The Synthesis of Carboxymethyl Chitosan-Pectin Film as Adsorbent for Lead (II) Metal

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

***Abstract*—The aim of this study was to develop a procedure for preparing film polyelectrolyte complex pectine/chitosan with increased sorption capacity for heavy metal ions which could be used as adsorbent to remove lead (II) ion in waste water. A film of the polyelectrolyte complex between chitosan and pectin were prepared by mixing the complex of both polysaccharides. Firstly, chitosan was grafted with acetate to form carboxymetyl chitosan (CMC). Subsequently, CMC is mixed with pectin to form CMC/pectin film. The result showed that the optimum mass ratio of CMC:pectin to synthesis CMC-Pectin film was 70:30%, optimum adsorbent mass to adsorb Pb (II) was 10 mg with 70% of adsorption and adsorption capacity was 30.1 mg/g. Optimum contact time to adsorb Pb (II) was 75 minutes with 87% of adsorption and adsorption capacity was 40.0 mg/g. Optimum pH to adsorb Pb (II) was at pH 5 with 93% of adsorption and adsorption capacity was 42.7 mg/g.**

***Index Terms*—CMC, pectin, CMC-pectin film, adsorbent, lead (II) metal ion.**

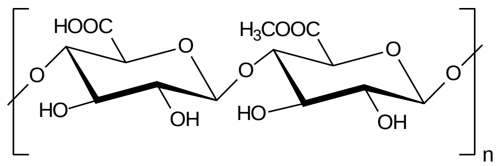
I. Introduction

The rapid industrial development and the using of various metallic materials have a negative impact, namely the emergence of cases of environmental pollution caused by waste containing heavy metals [1]. This pollution can cause harm and disturbing people who live around the industry. Refining metal factory, metal plating, painting and manufacture of battery are a source of heavy metal contaminants. Waste containing the remains of these heavy metals are dangerous if not be done properly and the processing is very harmful because it pollutes the environment especially with the nature of the toxicity.

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 a-(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 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

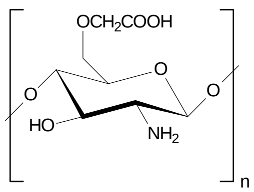
Manuscript received July 31, 2013; revised September 29, 2013.

B. Hastuti is with the Doctorate Program, 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.

DOI: 10.7763/IJCEA.2013.V4.323

chitosan derivative forming semi permeable membranes and films [11].



Scheme 2. Structure of carboxymethyl chitosan.

Interactions occur between polyanions and polycations, leading to the formation of a polyelectrolyte complex (PEC). As a positively charged polysaccharide, chitosan has been incorporated with pectin to fabricate various composite materials [12] and [13]. In addition to ionic interactions, there are other types of interactions that can form between amino groups and carboxyl groups, such as hydrogen bonds and covalent bonds formed using specific conjugating chemicals, like 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS) [14].

II. Materials and Method

A. Materials

The pectin used was obtained from local pectin from orange peels. And chitosan used was obtained from local chitosan from crab shell.

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 hours. 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:

Dissolving 0.2 g of pectin in 10 ml acetic acid 5% v/v were homogenized. CMC dissolving 0.2 grams of acetic acid in 10 ml of 5% v/v were homogenized. CMC and pectin gel mixed and stirred for 2 h. and poured in a Petri dish and dried to the oven for 5 hours at 40 ^{o}C. Add 5 ml of 1 M NaOH and let stand for 12 hours. Washing the film with distilled water and then dried to the oven for 2 hours at 40 ℃. Obtained adsorbent functional group characterized by using infrared spectroscopy.

Synthesis of Film CMC-pectin is done by using a variation of the mass ratio CMC: pectin as in the following Table I.

TABLE I: Variation of Ratio Mass CMC and Pectin

Samples	Mass ratio CMC:pectin	Mass of CMC (g)	Mass of Pectin (g)
A	50% : 50%	0,20	0,20
B	70% : 30%	0,28	0,12
C	40% : 60%	0,16	0,24
D	30% : 70%	0,12	0,28
E	60% : 40%	0,24	0,16

Adsorption process is done with a variety of adsorbent mass, contact time, and pH. A mass variation used were 5, 10, 15 and 20 mg. Variation of contact time used was 15, 30, 45, 60, 75, 90, and 120. While the pH variations used were 2, 3, 4, 5, 6, 7, and 8. Initial concentration of Pb (II) was 50 ppm by volume of 10 ml. Analysis of the adsorbed ion content determined by atomic absorption spectrophotometry.

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 groups of carboxylic and chitosan amine groups. It is a very reactive material that can bind a metal by forming a complex compound. Composite pectin with chitosan forms stable polyelectrolyte complexes [15]. Interaction between active group COO- of pectin and active group $-NH_2$ of chitosan complement the character of these macromolecules. Its complexes usually have a rigid structure that is very different from its original properties.

A. Characterizations

The film of pectin-CMC was prepared using the membrane method. The FTIR spectra of chitosan (Fig. 1a) show absorption peaks at 3464 cm^{-1} 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^{-1} is the stretching vibration of C-H group methylene and at 1026.13 cm^{-1} is the C-O group. Another Uptake of chitosan look at wave numbers 1651.07 cm^{-1} indicate the presence of amide groups (-NHCO)[10] and [16]

Fig. 1b, CMC shows absorption of peaks IR spectra at wave numbers 3464.15 cm^{-1} which is the absorption of the -OH stretching vibration that overlap with the -NH stretching vibration absorption. Peak absorption of CH stretching vibration shifted from 2877.79 cm^{-1} to 2924.09 cm^{-1}. Increasing the absorption peak of carbonyl bands (stretching C = O) at 1740 cm^{-1} indicates the addition of a carboxylic group (-COOH) which means it has been formed CMC. From all these data it can be concluded that it has formed CMC result of synthesize chitosan with chloroacetic acid [10] and [16].

FTIR spectra of pectin in Fig. 1c show a broad absorption band at 3387.00 cm^{-1}, indicates the range of the OH group vibrations. Ribbon at 1064.71 cm-1 is the stretching vibration of the-CO^{-}. Absorption at 1627.92 cm^{-1} is an absorption of group –COOH [17], [18] and [19]

Characteristics of film CMC-Pec using FTIR shows that it has an active force hydroxide (-OH) indicated by the spectra with wave numbers 3464 cm^{-1} and the active carboxylic group (-COOH) at wave number 1635 cm $^{-1}$ and bands related to C=O stretching of the ester could be observed at 1751 cm^{-1} [20],[21] and [22].(Fig. 1 d).

B. Influence of Mass Ratios

Fig. 2 shows the ratio mass between of pectin with CMC. From these Fig the optimum mass ratio between the pectin: CMC is 30%: 70% (Fig. B) showing the greatest intensity of absorption at a wavelength of 3400 (-OH) and 1600 (C = O) and 1700 ($-OCH_3$).

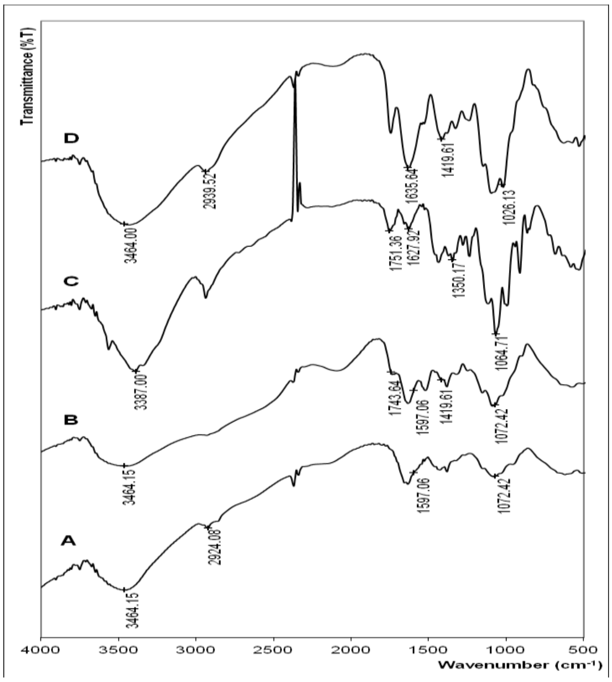


Fig. 1. FTIR spectra of film pec-CMC: a. chitosan, b. CMC, c. pectin, d. film pectin-CMC

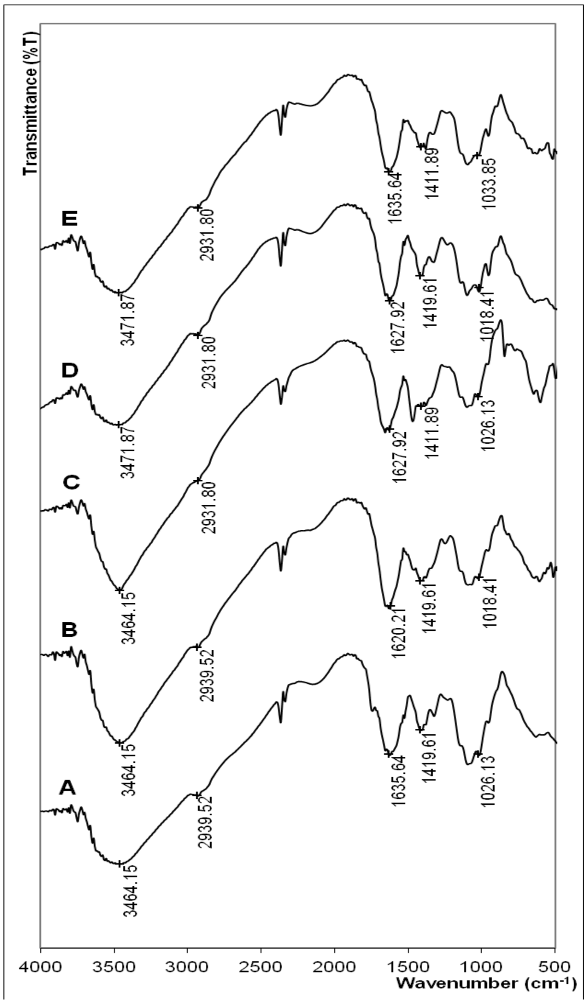


Fig. 2. FTIR spectra of % ratio mass: CMC: pectin: A. 50:50; 70:30; 40:60; 30:70; 60:40

C. Determination of Optimum Adsorbent Mass

The relationship between the mass of adsorbent upon adsorption capacity in Fig. 3 and percentage Pb (II) adsorbed show in Fig. 4. It shows at 5-10 mg adsorbent mass absorption levels are increasing rapidly due to the growing number of adsorbent process of diffusion and binding of the better adsorbate molecules and adsorbent mass reaches a maximum at 10 mg. At 10-20 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 10 mg with a metal ion concentration of Pb (II) adsorbed at 70% and the adsorption capacity of 30.16 mg/g.

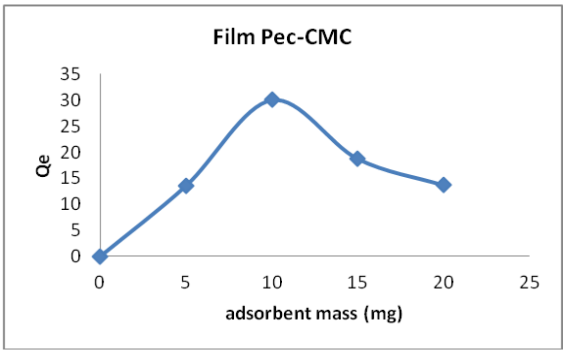


Fig. 3. Graph of adsorbent mass vs. adsorption affectivity.

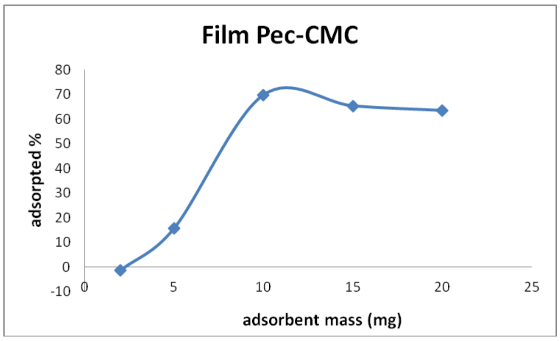


Fig. 4. Graph of mass adsorbent vs. % adsorbed.

D. 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. 5 and Fig. 6.

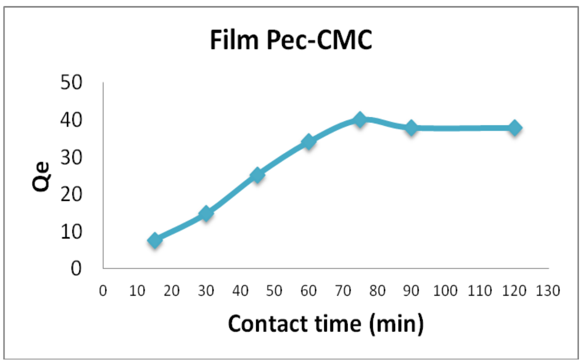


Fig. 5. The relationship between contact time of Pb (II) ion with adsorption capacity(Qe)

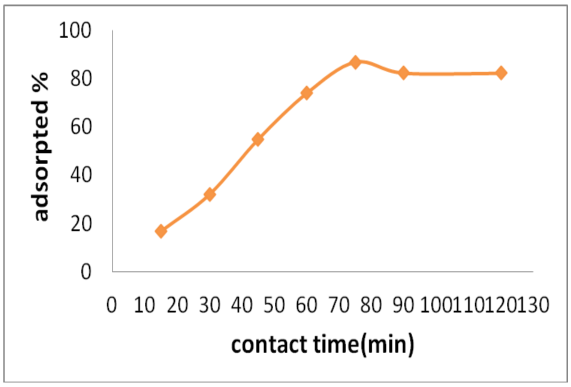


Fig. 6. The relationship between contact time of Pb(II) ion with % adsorbed

Contact time is important to determine of the adsorption process, because it allows better mechanism the diffusion process and binding of adsorbate molecules. Variation contact time used was 15, 30, 45, 60, 75, 90, and 120 minutes. On 15th minute, the film adsorbed Pb (II) ion with adsorption capacity of 7.75 mg/g and adsorption is 17 %. The binding process is going well with increasing time and then reached the optimum time in the 75th minute with 87 % absorption and adsorption capacity of 40.0 mg/g. In the 75th minute a perfect mixing occurs so that the films CMC-pectin can absorb Pb (II) optimally. After 75 minutes into a decline due to desorption the metal ion adsorbents release that Pb (II) which has been adsorbed because the pores of adsorbent was saturated by the Pb(II).metal ions

E. Determination of Optimum pH

Fig. 7 and Fig. 8 show the relationship between pH solution vs. adsorption capacity and the percentage of Pb (II) adsorbed.

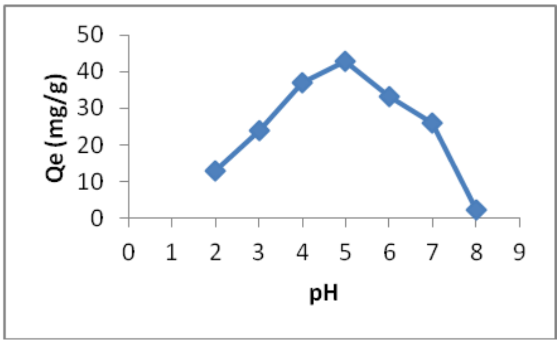


Fig. 7. Graph of the relationship between pH solution vs. adsorption capacity

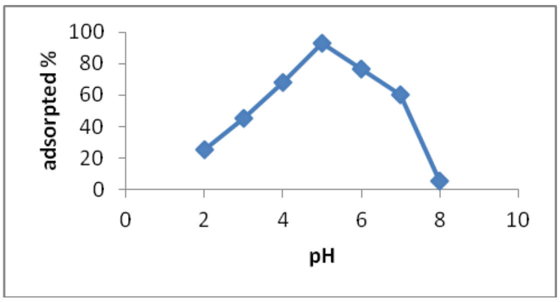
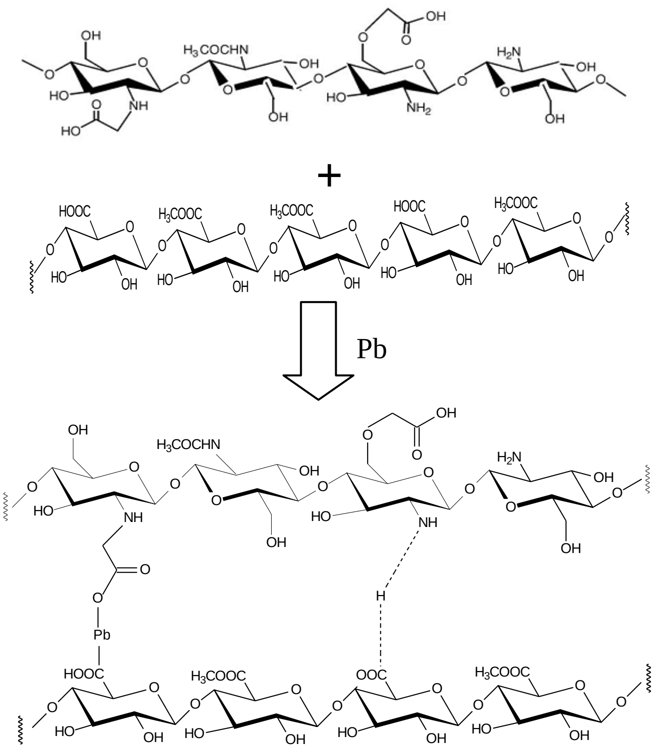


Fig. 8. Graph of the relationship between pH solution vs. percentage of Pb (II) adsorbed

The degree of acidity or pH of the solution is one of the important factors that determine the performance of the adsorbent in the adsorption process pH value is too low or too high will make optimum adsorbent unable to work. From Fig. 7 and 8 obtained results that on pH 2 adsorption percentage of the film is 25.1% with adsorption capacity is 13.0760 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 93% and the adsorption capacity is 42.7 mg/g. Furthermore at pH 6, the adsorption percentage decreased to 76.5 % and the adsorption capacity is 33.4 mg/g. It is caused of the condition that higher pH, the solution have more -OH ions in the solution. The existence of these ions causes Pb (II) ions are hydrolyzed and forms $Pb(OH)_3$. The percentage adsorption decreases sharply when the pH is raised back to 8, in which the obtained percentage adsorption is 5.4% and adsorption capacity is 2.1 mg/g.

F. Films Pectin-CMC as Adsorbent of Pb(II) Metal Ion

CMC-pectin film potentially enough to be used as an adsorbent because of the active group -OH and –COOH. It can interact with components of the adsorbate. Adsorption Film toward Pb (II) metal ion occurs between the -COOH groups of pectin and CMC with Pb (II) metal ions by chelating agent reaction as shown Fig. 3:



Scheme 3. The reaction of Pec-CMC bonded Pb metal ion

IV. Conclusion

Film of the Polyelectrolyte complex between chitosan and pectin were prepared by mixing the complex of both polysaccharides. Firstly chitosan was grafted with acetate to form a carboxymetyl chitosan (CMC) to increase active group as adsorbent. CMC mix with pectin to form polyelectrolyte film CMC/pectin Film pectin/chitosan able to increase sorption capacity for heavy metal ions which could be used as adsorbent to remove Pb (II) 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 to support.

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," *Jurnal Komunikasi Penelitian*, vol. 17, no. 4, pp. 66-72, 2005

[3] F. L. 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, 2015.

[5] S. E. Bailey, T. J. R. M. Olin, Bricka, and D. D. Adrian, *Water Res*, vol. 33, pp. 2469, 1999

[6] W. Stumm and J. J. Morgan, *Aquatic Chemistry*, 3nd edition, Canada: John Wiley and Sons, Inc, 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. Mu˜noz, "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. D. Abreu and S. P. C Filho, "Preparation and Characterization of Carboxymethylchitosan," *Polímeros*: *Ciência e Tecnologia*, vol. 15, no. 2, pp. 79-83, 2005

[12] M. Z. Elsabee, E. S Abdou, K. S. A Nagy, and M. Eweis, "Surface modification of polypropylene films by chitosan and chitosan/pectin multilayer," *Carbohydrate Polymers*, vol. 71, no. 2, pp. 187-195, 2008

[13] M. Hiorth, T. Versland, J. Heikkila, I. Tho, and S. A. Sande, "Immersion coating of pellets with calcium pectinate and chitosan," *International Journal of Pharmaceutics*, vol. 308, no. 1-2, pp. 25-32, 2006

[14] L. Richert, F. Boulmedais, P. Lavalle, J. Mutterer, E. Ferreux, G. Decher, "Improvement of stability and cell adhesion properties of polyelectrolyte multilayer films by chemical cross-linking," *Biomacromolecules*, vol. 5, no. 2, pp. 284-294, 2004

[15] S. S. Rashidova, R. Y. Milusheva, L. N. Semenova, M. Y. Janova, N. L. Voropaeva, Vasilyeva, S. Faizieva, and I. N. Ruban, "Characteristics of interactions in the pectin–chitosan," *Sys. Chromatogr.*, vol. 59, pp. 779-782, 2004

[16] 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.

[17] 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 physicaleenzymatic extractions," *Food Hydrocolloids*, vol. 29, pp. 160-165, 2012.

[18] W. W. Wai, F. M. Abbas, A. Karkhi, and A. M. Easa, "Comparing Biosorbent Ability of Modified Citrus and Durian Rind Pectin," *Carbohydrate Polymers*, vol. 79, pp. 584-589, 2010.

[19] 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.

[20] 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

[21] 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

[22] C. Bernabe, W. Peniche, and A. Monal, "Swelling behavior of Chitosan/Pectin Polyelectrolyle Complex Membrannes, Effect of Thermal Cross-linking," *Polym. Bull*., vol. 55, pp. 367-375, 2005

B. Hastuti was born in Sukoharjo, (Indonesia) on 06th August, 1978. She received his master's degree in Analytical Chemistry from the Universitas Gadjah Mada, Indonesia. At present, she is doing Ph.D. in Department of Chemistry, FMIPA, Universitas Gadjah Mada under the supervision of Prof, Dr. Mudasir, M.Eng., Dr. Dwi Siswanta, and Prof. Dr. Triyono, SU. Her area of interest is natural polymer material.