

# Reducing Levels of Methyl Orange Dye using Crosslinked Chitosan–Tripolyphosphate

Mardiyah Kurniasih<sup>1,\*</sup>, Anung Riapanitra<sup>1</sup>, Riyanti Riyanti<sup>2</sup>, Dwi Kartika<sup>1</sup>, Dena Rositasari<sup>1</sup>

<sup>1</sup>Chemistry Department, Faculty of Mathematics and Natural Sciences, Jenderal Soedirman University, Indonesia

<sup>2</sup>Faculty of Fisheries and Marine Science, Jenderal Soedirman University, Indonesia

\*Corresponding author: mardiyah.kurniasih@unsoed.ac.id

## ABSTRACT

Chitosan in acid was polycationic and can react with negative charges like tripolyphosphate. Tripolyphosphate was a crosslinking agent with low toxicity. This study was to review the ability of crosslinked chitosan-tripolyphosphate (Cs–TPP) in reducing the color levels of methyl orange. Synthesizing Cs–TPP was conducted by reacting chitosan solution with acid tripolyphosphate. The Cs–TPP was characterized using FTIR and determined for its molecular mass. The adsorption study of methyl orange was conducted at various pH, contact times, and the determination of adsorption isotherm. The spectra IR analysis showed that there was adsorption of –PO groups in the Cs–TPP in the area of 1026  $\text{cm}^{-1}$ . The molecular mass of Cs–TPP was  $345.24 \times 10^3 \text{ g/mol}$ . Cs–TPP optimally absorb methyl orange at pH 7 and a contact time of 120 minutes, with presence removal of 47.36%, and followed the Freundlich adsorption isotherm pattern.

**Keywords:** adsorption, chitosan, crosslinked chitosan-tripolyphosphate, methyl orange.

## 1. INTRODUCTION

Various industries will influence the economy of a society by increasing the standard of living. On the other hand, those industries can cause problems to the environment. One of the industrial wastes is dye waste. The dye waste can harm the environment because it is non-degradable, toxic, and stable [1]. Therefore, they need to be treated before their waste is disposed of. Chemical and food industries generate wastewater that contains methyl orange dye [2]. Methyl orange is an anionic [3] and carcinogenic dye [4]. Therefore, it is necessary to take serious action to remove this waste. The removal process must be simple, efficient, and cost-effective [3]. The azo dye methyl orange is an aromatic and heterocyclic compound that contains a double bond between nitrogen atoms [5]. Depending on the pH of the solution, MO chromophores appear as anthraquinones or azo compounds [4]. Figure 1 shows the structures of methyl orange.

A lot of methods have been developed to handle the dye waste; one of them is adsorption. Adsorption is one

effective method to eliminate dye from wastewater [10] and one of the best alternatives to deal with dye pollution [11].

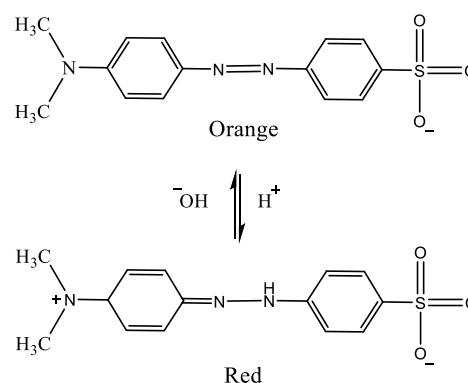


Figure 1. Structures of methyl orange

Scientists and commercial practitioners have been interested in the use of chitosan since the search for renewable materials. A linear polysaccharide chitosan is a polysaccharide with  $\beta$ -(1-4)-linked D-glucosamine and

N-acetyl-d-glucosamine randomly distributed throughout [6]. Chitosan is the product of chitin deacetylation [7]. Chitosan's amino group protonates in acidic to neutral solutions, causing the polymer to be water-soluble at these pH levels [6]. Chitosan nanoparticles can be created by using crosslink with tripolyphosphate to produce crosslinked chitosan-tripolyphosphate (Cs-TPP) [8]. An increased amount of crosslinking agent will change the strength of the crosslink when TPP and chitosan ion interact electrostatically [9].

The chitosan-based adsorbent has a high capacity of adsorption towards many dyes. Chitosan powder and chitosan beads can adsorb rhodamine B, each is at 0.655 mg/g and 0.603 mg/g [12]. Adsorption using chitosan can adsorb tartrazine as many as 4.22 mg/g [11]. Cs-TPP can reduce congo red dye by as much as 87.20% and methylene blue as much as 81.90% [10]. It has been previously reported that Cs-TPP can reduce the levels of heavy metals Ni(II) [8], so it is possible to use Cs-TPP to reduce the levels of dyes, especially methyl orange. Based on the description above, it is necessary to research to determine the ability of Cs-TPP to reduce methyl orange levels. Effects of pH, contact time, and the determination of adsorption isotherm were reviewed in this study.

## 2. METHODOLOGY

### 2.1. Materials and instruments

The materials used in this study were chitosan (purchase from CV Chemix Pratama, DD 77.03%)  $\text{Na}_5\text{P}_3\text{O}_{10}$  (Merck), methyl orange (Merck),  $\text{CH}_3\text{COOH}$  (Merck), and  $\text{AgNO}_3$  (Merck). The instruments used were Fourier Transform Infra-Red Spectrophotometer (FTIR) Shimadzu 8201 and Spectrophotometer Ultraviolet-visible (UV-visible) Shimadzu 1240.

### 2.2. Synthesis of Cs-TPP

A 2% chitosan solution was added with 10% TPP in pH 3 with a 3:1 ratio. The mix was then stirred for 15 minutes. The deposit was then strained and washed using distilled water. The deposit of Cs-TPP was dried at 40 °C [8]. Cs-TPP was analyzed using FTIR.

### 2.3. Adsorption experiments

Prepared a solution of 100 ppm of methyl orange. That solution was then diluted to 12 ppm and then measured for its absorbance at the wavelength range of 300-600 nm using spectrophotometer UV-visible to get the maximum wavelength ( $\lambda_{\text{max}}$ ).

The adsorption experiment has three stages, namely determination of the optimal pH value, determination of the effect of time, and determination of the determination of adsorption isotherm. Adsorption was carried out by

reacting 40 ml of 20 ppm methyl orange with 1 g of Cs-TPP in a 100 ml beaker. The adsorption of the dyes was studied in various pH (4, 3, 4, 5, 6, and 7), various times (20, 40, 60, 80, and 100 minutes), and various dye concentrations (10, 20, 30, 40 and 50 ppm). The methyl orange dye concentration was measured by spectrophotometer UV-visible. Equation (1) calculates the percent removal:

$$\% \text{ Removal} = \frac{(C_i - C_f)}{C_i} \quad (1)$$

where  $C_i$  is the initial concentration of methyl orange and  $C_f$  is the concentration of methyl orange after the adsorption process.

## 3. RESULT AND DISCUSSION

### 3.1. Synthesis of crosslink chitosan-tripolyphosphate (Cs-TPP)

Chitosan modification can be done by crosslinking to increase its adsorption ability [8]. The negative groups of tripolyphosphate can bind  $-\text{NH}_2$  groups from chitosan spontaneously at the mechanical stirring at room temperature. This technique can be carried out at the solution media simply and easily. Cationic chitosan can interact with multivalence counter ions, like tripolyphosphate, through intermolecular and intramolecular bonds with ionic reactions.

The Cs-TPP (**Figure 2**) in this study was created by reacting chitosan solution with pH 3 tripolyphosphate solution. The Cs-TPP made in acid conditions will have a higher density compared to that made in alkali conditions [8]. When sodium tripolyphosphate is dissolved in water will give hydroxyl and TPP ions. The interaction between polycationic chitosan and tripolyphosphate ions will result in a complex polycationic-multivalent anion, which is Cs-TPP. Cs-TPP depends on the cations site availability and the number of negative sites. Therefore, the pH solution influences the Cs-TPP synthesis greatly. The interaction of chitosan and tripolyphosphate ions will occur in an ionic crosslink at low pH while at high pH will go through a deprotonation mechanism [13].

The synthesized Cs-TPP was characterized using FTIR (**Figure 3**). The analysis using FTIR was used to find the uptake characteristics of Cs-TPP. IR spectra for Cs-TPP showed that the uptake widened at the wavenumber of  $3433 \text{ cm}^{-1}$ , which is related to stretching vibrations of  $-\text{OH}$  and  $-\text{NH}$  functional groups involved in H-bonding [14]. The peaks identified at  $2931 \text{ cm}^{-1}$  were caused by stretching vibrations of  $\text{CH}_3$  groups, both asymmetric and symmetric. Wavenumbers  $1635 \text{ cm}^{-1}$  and  $1543 \text{ cm}^{-1}$  come from N-H vibrations due to asymmetric or symmetric N-H deformation of  $-\text{NH}_3^+$ . Bands in the range of  $1800-1500 \text{ cm}^{-1}$  probably cover the vibrational bands in the amide I and amide II [14]. The peak of C-O coming from C-O-C or C-O-H was identified at the

wavenumber of  $1095\text{ cm}^{-1}$ , while the range of oxygen bridge was identified at the wavenumber of  $1026\text{ cm}^{-1}$  which showed the range vibration P–O.

### 3.2. Adsorption Study of Dyes

In batch sorption equilibrium experiments, the adsorption of methyl orange on Cs–TPP was investigated. In successive batches, pH, contact time, and the adsorption isotherm were investigated. Adsorb study was initially begun by determining the wavelength and standard curve. Determining the maximum wavelength ( $\lambda_{\text{max}}$ ) was necessary to set the maximum uptake of the solution towards the ray at a particular wavelength. Every molecule has a different wavelength depending on its structure and its nature in the solution. The result of  $\lambda_{\text{max}}$  for methyl orange is  $426\text{ nm}$  (Figure 4).

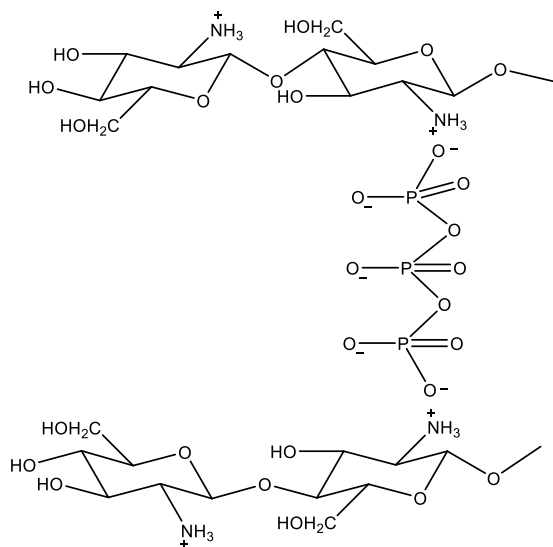


Figure 2. Structure of Cs–TPP

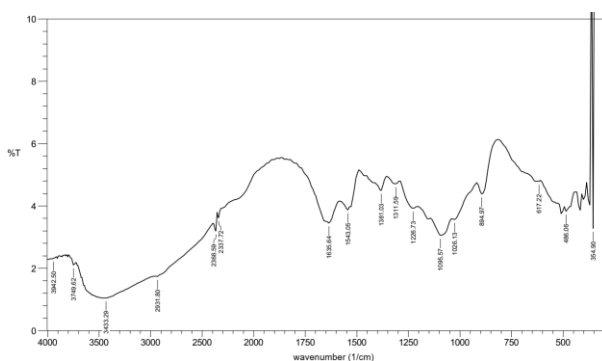


Figure 3. IR spectra of Cs–TPP

pH solution is an important factor to determine the charge of Cs–TPP, dissociation of methyl orange, and to determine the absorbent’s successful performance to adsorb the solution. The pH values which are too low or too high will cause Cs–TPP not to optimally reduce the levels of methyl orange. Figure 5 shows the effect of pH

solution on the ability of Cs–TPP to reduce the levels of methyl orange.

Figure 5 shows that the increase of pH will cause the amount of adsorbed methyl orange to increase to the optimum condition at pH 7. When the pH of the solution is greater than the pKa of methyl orange (3.76), more sulfonates groups will be dissociated from methyl orange so more will interact with Cs–TPP active sites and this will cause the adsorption percentage to increase. The more increased the pH, the less Cs–TPP cationic side. The percent removal of methyl orange at pH 7 and a contact time of 60 minutes was 45.46% with an adsorption capacity is 0.59 mg/g. The further adsorption of methyl orange will be carried out at pH 7. There are several ways in which Cs–TPP interacts with methyl orange, including electrostatic bonds (Figure 6) and hydrogen bonds (Figure 7).

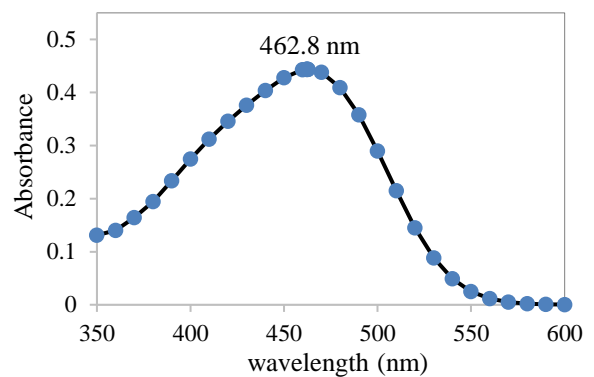


Figure 4. Determination of the maximum wavelength of methyl orange

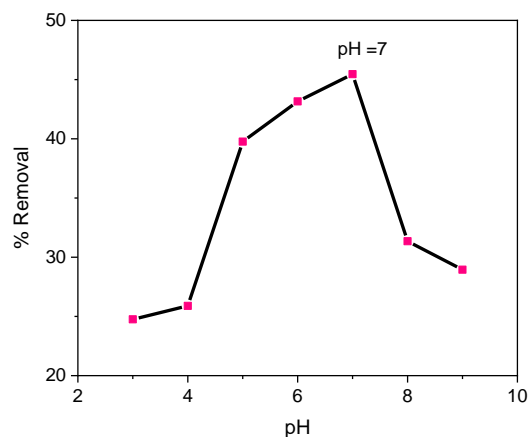
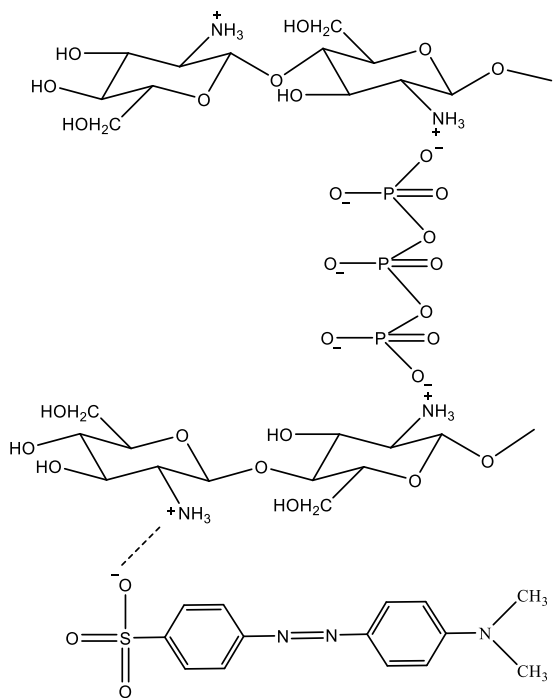
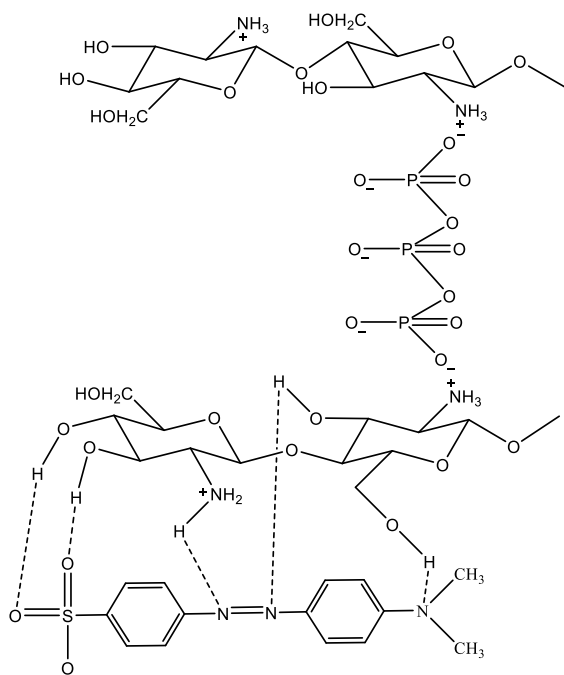


Figure 5. The effect of pH on percent removal of methyl orange

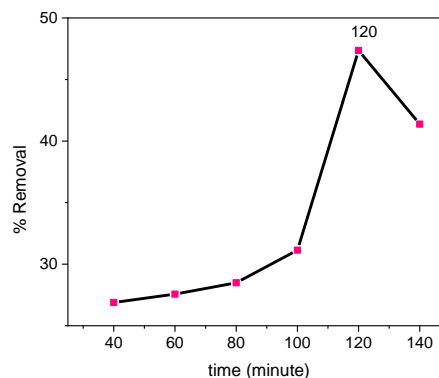


**Figure 6.** The electrostatic bond between Cs-TPP with methyl orange



**Figure 7.** The hydrogen bond between Cs-TPP with methyl orange

The optimum contact time is the time when the adsorbate's adsorption to the adsorbent's surface occurs maximally. The various times are carried out to find out the length of time needed for maximal adsorption at pH 7 (optimum pH). The percent removal of methyl orange increases along with the increasing time and eventually, it reaches its maximum adsorption (**Figure 8**).



**Figure 8.** The effect of contact time on percent removal of methyl orange

The longer contact time enables diffusion and the adsorption of adsorbate molecules to occur well. The percent removal of methyl orange at pH 7 and a contact time of 120 minutes was 47.36%. After reaching the optimum time, the adsorbent experiences decreasing percent removal on dyes. This decreasing ability is because the active side of Cs-TPP has been saturated by dyes so that it cannot absorb them again.

Analyze the interaction between the adsorbate and an adsorbent, the adsorption isotherm is essential [2]. In the determination of adsorption isotherm, the initial concentration of the methyl orange solution was varied. There are some isothermal adsorption equations commonly used to find out the phenomena that happen from adsorption, which are isothermal adsorption Langmuir (Equation 2) and isothermal adsorption Freundlich (Equation 3)[15].

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (2)$$

The  $q_e$ ,  $C_e$ ,  $q_m$ , and  $K_L$  are adsorption at equilibrium (mmol/g), the concentration at equilibrium (mmol/L), maximum adsorption (mmol/g), and adsorption equilibrium constant (L/mol), respectively.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

There are two constants in Freundlich adsorption,  $K_F$  and  $n$ . Based on equation 2, a  $\frac{C_e}{q_e}$  vs  $C_e$  curve can be made (**Figure 9**). While Equation 3 can be used to make a curve of  $\log q_e$  vs  $\log C_e$  (**Figure 10**). How to determine the kinds of adsorption is conducted by comparing the determination coefficient ( $R^2$ ) with its adsorption capacity.

Based on the determination coefficient, the adsorption model of methyl orange followed Freundlich's isothermal adsorption as well. The Freundlich isotherm model also occurs when methyl orange is adsorbed with modified xanthan gum [4] and crosslinked chitosan [chit-cl-Poly (AA-co-Am)] [16]. The Freundlich model showed the adsorbate's layers formed on the adsorbent's surface

were multilayer. This model also described that the adsorption on the surface was heterogenic, in which not all adsorbent surface has the adsorption power.

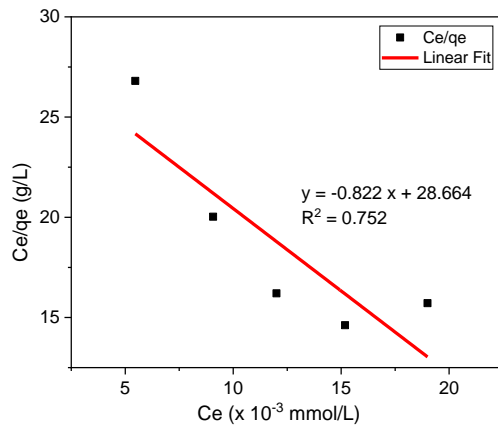


Figure 9. The curve of Langmuir adsorption isotherm

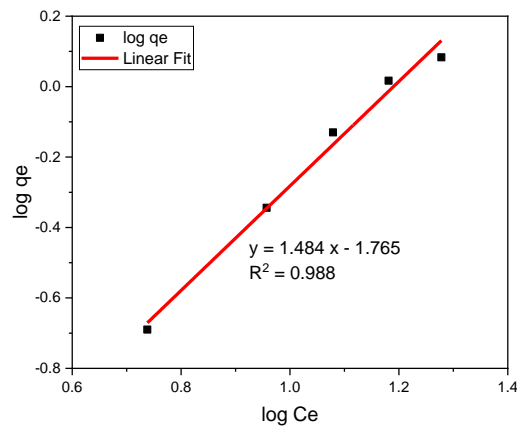


Figure 10. Curve of Freundlich adsorption isotherm

#### 4. CONCLUSION

Cs-TPP can be synthesized by reacting chitosan solution with TPP solution. By using a TPP solution with an acidic pH, ionic crosslinks will be obtained. Cs-TPP can reduce levels of methyl orange by 47.36%. The interactions that occur between Cs-TPP and methyl orange are electrostatic bonds and hydrogen bonds. Based on the results of the study, Cs-TPP has the potential to be used in reducing methyl orange levels in wastewater.

#### AUTHORS' CONTRIBUTIONS

MK designed the EXPERIMENT and WROTE the manuscript. DR carried out the EXPERIMENT, RR and DK performed the CALCULATIONS, and AR SUPERVISED the project.

#### ACKNOWLEDGMENTS

Thanks to the financial support provided by Universitas Jenderal Soedirman through the "Peningkatan Kompetensi " grant with contract number 14077/UN23.14/PN/2016.

#### REFERENCES

- [1] V. K. Gupta, R. Jain, A. Nayak, S. Agarwal, M. Shrivastava, Removal of the hazardous dye-Tartrazine by photodegradation on titanium dioxide surface, *Mater. Sci. Eng. C*, vol. 31, pp. 1062–1067, 2011, doi: 10.1016/j.msec.2011.03.006.
- [2] S. S. Shah, T. Sharma, B. A. Dar, R. K. Bamezai, Adsorptive removal of methyl orange dye from aqueous solution using populus leaves: Insights from kinetics, thermodynamics and computational studies, *Environ. Chem. Ecotoxicol.*, vol. 3, pp. 172–181, 2021, doi: 10.1016/j.enceco.2021.05.002.
- [3] R. Lafi, A. Hafiane, Removal of methyl orange (MO) from aqueous solution using cationic surfactants modified coffee waste (MCWs), *J. Taiwan Inst. Chem. Eng.*, vol. 58, pp. 424–433, 2016, doi: 10.1016/j.jtice.2015.06.035.
- [4] F. Lian, M. Zheng, M. Chen, Y. Zhu, L. Zhang, B. Zheng, Modified xanthan gum for methyl orange uptake: Kinetic, isotherm, and thermodynamic behaviors, *Int. J. Biol. Macromol.*, vol. 165, pp. 2442–2450, 2020, doi: 10.1016/j.ijbiomac.2020.10.147.
- [5] A. H. Jawad, S. S. A. Norrahma, B. H. Hameed, K. Ismail, Chitosan-glyoxal film as a superior adsorbent for two structurally different reactive and acid dyes: Adsorption and mechanism study, *Int. J. Biol. Macromol.*, vol. 135, pp. 569–581, 2019, doi: 10.1016/j.ijbiomac.2019.05.127.
- [6] S. O. Majekodunmi, E. O. Olorunsola, C. C. Uzoaganobi, Comparative Physicochemical Characterization of Chitosan from Shells of Two Bivalved Mollusks from Two Different Continents, *Am. J. Polym. Sci.*, vol. 7, no. 1, pp. 15–22, 2017, doi: 10.5923/j.ajps.20170701.03.
- [7] M. Kurniasih, Purwati, R. S. Dewi, Toxicity tests, antioxidant activity, and antimicrobial activity of chitosan, *IOP Conference Series: Materials Science and Engineering*, 2018, vol. 349, no. 1, doi: 10.1088/1757-899X/349/1/012037.
- [8] M. Kurniasih, K. Riyani, T. Setyaningtyas, I. Sufyana, Adsorption of Ni (II) Ions Using Crosslink of Chitosan Tripolyphosphate, *J. Rek. Kim. dan Ling.*, vol. 13, no. 2, pp. 174–181, 2018, doi: 10.23955/rkl.v13i2.11725 Adsorpsi.

- [9] C. Pan, J. Qian, C. Zhao, H. Yang, X. Zhao, H. Guo, Study on the relationship between crosslinking degree and properties of TPP crosslinked chitosan nanoparticles, *Carbohydr. Polym.*, vol. 241, no. April, p. 116349, 2020, doi: 10.1016/j.carbpol.2020.116349.
- [10] T. T. Kyaw, K. S. Wint, K. M. Naing, Studies on the Sorption Behavior of Dyes on Cross-linked Chitosan Beads in Acid Medium, in 2011 International Conference on Biomedical Engineering and Technology IPCBEE, 2011, vol. 11, pp. 174–178.
- [11] M. F. J. D. P. Tanasale, J. Latupeirissa, R. Letelay, Adsorption of Tartrazine Dye by Active Carbon from Mahogany (*Swietenia Mahagoni Jacq*) Rind, *Ind. J. Chem. Res.*, vol. 1, pp. 104–109, 2014.
- [12] M. Kurniasih, A. Riapanitra, A. Rohadi, Adsorption of Rhodamine B using powder and beads chitosan adsorbents, *Sains dan Mat.*, vol. 2, no. 2, pp. 27–33, 2014.
- [13] D. R. Bhumkar, V. B. Pokharkar, Studies on effect of pH on cross-linking of chitosan with sodium tripolyphosphate: A technical note, *AAPS Pharm.Sci.Tech*, vol. 7, no. 2, pp. E138–E143, 2006, doi: 10.1208/pt070250.
- [14] M. Gierszewska, J. Ostrowska-Czubenko, E. Chrzanowska, pH-responsive chitosan/alginate polyelectrolyte complex membranes reinforced by tripolyphosphate, *Eur. Polym. J.*, vol. 101, no. February, pp. 282–290, 2018, doi: 10.1016/j.eurpolymj.2018.02.031.
- [15] T. Kameda, R. Honda, S. Kumagai, Y. Saito, T. Yoshioka, Adsorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  by tripolyphosphate-crosslinked chitosan-modified montmorillonite, *J. Solid State Chem.*, vol. 277, no. February, pp. 143–148, 2019, doi: 10.1016/j.jssc.2019.06.002.
- [16] P. Kumar, S. Gihar, B. Kumar, D. Kumar, Synthesis and characterization of crosslinked chitosan for effective dye removal antibacterial activity, *Int. J. Biol. Macromol.*, vol. 139, pp. 752–759, 2019, doi: 10.1016/j.ijbiomac.2019.08.058.