Syntheses of Chitosan Macropore and Application as Procion Red Dyes Adsorben

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Abstract. The purpose of this research is to conduct syntheses of chitosan macropore using epichlorohydrin (ECH) as crosslinker and KCl as porogen. The synthesis process was done through three stages: first, chitosan dissolved in acetic acid and added KCl as porogen; second, crosslinking chitosan using epichlorohydrin and third, washing of chitosan crosslinked by aquadest to release KCl to produce pore. Chitosan and modified chitosan was characterized solubility on acid medium, functional groups using fourier transform infra red (FTIR), and photo micrograph using scanning electron microscopy (SEM). Chitosan dissolved on acetic acid 5% medium, but chitosan-ECH and chitosan macropore insoluble. The FTIR spectrum of chitosan and chitosan modified there are no significant differences because they have same of functional groups. SEM micrograph of chitosan and chitosan-ECH showed smooth surface, but addition KCl as porogen on modified chitosan produced pore in the surface of adsorben. Adsorption experiments were conducted to study the removal of procion red dyes and optimum adsorption conditions were obtained at pH 2. Chitosan, chitosan-ECH and chitosan macropore showed percentage adsorption for procion red respectively were 68.0%, 61.0% and 78.8%. Chitosan modification with crosslinking and porogen addition proved to improve stability and adsorption ability of chitosan.

1. Introduction
The development of textile industry in Indonesia is increasing rapidly. The textile industry absorbs 1.3 million workers. Improvement of the textile industry will also increase the pollution of dyes waste as a byproduct of the staining process [1]. The dyeing process in the textile industry will produce 10-15% of the dyestuff as waste [2]. Synthetic dyes are used in the textile industry for reasons of cheap, durable, easy to obtain, and easy to use. However, the resulting waste is colorful and difficult to degrade [3].

Dye waste will reduce the sunlight entering the water and prevent photosynthesis. This will result in decreased water quality and reduced dissolved oxygen. Dye waste can cause health problems like allergies, skin irritation, cancer, and mutations in humans [4]. One of the dyestuffs in the textile industry is Procion Red which is used as a fabric dye [5].

There are several methods developed to reduce the dyestuff levels in water pollution such as coagulation and flocculation, filtration, adsorption, advanced oxidation, ion exchange, and biological treatment [6,7,8]. From some of these methods, adsorption is considered one of the most promising
alternatives to remove dyes from aquatic waste due to its ease of operation, high efficiency, and can be regenerated [9].

One of the most commonly used as adsorbents is chitosan. Chitosan is a compound with the chemical formula of poly-(2-amino-2-dioxy-β-D-glucose) [10]. Chitosan is obtained from deacetylation of chitin and is a natural polysaccharide found in crustaceae such as shrimp, crab, lobster, and marine industry [11]. Chitosan is an abundant, cationic adsorption method of biopolymer dye, high adsorption capacity, macromolecular structure, and easily modified. The presence of amino and hydroxyl groups in chitosan showed a high potential for dye adsorption [12].

Modification of chitosan aims to prevent the adsorbent from being acidic and one of the chitosan modifications is carried out by crosslinking [13]. Some crosslinking agents were used as crosslinker among other are epichlorhydrin (ECH), glutaraldehyde (GLA), ethylene glycol diglycidyl ether (EDGE) and bisphenol a diglycidyl ether (BADGE) [14,15,16]. Epichlorhydrin (ECH) is a widely used compound in chitosan crosslinking. ECH binds the -OH group to chitosan so as not to bind to the main adsorption sites of chitosan ie -NH₂ [17]. The crosslinker may reduce the absorption capacity due to the binding of the active group [18]. To increase the adsorption capacity, chitosan is modified to produce pores on the chitosan surface useful for capturing dyes to be absorbed.

Porogen (pore generator) is used to produce pore membranes. In the preparation of absorbent membranes, porogens play two roles: increased internal absorption capacity (pore) and increased dispersivity [19]. Modification of chitosan with the addition of porogen has been widely performed, for example chitosan with porogen poly (vinyl pyrrolidone) (PVP) [19], porogen poly (ethylene glycol) [19], porogen silica [20], NaCl, KCl and sodium bicarbonate or NaHCO₃ [21,22,23]. The porogenic modified chitosan will be able to enlarge the porosity of the chitosan membrane thereby increasing the chitosan adsorption capacity [20]. One of the porogen used to produce pores on chitosan membranes is potassium chloride. Potassium chloride (KCl), an inorganic porogen such as NaCl that can produce small surface area with high porosity [20]. This has been proven that the addition of porogen NaCl can form pore structure on chitosan membrane [21].

In this paper, chitosan modification was done by crosslinking using ECH and addition of KCl as porogen. The resulting chitosan membrane was used as a procion red dyes adsorbent. Procion red is a reactive dyes and have huge structure. Procion red can bind on the active group of chitosan especially hydroxyl and amine groups. The structure of chitosan and procion red dyes showed on the Fig 1.

![Structure of chitosan and procion red](image)

**Figure 1.** Structure of chitosan and procion red

2. **Experimental Details**

Material was used in this research are: Chitosan flakes (DD>75), BADGE were obtained from Sigma-Aldrich Germany, epichlorhydrin, ethanol absolute, KCL, acetic acid, procion red, NaOH pellet, HCl 37%, citric acid and isopropanol, were obtained from E Merck Germany, whatman no 42 filter paper, and aquabides obtained from Central Laboratory, Sebelas Maret University.
Instruments used in this study were pH meter (Mettler PB 3000 Type ER-182), Shaker (Marus Instrumenten), Oven (Heraeus), analytical balance (Mettler Toledo AB54-S), FTIR Spectrophotometer (Shimadzu 8201PC), UV-Vis Spectrophotometer Shimadzu JSM 6360 LA.

Modification chitosan was done as follows. Chitosan (CTS) (1 g) dissolved on the 40 mL acetic acid 2 % and stirred for 2 hours. KCl (size < 100 mesh) 15 g added to solution and stirred for 2 hours. Epichlorhydrin (ECH) (0.5 mL) was added to the solution and stirred for 2 hours. The solution is poured into a petridisc, held for 24 hours in the desiccator. Petridisc were heated at 90°C for 4 hours. The formed membranes are picked up and washed with distilled water and ethanol. The membrane was crushed and filtered with a size of 100 mesh. This product as CTS-ECH-KCl was characterized using FTIR and SEM. As a comparison we performed crosslinking chitosan using ECH without the addition of porogen (CTS-ECH).

The effect of pH were performed at controlled pH (2.0 to 6.0) using buffer. The adsorbent 50.0 g and 25.0 mL procion red (25.0 mg/L) solution on the erlenmeyer was shaked for 2 hours at 40 rpm. Concentration procion red was analyzed using UV-Vis Spectrophotometer at wavelength 566 nm.

3. Result and Discussion

Chitosan and modified chitosan was studied solubility in acid (acetic acid 2%). Chitosan was soluble in acid but CTS-ECH and CTS-ECH-KCl was insoluble. This was showed that crosslinking chitosan increased stability of chitosan. Characterization of modified chitosan was done by using Scanning Electron Microscopy (SEM) and Fourier Transform Infra Red (FTIR) spectrophotometer to determine the differences of physical character and functional groups between chitosan, chitosan crosslinked and chitosan macropore. The SEM photomicrograph is shown in Fig. 1 and spectrum FTIR in Fig. 2.

![Photomicrograph SEM of (A) CTS, (B) CTS-ECH, (C) CTS-ECH -KCl](image)

Photomicrograph of CTS and CTS-ECH membrane showed a smooth surface. There were no pore in that adsorbents. Membrane CTS-ECH smoother than CTS because ECH as a crosslinker will close pore of chitosan. Surface CTS-ECH-KCl has showed that pore structure was formed. Surface of CTS-ECH-KCl was increasing and contact between adsobent and adsorbat become easily. Macropore chitosan has been syntheses beside increase stability of chitosan also interaction adsorbent and adsorbat.
Fig. 3 showed FTIR spectrum of chitosan. The peak at wave number 1634 cm\(^{-1}\) is characteristic vibration of C=O from amide, that is overlap with NH vibration at 1593 cm\(^{-1}\). The peaks at 3335 cm\(^{-1}\) showed the stretching vibration of \(-\text{OH}\) and \(-\text{NH}\) groups. The peak at 2867 cm\(^{-1}\) is characetize to \(-\text{CH}\) stretching vibration of \(-\text{CH}\) and \(\text{CH}_2\) [24]. There are no significant difference between spectrum FTIR CTS-ECH with CTS, because both of them have same functional groups. Spectrum of CTS-ECH-KCl showed change at 1381 cm\(^{-1}\) assigned to interaction K\(^+\) with amine and hydroxyl groups.

Adsorption procion red dyes studied the effect of pH using batch method. Adsorption was done in the pH range between 2 to 5. As shown in Fig. 3, the adsorption of procion red was highly dependent on the pH because pH can affect the charge of procion red and functional groups of adsorbent. Chitosan have amine (pKa 6.2) and hydroxyl groups as active site [24]. The optimum adsorption procion red on chitosan was at pH 2, and adsorption on CTS-ECH and CTS-ECH-KCl were at pH 4. Effect of pH on adsorption ability of procion red showed at Fig. 4.

![Figure 3. FTIR spectrum of CTS, CTS-ECH and CTS-ECH-KCl](image)

Chitosan macropore (CTS-ECH-KI) have higher adsorption ability for procion red than chitosan and CTS-ECH. The ability adsorption procion red on CTS, CTS-ECH and ECS-ECH-KI were 68.0%, 61.0% and 78.8% respectively. The formation of macropore will make the interaction between dyes.

![Figure 4. The effect of pH solution on adsorption ability of procion red on CTS, CTS-ECH and CTS-ECH-KCl](image)
and chitosan become better. Dyes can be adsorbed on the pores of the chitosan, resulting in higher adsorption capacity. Adsorption capacity procion red on chitosan crosslinked (CTS-ECH) decreased because the surface of chitosan was covered by a crosslinker that reduces the interaction of dye and active sites.

4. Conclusion
Synthesis chitosan macropore can be done successfully. Chitosan macropore is insoluble in acid, and higher adsorption ability than chitosan.

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