

Synthesis of Chitosan Magnetic Nanoparticles using Glutaraldehyde and Tripolyphosphate as Crosslinker

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ABSTRACT

Chitosan is an abundant natural polymer, which able to adsorb Pb^{2+} . However, chitosan has the drawback of being unstable in acid and alkaline conditions, so it needs cross-linking. In this article, we will compare the usage of two crosslinkers, glutaraldehyde (GD) and tripolyphosphate (TPP), to solve these issues. The synthesis of chitosan magnetic nanoparticles was carried out by co-precipitation with the addition of glutaraldehyde under acidic conditions and the addition of TPP under alkaline conditions. The results showed that the FTIR spectrum gave characteristic bands at 3131.96 cm^{-1} (OH and NH), 1635.86 cm^{-1} (C=O), 1401.97 cm^{-1} (CN), $\sim 1110\text{ cm}^{-1}$ (COC), and $\sim 617\text{ cm}^{-1}$ (Fe-O). SEM analysis showed that the surface morphology of CMNP-GA particle aggregation was clear more than that of CMNP-TPP. The size of the synthesized nanoparticles was determined by PSA analysis, which was $131.95\text{ }\mu\text{m}$ and $137.10\text{ }\mu\text{m}$, respectively. The results of the XRD analysis showed that, in addition to the Fe_3O_4 and chitosan phases, the produced CMNP also contained $\gamma\text{-Fe}_2O_3$ phase, which was considered to be caused by Fe_3O_4 oxidation.

Keywords: nanoparticle, chitosan, magnetic, glutaraldehyde, tripolyphosphate

INTRODUCTION

Chitosan is a linear biopolymer consisting of β -(1-4)-2-amino-2-deoxy-D-glucopyranose [1]. Chitosan is a biodegradable and ecologically friendly polymer [2], which has a high adsorption ability due to the presence of NH_2 and OH groups as active sites [3] for metal ion adsorption [4]. However, chitosan is unstable in both acidic and alkaline conditions which cause the interaction between metal ions and the chitosan surface to be weak, so further modification is needed [3]. Chemical modification such as crosslinking can improve the adsorption performance of chitosan [5]. In this study, we will synthesize chitosan crosslinked with glutaraldehyde (GA) and tripolyphosphate (TPP) for Pb^{2+} adsorption. The two crosslinkers have different types of bonds. Glutaraldehyde forms a Schiff base with chitosan, while TPP forms an ionic interaction with chitosan [6]. Glutaraldehyde as a crosslinker has two carbonyl groups C=O which will bind to the NH_2 group of chitosan and the reaction formed is an imine bond (C=N) [7]. Generally, glutaraldehyde is reacted with chitosan under acidic conditions [8]. In contrast to glutaraldehyde, TPP has a negative group $(P_3O_{10})^{5-}$, if in an alkaline condition ($pH > 9$) it will interact electrostatically with the NH_3^+ group of chitosan [5] which is formed by dissolving under acidic conditions, so it has a high cross-charge density with chitosan [9].

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Physical modification is also carried out by coating chitosan on solid surfaces such as magnetic nanoparticles [10]. Magnetic nanoparticles are materials consisting of magnetic elements such as Fe_3O_4 with a size of 1-100 nm which can be controlled using an external magnetic field [11]. Magnetic Fe_3O_4 is one of the iron oxidation phases which has the greatest magnetic properties compared to other phases, which have excellent biocompatibility and biodegradability [12]. Fe_3O_4 is made up of $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ is composed of a trivalent Fe^{3+} ion and a divalent Fe^{2+} ion [13]. Chitosan and Fe_3O_4 are combined to generate a chitosan- Fe_3O_4 composite that covers chitosan's weaknesses and improves its performance as a solid phase [14]. Cheng Liu explained that the addition of magnetic nanoparticles as a solid phase showed good dispersibility, and facilitated the isolation of the analyte solution by an external magnetic field [15]. Chitosan- Fe_3O_4 is formed based on the electrostatic interaction between the NH_3^+ group of chitosan with OH^- on the surface of Fe_3O_4 . Synthesis of chitosan magnetic nanoparticles can be carried out by in-situ and ex-situ co-precipitation [16]. In this process, Fe_3O_4 will precipitate by forming a core with high surface energy and rapidly adsorbing the well-soluble chitosan polymer. Under these conditions, a uniform layer of chitosan polymer is assembled by physical cross-linking induced by electrostatic interactions on the Fe_3O_4 core [17].

In this research, the synthesis of chitosan magnetic nanoparticles with glutaraldehyde and tripolyphosphate crosslinkers will be carried out. This paper aims to compare CMNP-GA and CMNP-TPP which are formed based on their characteristics. The chemical groups in CMNP were identified using the FTIR method. The morphological properties were observed through SEM images and the CMNP sizes were determined with PSA measurements. Crystal structures of CMNP were analyzed by XRD.

EXPERIMENT

Chemicals and instrumentation

Chemicals used in this study are chitosan, sodium tripolyphosphate, glutaraldehyde, iron(III) chloride hexahydrate, iron(II) sulfate heptahydrate, ammonium hydroxide 25%, Glacial Acetic Acid 98%. Distilled water was used to make all the solutions. All of the compounds were sourced from Merck and were of the analytical reagent grade.

The apparatus used in this study are Fourier Transform-Infrared Spectrometer (Shimadzu 8400S), Scanning Electron Microscopy (Hitachi TM-3000), Particle Size Analyzer, X-Ray Diffraction (PANalytical: E'xpert Pro), shaker (DLAB SK-0330-Pro), oven (Yenaco), thermometer, magnetic stirrer, analytical balance, and glassware. The pH values of the solutions were measured by a digital pH meter (Inolab).

Synthesis of CMNP

The CMNP-TPP was synthesized with the main steps as follows. Chitosan solution was made by continuously stirring 0.1 g chitosan in 100 mL of 0.5 % (v/v) acetic acid glacial solution. 5.40 g $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and 2.78 g $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (2:1), each dissolved in 25 mL distilled water, were added to the chitosan solution and stirred at 1000 rpm for 30 minutes at 40 °C. The reaction system was then filled with 40 mL of ammonium hydroxide at a concentration of 25% (m/v). After 60 minutes, the reaction system's temperature was raised to 60 °C, and 1 mL of 1% STPP was added to the system with continuous stirring at 1000 rpm for 90 minutes. For CMNP-GA, the crosslinking process was carried out in acidic conditions, namely 1 ml of 1% GA solution was added to the chitosan solution, stirred for 60 min at 40 °C for 5 hours. In another glass, 5.40 g of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and 2.78 g of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (2:1), which were dissolved in

25 mL of distilled water, respectively, stirred, and 40 mL of 25% (m/v) ammonium hydroxide was added dropwise with continuous stirring at 1000 rpm for 60 min. After that, the magnetic solution was added to the chitosan solution, stirred for 60 min at 60 °C. The resulting MCNP was separated by a magnet field and dried in an oven at 60 °C for 5 hours.

RESULT AND DISCUSSION

Characterization of CMNP

Chitosan was crosslinked using GA and TPP, then the CMNP was analyzed using FT-IR, SEM, PSA, and XRD. The IR spectrum of chitosan, CMNP-GA, and CMNP-TPP were shown in Figure 1. This data identifies the formation of chitosan, CMNP-GA, and CMNP-TPP. Chitosan spectra showed absorption at wavenumbers 3385.83 cm^{-1} and 1635.86 cm^{-1} . The wavenumber 3385.83 indicates the presence of OH and NH_2 groups, while the wave number 1635.86 indicates the NH bending vibration. The functional groups spectra appear in the wavenumbers between CMNP-GA and CMNP-TPP tend to be similar. The wavenumber of CMNP-GA and CMNP-TPP [KBr pellet ($\nu_{\text{max}}/\text{cm}^{-1}$): 3131.96 cm^{-1} (OH and NH_2), 1635.86 cm^{-1} (NH bending), 1401.97 cm^{-1} (CN), ~1110 cm^{-1} (C-O-C), and ~617 cm^{-1} (Fe-O)] [18]. However, the NH stretching vibration that appeared at 3385.83 cm^{-1} didn't appear on spectra IR of CMNP-TPP. The existence of C-O-C bonds indicates the occurrence of cross-links between chitosan. The interaction of chitosan with GA or TPP is evidenced by a shift in the wavenumber in the FTIR spectrum.

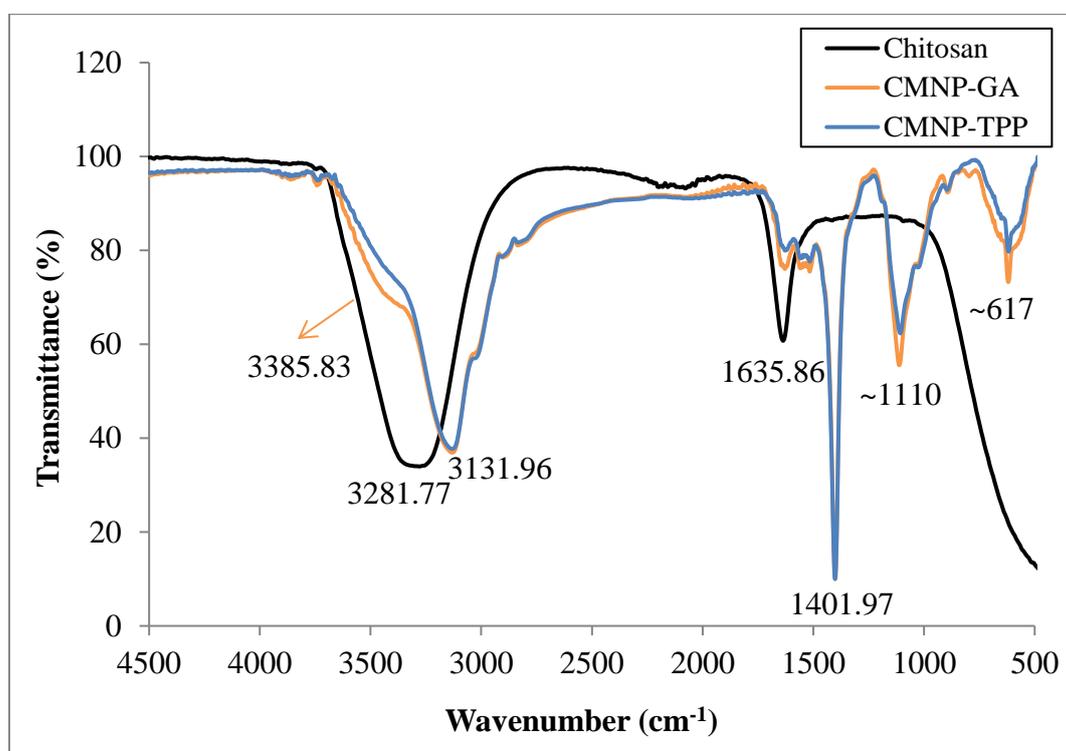


Figure 1. IR spectrum of chitosan, CMNP-GA, and CMNP-TPP

In order to evaluate the surface morphologies of the materials, SEM micrographs of CMNP-GA and CMNP-TPP were recorded (Figure 2). As can be observed in Figure 2, the results of the SEM analysis of CMNP-GA and CMNP-TPP have irregular spherical

morphology with different particle sizes. The presence of a bigger particle size is due to the crosslinker establishing crosslinks not only between particles in one nanoparticle, but also between nanoparticles so that the nanoparticles combine to form a larger size. CMNP-GA showed more pronounced particle aggregation compared to CMNP-TPP, which was caused by GA crosslinking through chemical bonds while TPP crosslinking was caused by ionic interactions thus forming weaker bonds.

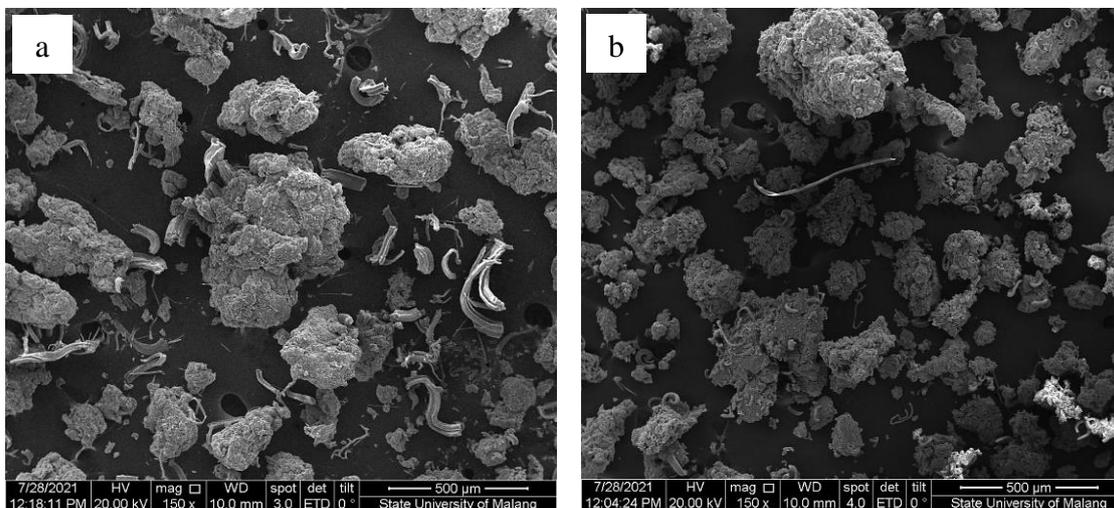


Figure 2. SEM micrograph of (a) CMNP-GA (b) CMNP-TPP

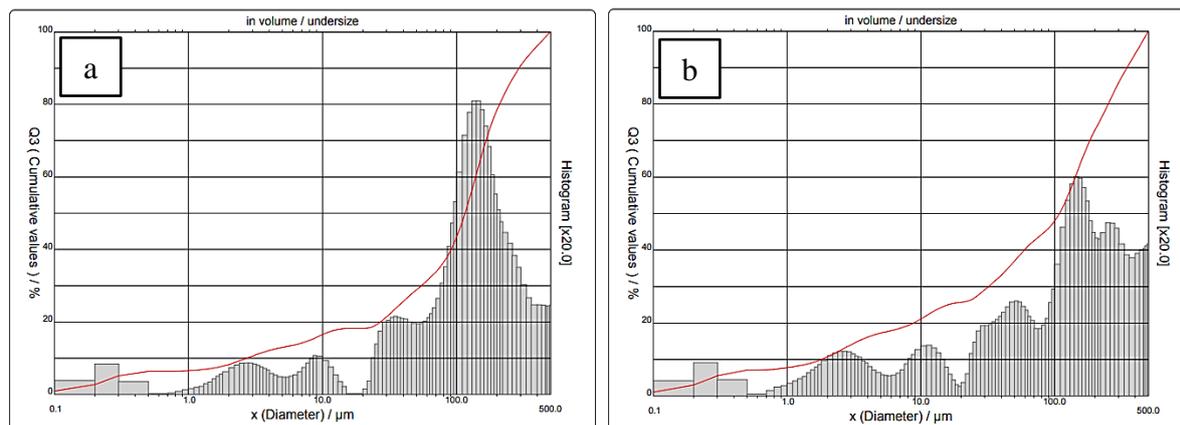


Figure 3. PSA distribution analysis of (a) CMNP-GA (b) CMNP-TPP

The particle size of CMNP was also measured by PSA as shown in Figure 3. CMNP-GA produces a particle size distribution with an average diameter of 131.95 μm , were in the 10% range measurement results in a diameter measuring 2.71 μm , in the 50% range measurement results in a diameter of 115.45 μm , and the 90% range measurement results in diameter measuring 292.71 μm . While CMNP-TPP produces a particle size distribution with an average diameter of 137.10 μm , which in the 10% range results in diameter of 1.79 μm , in the 50% range it produces a diameter of 108.32 μm , and the 90% range it produces a diameter of 347.74 μm . Thus, the particle size distribution of CMNP-GA and CMNP-TPP formed is in the range of microparticle size, namely 1-5000 μm [19].

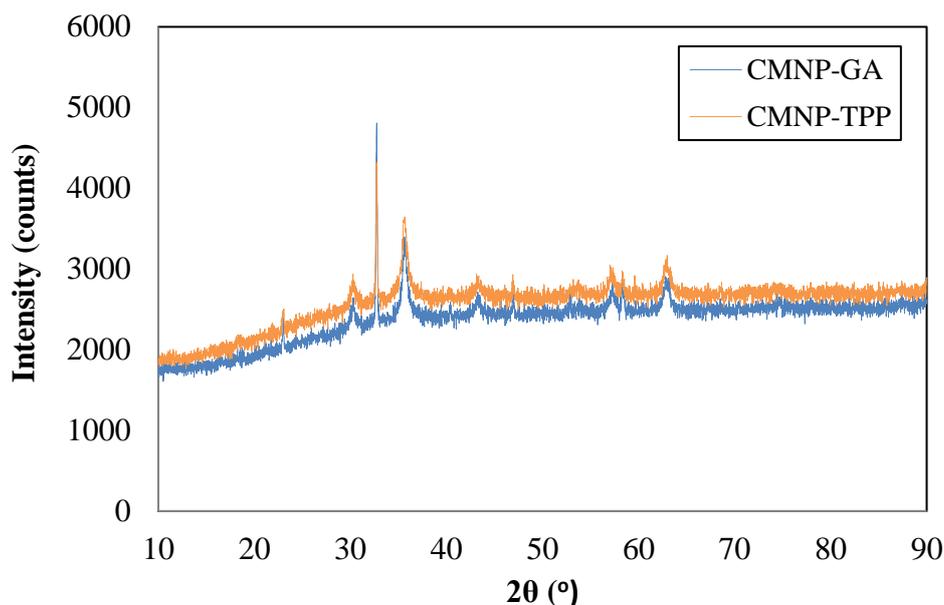


Figure 4. Diffractogram of CMNP-GA and CMNP-TPP

The crystal structure of CMNP was characterized using XRD. XRD diffractograms of CMNP-GA and CMNP-TPP are shown in Figure 4. Based on these diffractograms, it can be seen that in the CMNP-GA and CMNP-TPP samples there are diffraction peaks in the lattice plane (220), (311), (222), (400), (333), and (440). The diffraction peaks correspond to the crystalline pattern of the Fe_3O_4 phase, according to the standard Fe_3O_4 data (ICSD: 26410), which shows that both CMNPs contain the Fe_3O_4 phase. In addition, there are several other peaks with a smaller intensity which are thought to be maghemite ($\gamma\text{-Fe}_2\text{O}_3$), which is adjusted to the standard $\gamma\text{-Fe}_2\text{O}_3$ (ICSD: 172905)[20]. The formation of another iron oxide phase is due to the occurrence of Fe_3O_4 oxidation. Meanwhile, there is a peak at 2θ around 23° which is a characteristic peak for chitosan. The process of adding crosslinking of chitosan with GA and TPP did not affect the crystal structure of Fe_3O_4 .

CONCLUSION

This research synthesizes chitosan magnetic nanoparticles cross-linked with glutaraldehyde and tripolyphosphate as solid phases. The IR spectra of chitosan magnetic nanoparticles bound to GA and TPP did not show a significant difference, namely having a wavelength of 3131.96 cm^{-1} (OH and NH), 1635.86 cm^{-1} (C=O), 1401.97 cm^{-1} (CN), $\sim 1110\text{ cm}^{-1}$ (COC), and $\sim 617\text{ cm}^{-1}$ (Fe-O). The characteristics of chitosan magnetic nanoparticles with GA and TPP crosslinkers form crystals bound to chitosan with irregular spherical morphology. The particle size of CMNP-GA is smaller than that of CMNP-TPP, namely $131.95\text{ }\mu\text{m}$ for CMNP-GA and $137.10\text{ }\mu\text{m}$ for CMNP-TPP.

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