Poultry keratin based decolorants for dyeing wastewater treatment

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ABSTRACT

One of the challenges in wastewater treatment is the low efficiency in decoloring dyeing wastewater. Chicken feather, as a waste material, has a great potential in decoloring the dyeing wastewater. In this study, a lab synthesized dyeing wastewater prepared with acid blue-A dye was treated with a chicken feather keratin-based composite decolorant KA (keratin agent) using batch decoloration techniques. A modified KA (MKA) was also developed to improve the decoloration efficiency. The decoloration performance of the two decolorants was then evaluated in terms of decoloring rate, at various decolorant dosages, pH, reaction temperature and time. Under optimal conditions, the decoloration rates of the KA and MKA in treating the dyeing wastewater were 91.8% and 94.3%, respectively. IR and TEM results indicated that the KA and MKA decolorants removed the dye stuff from the dyeing wastewater by physical adsorption as well as chemical reactions.

Keywords: Keratin; Poutry feather; Decolorant; Dye; Dyeing wastewater; Decoloring; Treatment

1. INTRODUCTION

Water pollution caused by the color effluents discharged from textile dye manufacturers and textile dyeing mills is one of the major environmental concerns in the world today. 1 Textile dyeing wastewater is difficult to treat. Color removal 2 of the dyeing wastewater is especially difficult due to its complex characteristics, large volume, high content of organic pollutants, dark color, and unstable properties. A number of techniques have been developed to remove different types of dyes from wastewater. 3,4 One technique, a physicochemical method, removes different types of dyes through adsorption, 5,6 electrocoagulation, 7 oxidation 8 and photocatalytic decolorization. 9-9 Recently, the adsorption technique has been gaining more attention since it can be widely used in different dyeing wastewater treatments, and it is versatile and easily to be implemented. 10 Various potential adsorbents have been studied, such as activated carbon, 11,12 clays, 13 agricultural solid wastes 14,15 and fly ash. 16 However, more research is needed to develop more cost-effective dye absorbents.

Poultry Feather is a solid waste produced from slaughterhouses. It is estimated that the annual production of poultry feather is more than 8.5 billion tons in the world. 17 Traditionally, the majority of the feather is being dumped into landfills, which is expensive to operate and has harmful impacts on the environment. In addition, poultry feather is rich in protein which breeds flies and viruses. For these reasons, there has been an increased interest in the utilization of feather keratin. 18 For instance, feather was used to decolor or filtrate toxic pollutants 19 and dyes from dyeing wastewater. 20 The poultry feather may be activated and used directly without extracting the keratin. 21 Limited studies have been found in the literature on the extraction of keratin and its chemical and physical properties in relation to the disulphide bonds and cross-linkages of feathers.

In this study, two kinds of composite decolorants were prepared by hydrolyzing the poultry feather in sodium hydroxide solution to extract the kerating protein which was modified to have improved decoloring properties. The performance of the feather keratin based decolorants in treating a simulated dyeing wastewater was assessed by the absorbance and decoloring rate of the treated wastewater. The process parameters including decolorant dosage, pH, temperature and contact time were investigated to optimize the decoloring process. The treated dyeing wastewater, feather keratin decolorants and resulting sludge were examined by infrared spectrum (IR), transmission electron microscopy (TEM), and the underlining decoloring mechanism was discussed.

2. MATERIALS AND METHODS

2.1 Materials

Chicken feathers were collected from a slaughterhouse in Yulin. An acid blue-A dye sample was obtained from a dye chemical plant in Shanghai of China, and a dye-fixing agent (DE) from Shanghai TianTan Auxiliaries Co., Ltd. Analytical reagent grade hydrochloric acid (HCl), sodium dithionite (NaHSO 3) and sodium hydroxide (NaOH) were purchased from Chemicals Ltd, Xi’an (China).

2.2 Experimental procedures

Two different composite decolorants were prepared for the lab trials in this study. The first decolorant (KA) was prepared by following steps: 1) the feathers were treated first with 40% hydrochloric acid at 75 °C for 90 min; 2) and then with 30% sodium bisulfite solution at 75 °C for 90 min; 3) and then hydrolyzed with 20% sodium hydroxide...
solution at 80°C for 40 min. The liquid extract from the last step contained 0.8 g/L of poultry keratin, and it was designated as KA.

The second decolorant (MKA) was prepared by mixing the KA (0.8 g/L) with DE (0.6 g/L) in a rotary reactor (500 mL) at 80 °C for 30 min, at a rotating speed of 120 r/min. DE was a positively charged cationic polymeric quaternary ammonium salt with an epoxy group, and the KA had polar groups in the main chain such as -COOH, -NH2, -OH and peptide bond (-CONH-). Thus, the epoxy group of DE can readily react with the amino and hydroxy groups of KA to produce MKA, which can absorb or embed dye molecules in micelles by electrostatic attraction, hydrogen bonding, Van der Waals’ force and hydrophobic force.22,23

The decoloration experiment was carried out in glass beakers with 100 mL synthesized dyeing wastewater of 60 mg/L dye concentration, according to the National Standard Method and relative literature.16 The pH of the mixture was adjusted to a desired level by adding hydrochloric acid or sodium hydroxide solutions, and it was maintained at the level throughout the whole reaction period. A PHS-3C model pH meter was used to monitor the pH value. The reaction temperature was also maintained at a constant level as desired. After the decoloration treatment, the wastewater was filtered and measured for absorbance. The absorbance of the original and treated dyeing wastewater was determined at 635 nm wavelength with a UV-2401PC series spectrophotometer (SHIMADZU Co., Ltd). All experiments were repeated three times for each condition, and the average value was reported.

The decoloring rate of the treatment was calculated from the change in the absorbance of the synthesized dyeing wastewater before and after the treatment. The decoloring rate was calculated as

\[
R = (1 - \frac{A_i}{A_0}) \times 100\%
\]

Where R is the decoloring rate; \(A_0\) and \(A_i\) are the absorbance of the dyeing wastewater before and after the treatment at 635 nm; \(m\) and \(n\) are dilution factors for the dyeing wastewater.

3. RESULT AND DISCUSSION

3.1 Optimization of process parameters

3.1.1 Effect of pH

The pH of an adsorption process is an important process parameter to be controlled to obtain maximum performance.25 Figure 1 shows the effect of pH on the decoloring rate in a wide range from pH 1 to pH 12, with 600 mg/L KA or 600 mg/L MKA, under ambient temperature (20 °C) for 30 min. The results show that the decoloring rate increased first with increasing decolorant dosage, and then started to decrease when the dosage was higher than 400 mg/L for the KA system, and 1400 mg/L for the MKA system. The maximum decoloring rates were 91% and 92.8% for the KA and MKA systems, respectively.

3.1.2 Effect of decolorant dosage

In Figure 2, the decolorant dosage was varied from 40 to 1000 mg/L for KA at pH 2, and 400 to 1600 mg/L for MKA at pH 8, and the temperature was fixed at 20°C. The results show that the decoloring rate increased first with increasing decolorant dosage, and then started to decrease when the dosage was higher than 400 mg/L for the KA system, and 1400 mg/L for the MKA system. The maximum decoloring rate was 91% and 92.8% for the KA and MKA systems, respectively.

3.1.3 Effect of reaction temperature

Figure 3 shows the impact of reaction temperature on the decoloring rate from 20°C to 70°C, with 400 mg/L KA at pH 2, or with 1000 mg/L at pH 8. The results show that as the temperature increased from 20 to 30 °C, the decoloring rate increased slightly, and then decreased rapidly when the temperature increased further from 30 to 70 °C. The maximum decoloring rates were 92% for KA and 93% for MKA, both of which were obtained at 30°C. A moderately higher temperature (e.g. 30 °C) might favour the interaction between the dye molecules and the decolorants, without ruining the flocs formed in the adsorption process. However, when the temperature was too high (above 30
°C), the flocs formation might be disturbed, resulting in a lower decoloring rate.

3.1.4 Effect of contact time

Figure 4 compares the decoloring rate of KA and MKA at various reaction times, in the range from 5 to 120 minutes. The decolorant dosage and reaction pH were fixed at 400 mg/L and 2 for the KA system, and 1000 mg/L and pH 8 for the MKA system. The results show that the decoloring rate increased rapidly with the increase of the reaction time in the first 30 minutes, and then leveled off and reached a plateau at 90 minutes, which was true for both the KA and MKA processes.

3.2 Decoloring Mechanism

3.2.1 IR spectra

Infrared spectra of the KA and MKA decolorants are shown in curve 5 and curve 4, respectively, in Figure 5. The absorption peaks at 3377.7 cm⁻¹ and 1638.3 cm⁻¹ were attributed to the O-H and C=O vibration. The vibration absorption of the C-H on the peptide chain and the N-H bending vibration peaked at 1463.1 cm⁻¹ and 1409.7 cm⁻¹, respectively, both of which intensified and shifted slightly to the lower wave numbers. The absorption peak at 1650 cm⁻¹ was responsible for the S-H groups in the spectrum for KA disappeared in the spectrum for MKA, indicating that the dye-fixing agent DE had reacted with KA in the decolorant preparation process.

The IR spectra for the sludge samples from the treatments of the dyeing wastewater with KA or MKA are shown by the curves 2 and 3 in Figure 4, respectively. In both cases the absorption bands were intensified and slightly shifted to lower wave numbers. Both spectra had the characteristic absorption peak of the acid blue A at 2359.5 cm⁻¹, which shows that the decolorant KA and MKA had interacted with the acid blue dye.¹⁸,¹¹

The DE fixing agent had a plurality of reactive epoxy functional groups, which can interact with the amine and hydroxyl groups under alkaline conditions. The DE fixing agent also contained multiple quaternary ammonium cationic groups. It was expected that DE would crosslink keratin and impart cationic charges to the decolorant. The introduction of the cationic groups to the protein molecules of the keratin decolorant increased the electrostatic attraction between the keratin decolorant and anionic dye molecules,¹² and thus facilitated the absorption and flocculation of the dye stuff in decoloration process.
The chemical structural of DE:

Its simplified form:

The reactions of DE with the hydroxyl and amine groups of KA may be described as:

\[ P-\text{NH}_2 + \overset{\text{H}_2\text{O}}{\overset{\text{CH}-\text{CH}_2-N(R_3)Cl^-}{\text{O}}} \rightarrow P-\text{NH}-\text{CH}_2-\text{CH}_2-N(R_3)Cl^- \]

The dye (Acid Blue A) contained sulfonate groups and was an anionic dye. The reactions of MKA with the anionic dye may be described as follows.

\[ D-\text{SO}_4\text{Na}^+ + P-\overset{\text{OH}}{\overset{\text{NH}-\text{CH}_2-\text{CH}_2-N(R_3)Cl^-}{\text{O}}} \rightarrow \]

\[ \left[ D-\text{SO}_4\right]^+ \left[ P-\overset{\text{OH}}{\overset{\text{NH}-\text{CH}_2-\text{CH}_2-N(R_3)}{\text{O}}} \right]^+ + \text{NaCl} \]

These chemical reactions, as well as the electrostatic attraction, Van der Waals force and hydrogen bonds between the decolorant and the anionic dye molecules played important roles in the decoloration of the dyeing wastewater with MKA.

3.2.2 TEM analyses

The KA decolorant particles shown in the transmission electron microscopic (TEM) image in Figure 6a were in separate granule form, while the MKA decolorant particles were in cluster form (Figure 6b). The network structure of the MKA decolorant provides further evidence for the strong physical/chemical interaction between KA and DE. This also explains the improved decoloring performance of MKA in treating the dyeing wastewater. The TEM image of the sludge from the decoloring process with MKA (Figure 6d) had more compact structure than that from the KA process (Figure 6c), which explains the much faster settlement of the flocs formed in the decoloring process with MKA than with KA.
4. CONCLUSIONS

Two poultry keratin-based decolorants (KA and MKA) were successfully prepared in the lab and evaluated in treating a dyeing wastewater synthesized with an acid blue-A dye. It was found that the modified keratin decolorant MKA had a superior decoloring performance than the original keratin decolorant KA extracted from poultry feather. The decoloring rate of the dyeing wastewater was up to 90% with KA, and up to 92.5% with MKA, under the conditions in current study. It was also found that the KA was more effective in acidic conditions. While the MKA performed better in a neutral to alkaline medium. The IR and TEM results support the hypothesis that there were strong physical/chemical interaction between the KA decolorant and the DE dye fixing agent.

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