by chitosan or PECTIN separately.

#### ACKNOWLEDGMENT

The authors would like to thank Directorate General of Higher Education (DGHE), Department of National Education Republic Indonesia for supporting the funding. The authors would like also to thank to Universitas Sebelas Maret and Universitas Gadjah Mada for facility and permission in this study.

#### REFERENCES

- [1] N. Das, R. Vimala, and P. Karthika, "Biosorption of heavy metal," *Indian Journal of Biotechnology*, vol. 7, no. 4, pp. 159-169, 2008.
- [2] E. Naria, "Mewaspadai dampak bahan pencemar timbal (Pb) di lingkungan terhadap kesehatan," *Journal Komunikasi Penelitian*, vol. 17, no. 4, pp. 66-72, 2005.
- [3] F. Lian Fu and Q. Wang, "Removal of heavy metal ions from wastewaters: A review," *Journal of Environmental Management*, vol. 92, pp. 407-418, 2011.

- [4] M. M. Fares, Y. R. Tahboub, S. T. Khatatbeh, and Y. M. A. Haija, "Eco-Friendly, vascular shape and interpenetrating poly (Acrylic Acid) grafted pectin hydrogels; biosorption and desorption investigations," *J. Polym. Environ.*, vol. 19, pp. 431-439, 2011.
- [5] S. E. Bailey, T. J. R. M. Olin, Bricka, and D. D. Adrian, "A review of potentially low-cost sorbents for heavy metals," *Water Res.*, vol. 33, p. 2469, 1999.
- [6] W. Stumm and J. J. Morgan, *Aquatic Chemistry*, 3<sup>rd</sup> edition, John Wiley and Sons, Inc, Canada, 1996.
- [7] C. M. G. C. Renard, M. J. Crepeau, and J. F. Thibault, "Structure of repeating units in the rhamnogalacturonic backbone of apple, beet and citrus pectins," *Carbohydrate Research*, vol. 275, pp. 155-165, 1995.
- [8] M. S. Rodriguez, A. L. Zalba, and E. A. Debbaudt, "New Chitosan-Calcium Pectinate Pellets and their adsorption capacity," *J. Colloid. Polym.*, vol. 285, pp. 119-124, 2006.
- [9] Y. N. Mata, M. L. Blázquez, A. Ballester, F. González, and J. A. Muñoz, "Sugar-Beet pulp pectin gels as biosorbent for heavy metals: Preparation and determination of biosorption and desorption characteristics," *Chemical Engineering Journal*, vol. 150, pp. 289-301, 2009.
- [10] V. K. Mouryaa, N. N. Inamdara, and A. Tiwarib, "Carboxymethyl chitosan and its applications," *Adv. Mat. Lett.*, vol. 1, no. 1, pp. 11-33, 2011.
- [11] F. R. De Abreu and S. P. C. Filho, "Preparation and characterization of carboxymethylchitosan," *Polímeros: Ciência e Tecnologia*, vol. 15, no. 2, pp. 79-83, 2005.
- [12] N. Li and R. Bai, "Novel modification of chitosan hydrogel beads for improved properties as an adsorbent. departemen of chemical and biomolecular engineering," National University of Singapore, 2004, pp. 203-210.
- [13] E. Ardelean, R. Nicu, D. Asandei, and E. Bobu, "Carboxymethyl-Chitosan as consolidation agent for old documents on paper support," *European Journal of Science and Theology*, vol. 5, no. 4, pp. 67-75, 2009.
- [14] J. Lim, J. Yoo, S. Ko, and S. Lee, "Extraction and characterization of pectin from Yuza (Citrus junos) pomace: A comparison of conventional-chemical and combined physicoenzymatic extractions," *Food Hydrocolloids*, vol. 29, pp. 160-165, 2012.
- [15] W. W. Wai, F. M. Abbas, Al Karkhi, and A. M. Easa, "Comparing biosorbent ability of modified citrus and durian rind pectin," *Carbohydrate Polymers*, vol. 79, pp. 584-589, 2010.
- [16] A. Kumar and G. S. Chauhan, "Extraction and characterization of pectin from apple pomace and its evaluation as lipase (Steapsin) Inhibitor," *Carbohydrate Polymer*, vol. 82, pp. 454-459, 2010.
- [17] F. Bigucci, B. Luppi, M. S. Cerchiarac, G. L. Bettinetti, and R. V. Zecchia, "Chitosan/pectin polyelectrolyte complexes: Selection of suitable preparative conditions for colon-specific delivery of vancomycin," *J. Pharm. Sci.*, vol. 35, pp. 435-441, 2008.
- [18] A. Ghaffari, K. Navaee, M. Oskoui, A. Bayati, and M. R. Tehrani, "Preparation and characterization of free mixed-film of pectin/chitosan/Eudragit\_ RS intended for sigmoidal drug delivery," *J. Pharm. and Biopharm.*, pp. 175-186, 2007.
- [19] C. Bernabe and W. Peniche, "Argueles-Monal, Swelling behavior of Chitosan/pectin Polyelectrolyte Complex Membranes, Effect of Thermal Cross-linking," *Polym. Bull.*, vol. 55, pp. 367-375, 2005.



**B. Hastuti** was born in Sukoharjo, Indonesia on August 6, 1978. She received her master's degree in analytical chemistry from the Universitas Gadjah Mada, Indonesia. At present, she is doing Ph.D. in the Department of Chemistry, FMIPA, Universitas Gadjah Mada under the supervision of prof. Dr. Mudasar, M.Eng., Dr. Dwi Siswanta, and prof. Dr. Triyono, SU. Her area of interest is natural polymer material.

She is also a lecturer of chemistry program, science and mathematics education major, Faculty of Teacher Training and Education, Universitas Sebelas Maret.



**Mudasir** was born in Kendal, Indonesia on August 19, 1963. He received his undergraduate's degree in the Department of Chemistry from the Universitas Gadjah Mada, Indonesia in 1986, master's degree at Keio University, Japan in 1990 and doctor degree's at Keio University, Japan in 1993. His areas of interest are development method of analytical Chemistry instrument and development of natural polymer material. He is a professor of Chemistry Department, Science and Mathematics Faculty

Universitas Gadjah Mada.



**Dwi Siswanta** was born in Klaten, Indonesia on February 2, 1965. He received his undergraduate's degree in the Department of Chemistry from the Universitas Gadjah Mada, Indonesia in 1988, master's degree at Keio University, Japan in 1992 and doctor degree's at Keio University, Japan in 1998. His areas of interest are development method of analytical chemistry instrument and development of natural polymer material. He is an associate professor of the Chemistry Department, Science and Mathematics Faculty Universitas Gadjah Mada.



**Triyono** was born in Magelang, Indonesia on September 21, 1960. He received his undergraduate's degree in the Department of Chemistry from the Universitas Gadjah Mada, Indonesia in 1983, master's degree at the Department of Chemistry from the Universitas Gadjah Mada, Indonesia in 1987 and doctor degree's at Innsbruck University, Austria in 1993. His area of interest is mical catalysts. He is a professor of Chemistry Department, Science and Mathematics Faculty Universitas Gadjah Mada.