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Research Paper

# The Effect of Tripolyphosphate as a Chitosan Cross-Linker on Cadmium (II) Ion Adsorption

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## ABSTRACT

Chitosan is a biosorbent for heavy metal ions, but its adsorption performance remains unsatisfactory. Modification of chitosan is expected to address this issue. In this study, chitosan was cross-linked with tripolyphosphate (TPP) at various concentrations and applied as a Cd (II) adsorbent. The characteristics of the chitosan powder were analyzed using an FTIR spectrophotometer to determine the degree of deacetylation of chitosan. FTIR spectra were also used to determine the functional groups of chitosan and tripolyphosphate-cross-linked chitosan. Tripolyphosphate in the form of sodium tripolyphosphate was varied with chitosan in ratios of 1:0, 2:1, and 1:1. The optimum conditions were obtained at pH 5 with 12 hours of contact time for a 1:0 ratio and 3 hours for ratios of 1:1 and 2:1. The maximum adsorption capacity of chitosan crosslinked with sodium tripolyphosphate with chitosan: sodium tripolyphosphate ratios of 1:1, 2:1, and 1:0 for Cd (II) ion adsorption was 333.3, 166.67, and 28.57 mg/g, respectively. The results showed that the greater the mass of sodium tripolyphosphate, the higher the maximum adsorption capacity.

***Keywords:*** chitosan, crosslinking, tripolyphosphate, Cd adsorption

## INTRODUCTION

Heavy metal waste is non-biodegradable and pollutes the environment. Various methods to remove heavy metals include filtration, precipitation, adsorption, electrodeposition, and membrane filtration. Among these, adsorption is widely used because it is effective, inexpensive, and efficient (Minceva et al., 2007; Rahayu and Khabibi, 2016). Biopolymer adsorbents are especially attractive since they are natural, non-polluting, and effective for removing heavy metals from industrial waste (Mohanrasu et al., 2025; Shabbirahmed et al., 2025).

Chitosan is a non-toxic, biodegradable, and biocompatible biopolymer (Ikhsan et al., 2024). It has active amine ($NH_2$) and hydroxyl (OH) groups that bind heavy metal ions (Putra et al., 2014). Chitosan is obtained by deacetylating chitin from shrimp or crab shells. Highly deacetylated chitosan is more beneficial than chitin because it chelates heavy metal ions more effectively. However, highly deacetylated chitosan is also very expensive (Kaminski et al., 2008). One way to address this is to physically or chemically modify chitosan (Khabibi et al., 2022).

Several modifications to chitosan have been carried out. Khabibi at al. (2022) modified chitosan by adding citric acid as an adsorbent for Cu (II). Druzynska and Czubenko (2008) modified chitosan with sodium tripolyphosphate to adsorb Cu (II) and Zn (II). Chitosan-tripolyphosphate membranes had greater adsorption capacity for Cu (II) and Zn (II) than pure chitosan membranes.

In this study, chitosan cross-linked with tripolyphosphate was prepared and used to adsorb Cd (II) ions. The maximum adsorption capacity was determined using the Langmuir isotherm curve (Acharya et al., 2023; Alsehli et al., 2020). Adsorption capacity depends on pH, contact time, and crosslinking agent (Kong et al., 2025; Trikkaliotis et al., 2022). Optimal conditions were determined by varying pH, contact time, and sodium tripolyphosphate mass to assess their effect on chitosan's adsorption capacity for Cd (II) ions.

## MATERIALS & METHODS

### Materials and Equipment

The materials used in this study included: distilled water, $CH_3COOH$ 98% (Brataco) p.a., $3CdSO_4.8H_2O$ (Merck) p.a., HCl (Merck) p.a., chitosan (Brataco), sodium tripolyphosphate ($Na_5P_3O_{10}$) (Merck) p.a., NaOH (Merck) p.a., and Pb $(CH_3COOH)_2.3H_2O$ (Merck) p.a.

The laboratory equipment used included glassware, aluminum foil, a Shimadzu 820 IPC FTIR, litmus paper, filter paper, a Lab Tech magnetic stirrer, an oven, pH paper, a JSM 6360LA scanning electron microscope (SEM), a shaker, a PE 3310 atomic absorption spectrophotometer (AAS), and an analytical balance.

### Procedure Research

Two grams of chitosan powder were dissolved in 75 ml of 1% acetic acid in three beakers until homogeneous. Then, 0 g, 1 g, and 2 g of sodium tripolyphosphate were dissolved in 25 ml of distilled water, and the mixture was stirred with a magnetic stirrer until homogeneous. The resulting viscous solution was then added dropwise to 400 mL of ethyl acetate, and the mixture was stirred for 45 minutes at high speed. The chitosan-tripolyphosphate granules were then decanted. The resulting granules were then dried in an oven at 30°C until a constant weight was reached (Phromsopha and Baimark, 2010). The resulting chitosan-tripolyphosphate was tested using SEM and FTIR. The resulting chitosan-tripolyphosphate was used as an adsorbent for Cd (II) and Pb (II) at the optimum pH and contact time.

In each experiment, 0.15 g of adsorbent was placed in a 250 ml Erlenmeyer flask. Then, 15 ml of Cd (II) solution at concentrations of 200, 300, 400, 500, or 600 ppm was added at the adsorbent's optimum pH. The flask was then shaken at 150 rpm for the optimum contact time. After shaking, the mixture was filtered, and the filtrate was analyzed using AAS. This process was repeated for adsorbents with varying chitosan-to-sodium tripolyphosphate mass ratios.

## RESULT AND DISCUSSION

Chitosan was analyzed by FTIR to identify functional groups and to determine the degree of chitosan deacetylation using the Domsky and Robert baseline method (Serkan, 2007). The FTIR spectra of chitosan are shown in Figure 1. The degree of deacetylation of chitosan was determined to determine the percentage of acetyl groups that had been removed from the chitin structure and replaced by amine groups.

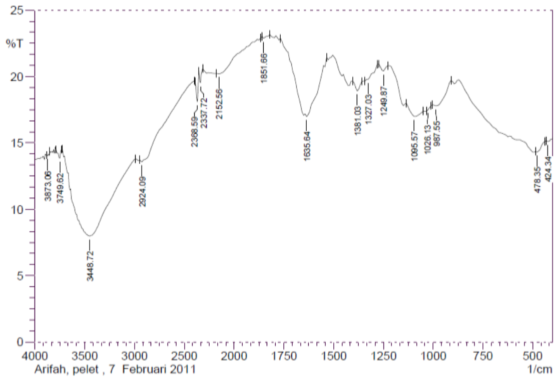


**Figure 1. Chitosan spectra**

The functional groups present in chitosan can be identified from the wavenumbers they display. The number of functional groups observed in the FTIR spectra is shown in Table 1.

**Table 1. Functional Groups in the FTIR Spectra of Chitosan**

| Wave Number(cm$^{-1}$) | Functional Groups |
|---|---|
| 3448,72 | O-H stretch dan N-H stretch |
| 2924,09; 2877,79 | C-H stretch |
| 1635,64 | C=O stretch, N-H bend |
| 1381,03; 1342,46 | C-N ulur dan OH bend |
| 1257,59; 1080,14 | C-O-C stretch |

According to Yaqin et al., (2022), the typical functional groups of chitosan are found in the peak at 3448.72, indicating the OH and N-H stretching functional groups, and the peak at 1651.07, indicating the N-H bending functional group. Based on the calculation of the degree of deacetylation using the baseline method, the degree of deacetylation was 82%.

### Preparation of Sodium Tripolyphosphate-Modified Chitosan

Chitosan with a deacetylation degree of 74% was modified using sodium tripolyphosphate. Chitosan dissolves in dilute acetic acid due to the interaction between the two, forming hydrogen bonds, which protonate the amine groups in chitosan into $NH_3^+$ groups.

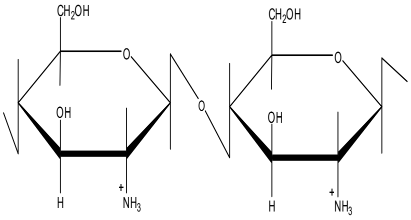


**Figure 4. Protonation of chitosan amine groups**

During chitosan dissolution in acetic acid, sodium tripolyphosphate was dissolved in distilled water and used as a crosslinking agent. According to Bhumkar and Pokharkar (2006), sodium tripolyphosphate dissociates in distilled water, forming tripolyphosphate polyanions. The process of forming chitosan-TPP granules was carried out in ethyl acetate. Stirring with a magnetic stirrer at high speed aimed to form smaller chitosan-tripolyphosphate granules to increase their surface area and, consequently, their adsorption capacity. Ethyl acetate is used in the formation of chitosan-tripolyphosphate granules because chitosan and tripolyphosphate ions have low solubility in ethyl acetate (Phromsopha and Baimark, 2010). The resulting chitosan-tripolyphosphate granules are dried in an oven at 300°C until a constant weight is reached. According to Druzynzka et al. (2008), the bond formation between chitosan and tripolyphosphate ions can be predicted as Figure 5.

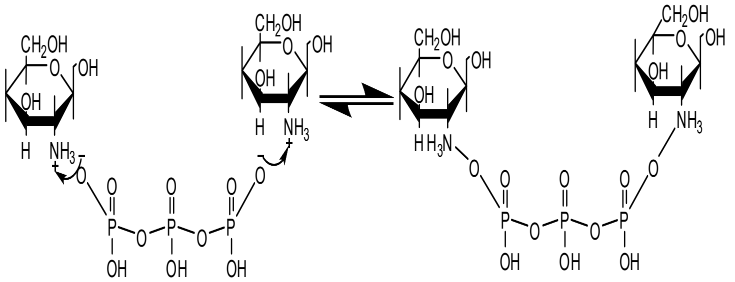


**Figure 5. Bonding of chitosan with tripolyphosphate**

The more active groups in an adsorbent, the more metal ions will be bound. Chitosan itself already has an amine group ($NH_2$), which has a lone pair of electrons on the N atom that can be donated, making the amine group in chitosan a Lewis base (Hsu et al., 2024). The presence of tripolyphosphate will add a phosphate functional group $(P_3O_{10})^{5-}$. Tripolyphosphate is a polyanion $(P_3O10)^{5-}$ that, in addition to binding to the $NH^{3+}$ group of chitosan (Phromsopha and Baimark, 2010), can also donate hydroxyl groups to attract metal ions (Druzynzka et al., 2008).

### Characterization of Chitosan-Tripolyphosphate

According to Figure 6, the FTIR spectra of chitosan-tripolyphosphate show a peak at 1558.72 cm$^{-1}$. This indicates the presence of an N-O functional group, which refers to a bond between a nitrogen atom (from the ammonium ion in chitosan) and an oxygen atom (from the tripolyphosphate ion) at the cross-linking point. The peak at 1153.34 cm$^{-1}$ corresponds to a P=O functional group, which is a phosphorus-oxygen double bond on the tripolyphosphate ion. This shows that the tripolyphosphate ion has been bound to chitosan (Bhumkar and Pokharkar, 2006).

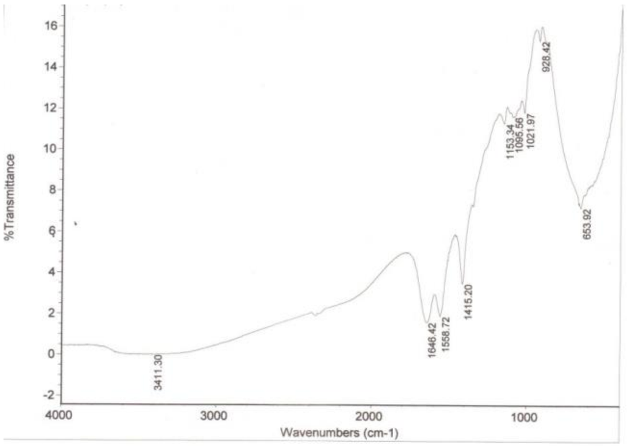


**Figure 6. FTIR Spectra of Chitosan-Tripolyphosphate**

### Application of chitosan-tripolyphosphate as a Cd (II) adsorbent

### Determination of optimum pH

The optimum pH was determined to be 2-7, with a pH interval of 1. The effect of pH on the adsorption of Cd (II) metal ions can be seen in Figure 7.

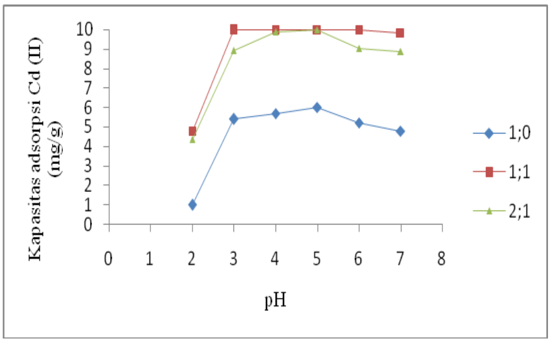


**Figure 7. Graph of Cd (II) metal ion adsorption at various pH values**

Figure 7 shows a tendency for the adsorption process to increase at pH 2-5 and decrease after pH 5. This trend can be explained by the speciation of Cd metal in the pH range 1-9, as shown in the Pourbaix diagram, indicating that the Cd metal is present as Cd (II), which allows it to bind to the chitosan-tripolyphosphate adsorbent. The ion-exchange adsorption process is influenced by the number of protons in the solution. At an acidic pH (pH 2), many H$^+$ protons can bind and cover the surface of the active NH$_2$ groups on chitosan and the hydroxyl groups on tripolyphosphate. This results in competition between Cd (II) ions and hydrogen ions for the active sites of the amine and hydroxyl groups. This results in fewer Cd (II) ions being adsorbed, thereby decreasing the efficiency of Cd (II) removal. As the solution pH increases, the number of H$^+$ ions decreases, allowing Cd (II) ions to bind to the amine and hydroxyl groups of chitosan-tripolyphosphate, thereby increasing metal adsorption.

Cd (II) ion adsorption decreases at pH values above 5 because increasing pH increases the number of OH- ions, thus strengthening the interaction between Cd (II) and OH$^-$ ions. This interaction between Cd (II) and OH$^-$ ions reduces the amount of Cd (II) bound to chitosan-tripolyphosphate. At pH values above 9, Cd (II) ions bind to hydroxide ($OH^-$) groups, forming a Cd $(OH)_2$ precipitate. In this study, the optimum pH for Cd (II) ion adsorption was 5. This is possible because at pH 5, the concentrations of $H^+$ and $OH^-$ ions in solution are not too high, allowing Cd (II) ions to bind to the sorbent in optimal amounts. The optimum adsorption of Cd (II) ions for a 1:1 chitosan:tripolyphosphate mass ratio was 9.99, 2:1 was 9.98, and 1:0 was 6.01 mg/g.

### Determination of Optimum Contact Time

Adsorption of Cd (II)] using sodium tripolyphosphate-modified chitosan was carried out over 3–15 hours at 3-hour intervals to determine the optimum contact time. The optimum time was determined at pH 5, which is considered the optimum pH. The effect of contact time on the adsorption of Cd (II) metal ions can be seen in Figure 8.

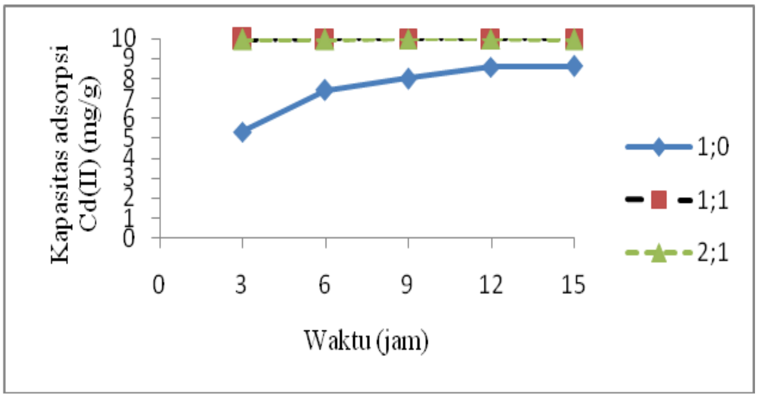


**Figure 8. Graph of Cd (II) metal ion adsorption over time variations.**

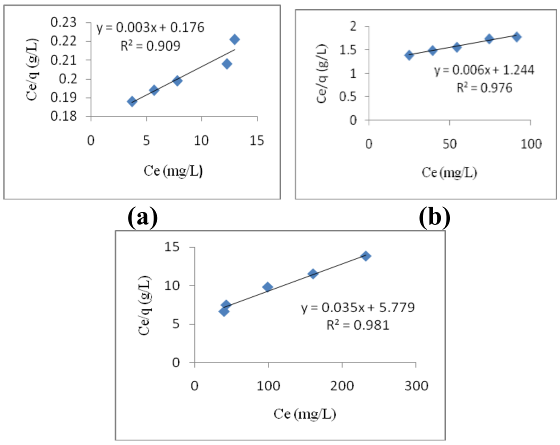
Figure 8 shows that the contact time for Cd (II) adsorption on pure chitosan increased from 3 to 12 hours, then stabilized at 12-15 hours. Meanwhile, for chitosan-tripolyphosphate, the contact time reached stability at 3 hours. At the optimum time, Cd (II) adsorption for a 1:1 chitosan:sodium tripolyphosphate mass ratio variation had an adsorption capacity of 9.998 mg/g, while at 2:1 it was 9.980 mg/g, and for chitosan without the addition of sodium tripolyphosphate, the adsorption capacity was 8.58 mg/g.

Determining the optimum contact time of Cd (II) metal ions for pure chitosan adsorbent without the addition of sodium tripolyphosphate, the contact time of 3 hours to 12 hours of adsorption increased because the active groups of the adsorbent were limited, requiring a longer time for the adsorbent and adsorbate to interact with each other. Meanwhile, for the adsorbent with the cross-linking agent sodium tripolyphosphate, the optimum contact time was 3 hours. This is because the active groups in chitosan-tripolyphosphate are more numerous than in pure chitosan, so the opportunity for metal ions to bind to these active groups is greater, causing chitosan-tripolyphosphate to reach its highest adsorption capacity within 3 hours. The longer the contact time between the adsorbent and adsorbate, the more molecules are adsorbed, until the maximum adsorption capacity is reached (Sepehran et al., 2008).

### Determining Maximum Adsorption Capacity

The adsorption of Cd (II) ions increases with the initial concentration of the metal solution, resulting in a higher adsorption capacity of sodium tripolyphosphate-modified chitosan until all active sites are saturated. This process follows the Langmuir isotherm pattern and is thought to occur in a monolayer. When the adsorbate saturates the adsorbent layer, the number of bound molecules does not exceed the number of active sites on the adsorbent surface (Ezzati et al., 2023).

Adsorption of Cd (II) ions with varying masses of sodium tripolyphosphate yields different adsorption capacities. The Cd (II) adsorption capacity graphs are presented in Figure 9.



**(a)** **(b)**

**(c)**

**Figure 9. Langmuir Cd (II) isotherm graph (a) 1:1 (b) 2:1 (c) 1:0**

Figure 9 showed that the adsorption capacity of Cd (II) metal ions on the chitosan-tripolyphosphate adsorbent with varying masses of sodium tripolyphosphate can be determined from a straight-line equation. The adsorption capacity values for Cd (II) ions at various mass ratios of chitosan and sodium tripolyphosphate of 1:1, 2:1, and 1:0 are, respectively. The mechanism of metal ion binding by sodium tripolyphosphate-modified chitosan can be inferred from Figure 10.

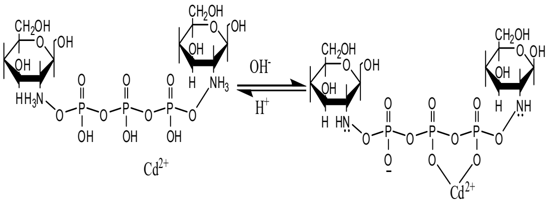


**Figure 10. Mechanism of Cd (II) adsorption reaction by tripolyphosphate-modified chitosan**

## CONCLUSION

Sodium tripolyphosphate-modified chitosan has been successfully synthesized with a mass ratio of 1:1 and 2:1. For its application as a Cd (II) adsorbent, the optimum adsorption conditions were obtained at pH 5 and a contact time of 12 hours for pure chitosan, while for chitosan-tripolyphosphate, the maximum adsorption capacity of chitosan-tripolyphosphate at ratios of 1:1, 2:1, and 1:0 for Cd(II) was 333.3, 166.7, and 28.57 mg/g, respectively. The highest adsorption capacity was achieved at a ratio of 1:1. The higher the tripolyphosphate content, the higher the capacity.

## *Declaration by Authors*

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**Conflict of Interest:** No conflicts of interest declared.

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