Synthesis and Charactherization of Chitosan-Tripolyphosphate from Clam Shells (*Cerithidea obtusa)* and Its Application to Sorption of Cadmium Ion

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Abstract

Synthesis and characterization of chitosan-tripolyphosphate (Chi-TPP) from Clam Shells (Cerithidea obtusa) and its application to sorption of cadmium ion has been researched. The Chi-TPP was synthesized using gelation methods by addition tripolyphospate 0,1%. The chitosan was prepared by deacetylation from chitin and this was isolated from Clam Shells (Cerithidea obtusa). The Chi-TPP was characterized using Fourier Transform Infra-Red (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). FTIR characterization was indicated the appearance peak of a N-H vibration at 1635 cm^{-1}, functional group of NH_3^+ deformation at 1534 cm^{-1}, streching vibration of a –C-O- at 1072 cm^{-1} and vibration of P-O at 1026,91 cm^{-1} was indicated the presence of TPP. XRD pattern of Chi-TPP showed broad diffraction peaks at 2Ɵ values of 19.85º, which are thypical fingerprints of Chi-TPP. The lower intensity of Chi-TPP was revealed that its was amorphous. SEM image of Chi—TPP showed cross-linker TPP on chi and stabilizes them. The sorption application of cadmiun ions on Chi-TPP was optimum at pH 4 ie 29.12 mg/g.

Keywords: *chitosan-tripolyphosphate, Clam Shells, cadmium ion*

Introduction

Clam shells (*Cerithidea obtusa)* is clam-spesies from Potamididae familiy and existing is very abundant in beach of Pondong Village, Paser Regency, East Kalimantan. The shells as a waste and unutilized. The utilization of shells waste is processed into chitin and chitosan product. Chitin is poly (β-(1→4)-*N*-acetyl-D-glucosamine from the shell of clam, crab and shrimp. Chitin is collected by deproteinization and demineralization of crustaceans' wastes. The deacetylated form of chitin is chitosan. The result of dyacetilation produces many functional group of amine ($-NH_2$) dan hydroxil (-OH) (Dutta, *et al.*, 2004). Compared with chitin, chitosan have higher solubility, lower crystallinity, degree of deacytilation, particle size, formation of particle and agregation (Tiyaaboonchai, 2003).

Application of chitosan exhibits the promising to removing of organic ang inorganic polutant like dyes, phenol and heavy metal (Bhatnagar *et al.*, 2009], Pb dan Pt (Kondo, *et al.*, 2015), Fe(II) and Mn(II) (Ali *et al.*, 2018). The removing capacity is due to the presence of functional group that can form to coordination bonds (Kondo, *et al.*, 2015). The properties of chitosan exhibits biodegradle, non-toxic, biocompatible and can be resized in nano-size. Modification of chitosan into chitosan nanoparticle with a crosslinker can expands its usefulness as drug delivery (Kavaz, 2010). organ transplants and restoring organ function (Kumar and Koh 2012) and efficient sorption of heavy metal (Holban *et al.*, 2016).

Synthesis of chitosan nanoparticle have five methods are presently available are ionic gelation method, microemulsion, emulsifcation solvent diffusion, polyelectrolyte complex and reverse micellarmethod (Tiyaboonchai, 2003). The most widely used method is ionic gelation method. This method utilizes the electrostatic interaction between the amine group of chitosan and a negatively charged group of polyanion such as tripolyphosphate (TPP) (Bhumkar and Pokharkar, 2006). The TPP is a type of harmless anionic crosslinker and can interact by inter- and intramolecular with chitosan to provide better spherical morphology, increase the fexibility of the polymer increase its stability (Koiparambil and Shanavas, 2017).

In this work, isolation of chitin from Clam shells (*Cerithidea obtusa,) and tranformed into chi. , chitosan-TPP* was prepared using gelation method and characterized by functional group using FT-IR, crystal structure using XRD, and morphological surface using SEM. The effect of pH to application sorption on Chi-TPP.

Materials and Methods

Materials

Clam Shells (*Cerithidea obtusa)* was collected from beach Pondong Paser, Analytical grade NaOH, HCl, tripolyphosphate (TPP), CH_3COOH 25% and Cadmium.

Preparation of chitin and chitosan

Chitin from Clam Shells (*Cerithidea obtusa)* was prepared by a demineralization and deproteination. The product was transformed into chitosan by deacetylation process. The resulting of chitosan was separated, washed with distilled water to neutral pH.

Synthesis of Chi-TPP

Five grams of chi were dissolved into 25 mL CH_3COOH 1% and then 5 mL croslinker of tripolyphosphate (TPP) was added into chi solution. The mixture was shaked by magnetic stirer for 1 hour to homogeneous. After the completion of the reaction, the product of Chi-TPP was washed by deionized water to neutral.

Characterization.

The functional group of Chi-TPP was analyzed by Shimadzu 8201 PC Fourier transform spectrometer (FTIR). The crystal structure were characterized by Shimadzu X-ray diffraction (XRD) using CuKα radiation (λ = 1.5406 Å) operated at 40 kV and 30 mA). Morphological surface was examined by JEOL SSM-6510 LA Scanning electron microscopy (SEM)

The sorption of cadmium ion on Chi-TPP.

Sorption application of optimum pH was carried out by a batch adsorption method. A series of 50 mg.L^{-1} cadmium ion were adjusted to pH 2; 3; 4; 5; 6; 7; 8; 9; 10; 11 by adding HCl or NaOH solutions. Interaction of cadmium solution on 20 mg of Chi-TPP by shaking for 120 minutes. After adsorbent was separated, concentration of cadmium was analyzed using AAS.

Results and Discussion

Calm shells (*Cerithidea obtusa*) were obtained from beach of Pondong Village, Paser, East Kalimantan. The size of shell is 5 cm, blackish brown color and existing is very abundant and unutilized. Isolation of chitin from Calm shells (*Cerithidea obtusa*) by a demineralization and deproteination and then was transformed into Chi by deacetylation. The Chi-TPP was synthisized by gelation method that is the complexation of Chi with TPP as a crosslinker. The form physical of Chi and Chi-TPP were the same, but coloring of Chi-TPP is more white and easily to dissolve in acetate acid solution. The form physical of Chi and Chi-TPP are shown in Fig.1.

Figure 1. material of a) Chi and b) Chi-TPP

Material of Chi-TPP was successfully complexed by the gelation method which was indicated change in the characteristics of the FTIR, XRD and SEM analysis. The FT-IR spectra of chitin, Chi, Chi-TPP are shown in Fig.2.

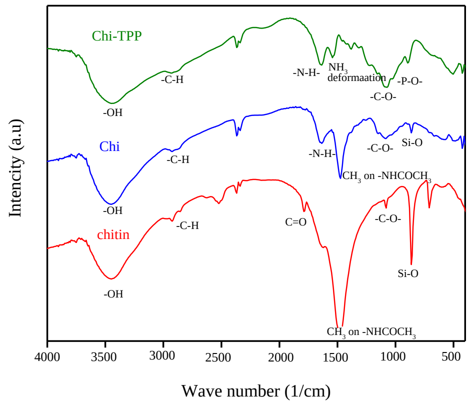

Figure 2.. FTIR Spectra of chitin, Chi and Chi-TPP

The functional group of chitin has a wavenumber at 3425 cm^{-1} due to the -OH groups. The -CH_2 group was showing at 2924 cm^{-1} as attributed to the symmetrical stretching, the band at 1473 cm^{-1} was -CH_3 group on amide (-$NHCOCH_3$), wave number at 1798 cm^{-1} due to the C=O group on amide (-NHCO) and then at 1080 cm^{-1} the stretching vibration of C-O-C in glucose circle. The impurities spectra of silica mineral on chitin at wave numbers 864, 11 cm^{-1} and 709,80 cm^{-1}. (Silverstein *et al.*, 1981).

The FTIR spectra of Chi has similar to a chitin, this has a wavenumber at 3448 cm^{-1} due to the -OH groups, -CH_2 group at 2931 cm^{-1}, stretching vibration of C-O-C at 1087 cm^{-1}, CH_3 group on amide (-$NHCOCH_3$) at 1473 cm^{-1}, wave number at 1798 cm^{-1} due to the C=O group on amide (-NHCO). (Silverstein dkk, 1981) and then presence of silica mineral at wave number 864 cm^{-1}. The difference FTIR spectra of chitin and Chi was loss of C=O group of amida (-NHCO-) ((Silverstein *et al.*, 1981).

Characteristic FTIR spectra of Chi-TPP has peak at 1534 cm^{-1} was assigned to deformation of -NH, the band at 1651 cm^{-1} was bending vibration of N-H group from amine ($-NH_2$) (11) and vibration of P-O on TPP at 1026 cm^{-1}. The loss FTIR spectra of Chi-TPP were C=O group, CH3 group on amide ($-NHCOCH_3$) and impurities of silica mineral. (Silverstein *et al.*, 1981). The XRD pattern of Calm shells, Chi and Chi-TPP are shown in Fig.3.

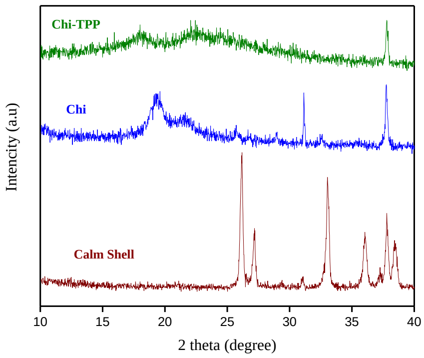

Figure 3.. XRD pattern of Clam shells, Chi and Chi-TPP (magnification 10.000x)

The difraction of Calm Shell has crystalline structure because there are still many minerals. XRD pattern of Chi has two characteristic peaks at 10,15^o and 19,94^o but still has impurities in peaks at 32o and 38^o. The characteristic XRD pattern of Chi-TPP has a broad at 19,85^o and 23.50^o. (Bhumkar dan Pokharkar, 2006). Difraction of Chi is crystallite structure, Cross-linking of TPP on Chi where these two peaks disappeared in XRD pattern of Chi-TPP, which indiates amorphous shape.

SEM image of Chi and Chi-TPP are shown in Figure 4. The morphological surface of Chi has rigid colloid-shaped and then SEM image of Chi—TPP showed threads-shaped of cross-linker TPP on chi-surface and stabilizes them.

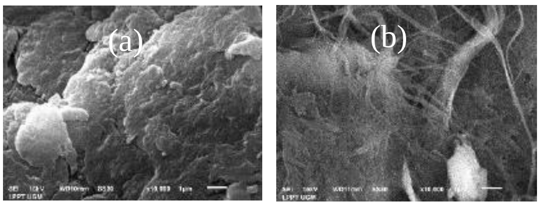

Figure 4.. SEM image of Chi and Chi-TPP

Determination of the optimum pH was carried out to determine the optimum pH conditions to adsorb cadmium ion using Chi-TPP. The effect of pH adsorption of cadmium ion on Chi-TPP are shown in Fig.5

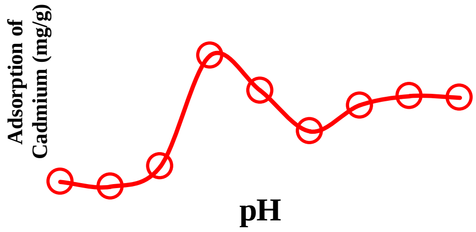

Figure 5.. The Effect of pH adsorption of cadmium ion on Chi-TPP

Based in Figure 5, pH range experiment was varied from 1.0-9.0. At low pH, ion H^+ has high concentration and compete with Cd ion for sorption. Hovever, if pH solutions was increased, the sorption of Cd was increased because concentration of ion H^+ due to decreased. Optimum pH for sorption of Cd ion on Chi-TPP at pH 4.0 Increasing the pH futher was resulted in a decreased for sorption until at pH 7. At pH 8 -9, the sorption of cadmium ion was increased because cd ion has was started to precipitate (Seyedi *et al.*, 2013)

Conclusions

The succesfull isolation of chitin from Clam Shells (*Cerithidea obtusa)* and synthesis of Chi-TPP from chitin. XRD pattern of Chi-TPP has characteristic peak is amorphous shape. SEM image of Chi-TPP is rigid-colloid with cross-linking of TPP. Optimum pH Adsorption of cadmium ion on Chi-TPP at pH 4.

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