Adsorption Study for Removal of Acid Orange Dye using Modified Nano Chitosan

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Abstract. So far the application of chitosan as an adsorbent still uses microscale chitosan adsorbent. The microscale chitosan has not adsorbed waste maximally either to the weight of the adsorbent usage or the target adsorption capacity. Nanoscale adsorbent size has not been widely used, especially as an adsorbent of dyes waste. Therefore, through micro-size reconstruction into nano chitosan will provide maximum opportunities in its utilization. This study reconstructs the size of chitosan into nanochitosan and binds crosslinking with phosphate. Synthesis using ionic gelation method. The crosslinked results were characterized using FTIR, PSA and SEM-EDX instruments, followed by parameter optimization including pH optimization, interaction time, adsorption capacity and application. The amount of absorbed dye concentration was analyzed using UV-Vis spectrophotometer. The measurement results showed that the physical reconstruction of chitosan was successfully carried out with a wavelength range of 246nm-260nm as an indication of nanochitosan adsorbent at pH 7-9 using 5% nanochitosan. It was concluded that the nanochitosan from the synthesis could be reused for 2 times, with desorption percentage of 86%.

Keywords: ionic gelation, nanochitosan, adsorption, methyl orange

1. Introduction
Chitosan is a type of natural polymer produced from chitin deacetylation process, discovered first by Rouget in 1859, is an important and very abundant polysaccharide biopolymer [1]. Chitosan is biodegradable, biocompatible, non-toxic and environmentally friendly [2]. Referring to the nature of chitosan, chitosan can be applied in various fields of modern industry (pharmaceutical, biochemistry, cosmetics, food industry, and textile industry) and continues to be developed, including modifying chitosan chemically or physically. Chemical modification results in improved stability of chitosan through functionalization of existing functional groups, and improvement of chitosan pore size. A physical modification that is reconstructing the particle size becomes smaller for widely applications. Therefore, the development of physical modification leads to nanoscale forms [3]. Limited application of nanochitosan, such as physical instability (aggregation/particle fusion) and/or chemistry, the concern is only on the longtime of storage. Therefore, the water content should be removed. Freeze-drying is the most often process used to change a solution or suspension become nano solids so that they are stable when distributed and/or stored for application purposes [4].
The synthesis of nanoparticles is generally carried out with the bottom-up technique which is that atoms or molecules or clusters are assembled to form the desired nanometer-sized particles [5]. Nanochitosan synthesis with the bottom-up technique using several methods such as emulsion cross-linking, precipitation, spray drying, emulsion-droplet coalescence method, ionic gelation, micellar, and polyelectrolyte complex [6]. Various crosslinkers can be used to improve the stability of chitosan such as CaCl$_2$, glutaraldehyde, epichlorohydrin, and tripolyphosphate[7][8]. However, the synthesis of nanochitosan using citric acid as a solvent and tripolyphosphate cross-linking so far has not been conducted. The ionic gelation methods are selected due to the simplicity and can be controlled, and the tripolyphosphate is selected as a crosslinker due to its compatible properties [9].

2. Materials and Method

2.1 Chemicals and instruments
The materials used were chitosan (shrimp, DD 85%), citric acid (C$_6$H$_8$O$_7$(s)), sodium tripolyphosphate, Tween 80 (surfactant), hydrochloric acid (HCl$_{(l)}$) 2N. Magnetic stirrer, UV-Vis spectrophotometer, Fourier Transform Infrared (FTIR) spectrophotometer, and SEM-EDX.

2.2 Synthesis of nanochitosan
Chitosan dissolved in citric acid 50 mg while adding 25 mL of tween solution 5% drop by drop. Tripolyphosphate solution 10 mL of 0.1% was added to form a suspension. The obtained suspensions were then analyzed using a UV-Vis spectrophotometer at a wavelength range of 200-400 nm and calculated [10][11]. The suspension of nanoparticles was dried using a freeze dryer at -40°C for 48 hours. The nanochitosan powder will be used for optimization of adsorption parameters including pH optimization, contact time and adsorption capacity.

2.3 Parameter optimization (pH, contact time and concentration)
Nanochitosan 3 g interacted with 50 mL of the acid orange dye solution at a variation of pH 3 to pH 12. The filtrate was then analyzed using a UV-Vis spectrophotometer. The optimum pH obtained will be used to optimize contact time with variations of time, i.e., 10, 20, 30, 60, 90 and 180 minutes. Adsorption capacity was determined by optimizing concentrations of 20, 50, 100, 150 and 200 ppm with a volume of 50 mL, at optimum pH and contact time. The filtrate was then analyzed using UV-Vis spectrophotometer. Recovery test was determined by repeated adsorption until adsorption capacity is less than 50%, followed by an application using laboratory scale liquid waste samples.

3. Results and Discussion
Chitosan nanoparticles are solid particles with a size range of 10-1000 nm [5]. Nanochitosan in this study has been successfully reconstructed; it was shown in the Uv-Vis spectra obtained in the range at 246-260 nm by using dissolution of chitosan with concentration 5% citric acid. Nanochitosan was dried using a freeze-drying process for 6-10 hours, the emulsion obtained gradually was dried up, and the water content is reduced and produced particles with nano sizes. Figure 1 shows the chitosan sizing process using ionic gelation method.
Ionic gelation method with polyelectrolyte complexes has several advantages, such as simple and without organic solvents or high shear forces. The crosslinking method is generally used to avoid toxicity from reagents and other undesirable effects. The mechanism of chitosan nanoparticles formation by ionic gelation method is based on the electrostatic interaction between the chitosan amine group and the tripolyphosphate negative charge group. Ionic gelation method in this study was carried out by dissolving chitosan in a citric acid solution at a concentration of 5% for 24 hours to obtain chitosan cation, then dripped slowly into the TPP polyanionic solution during stirrer. Complex reactions through ionic gelation and precipitation formed beads particles. Thus, the nanoparticles are formed spontaneously due to mechanical stirring at room temperature.

The freeze-drying process changes the suspension into dry particles by using a cold drying process using a temperature of -40°C for 48 hours to form the nanochitosan powder. The result of The wavelength measurement results for the nanochitosan concentration of 5% citric acid was stable for 360 minutes. The product nanochitosan and chitosan powder are shown in Figure 2. Izu et al. [12] reported smaller nanoparticles by using acetic acid concentrated 1%. As a result, the particle size around 62.8 nm, meanwhile, Elshokyet [13] reported getting the size of the particle 400-450 nm by increasing concentration 2%. The difference in the particle size obtained is possible due to the different drying processes and different acids. The IR spectra showed that several functional groups owned by the synthesized nanochitosan, and the full interpretation could be seen in Table 1.

![Figure 1. Ionic gelation method](image1.jpg)

![Figure 2. Chitosan powder (A) and nanochitosan powder (B)](image2.jpg)
Table 1. Interpretation data of FT-IR spectra, for chitosan, chitosan-citric, and nanochitosan

| Type of absorption            | Wave number (cm\(^{-1}\)) |
|-------------------------------|-----------------------------|
| OH (H-bond)                   | Chitosan: 3450, Chitosan-citric: 3417, Nanochitosan: 3441 |
| Stretching C=O amide          | Chitosan: 1653, Chitosan-citric: 1640, Nanochitosan: - |
| Bending NH amine              | Chitosan: 1598, Chitosan-citric: 1554, Nanochitosan: 1627 |
| Stretching C=O carboxylic     | Chitosan: 1718, Chitosan-citric: 1728, Nanochitosan: 1222 |

The results of the functional group analysis using FTIR spectrophotometer showed that the active site of chitosan at a wave number of 1598 cm\(^{-1}\) as an amine group (\(-\text{NH}_2\)), was a bending vibration of the specific N-H chitosan. After dissolving with citric acid, a new absorption with strong intensity appeared at a wave number of 1718 cm\(^{-1}\) was a stretching vibration of the carbonyl group C=O carboxylic, indicating that there was an interaction of citric acid with chitosan were O- atoms reacted with the \(\text{NH}_2\) group protonated to \(\text{NH}_3^+\) from chitosan. The formation of nanochitosan was characterized by the emergence of new absorption for stretching vibration of the P=O group at the wave number of 1222 cm\(^{-1}\). It showed that the \(\text{NH}_2\) group was protonated and formed \(\text{NH}_3^+\) and has been crosslinked with O- atoms from Na-TPP.

![Chemical structures](image)

**Figure 3.** Illustration of interaction between chitosan-citric with tripolyphosphate

The most important characteristics in the nanoparticle system are expressed in the polydispersity index with a range of 0-1. Polydispersity index values close to 0 indicate a homogeneous size dispersity, and the polydispersity index values of more than 0.5 indicate high heterogeneity [14]-[16]. Crosslinking prevents the formation of particles at micro size and concentration should be used as low as possible to obtain the particle size below 100 nm, and droplets are carried out as quickly as possible in the ionic gelation reaction process to prevent solidification.
Figure 4. Characterization result of Porous surface Area (left), morphology (SEM-1000x -middle) and TEM (200X- right)

Based on the data obtained, the size of nanochitosan particles was in the range of microparticles with heterogeneous particle distribution, low stability and aggregate formation [17]. Polydispersity index values were quite high, but several were below the value of 1, indicated a good level of uniformity. Polydispersity index > 0.7 states a nanoparticle system with a very large particle size distribution [18]. Morphology analysis using TEM and SEM showed the surface of the adsorbent was not uniform as well as SEM (Figure 4). However, UV-Vis spectrophotometer measurements showed the range of nano-size wavelength. It is possible due to the influence of mechanical movement during the freeze dryer process, freezing and drying, and the powder form caused nanochitosan aggregation process. These indications are reinforced by, that the size and distribution of nanochitosan with an acetic acid increase after freeze-drying, compared to the initial size of nanoparticles[19]. Nanochitosan optimization results showed in 5% concentration of citric acid was stable for 360 minutes at pH 7-9 and interaction time of 120 minutes. The results of the analysis and characterization of PSA obtained a particle size of 7270 nm and polydispersity index (PI) of 0.7740.

4. Conclusion
The results of sizing reconstruction showed the formation of nanochitosan based on the results of UV-Vis spectrophotometer analysis obtained maximum absorption at a wavelength range of 246-260 nm. FT-IR analysis showed a shift in the active site absorption peak C=O as amide, C=O as carboxylic, NH as amine and P=O showed nanochitosan. The parameter optimization showed the optimum pH range of 7-9 and the interaction time of 120 minutes. PSA analysis results obtained the average particle size of 1981-7270 nm. The synthesized nanochitosan can be reused 2x with the desorption percentage of 86%.

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