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EFFECT OF CHITOSAN CONCENTRATION ON MACROPOROUS CHITOSAN-TPP BEADS TOWARD TURBIDITY, DYE CONTENT, AND COD OF SASIRANGAN WASTEWATER

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ABSTRACT

This research was carried out to determine the effect of chitosan concentration in synthesising crosslinked tripolyphosphate (TPP) macropore beads on turbidity, dye content, and Chemical of Demand (COD) Sasirangan wastewater. Macroporous chitosan-TPP beads were synthesised from chitosan solution with various concentrations of 2%, 3%, 4%, and 5% and added $NaHCO_3$ as a porogen, then dripped into 0.75% tripolyphosphate solution. It was further interacted with Sasirangan wastewater by adsorption method with its effect analysed by using the turbidity value, dye content, and COD. The results showed that beads with a 3% chitosan concentration were the most effective in reducing the turbidity, dye content, and COD value. Furthermore, using a more than 3% chitosan concentration indicates reduced effectiveness. Macroporous Chitosan-TPP beads were able to produce a decrease in turbidity, dye content and COD by 81.21%, 55.44%, and 59.37%.

Keywords: *chitosan beads, sasirangan wastewater, turbidity, dye content, COD.*

INTRODUCTION

Sasirangan industry is a typical textile industry in South Kalimantan, mainly produced on a small scale or at home. Its production development has numerous positive and negative impacts on the welfare of the people of South Kalimantan. One of the negative impacts is the occurrence of environmental pollution due to the disposal of unprocessed wastewater from various kinds of chemicals in the production process, such as dyes, naphthol, caustic soda, and other materials. These are the primary sources of pollution because only a small part is absorbed in textile products, while most are wastewater (liquid waste) [1]. Textile industry wastewater contains pollutants that can affect environmental quality, such as Total Suspended Solids (TSS), dye content, turbidity, temperature, odor, microorganisms, Biological of Demand (BOD), Chemical of Demand (COD), Dissolved Oxygen (DO), ammonia (NH_3), sulfides, phenols, pH, heavy metals. These are usually acidic, basic, dark in color with high organic matter content, and contain synthetic materials that are difficult to decompose by microbes [2].

Wastewater discharged by the Sasirangan fabric industry needs to be treated before being discharged into the waters. During the manufacturing process, the principles of coagulation and flocculation using chemicals such as ferrous sulfate and poly aluminium chloride cause environmental pollution. [3]. Therefore, there is a need for alternative methods for treating Sasirangan wastewater, such as using natural materials, such as chitosan, which are environmentally friendly and substitute for chemicals. [4].

Chitosan is used in various waste treatment methods, including adsorbents, flocculants and membranes. Chitosan was chosen as an adsorbent because of its high surface area [5]. According to literature studies, chitosan has the highest potential compared to other adsorbents due to hydroxyl and amine groups along the polymer chain. However, chitosan is less stable or more soluble, especially at acidic pH. Some researchers have reported that crosslinking chitosan can prevent chitosan from dissolving in acids. Modification of chitosan in the form of crosslinked beads can be carried out by adding a crosslinking agent. Commonly used crosslinkers in the adsorption process include glutaraldehyde [6], [7], epichlorohydrin [8], and glyoxal [9], [10]. However, these cross-linking agents are known to be toxic. Glutaraldehyde is neurotoxic [11], epichlorohydrin is carcinogenic [12], and glyoxal is mutagenic [13]. An alternative environmentally friendly crosslinker is sodium tripolyphosphate (STPP) [14].

Sodium tripolyphosphate interacts with chitosan via electrostatic interactions to form an ionic crosslinking network, creating a highly stable bead structure and reducing the time required for bead formation [15], [16]. However, bead crosslinking can also reduce the adsorptive capacity of chitosan to adsorb molecules, as most of the active sites of chitosan are widely used to bind to crosslinking agents [7]. In addition, crosslinking also causes chitosan to experience a decrease in porosity [8]. Therefore, there is a need to increase the adsorption capacity. One possibility is to add porogen.

Porogen acts as a pore-forming agent that can provide active groups on the surface of the adsorbent and interact with adsorbed molecules [5]. The addition of porogen as a pore template can prevent or reduce pore shrinkage during the crosslinking process [17]. One porogen is baking soda, and baking soda bubbles can be created during polymerisation to make the pores large and uniform [9]. The larger the pores formed, the more likely adsorbed molecules will be adsorbed. The production of macropolar chitosan using STPP as a crosslinking agent and sodium baking soda as a porogen not only contains metal ions but also adsorbs larger sized molecules such as humic acid molecules [11] and dyes such as methyl orange [18], rhodamine B, safranin O [14]. Therefore, it was developed as an adsorbent that can be used.

Based on the explanation above, this study made macropore chitosan using STPP as a crosslinker and sodium bicarbonate as a porogen. In addition, the effect of chitosan concentration on the cross-linking ability of macropore tripolyphosphate chitosan grains on the turbidity value, dye content, and COD of sasirangan wastewater was also studied.

METHODS

Data were collected from wastewater reservoirs in the sasirangan fabric industry in the Banjarmasin area of South Kalimantan. This research was carried out using 5 litres of various samples put in a jerry can close and stored in a closed condition in a dry place protected from direct light. Before interacting with macropores chitosan-TPP beads, the turbidity, dye content, and COD parameter values were first analysed as initial data.

The synthesis of macropore chitosan-TPP beads was carried out according to the procedure used [11] with several modifications. A total of 1 gram of chitosan was dissolved in 50 mL of 2% (v/v) acetic acid, stirred until homogeneous to produce a 2% solution. It was then added to 2 grams of $NaHCO_3$, stirred again for ± 30 seconds, and dripped dropwise into 100 mL of 0.75% (w/v) Na-TPP solution using a burette to form beads allowed to stand for 24 hours. Beads were filtered and washed using distilled water until the pH was neutral, while its surface was dried with filter paper. The same procedure was carried out to make chitosan solutions with 3%, 4%, and 5% concentrations with the same acetic acid, $NaHCO_3$, Na-TPP solution.

A total of 5 beakers containing 100 mL of Sasirangan wastewater samples were prepared, with four beakers added to macropore chitosan-TPP beads concentrations of 2%, 3%, 4%, and 5% (w/v), respectively. Furthermore, 1 cup without beads was added as a negative control, stirred at 45 rpm for 30 minutes and allowed to stand for 24 hours. Macroporous chitosan-TPP beads were separated from the solution by filtering with Whatman 42 filter paper. The filtrate was measured for turbidity, dye content, and COD using a turbidimeter, UV-Vis spectrophoto-meter, and a test method based on SNI. 6989.73:2009, respectively.

RESULTS AND DISCUSSION

Sasirangan industrial wastewater with many hazardous pollutants discharged without any prior treatment into the surrounding water bodies. These activities are often carried out by craftsmen using the traditional manufacturing process, which discharges poorly processed waste into the environment. This waste consists of pollution parameters that exceed the government's quality standard of textile industry waste-water. Table 1 shows the pre-analysed turbidity, dye content, and COD values.

Table 1. The analysis results of turbidity, dye content, and COD in samples of Sasirangan wastewater.

No	Parameter	Method	Score
1	Turbidity	Turbidimeter	41,2 NTU
2	Dye Level	UV-Vis$_{400}$	0,496 (absorbance)
3	COD	Titrimetric	276,9 mg/L

Table 1 shows the initial data used to determine macropore chitosan-TPP beads' ability to reduce turbidity, dye content, and COD of Sasirangan wastewater by the adsorption method.

The TPP-chitosan beads synthesis method was carried out in 2 stages. The first is dissolving it in 2% (w/v) acetic acid through the chitosan polymer matrix to form a bulging mass. Furthermore, it is solvated to form a gel, which quickly breaks to form a thick solution of chitosan [19]. In the second stage, the chitosan solution was added with sodium bicarbonate as a porogen because it can be quickly released after the foam is formed [7].

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \quad \text{... (1)}$$

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \quad \text{... (2)}$$

Chitosan, with the addition of porogen, has a more extraordinary ability to adsorb dye molecules because the pores produced are larges; therefore, the surface area of the adsorbent is wider than chitosan and has more active sites [18]. The addition of this porogen produces macroporous beads.

This foaming chitosan solution was then dropped into a 0.75% (w/v) sodium tripolyphosphate solution at the original pH to produce macroporous beads using a burette. Chitosan interacts with TPP to form TPP-chitosan through intermolecular and intra-molecular bonds with ionic reactions. Ionic crosslinking between chitosan and TPP occurs under acidic or basic pH conditions [20].

In acidic conditions, the $-NH_2$ group in chitosan is protonated to become $-NH_3^+$, causing the crosslinking interaction between the –NH3+ chitosan and the TPP ion to become denser [15], as shown in Figure 1.

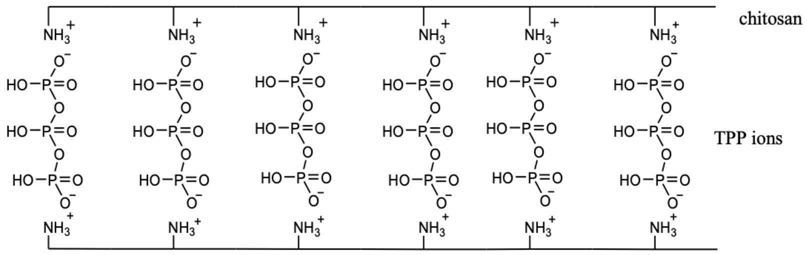

Figure 1. The shape of the TPP-molecular ladder chitosan due to crosslinking with TPP at acidic pH.

The crosslinking between chitosan and TPP in this research was conducted at pH 8 - 9. The $-NH_3^+$ in chitosan is deprotonated; therefore, the dominant group becomes $-NH_2$ [21], as shown in Figure 2.

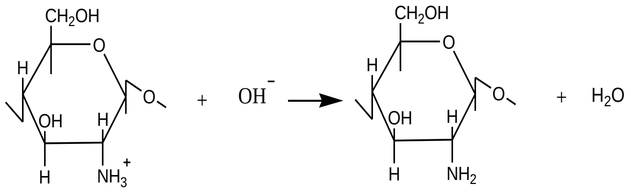

Figure 2. Deprotonation reaction of TPP-chitosan beads

The TPP-chitosan beads are porous and less tight (loop-shaped) [15]. The crosslinking model between chitosan and TPP under alkaline conditions is shown in

Figure 3. The above model is more profitable, assuming it is used as an adsorbent for macromolecules such as dyes because the pores are relatively large. However, many active groups of chitosan are still used to interact with adsorbate molecules.

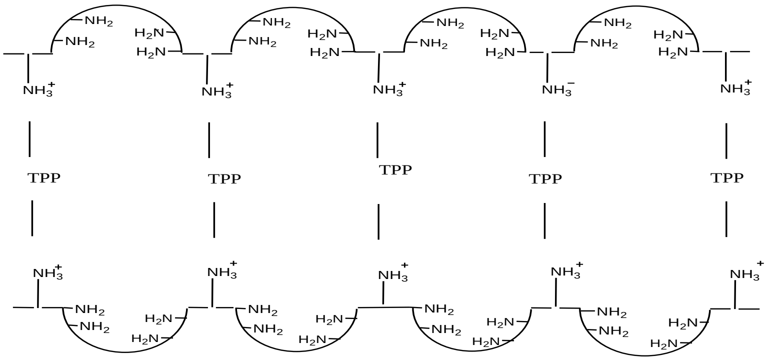

Figure 3. The shape of the TPP-chitosan molecular loop is due to crosslinking of chitosan with TPP at alkaline pH [15].

Effect of Chitosan Concentration on Macropore Chitosan-TPP Beads on Turbidity Value, Dye Content, and COD of Sasirangan Wastewater

Using the optimum concentration of chitosan solution in the manufacture of macropore chitosan-TPP beads is necessary for the efficiency of the sasirangan wastewater treatment. This research studied the effect of variations in chitosan concentrations of 2%, 3%, 4%, and 5% to obtain a dose of 10 g/L, 15 g/L, 20 g/L, and 25 g/L, respectively, for 100 ml of waste. The analysis results of turbidity values, dye content, and COD on sasirangan waste samples after treatment are shown in Table 2.

The data in Table 2 is further processed into a graph to determine the effect of chitosan concentration in beads on the decrease in turbidity, dye content, and COD values on the initial data of sasirangan wastewater. These graphs are shown in Figures 4, 5, and 6.

Table 2. The analysis results of Sasirangan wastewater after treatment with macropore chitosan-TPP beads

No	Sample	Turbidity (NTU)	dye content (Absorbance)	COD (mg/L)
1	Negative control	20,70	0,367	134,4
2	C-TPP 2%	9,99	0,357	262,5
3	C-TPP 3%	7,74	0,221	112,5
4	C-TPP 4%	8,41	0,275	500,0
5	C-TPP 5%	13,50	0,356	562,0

Description:
C-TPP 2% = Macropore chitosan-TPP beads with 2% chitosan concentration
C-TPP 3% = Macropore chitosan-TPP beads with 3% chitosan concentration
C-TPP 4% = Macropore chitosan-TPP beads with 4% chitosan concentration
C-TPP 5% = Macropore chitosan-TPP beads with 5% chitosan concentration

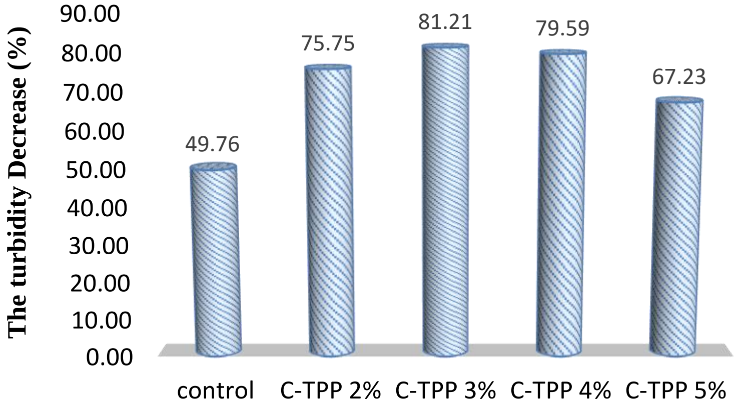

Figure 4. The effect of chitosan concentration in the manufacture of beads on the decrease in the turbidity value of Sasirangan wastewater

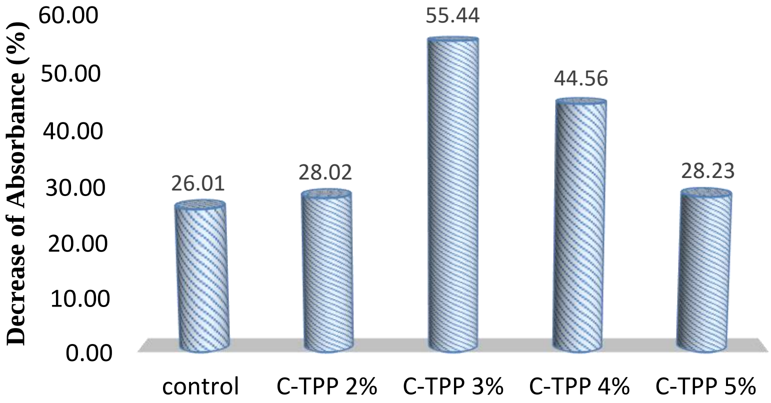

Figure 5. The effect of chitosan concentration in the manufacture of beads on the decrease in the absorbance value of Sasirangan wastewater

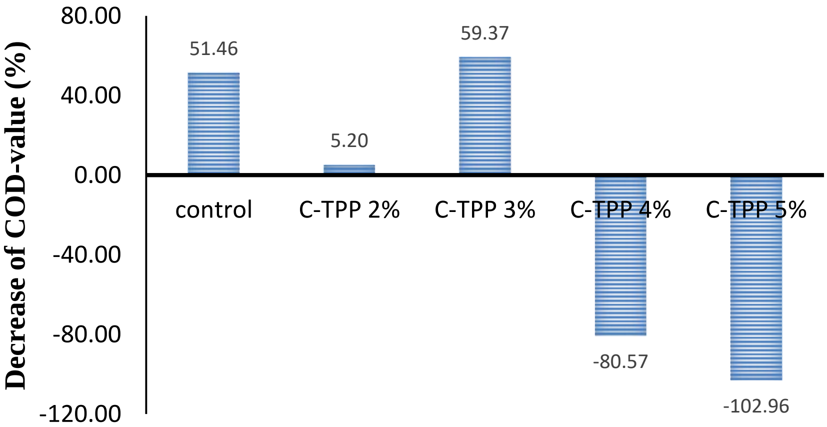

Figure 6. The effect of chitosan concentration in granules on decreasing the COD value of Sasirangan wastewater

In general, turbidity, dye content, and COD of sasirangan wastewater are caused by suspended organic and inorganic substances. Inorganic substances usually come from dissolved metals, while organic is obtained from dyes, cellulose fibres, and other auxiliary chemicals used in colorings such as naphthol and caustic soda. Table 1 shows that the initial analysis of turbidity, dye content, and COD in the Sasirangan waste samples used has a reasonably high value.

Sasirangan wastewater comes from dying and staining fabrics, while the dye content parameter is essential in determining the quality of processed waste products. Since the waste liquid of sasirangan contains a large amount of dye mixture, it is impossible to measure the dye concentration in the waste liquid. However, the absorbance value can estimate with a UV-Vis spectrophotometer to analyse the decrease in dye content. Based on Lambert Beer's law, the dye concentration is directly proportional to the absorbance [22]. Therefore, absorbance values measured at maximum wavelengths can be used to determine semi-quantitatively the reduction or increase in dye content in waste before and after treatment.

Based on Figures 4, 5, and 6, the optimum decrease in turbidity, dye content, and COD on the use of beads with a concentration of 3% chitosan reduces the turbidity, dye, and COD sasirangan wastewater by 81.21%, 55.44% and 59.37%. The ability of beads with a 2% chitosan concentration is still lower than 3%, and this decrease causes a decrease in the number of active groups that play a role in the adsorption of substances. The decrease in percentage was also reduced using 4% and 5% chitosan concentrations. Regarding the crosslinking between chitosan and TPP, as shown in Figure 7 [21], the beads' stability is influenced by the concentration or amount of TPP in the chitosan TPP beads [11]. In this study, the chitosan concentration was changed while possession the TPP concentration was constant barely. The higher the chitosan concentration used, the lower the concentration of TPP ions in the beads, resulting in an insufficient crosslinking agent to achieve bead stability. As a result, some chitosan is easily separated and dissolved in the waste.

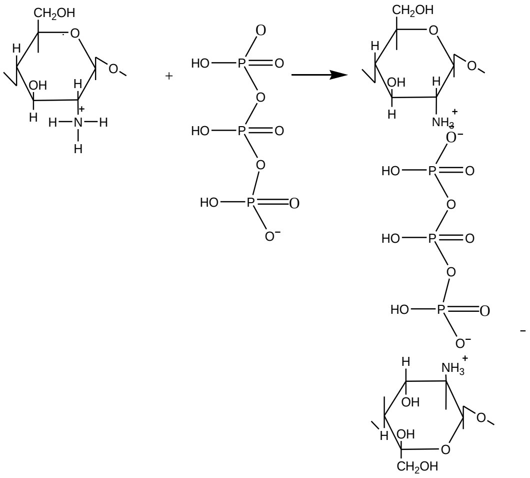

Figure 7. Ionic interaction of chitosan with TPP

COD analysis was carried out using the SNI.6989.73:2009 procedure, with the organic and inorganic compounds in the test sample oxidised by Cr2O72- in closed reflux. The excess potassium dichromate that is not reduced is then titrated with a solution of ferrous ammonium sulfate (FAS) using a ferroin indicator. The required amount of oxidant is expressed in oxygen equivalents (O_2 mg/L). Based on Figure 6, only beads with a concentration of 3% could reduce the COD value by 59.37%. However, it was also ineffective where the decreasing percentage differences were similar to the negative control. Ion-crosslinked beads, such as Chitosan-TPP beads, cannot be used to reduce COD because they are easy to separate and dissolve in waste [21]. Chitosan polymers have many primary alcohol groups, secondary alcohols, and amine groups [23]. Primary alcohol groups are oxidised to aldehydes and carboxyl groups, secondary alcohol groups are oxidised to ketones [23], and amine groups are oxidised to an amine oxide-type [24]. Based on this, the reagents can oxid the chitosan for COD analysis. Therefore, the release of chitosan into the waste sample increases the COD value. Further research needs to be carried out to examine the effect of crosslinking concentration, type of crosslinker, and the number of beads interacting with sasirangan wastewater.

CONCLUSION

In conclusion, the macropore chitosan-TPP bead can reduce turbidity, dye content, and optimum COD at a concentration of 3%, which is equivalent to a dose of 15g/L. It also decreases the turbidity, dye content, and COD by 81.21%, 55.44%, and 59.37%, respectively. However, it is less effective for concentrations of more than 3% due to the type of cross-linkage between chitosan and TPP, which is ionic. The concentration of TPP remains constant for each variation, causing the partial release of chitosan from beads.

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