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The Interaction Mechanism of Papaya Seeds (*Carica papaya* L.) as a Natural Coagulant and Remazol Red Under Different pH Conditions

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Abstract

Batik wastewater contains a high concentration of dye that comes from the batik dyeing process. In this study, papaya seeds were applied as a natural coagulant to reduce the concentration of remazol red in batik wastewater. Dried papaya seeds were characterized using Fourier Transform Infrared Spectroscopy (FTIR). The coagulation method used the batch method in the pH range of 1-6. The FTIR spectra showed that the papaya seeds contained compounds with $-NH_2$ and -COOH functional groups. The results of coagulation showed that the pH of batik wastewater had an effect on the ability of papaya seeds to reduce the concentration of remazol red. The optimum pH condition was obtained at pH 2 with a decrease in the concentration of remazol red by 96.1%. The interaction that occurs between the coagulant of papaya seeds and the remazol red of batik wastewater is through electrostatic interactions.

Keywords: Coagulation, Papaya seeds, Remazol red, Batik wastewater, Interaction mechanism

INTRODUCTION

Remazol red is the most widely used dye in the batik industry. Remazol red is an anionic dye. This dye has high stability so it is difficult to degrade naturally (Safitri & Rahmayanti, (2020); Maya Rahmayanti, Nurhikmah, & Larasati, (2021). Batik wastewater containing remazol red dye if discharged into the environment can last a long time and accumulate to a certain concentration level and cause negative impacts on the environment (Pembayun & Rahmayanti, 2020); (Pambudi, Prayogo, Nadjib, & Ediati, (2021); Tanasale, Sutapa, & Topurtawy, (2014); Bijang, Nurdin, Latupeirissa, Aziz, & Talapessy, (2022).

One of the effective methods to reduce organic compounds is the coagulation method. The coagulation method has advantages, namely the process is simple, the cost is relatively cheaper and is able to absorb organic pollutants such as dyes (M Rahmayanti, 2021). Coagulation method is colloid stabilization with the addition of coagulant. Coagulant has a charge opposite to the charge of the colloidal particles causing an attractive force. Finally, the colloidal particles will bond and agglomerate (Pembayun & Rahmayanti, 2020).

The coagulant commonly used for waste treatment is alum. The use of alum is very effective in purifying water, but recently the use of alum is known to contain aluminum residues that are harmful to health. According to Jeyakumar, 2014 the use of synthetic coagulants has disadvantages, namely expensive processing costs, non-biodegradable and can cause serious health impacts such as Alzheimer's disease. Therefore, natural coagulants were chosen to reduce processing costs and minimize negative impacts on the environment and human health.

Papaya seeds can be used as a natural coagulant because of their protein content. The advantages of using papaya seeds as a natural coagulant are biodegradable, economical, and can reduce agricultural waste. The utilization of papaya seeds has not been widely developed as a dye coagulant (Tafera & Demissie, 2017). This study used natural coagulant of papaya seeds to reduce the concentration of remazol red in batik wastewater. The protein content in papaya seeds has an active group such as an amine ($-NH_2$) will undergo protonation to $–NH_3^+$ at acidic pH and act as a cationic polyelectrolyte (Kristianto, Kurniawan, & Soetedjo, 2018); (Hendrawati, Syamsumarsih, & Nurhasni, 2013). Charges of opposite and mutually neutralizing particles can be used to reduce the remazol red dye. Optimization of pH was carried out to obtain the optimum coagulation pH in reducing the concentration of remazol red in batik wastewater.

METHODOLOGY

Materials and Instrumentals

The tools used in this research were a set of glassware, sungu spoon, magnetic stirer, filter paper, Whattman 42 filter paper, pH meter, analytical balance, hot plate, vacuum pump, UV-Vis spectrophotometer (1800 double beam Shimadzu) and FTIR spectrophotometer (IR, Shimadzu Prestige-21). The materials used in this study were papaya seeds, remazol red, batik wastewater, sodium acetate trihydrate ($CH_3COONa.3H_2O$), and glacial acetic acid (CH_3COOH). The pH adjustment was carried out using a buffer solution.

Methods

Preparation of papaya seeds as a natural coagulant

Papaya seeds were dried in the sun for 5 days. The dried papaya seeds were crushed and stored in a clean and dry container. Papaya seeds characterization was carried out using an FTIR spectrophotometer (IR, Shimadzu Prestige-21).

Preparation of remazol red mother liquor

The remazol red mother liquor was prepared by dissolving 1 g of remazol red in
1000 mL of distilled water. The mother liquor was diluted into 10, 15, 20, 25, dan 30 ppm then used as standart solution.

Determination of the remazol red standart curve

The absorbance of remazol red standard solution with various concentrations of 10, 15, 20, 25, and 30 ppm was determined using a UV-Vis spectrophotometer. The linier equation of the standar curve was obtain by graphing the concentration versus absorbance.

Coagulation of remazol red in batik wastewater using papaya seeds

Papaya seeds as much as 0.0260 mg were put into 25 mL batik wastewater with variations in pH 1, 2, 3, 4, 5, and 6. The mixture was stirred using a magnetic stirrer. Stirring was carried out in two stages, namely fast stirring at 950 rpm for 5 min, and slow stirring at 125 rpm for 30 min. Furthermore, the concentration of remazol red in batik wastewater was analyzed using a UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Characterization of Papaya Seed Natural Coagulants

FTIR spectrophotometer was used to determine the functional groups contained in papaya seeds. Characterization of the functional groups of papaya seeds was carried out on papaya seed powder before and after the coagulation process. The FTIR spectra of the results of this study were presented in Figure 1. Figure 1 showed the absorption peaks that appeared in the papaya seed samples before coagulation (a), remazol red (b) and papaya seeds after coagulation (c). The Figure 1(a) and 1(c) showed absorption in the wavenumber area of 1635.54 cm^{-1} for the -C=O stretching vibration of -COOH and the stretching vibration of the -OH and -NH groups at the wavenumber of 3425.58 cm^{-1}. The presence of -C-H absorption was indicated by the appearance of absorption at a wavenumber of 2924.09 cm^{-1} and C-O vibrations at a peak of 1219.01 cm^{-1}. This study is in line with Kristianto et al., (2018) which characterized the functional groups of papaya seeds using FTIR with an absorption at a wavenumber of 3438.8 cm^{-1} for the stretching vibrations of -OH and -NH and an absorption at a wave number of 2925.8 cm^{-1} for the -CH group. According to Prihatinningtyas, (2013), the carboxyl, hydroxyl and amide groups in the polymer are the active components in the coagulant.

The presence of remazol red functional groups (1.b) was indicated by the appearance of specific absorption of -CN at 1211.30 cm^{-1}, absorption of the -N=N- group at wavenumber 1558.48 cm^{-1}, absorption of sulfite group at wavenumber of 1404.18 cm^{-1} and the absorption of the -S=O group at a wavenumber of 1126.43 cm^{-1}. The presence of the aromatic -C=C group was indicated by the appearance of absorption at a wavenumber of 1504.48 cm^{-1}, a stretching vibration of C-OH at an absorption of 3448.72 cm^{-1} and aliphatic ether absorption at a wavenumber of 1049,28 cm^{-1}. The uptake of remazol red from this study was in accordance with the results of the study of Waghmode, Kurade, Kabra, & Govindwar, (2012) which showed specific absorption for the sulfonic acid group at 1209.41 cm^{-1}, the sulfite group at wavenumber 1397.96 cm^{-1}, stretching vibration -N=N at wavenumber 1679.19 cm^{-1}, stretching vibration -CH at a wavenumber of 2889.94 cm^{-1} and the stretching vibration of aromatic -C-OH at a wavenumber of 3479.70 cm^{-1}.

Based on Figure 1, there is no difference in the amount of absorption that appears between the FTIR spectra of papaya seeds before and after coagulation. However, there are some absorption shifts. The shift that occurs is in the -OH and -NH groups, the absorption shifts from wavenumber 3425.58 cm^{-1} to 3425.50 cm^{-1}. In addition, a shift occurs in the absorption of C-O vibrations, before coagulation the absorption appears at a wave number of 1219.01 cm^{-1}, after coagulation it becomes 1256.30 cm^{-1}. The shift in wavenumber in the papaya seed spectra of interactions that occur between papaya seeds and remazol red is not through chemical bonds. Natural protein coagulants work in two ways, namely charge neutralization and particle bridging through the interaction of van der Waals forces or through electrostatic interactions (Hendrawati et al., 2013).

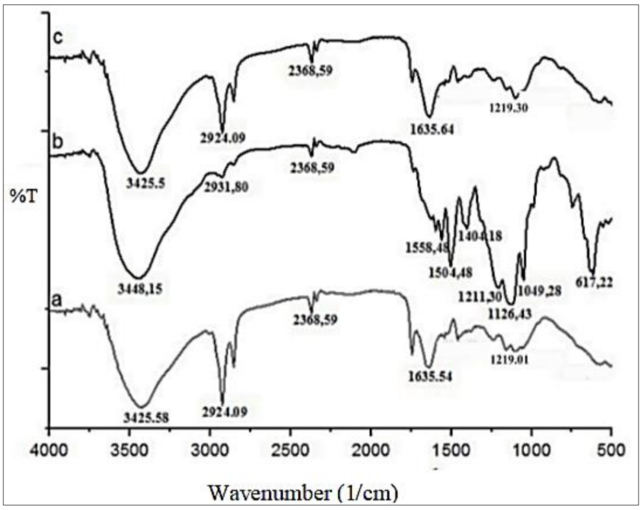

Figure 1. FTIR spectra of (a) papaya seeds before coagulation (b) remazol red and (c) papaya seeds after coagulation

Coagulation of remazol red in batik wastewater using papaya seeds

Coagulation of remazol red in batik wastewater using papaya seed as a coagulation was carried out at a pH range of 1-6 to determine the optimum pH conditions of coagulation. Based on this study, variations in the pH of batik wastewater have an effect on the percent reduction in the concentration of remazol red. Rapid stirring (950 rpm) was carried out in this study to ensure that the papaya seed coagulant was evenly distributed in the batik wastewater, so that microflocs were formed. Slow stirring (125 rpm) was carried out so that the small particles (microflocs) became larger clumps (macroflocs) and the formed flocs were stable.

The graph of the relationship between pH and % decrease in remazol red using natural coagulants of papaya seeds is presented in Figure 4. Figure 4 shows the reduction percentage of remazol red concentration in the pH range of 2-5 going well, namely 96.1%, 94.3%, 91, 7%, and 89.03%, respectively. Meanwhile at pH 1, the reduction percentage of remazol red concentration was lower at 79.1% and at pH 6 there was no decrease in the concentration of remazol red. This can be explained as follows: Papaya seeds have the main content of protein which is composed of amino acids. Amino acids have groups which in acidic conditions will experience protonation so that they will be positively charged $-NH_3^+$ and $-COOH_2^+$ while in alkaline conditions they will be deprotonated to $-NH^-$ and COO^- (El Boraei & Ibrahim, 2019); Hendrawati et al., (2013). This is causes in the pH range of 2-5 papaya seeds can reduce the concentration of remazol red better, because at this pH the $-NH_2$ and -COOH groups are protonated to $-NH_3^+$ and $-COOH_2^+$ and interact with the $-SO_3^-$ group of remazol red through electrostatic interactions. Furthermore, the higher of pH, the $-NH_2$ and -COOH groups were deprotonated to $-NH^-$ and COO^- and made it difficult to interact with the $-SO_3^-$ remazol red group through electrostatic interactions causes the reduction percentage of remazol red concentration to decrease.

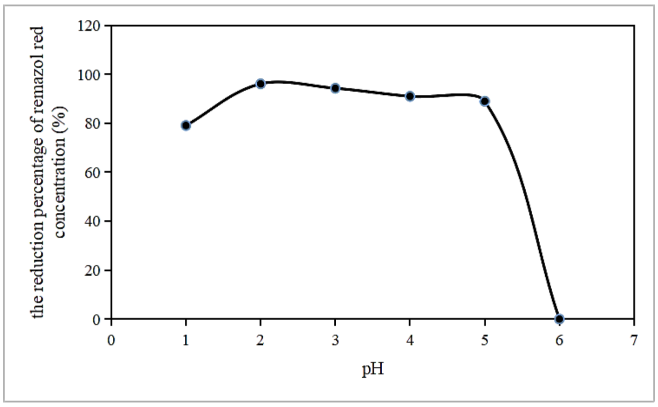

Figure 4. The relationship between pH of batik wastewater with the reduction percentage of remazol red concentration

At pH 6, the reduction percentage of remazol red concentration = 0%, because at this pH the $-NH_2$ and -COOH groups have been completely deprotonated to $-NH^-$ and COO^- so there is not electrostatic interaction with remazol red. At pH 1, the reduction percentage of remazol red concentration was lower than at pH 2-5 even though it was more acidic, this was because at pH 1, the $-NH_2$ and -COOH groups were not fully protonated. In this study, the optimum pH of remazol red coagulation in batik wastewater using papaya seed coagulation occurs at pH 2. At this pH, the $-NH_2$ and -COOH groups were fully protonated so that the interaction between remazol red and the coagulant was optimal.

Study of the interaction mechanism between Papaya Seeds (*Carica papaya* L.) with Remazol Red in Batik Wastewater Under Different pH Conditions

The natural coagulants of papaya seeds work in two ways, namely charge neutralization and particle bridging through the electrostatic interaction. Figure 5 presents an illustration of the interaction that occurs between the coagulant of papaya seeds and the sulfonate group of remazol red. The process of coagulation of remazol red dye occurs due to colloid destabilization.

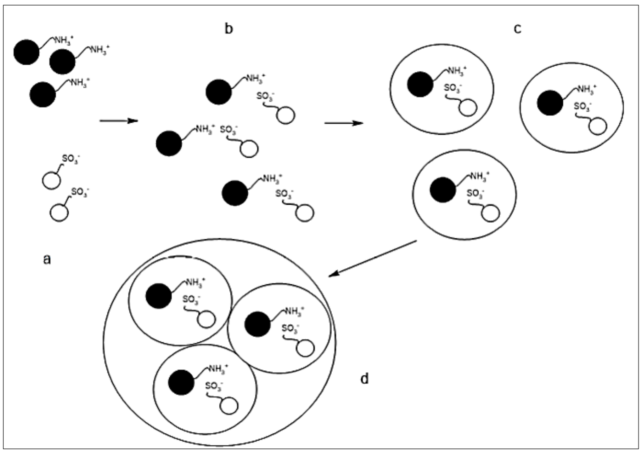

Figure 5. Illustration of coagulant interaction with remazol red in batik wastewater

The colloid destabilization process begins with (a) the presence of a different electric charge between the sulfonate group (SO_3^-) of remazol red and a positive charge (NH_3^+) of papaya seeds (b) there is an electrostatic attraction between the amino acid protein of papaya seeds which is positively charged (NH_3^+) with the sulfonate group of remazol red dye (SO_3^-) (Farooq & Velioglu, 1989) (c) a charge neutralization process occurs followed by a particle bridging process (d) the merging of microflocs into larger clumps of macroflocs (Fitriani, 2016).

Table 1. The Application of Natural Coagulants for Water to Reduce The Concentration of Remazol Red in Batik Wastewater

Natural coagulant	**Dye in batik wastewater**	**Optimum pH**	**The reduction percentage (%)**
Chitosan [1]	Rhemazol red	2	100
Tamarind seeds [3]	Rhemazol red	3	68.26
This research	Rhemazol red	2	96.1

Protein have long chains on one side of the adsorption on colloidal particles while the other side of the protein extends into the solution. This extended side provides the possibility to bond with other colloids to form bridges with other particles, thus forming larger flocs (Viessman & Hammer, 1985).

CONCLUSION

Papaya seeds have been successfully applied as a natural coagulant to reduce the concentration of remazol red in batik wastewater. The pH of batik liquid waste affects the reduction percentage of remazol red concentration. The optimum pH condition of the coagulation process occurred at pH 2 with a % decrease in remazol red concentration of 96.1%. The higher of pH, the $-NH_2$ and -COOH groups were deprotonated to $-NH^-$ and COO^- and made it difficult to interact with the $-SO_3^-$ remazol red group through electrostatic interactions causes the reduction percentage of remazol red concentration to decrease.

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