Synthesis and characterization of chitosan-pectin as adsorbent of dyes

B Hastuti¹, S Hadi², S N Afifah¹, B Mulyani¹
¹Department of Chemistry Education, Faculty of Teacher Training and Education, Universitas Sebelas Maret
²Department of Pharmacy, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret

E-mail: Budihastuti@staff.uns.ac.id

Abstract. Environmental pollution due to the disposal of colored substances can endanger both the environment and humans. For this reason, the presence of dyes pollutants needs to be reduced, where adsorption method has become one of the alternative. Research on synthesis of modified chitosan to pectin polyelectrolyte complex (PEC) Chi-Pec has been carried out in order to improve the characteristic of chitosan as adsorbent. The research was done by mixing chitosan solution in acetic acid with pectin solution in water for 3 hours stirring. The solution was then printed out into a polypropylene container and dried. The formed membrane was characterized using FTIR to identify functional groups, XRD and SEM to analyze their physical characteristic. The results showed that the Chi-Pec adsorbent had stability and resistance to the acidic environment. Characterization results using FTIR showed that the adsorbent has functional group of amine, carboxyl and hydrogen. The results of XRD show that the adsorbent was not crystalline. Furthermore, SEM data shows a solid structure of the adsorbent.

1. Introduction
Along with the establishment of Batik as a world heritage from Indonesia by UNESCO on October 2, 2009, nowadays the use of batik is not only on traditional events but also on various type of event [1]. This also has an impact on the growing development of the batik industry in Indonesia, especially in Solo. Most of them are home-based and small scale industries that do not have procedures for processing batik wastewater. It is have a bad impact in the form of water pollution due to processed dyes made in batik industry without processing [1]. Not only batik industry, other textile industries which in the process use dyes are also contributors to water pollution, especially rivers. In study of Septiono et. al., based on central java EPA, the biggest contributor to pollution in the Bengawan Solo River is textile industry, which is 41.5%. This number is indicated to come from activity industry, such as the garment industry, activities of dyeing process, spinning fabric and batik industry [2]. Therefore, the composition of dye in the aquatic environment must be reduced.
Some dyes have properties that can interfere with the environment because some dyes are toxic to some organisms [3]. Methylene blue (C_{16}H_{18}ClN_{3}S) is one type of dye that widely used in the textile industry. If the body is contaminated with these dyes in the long time it can cause vomiting, nausea, anemia and hypertension [4]. One way to reduce dyes in aquatic environment is by absorption. One of these absorption can use a membrane derived from chitosan and pectin synthesis.

Chitosan is the second abundant natural polysaccharide after cellulose. Chitosan dissolves in acids and has an amine group which is polycation. Pectin is a natural polysaccharide that is water soluble and has a carboxyl methylate group [5]. The carboxyl group from pectin causes pectin to act as polyanion and react with chitosan which acts as polycation to form a PEC (Pec-Chi) membrane [6]. In research, Chen et al. (2010) succeeded in synthesizing PEC Pec-Chi membrane and after the analysis was obtained the results of PEC (Pec-Chi) tensile test where the value was greater than that of pure chitosan. The synthesis result of PEC Pec-Chi modification were also carried out to improve the mechanical properties of each polymer. Research on synthesis of modified chitosan to pectin polyelectrolyte complex (Pec-Chi) has been carried out in order to improve the characteristic of chitosan as adsorbent of dyestuff, especially in methylene blue.

2. Experimental

2.1. Material
Chitosan, Pectin, Acetic acid 5%, Aquadest or Water, Methylene blue (C_{16}H_{18}ClN_{3}S) powder.

2.2. Procedure
2.2.1. Preparation of adsorbent
Synthesis of The PEC (Pec-Chi) was made by coservation method that combine chitosan and pectin to form stable adsorbent membrane. Chitosan 0.2 gram was dispersed in 10 mL of acetic acid 5 % and then stirring until 3 hours. Besides that, Pectin 0.2 gram was dispersed in 10 mL water and then stirring until 3 hours. After that, Chitosan solution was added to pectin solution and then stirring until homogeneous. After all the solution is mixed, then the mixture was printed out into polypropylene container and dried in oven. After dry, the film can be peeled off from the container. The PEC(Pec-Chi) adsorbent membrane was ready.

Figure 1. East Java EPA monitoring point in Begawan Solo and surrounding industry type.
(Source : Center Java EPA, 2014)
3. Result and Discussions

3.1. FTIR Characterization

-COOH group is the dominant active group in pectin, while the dominant active group of chitosan is –NH₂ group. Fourier Transform Infrared (FTIR) Spectroscopy are used to see how interaction between components and the result of synthesis polyelectrolyte complex PEC (Pec-Chi) membrane. From figure 2, it can be seen on three spectra in the region 3000-3700 cm⁻¹ can be observe a broad of hydrogen-bonded OH groups. In this area also can be observed NH group stretching vibrating which overlaps with OH vibration for chitosan spectra. In the area of 1500-1800 cm⁻¹ can be observed the stretching vibration of the carbonyl group on the band at 1643 cm⁻¹ for pectin (A). While in the chitosan (B) spectra, in the area of 1597 cm⁻¹ show stretching vibration of amide group. In the area around 1600-1500 cm⁻¹ in PEC (Pec-Chi)spectrum induces an amine group in wavelength 1419 cm⁻¹ that interacts with carboxyl group on 1597 cm⁻¹[7].

![FTIR spectra from membrane](image)

Figure 2. FTIR spectra from membrane: (a) Pectin (b) Chitosan (c) PEC(Pec-Chi)

3.2. Analysis of PEC Pec-Chi adsorbent by XRD

The phase form of the material from pure film (Pectin and Chitosan) and its modification, the membrane/film was tested using X-Ray Diffraction (XRD). XRD spectra result from pectin showed that the properties of pectin is amorphous, this was characterized by not sharp peaks found which
appeared anomaly, at peak \(2\theta=20^\circ\). The characterized phase of chitosan from the result of XRD test is semi-crystalline and have peak at \(2\theta=20^\circ\) and 30°. In the PEC (Pec-Chi), between pectin and chitosan, the characteristics of chitosan is disappear and the halodisperse is indicated of amorphous. This can be explained by the strong interaction like hydrogen bond and ionic interaction between pectin and chitosan with has destroyed the close packing of chitosan molecule for those formation of regular crystalline [8]. The presence of pectin in PEC (Pec-Chi) decreases the crystalline level of chitosan which is seen by the comparison of peak of each spectra.

![XRD test result from film](image)

**Figure 3.** XRD test result from film: (a) Pectin (b) Chitosan (c) PEC (Pec-Chi) membranes

### 3.3. SEM Analysis
Morphology of the PEC (Pec-Chi) adsorbent film, it can be seen using SEM test, both form the surface and cross section. From the result of SEM for surface appearance with 500X magnification both chitosan and pectin have small and homogeneous pores (figure B and C). As form PEC (Pec-Chi) films, the pores that owned are smoother and smaller compared to chitosan or pectin films. PEC (Pec-Chi) film also has a high complexity when compared to its pure component films. But if the film is viewed from a cross section the pores are more rough while the result seen from the surface of the pores are smaller. So it implys that PEC (Pec-Chi) film was potential used as an adsorbent candidate for dyestuffs.
4. Conclusion

Pec-Chi polyelectrolyte complex (PEC)Pec-Chi were prepared by coaservation combine both polysaccharides Pectin and Chitosan. Based on FTIR spectroscopy, the adsorbent have active group comprise and interaction of carboxylate and amine groups. The result of characterization using XRD, show that the PEC adsorbent is amorphous. Based on SEM analysis, the film adsorbent has small pores with a high complexity.

References
[1] Kusumawati N, Wijiastuti A, Rahmadyanti E 2012 *J Environ. Sci. Eng.* 1 672
[2] Septiono M A, Roosmini D, Salami H I R S, Ariesyadi D, Lufiandi 2016 *Industrial activities and its effects to river water quality (case study citarum, bengawan solo and brantas)*.
[3] Pathania D, Sharma S, Singh P 2017 *Arabian J. of Chem.* 10, S1445–S1451
[4] Hameed B H 2009 *J Hazard. Mater* 161 753-759
[5] Chen P, Kuo T Y, Kuo J R, Tseng Y P, Wang D M, Lai J Y, Hsieh H J 2010 *Carbohydr. Polym.* 82 12361242
[6] Ayuni N P S, Yuningrat N W, Andriani K Y 2016 *Jurnal Sains dan Teknologi.* 706 – 717
[7] Marudova M, MacDougall A J, Ring S G 2004 *Carbohydrate Research.* 339
[8] Ghaffari A, Navaee K, Oskoui M, Bayati K, Tehrani M R 2007. *European J. Pharm. and Biopharm* 175-186