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CHITOSAN CROSSLINKING FROM CLAM SHELLS (*Cerithidea obtusa)* WITH TRIPOLYPHOSPHATE FOR CADMIUM (II) ADSORPTION

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ABSTRACT

The study investigates chitosan crosslinking from clam shells (*Cerithidea obtusa*) with tripolyphosphate for cadmium (II) adsorption. Chitosan was prepared by deacetylating chitin using 60% NaOH and heating at 140°C for 60 minutes. Chitin was isolated from *Cerithidea obtusa* shells, an abundant waste in East Kalimantan. Crosslinking of chitosan with tripolyphosphate was synthesized via gelation methods, dissolving 5 g of chitosan in acetic acid and adding 0.1% tripolyphosphate as a crosslinker. The chitosan-tripolyphosphate characterisation was conducted using FTIR, XRD, and SEM. FTIR spectra revealed an N-H vibration at 1635 cm^{-1}, NH_3^+ deformation at 1534 cm^{-1}, C-O stretching at 1072 cm^{-1}, and P-O vibration at 1026.91 cm^{-1}, indicating the presence of tripolyphosphate in chitosan. The XRD pattern showed broad peaks at 19.85° and 23.50°, characteristic of amorphous chitosan-tripolyphosphate. SEM images depicted a flat sheet without pores and a tight surface. Cadmium (II) adsorption on chitosan-tripolyphosphate at an optimum pH of 4 followed a pseudo-second-order kinetic model. It adhered to the Langmuir isotherm model, with a maximum adsorption capacity of 27.8 mg/g. The results demonstrate that chitosan crosslinked with tripolyphosphate effectively for cadmium (II) adsorption.

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INTRODUCTION

Clam shells (*Cerithidea obtusa*) are a species from the Potamididae family and are abundantly found on the beaches of Pondong Village, Paser Regency, East Kalimantan. According to data from the Ministry of Maritime Affairs and Fisheries, the eight fish landing bases in East Kalimantan manage an average of 70 tons of shellfish daily. Shellfish production in East Kalimantan experienced a significant increase from 642.93 tons in 2020 to 647.57 tons in 2022 [1]. Local communities use clams as food but have yet to utilize the shells for other useful products, accumulating shell waste. The uncontrolled presence of clamshell waste on beaches leads to piles of shells, making the environment increasingly dirty and producing a foul odor due to the decomposition of remaining tissue attached to the shells [2]. Traditionally, people have used shells as decorative ornaments. However, this practice depends on market demand and is not the industry's primary focus [3]. Handling shell waste requires substantial operational and financial resources. The distance and transportation costs pose obstacles to storing shell waste. Decomposition of the shell requires high temperatures exceeding 1000°C, leading to high energy consumption due to the dominant CaCO3_33 content [4, 5]. One way to process shell waste is by converting shells into chitosan. Utilising shell waste to produce chitin and chitosan products has significant economic potential. For example, in collaboration with PT, Salona Selambai shell waste was utilized to make liquid chitosan in Bontang, East Kalimantan. Pupuk Kaltim [6]. This approach can also be developed in other areas of East Kalimantan, especially in the Paser area.

Chitin is a poly(β-(1→4)-N-acetyl-D-glucosamine) found in clams, crabs, and shrimp shells. Chitin is obtained by deproteinisation and demineralization of crustacean wastes. The deacetylated form of chitin is chitosan, which features many functional groups of amine (-NH2_22) and hydroxyl (-OH) [7, 8]. Compared to chitin, chitosan has higher solubility, lower crystallinity, a degree of deacetylation, particle size, and a propensity for particle formation and aggregation [9]. The application of chitosan is promising for the removal of inorganic heavy metal pollutants, such as Pb and Pt [11], Fe(II) and Mn(II) [12]. The removal capacity is due to the presence of functional groups that can form coordination bonds [10]. Chitosan also removes organic pollutants like dyes [13] and organic solutions [14]. Chitosan exhibits biodegradability, non-toxicity, and biocompatibility and can be resized to nano dimensions.

Five methods for synthesizing chitosan are currently available: ionic gelation, microemulsion, emulsification solvent diffusion, polyelectrolyte complex, and reverse micellar method [9]. The most widely used method is ionic gelation. This method is simple, requires inexpensive materials and equipment, and can be easily performed in a typical laboratory. Ionic gelation utilises the electrostatic interaction between the amine group of chitosan and a negatively charged group of a polyanion, such as tripolyphosphate [15]. Tripolyphosphate is a harmless anionic crosslinker that interacts inter- and intramolecularly with chitosan, providing better spherical morphology, increased polymer flexibility, and a stable bead structure [16]. A weight ratio of 0.5:0.25 between chitosan and tripolyphosphate results in smaller particle sizes [17]. Modification of chitosan crosslinking with tripolyphosphate enhances its usefulness in drug delivery [18], organ transplants and restoring organ function [19], and efficient sorption of heavy metals [20].

This work isolated chitin from clam shells (*Cerithidea obtusa*) and deacetylated by adding 60% NaOH and heating at 140°C for 60 minutes to process chitosan from chitin. Crosslinking chitosan with tripolyphosphate was prepared using the gelation method and characterized by functional groups using an FT-IR spectrometer, crystal structure using an X-ray diffractometer, and surface morphology using a scanning electron microscope. The effects of pH, kinetics model, and adsorption capacity of cadmium on chitosan-tripolyphosphate were also evaluated. This research aims to expand the application of chitosan in removing heavy metal cadmium (II). The application of chitosan for the adsorption of heavy metals reported in previous studies serves as a comparison for this research [21].

METHODS

1. Material Preparation

Clamshells (*Cerithidea obtuse*) were collected from Pondong Beach, Paser Regency, East Kalimantan, on Tuesday, March 10, 2020, under sunny weather conditions. The shells were washed with distilled water and air-dried indoors. Analytical grade reagents, such as sodium hydroxide and hydrochloric acid (37%), were used for chitin and chitosan preparation.

2. Chitin Extraction

Chitin was extracted from clam shells (*Cerithidea obtusa*) by demineralisation and deproteinisation. Initially, clam shells were ground into a fine powder using a mortar and pestle and sieved to 100 mesh. In the demineralization stage, 50 g of fine clam shell powder was added to 750 mL of 1 N hydrochloric acid solution and heated at 75°C for 60 minutes. During the deproteinization stage, 30.3 g of extract was added to 300 mL of 3.5% sodium hydroxide solution, heated at 85°C for 30 minutes, and then cooled to room temperature. The chitin was then transformed into chitosan by the deacetylation process.

3. Chitosan Synthesis

Chitosan was prepared by deacetylating 18 g of chitin with 360 mL of 60% sodium hydroxide solution, heating at 140°C for 60 minutes. The resulting chitosan was separated and washed with distilled water until a neutral pH was achieved.

4. Crosslinking of chitosan with tripolyphosphate

Five grams of chitosan were dissolved in 25 mL of 1% acetic acid solution. Then, 5 mL of 0.1% sodium tripolyphosphate solution was added to the chitosan solution. The mixture was stirred with a magnetic stirrer for 60 minutes until homogeneous. The chitosan-tripolyphosphate product was washed with deionized water until neutral.

5. Characterization Technique

The characterisation of chitosan-tripolyphosphate was performed using several analytical techniques. The functional groups of chitosan-tripolyphosphate were analyzed using a Shimadzu 8201 PC Fourier Transform Infrared (FTIR) spectrometer at wave numbers ranging from 500 to 4000 cm^{-1}. The crystal structure was characterized using a Shimadzu X-ray Diffractometer (XRD) with CuKα radiation (λ = 1.5406 Å), operated at 40 kV and 30 mA, and measured at 2θ angles ranging from 10 to 40 degrees. The surface morphology was examined using a JEOL SSM-6510 LA Scanning Electron Microscope (SEM).

6. Adsorption Study

The adsorption of cadmium on chitosan-tripolyphosphate was conducted using a batch method. A series of 50 mg/L cadmium (II) solutions were adjusted to pH levels of 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 by adding hydrochloric acid or sodium hydroxide solutions. A 20 mg sample of chitosan-tripolyphosphate was added to the cadmium (II) solutions and shaken for 120 minutes. After separation, the cadmium (II) concentration was analyzed using a Perkin Elmer Atomic Absorption Spectrometer. The adsorption kinetics were measured with an initial cadmium (II) concentration of 70 mg/L, adding 20 mg of chitosan-tripolyphosphate, with interaction times of 1, 2, 5, 10, 15, 30, 50, 100, 150, 200, 250, and 300 minutes.

7. Kinetic and Isotherm Model Analysis

The kinetics models of Lagergren’s pseudo-first-order and Ho’s pseudo-second-order were used to analyse the adsorption kinetics. The adsorption capacity was measured using the batch method with initial cadmium (II) concentrations of 1, 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg/L, adding 20 mg of chitosan-tripolyphosphate. Langmuir and Freundlich's isotherm models were used to analyse the adsorption capacity.

RESULTS AND DISCUSSION

1. Characterization of Chitosan-based Adsorbents

Clam shells (*Cerithidea obtusa*) were obtained from the beach of Pondong, Paser Regency, East Kalimantan. Clamshell waste affects the ecological and biological environment, resulting in dirtier surroundings and foul odors due to the decomposition of remaining tissue attached to the shells [2]. The clam shells used were approximately 5 cm in size, blackish-brown in colour, and abundantly available but unutilised. The clam shells were initially ground until smooth and sieved to 100 mesh. During the demineralization stage, the fine clam shell powder was added to a hydrochloric acid solution and heated at 75°C for 60 minutes. The purpose of this demineralisation is to remove minerals, specifically calcium carbonate, from the clam shells, as per the following reaction [22]:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

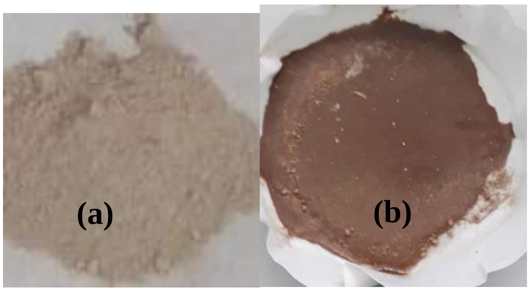

Figure 1. The physical form of a) Clamshells and b) Chitin

In the deproteinisation stage, the extract was added to a sodium hydroxide solution and heated at 85°C for 30 minutes. This stage aims to reduce the protein content in the clam shells by forming sodium proteinate and heating it to 85°C [22]. The transformation process of clam shells into chitin is marked by a physical change in the colour of the materials and the appearance of functional groups characteristic of chitin. FT-IR analysis revealed a wavenumber at 3425 cm^{-1} due to -OH groups, a symmetrical stretching of the -CH$_2$ group at 2924 cm^{-1}, a

$-CH_3$ group on amide ($-NHCOCH_3$) at 1473 cm^{-1}, C=O groups on amide (-NHCO) at 1798 cm^{-1} and 1627 cm^{-1}, a stretching vibration of C-O-C in the glucose ring at 1080 cm^{-1}, and impurities spectra of silica minerals at 864.11 cm^{-1} and 709.80 cm^{-1} [23], [24]. The physical forms of clam shells and chitin are shown in Fig. 1, and the FT-IR spectra of chitin are shown in Fig. 2.

Changing chitin into chitosan involves deacetylation by treating it with sodium hydroxide and heating it at 140°C for 60 minutes. The –OH group in sodium hydroxide can attack the acetyl group ($COCH_3$), particularly the carbon atom attached to C=O, releasing the acetyl group from chitin [22]. The changes in functional groups from chitin to chitosan are characterized by the appearance of C=O at 1635 cm^{-1} and a decrease in intensity of the $-CH_3$ group on amide ($-NHCOCH_3$) at 1473 cm^{-1} and silica mineral impurities at a wavenumber of 864 cm^{-1} [23], [24]. The FT-IR spectra of chitosan are shown in Fig. 2. The degree of deacetylation was measured using the FTIR method to identify hydroxyl and amide functional groups in chitosan, which play a crucial role in floc formation. In this study, the degree of deacetylation of chitosan from clam shells (*Cerithidea obtusa*) was 70.8%. Compared to other studies, the degree of deacetylation of chitosan from clam shells and crab shells has been reported to be 77.80% and 87.64% [25], or 72.85% for shrimp shells [22]. These values align with the Biochitosan Indonesia standard, which requires a degree of deacetylation above 70% [22]. A higher degree of deacetylation indicates a more significant loss of acetyl groups [25].

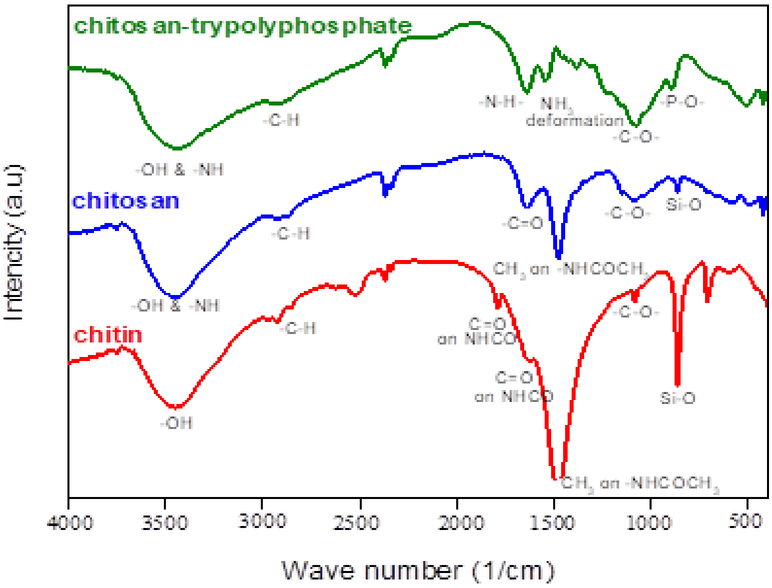

Figure 2. *FTIR Spectra of chitin, chitosan and chitosan-tripolyphosphate*

The chitosan-tripolyphosphate was synthesised using the gelation method, which involves the complexation of chitosan with tripolyphosphate as a crosslinker at a weight ratio of 2:1. Tripolyphosphate is preferred as a crosslinker because it avoids the use of toxic substances like glutaraldehyde or genipin. Tripolyphosphate is also commonly used as a crosslinker for scaffolds [26], microparticles [27], beads [28], and composite systems in biomedicine [29]. Phosphate groups are important for bone mineralization, and the degree of cross-linking can significantly influence the scaffold's homogeneity, porosity, hydrophilicity, and mechanical properties [26]. Another advantage of tripolyphosphate compared to sodium hydroxide is that it forms a more rigid structure due to the reaction of the amine group in chitosan with $P_3O_{10}^{5-}$, resulting in a faster and more stable reaction [30]. In this study, cross-linking between chitosan and tripolyphosphate was conducted under acidic pH conditions, where the $–NH_2$ group on chitosan is protonated to $-NH_3^+$, leading to cross-linking interactions between $-NH_3^+$ in chitosan and tripolyphosphate ions, resulting in a denser structure [31]. The cross-linking process under acidic conditions forms a chitosan-tripolyphosphate ladder, as shown in Fig. 3.

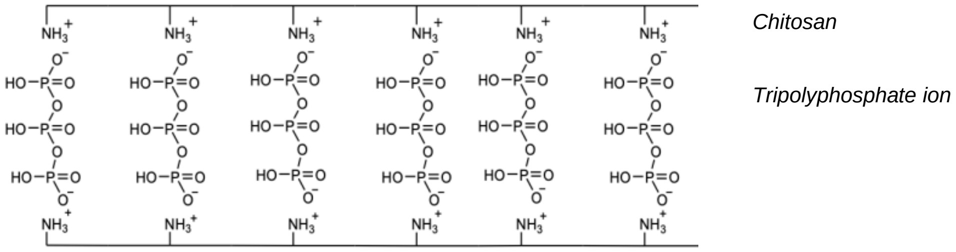

Figure 3. The form of the chitosan-tripolyphosphate ladder under acidic conditions

Table 1. The functional group of chitin, chitosan, and chitosan-tripolyphosphate

Functional group	**Wave number (cm^{-1})**		
	chitin	**Chitosan**	**chitosan-tripolyphosphate**
O-H streching	3425	3448	3448
C-H Stretching	2924, 2854	2931	2924
CH_3 on $NHCCCH_3$	1473	1473	-
C=O	1798 & 1627	1635	-
N-H bending	-	-	1630
Deformation NH_3^+	-	-	1534
C-O	1080	1087	1072
P-O	-	-	1026
Si-O	864	864	-

The adsorbent of chitosan-tripolyphosphate was successfully synthesized, as indicated by a change in the peak at 1534 cm^{-1}, attributed to the deformation of -NH, a band at 1651 cm^{-1} corresponding to the bending vibration of the N-H group from amine ($-NH_2$), and the vibration of P-O on tripolyphosphate at 1026 cm^{-1} [26]. The FTIR spectra of chitosan-tripolyphosphate showed the absence of the C=O group, the CH_3 group on amide ($-NHCOCH_3$), and silica mineral impurities [23], [24]. The physical appearance and color of chitosan and chitosan-tripolyphosphate are not significantly different. The FT-IR spectra of chitosan-tripolyphosphate are shown in

Fig. 2, and the physical forms of chitosan and chitosan-tripolyphosphate are shown in Fig. 4.

Figure 4. The form physical of a) chitosan and b) chitosan-tripolyphosphate

2. Analysis of Structural and Morphological Chitosan-based Adsorbents

The X-ray diffraction (XRD) analysis of clam shells revealed a crystalline structure indicative of the presence of various minerals. The XRD pattern of chitosan displayed two characteristic peaks at 10.15° and 19.94°, along with impurity peaks at 32° and 38°. In contrast, the XRD pattern of chitosan-tripolyphosphate exhibited broad peaks at 19.85° and 23.50°, signifying an amorphous form [11]. The crosslinking of chitosan with tripolyphosphate resulted in a structural transformation from crystalline to amorphous, attributed to a dense network structure formation. This decrease in crystallinity is due to the interpenetration of tripolyphosphate counter ions, where the polymer chains are cross-linked, forming a more compact structure [12]. The XRD patterns of clam shells, chitosan, and chitosan-tripolyphosphate are shown in Fig. 5.

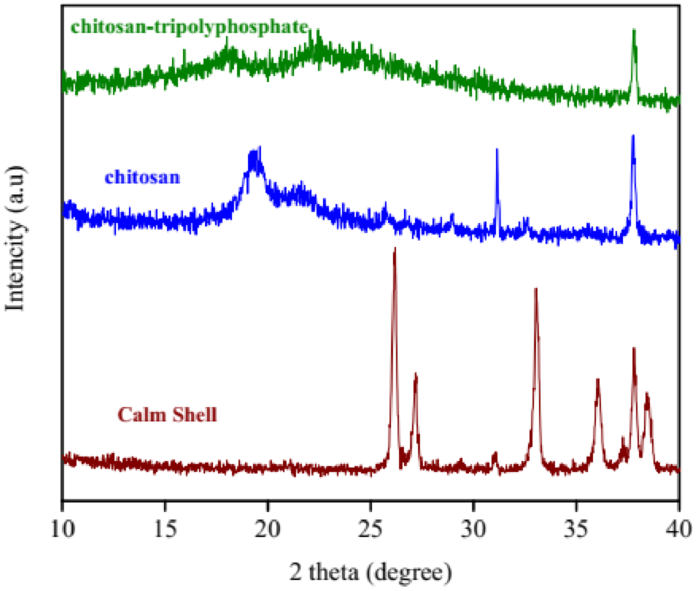

Figure 5. XRD pattern of Clam shells, chitosan and chitosan-tripolyphosphate

Scanning Electron Microscopy (SEM) images of chitosan and chitosan-tripolyphosphate are presented in Fig. 6. The surface morphology of chitosan appeared flat and dense, without pores [32]. In contrast, the SEM image of chitosan-tripolyphosphate displayed a thread-like structure on a thick surface. This change in surface morphology is due to the addition of the crosslinker, which enhances the strength and stability of chitosan [32].

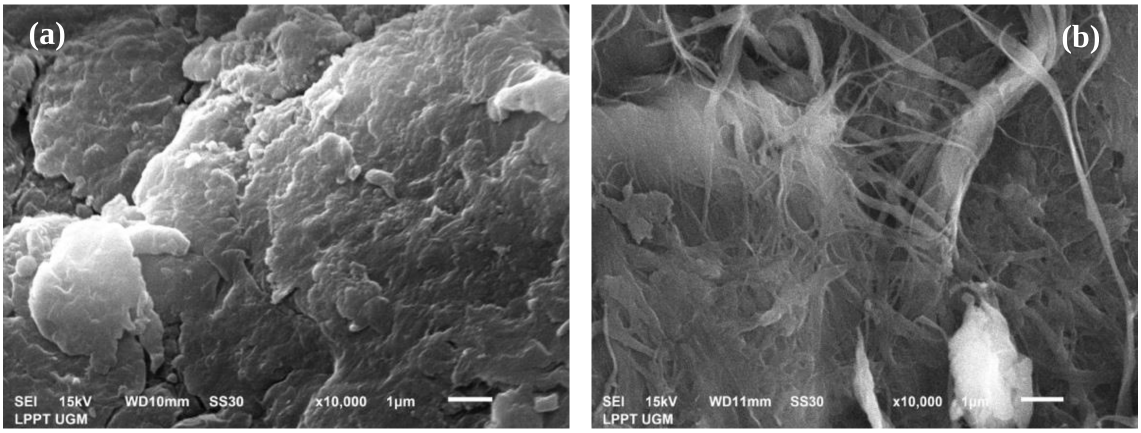

Figure 6. SEM image of a) chitosan and b) chitosan-tripolyphosphate

3. Adsorption Behavior and Mechanistic of cadmium (II) on chitosan-tripolyphosphate

The effect of pH on cadmium (II) adsorption on chitosan-tripolyphosphate was investigated over a pH range of 1.0 to 9.0. At low pH values (pH 1.0-2.0), the amine and tripolyphosphate groups in chitosan are protonated, resulting in competition between the high concentration of H^+ ions and cadmium (II) ions for adsorption sites. However, as the pH increases to 3.0, cadmium (II) sorption increases due to a decrease in H^+ ion concentration. The optimum pH for cadmium (II) ion adsorption on chitosan-tripolyphosphate was pH 4.0. Further increases in pH (pH 5.0-7.0) decreased sorption until pH 7.0. This behavior is attributed to the pKa of chitosan, which is 6.5. Below this pH, chitosan is protonated, enhancing cation adsorption. Excess H^+ ions compete with cadmium (II) cations at low pH. In contrast, at pH values above 4, the reduced protonation of chitosan surpasses the decrease in competitive adsorption of hydrogen ions. At pH 8-9, the sorption of cadmium (II) ions increased again as cadmium (II) ions began to precipitate. The effect of pH on cadmium (II) adsorption on chitosan-tripolyphosphate is shown in Fig. 7.

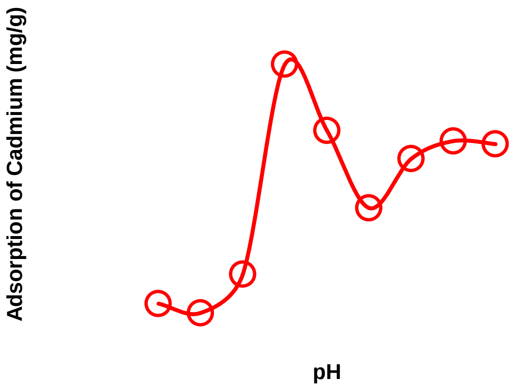

Figure 7. The effect of pH adsorption of cadmium (II) on chitosan-tripolyphosphate

The adsorption kinetics of cadmium (II) on chitosan-tripolyphosphate were analyzed using Lagergren's pseudo-first-order and Ho's pseudo-second-order models. The results indicated that cadmium (II) adsorption on chitosan-tripolyphosphate fits better with the pseudo-second-order model than the pseudo-first-order model. The excellent linearity (R^2) for the pseudo-second-order model was 0.996, with a rate constant of 0.01 g mg^{-1} min^{-1}. This finding aligns with previous research, which also reported that cadmium adsorption on chitosan and nano chitosan is more compatible with the pseudo-second-order model [33]. The pseudo-second-order kinetic model suggests that the rate-limiting step involves chemisorption, where valence forces exchange electrons between the adsorbent and adsorbate [32]. In contrast, other studies have shown that the adsorption of methyl orange on cross-linked chitosan with TPP fits better with the pseudo-first-order model, indicating a physical adsorption mechanism controlled by the rigidity of the cross-linked chitosan [34]. The kinetic models for cadmium (II) adsorption on chitosan-tripolyphosphate are shown in Fig. 8, and the kinetic parameters for both pseudo-first-order and pseudo-second-order models are presented in Table 2.

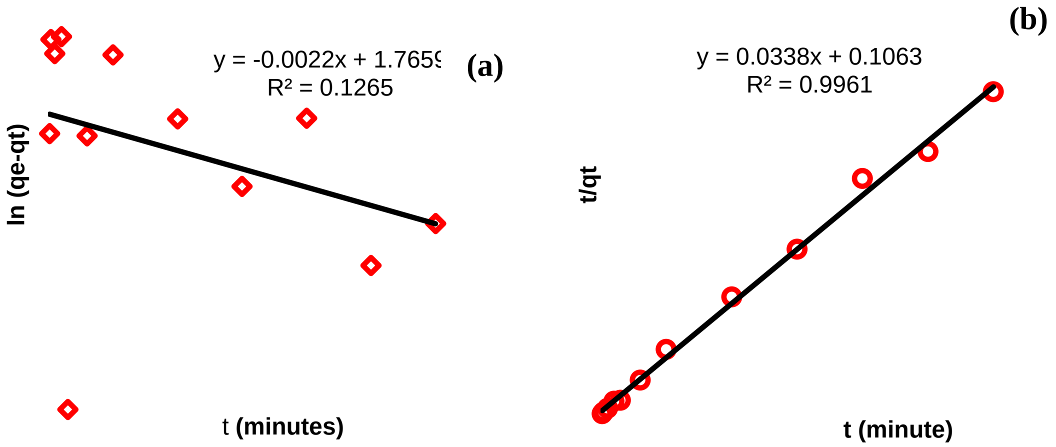

Figure 8. The plot of kinetics model for adsorption of cadmium (II) on chitosan-tripolyphosphate (a) Lagergren's pseudo-first-order, (b) Ho's pseudo-second-order

Table 2. Kinetic parameters of Lagergreen's pseudo-first-order and Ho's pseudo-second-order model for adsorption of cadmium (II) on chitosan-tripolyphosphate

Adsorbent	**Lagergreen's pseudo-first-order**			**Ho's pseudo-second-order**		
	q_m (mg/g)	**K_1 (min^{-1})**	**R^2**	**q_m (mg/g)**	**K_2 (g/mg.min)**	**R^2**
chitosan-tripolyphosphate	5,79	0,002	0,162	30,3	0,010	0,996

The adsorption capacity was examined by equilibrating an appropriate amount of the adsorbent with excess adsorbate under optimum conditions. The adsorption capacity of chitosan-tripolyphosphate was evaluated using the Langmuir and Freundlich isotherms. The Langmuir isotherm assumes that the adsorbent surface has a single type of site, predicting the formation of a monolayer of adsorbate on the adsorbent surface. In contrast, the Freundlich isotherm describes multi-site adsorption. Based on the calculation of the Langmuir and Freundlich isotherm parameters, it was found that the correlation coefficient R^2 was higher for the Langmuir isotherm model than for the Freundlich isotherm. Similar results have been reported in the literature, indicating that cadmium adsorption on chitosan and nano chitosan fits the Langmuir model better than the Freundlich model, suggesting monolayer adsorption [33]. The isotherm models for cadmium (II) adsorption on chitosan-tripolyphosphate are shown in Fig. 9, and the isotherm parameters are presented in Table 3.

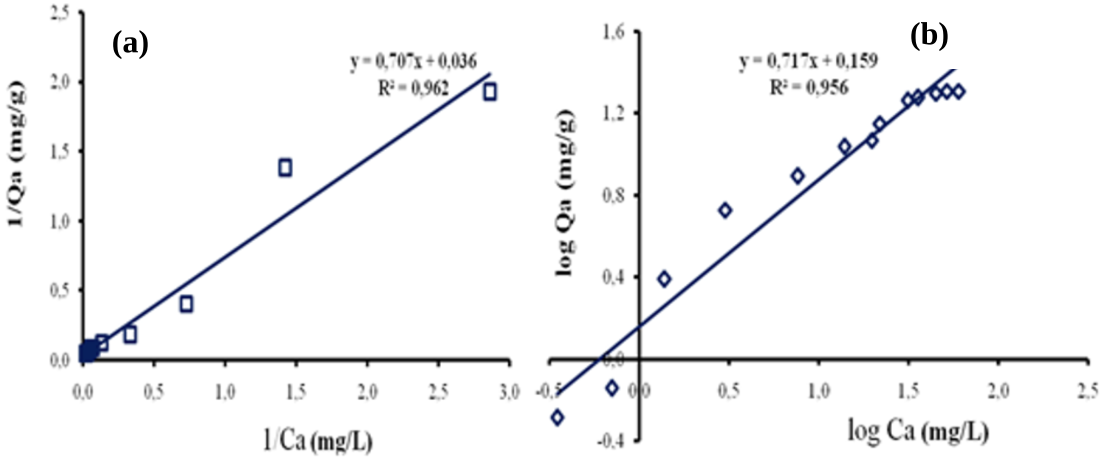

Figure 9. Plot of isotherm models for adsorption of cadmium (II) on chitosan-tripolyphosphate

Table 3. Isotherm parameters of adsorption of cadmium (II) on chitosan-tripolyphosphate by Langmuir and Freundlich

Adsorbent	Langmuir			Freundlich		
	Qm (mg/g)	K_L (L/mg)	R^2	Kf(mg/g).(mg/L)^n	n	R^2
chitosan-tripolyphosphate	27.8	0.002	0.,962	1.172	1.398	0.956

The experimental data suggest that cadmium (II) adsorption fits the Langmuir isotherm model, with an adsorption capacity of 27.8 mg/g. This indicates that adsorption occurs homogeneously through a single mechanism and forms a monolayer without interaction between the adsorbate molecules. Similar findings have been observed, where the adsorption isotherm of chitosan-tripolyphosphate for a binary solution of Cd (II) and Cu (II) followed the Langmuir isotherm, with an adsorption capacity of 87.5 mg/g. However, the presence of Cu (II) as a competitor reduced the adsorption of Cd (II) [35].

CONCLUSION

The successful isolation of chitin from clam shells (*Cerithidea obtusa*) and the synthesis of chitosan-tripolyphosphate from chitin were confirmed by characteristic functional group vibrations of N-H, C-O, and P-O. The XRD pattern exhibited broad peaks at 19.85° and 23.50°, indicating an amorphous structure. SEM images showed that chitosan-tripolyphosphate had a flat, non-porous, and dense surface. Cadmium (II) adsorption on chitosan-tripolyphosphate was optimal at pH 4. The adsorption kinetics followed a pseudo-second-order model, and the adsorption isotherm conformed to the Langmuir model with a maximum adsorption capacity of 27.8 mg/g. These results demonstrate the effectiveness of chitosan crosslinked with tripolyphosphate as an adsorbent for cadmium (II) removal. Future research should focus on producing nanosized chitosan from clamshell waste in East Kalimantan to exploit its enhanced benefits.

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