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# A MULTIFUNCTIONAL GELATIN-QUATERNARY AMMONIUM COPOLYMER EXHIBITING SUPERIOR ANIONIC DYE ADSORPTION FOR EFFICIENT EMISSION REDUCTION IN LEATHER TANNING PROCESS

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**Abstract.** Leather wastewater is one of the most polluting industrial emissions. An in-situ, green, and innovative strategy that limits dye emissions is required to replace subsequent waste management. A novel cationic protein with a high quaternary ammonium degree was designed and synthesized. The results show that at concentrations ranging from 3 to 15 wt%, this cationic protein rapidly and completely adsorbs Direct Purple N and Acid Black 24 within 5 min. A remarkable efficiency in removing Acid Red 73, Acid Golden G, Acid Lake Blue A, Acid Green, and Acid Orange II, with >96% removal rates, was achieved. The cationic protein was most accurately represented by the pseudo-second-order kinetic model. Acid Orange II (2000 mg L<sup>-1</sup>) and 15 wt% cationic protein were used in an actual tanning process. The residual concentration of Acid Orange II in the wastewater was 23.1 mg L<sup>-1</sup>. These results reflect that the emission reduction targets have been effectively achieved.

## 1 Introduction

The presence of pollutants in the environment can be attributed to both natural and anthropogenic sources<sup>1,2</sup>. Dyeing wastewater has drawn great public concern owing to its strong colority, high toxicity, carcinogenicity, degradation resistance, and easy accumulation in living organisms<sup>2,3</sup>, which has led to concerns about water pollution as a global challenge<sup>1,4</sup>. To date, many technologies, including membrane technologies<sup>5</sup>, adsorption<sup>6,7</sup>, biodegradation<sup>8</sup>, distillation<sup>9</sup>, photocatalysis<sup>10,11</sup>, and other approaches, have been utilized for the purification and remediation of polluted water.

The leather industry is one of the most polluting industrial sectors and generates enormous amounts of dye wastewater via the tanning process<sup>3,12-15</sup>. The volume wastewater of per kilogram of the tanned leather produced and the wastewater dye concentrations (>400 mg L<sup>-1</sup>) in the different wet-finishing process steps are generally high<sup>16</sup>. Leather wastewater has a high pH value and strong color, and comprises complex components. The main pollutants include heavy metals such as chromium, soluble proteins, dandruff, suspended matter, tannins, lignins, inorganic salts, oils, surfactants, dyes, and resins<sup>17-19</sup>. Therefore, it is very difficult to deal with such complicated sewage in a simple way. A cleaner and green tanning process has become the focus of attention in the leather industry<sup>20</sup>. Dye emissions can be minimized if the leather dyes in the tanning process are retained in the leather via sufficient adsorption; this will be an efficient and cleaner method to prevent water pollution. It will also be a green way to cater to the needs of the tanning industry. Therefore, the purpose of this study was to design and synthesize a new type of cationic protein that not only fully fills the leather but also quickly and firmly adsorbs dye molecules in large quantities, to prevent dye emissions.

In leather dyeing, direct and acid (anionic) dyes that contain functional groups such as benzene rings, and azo and sulfonate groups are mainly used<sup>21,22</sup>. Cationic compounds effectively adsorb

these anionic dyes through ionic interactions. Quaternary ammonium compounds are widely recognized cationic compounds because of their non-toxicity and strong antibacterial efficiency<sup>23</sup>. Moreover, it can be deduced that a high quaternary ammonium degree is beneficial for adsorption. In addition, copolymers are also suitable compounds to improve the performance of auxiliaries, particularly dyes, in the dyeing process<sup>24-27</sup>. These copolymers react with the substrates at multiple points to improve the uptake of chemicals; this has attracted the attention of researchers. Copolymers are very effective in adsorbing dyes because, unlike normal polymers, they contain mainly reactive groups in the backbone surrounded by linearly and randomly distributed side chains that can attract more adsorbents<sup>28</sup>. For the above reasons, a cationic protein that contains gelatin and quaternary ammonium salt components was designed and synthesized in this study, for dye adsorption in the tanning process. Gelatin polymers can be prepared via the hydrolysis of leather collagen<sup>29</sup>. Their homology effectively enhances their combination ability, which is very helpful to fill these cationic proteins into leather.

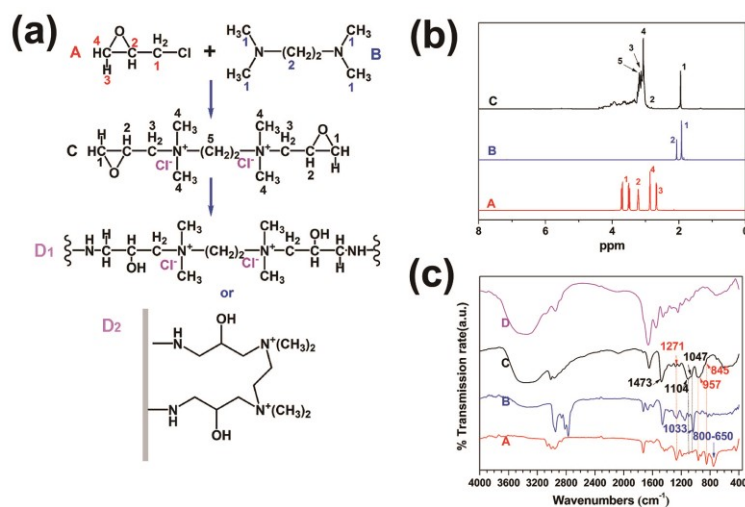
The objectives of this study were to synthesize a new type of cationic protein with a high quaternary ammonium degree, evaluate its adsorption kinetics and isotherm, demonstrate the feasibility of its use for dye adsorption, and realize trace dye emissions in an actual tanning process. A series of anionic dyes, including Acid Black 24, Acid Red 73, Acid Golden G, Acid Lake Blue A, Acid Green, Direct Purple N, and Acid Orange II, were used to investigate the adsorption capacity of the cationic protein. The residual concentrations of the dyes in the distillates indicated the dyes that were adsorbed efficiently; Direct Purple N and Acid Black 24 attained equilibrium rapidly (within 5 min). Acid Orange II (2000 mg L<sup>-1</sup>) was used in a tanning process. The residual concentration of this dye in the wastewater was 23.1 mg L<sup>-1</sup>. This result indicates that this dye is fully adsorbed by the cationic protein. Dye emission can therefore be prevented very effectively in the tanning process, which is beneficial to realize cleaner and green leather tanning.

## 2 Results and discussion

### 2.1 Synthesis of cationic proteins

The DEQAS was synthesized in 87% yield using epichlorohydrin and tetramethylethylenediamine at a molar ratio of 2.5:1. Then, it was used as the raw material to prepare the cationic protein. Chemical reactions occurred between the functional groups in gelatin and the DEQAS in a sodium hydroxide-water medium. During the cross-linking reactions, epoxy groups belonging to the DEQAS molecules reacted mainly with the free -NH<sub>2</sub> groups on the gelatin chains to form cross-linked products via a nucleophilic substitution pathway. Two possible structures of the cationic protein are described (Fig. 1a). The <sup>1</sup>H NMR spectra of epichlorohydrin, tetramethylethylenediamine, and the DEQAS are shown in Fig. 1b. The FTIR spectra of epichlorohydrin, tetramethylethylenediamine, the DEQAS, and the cationic protein (sample 2) are depicted in Fig. 1c. The bands in the 650-800 cm<sup>-1</sup> region can be assigned to the C-Cl groups in epichlorohydrin. The bands at 845, 957, and 1271 cm<sup>-1</sup> were attributable to the characteristic absorption bands of the epoxy ring in epichlorohydrin<sup>30</sup>, and were assigned to the 12μ, 11μ, and 8μ peaks, respectively. The bands at both 1047 and 1104 cm<sup>-1</sup> were attributed to contributions from the symmetric stretching of the C-O-C and skeletal vibrations of the C-O stretching, respectively. The sharp peak at 1033 cm<sup>-1</sup> was attributed to the C-N stretching of the tertiary amine group in tetramethylethylenediamine<sup>31</sup>. An absorption band at 1473 cm<sup>-1</sup> appeared due to the C-H functional groups of the methyl substituent of tetramethylethylenediamine or the quaternary ammonium groups. After the formation of the DEQAS, characteristic absorption bands of epoxy groups, and bands at 1047 and 1104 cm<sup>-1</sup> also appeared; however, the sharp peaks at 1033 cm<sup>-1</sup> and in the 650-800 cm<sup>-1</sup> region disappeared. These results indicated that a DEQAS was

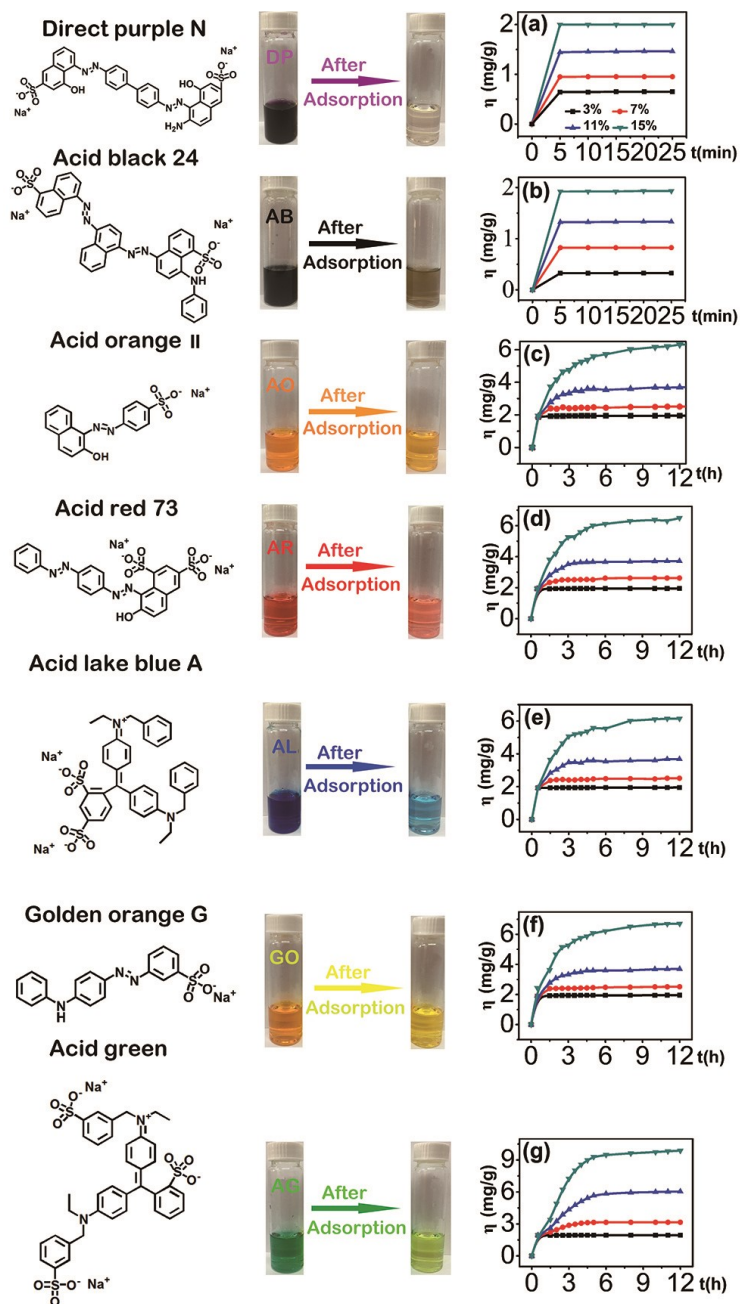
obtained. When the cationic protein was prepared, the bands at both 957 and 1104  $\text{cm}^{-1}$  disappeared. This result indicated that the epoxy groups were nearly completely consumed.



**Fig. 1.** (a) Synthesis of DEQAS and cationic protein (sample 2). (b) 400 MHz  $^1\text{H}$  NMR spectra of epichlorohydrin (A), tetramethylethylenediamine (B), and DEQAS (C) in  $\text{CDCl}_3$  at 25 °C. (c) IR spectra of epichlorohydrin, tetramethylethylenediamine, DEQAS, and cationic protein (sample 2, D<sub>1</sub> or D<sub>2</sub>).

## 2.2 Adsorption behavior of cationic protein

Since the cationic protein was designed with cationic branched quaternary ammonium groups that could attract anionic dyes, it could be used to evaluate the removal of various anionic dyes. The initial concentration of the dyes was 2000  $\text{mg L}^{-1}$ . The cationic protein (sample 2) showed a remarkable efficiency ( $\sim 100\%$ ) for removing Direct Purple N (**Fig. 2a**) and Acid Black 24 (**Fig. 2b**) within 5 min. Direct Purple N and Acid Black 24 attained adsorption equilibriums within 5 min. It is notable that a favorable cationic protein adsorption efficiency was maintained at concentrations of cationic protein ranging from 3 to 15 wt%. The maximum efficiencies for removing Acid Orange II (**Fig. 2c**), Acid Red 73 (**Fig. 2d**), Acid Lake Blue A (**Fig. 2e**), Golden Orange G (**Fig. 2f**), and Acid Green (**Fig. 2g**) were 95%, 90%, 90%, 91%, and 93%, respectively, within 30 min; adsorption equilibrium was quickly attained when the concentration of the dye ranged from 3 to 7 wt%, whereas about 6 h was needed for a higher concentration. These results suggest that the operation time should be increased when these five dyes are used in real industrial processes. **Fig. 2** shows that the remarkable adsorption efficiency of sample 2 increased with an increase in the contact time under various concentration levels. The color variations after filtering the dye solutions through the cationic protein (sample 2) films are displayed in **Fig. 2**.

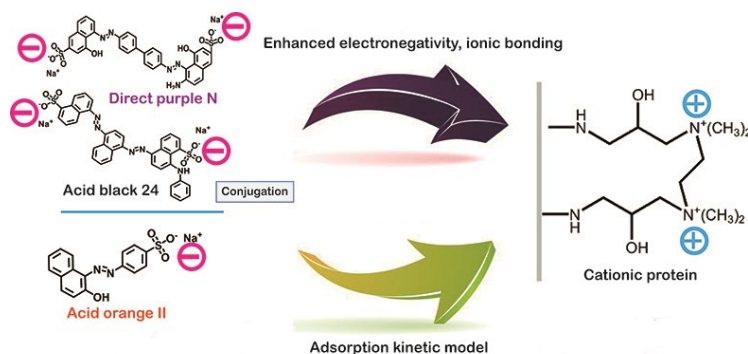


**Fig. 2.** Comparison of dye adsorption effects (the dye chemical formulae, standard solutions, and effluents are shown on the left, in the middle, and on the right, respectively). Adsorption equilibrium versus  $t$  curves for dyes: (a) Direct Purple N, (b) Acid Black 24, (c) Acid Orange II, (d) Acid Red 73, (e) Acid Lake Blue A, (f) Golden Orange G, and (g) Acid Green. The concentrations of the cationic protein (sample 2) were 3, 7, 11, and 15 wt%.

### 2.3 Re-tanning experiment in leather industry

$\pi$ - $\pi$  and  $p$ - $\pi$  conjugates built by aromatic, azo, and sulfonic acid groups exist in Direct Purple N, Acid Black 24, and Acid Orange molecules. This strong conjugated interaction enhances the electronegativity of the dye molecules<sup>32</sup>. The ionic bonds with positive charge that existed in the quaternary ammonium group were obviously improved (**Scheme 1**). In the adsorption experiment, the removal efficiencies for Direct Purple N, Acid Black 24, and Acid Orange were better. The results

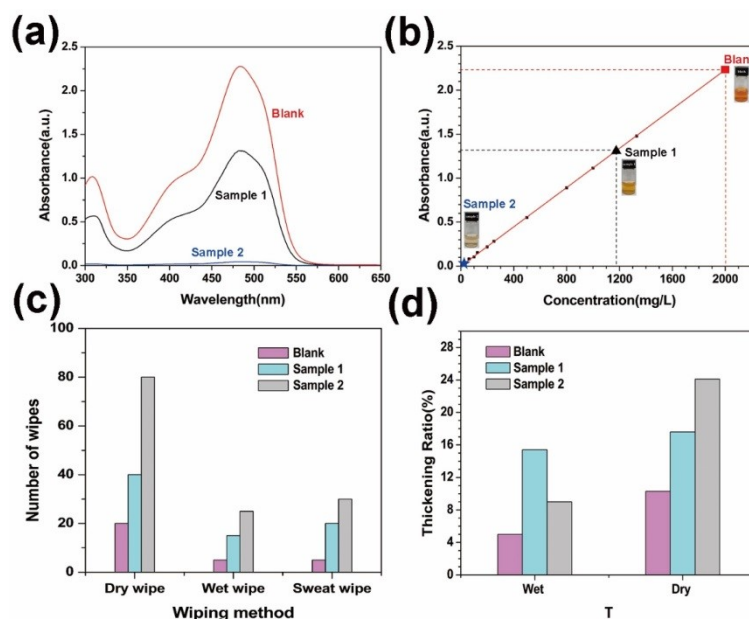
encouraged us to study the efficacy of the cationic proteins using real samples. Acid Orange II, which had a neutral adsorption capacity, was selected as the model dye to study the adsorption effect of the cationic proteins in a real tanning process. The cationic protein samples 1 and 2 were used in actual tanning experiments to compare their adsorption capabilities. The kinetic data suggested that a higher concentration of the cationic protein was beneficial for adsorption; considering the real needs of industrial conditions, the concentrations of samples 1 and 2 were set as 15 wt%, and the optimum adsorption period was identified as 2.5 h. The concentration of Acid Orange II was 2000 mg L<sup>-1</sup>. Use style 'Abstract': 10 pt Calibri, justified, flush left, two line space between Abstract and Author address. Make the word Abstract bold followed by a point.



**Scheme 1.** Ionic interaction between cationic protein (sample 2) and Direct Purple N, Acid Black 24, and Acid Orange II.

After the tanning experiments, the three wastewaters were collected. They were from the cationic protein-free system, sample 1-containing system, and sample 2-containing system. The wastewaters were analyzed using fluorescence spectroscopy (**Fig. 3a**). The results show that the maximum absorption peak of Acid Orange II is at 542 nm. The peak strength at 542 nm was lowest for the sample 2-containing system. This result indicates that the residual concentration of Acid Orange II was lowest in this system. The relative concentrations were quantified using the standard curve (**Fig. 3b**). The results showed that the residual concentration of Acid Orange II was 23.1 mg L<sup>-1</sup> in this system. In comparison, the residual concentration of Acid Orange II was 1188.7 mg L<sup>-1</sup> in the sample 1-containing system. In the cationic protein-free system, the dye was barely adsorbed.

Gelatin, which was the main component of the cationic proteins, is a hydrolysis product of leather collagen. The homology of gelatin and leather collagen leads to a strong combination force between them. There are many polar functional groups such as amino groups, carboxyl groups, and hydroxyl groups in gelatin and leather collagen. The close combination of these components can promote intermolecular hydrogen bonds, and thus improve the anti-wiping ability of the leather surface. In addition, a higher quaternary ammonium degree of the cationic protein can improve the ionic interaction between these positive and negative ions. **Fig. 3c** shows that the anti-wiping ability of tanned leather containing sample 2 under dry, wet, and sweat conditions is obviously enhanced. Similarly, the filling effect and tearing strength of this leather are also the best among those of all the samples (**Fig. 3d**).



**Fig. 3.** (a) UV analysis of wastewater from tanning process for blank, sample 1-containing system, and sample 2-containing system. (b) Concentration analysis of Acid Orange II in wastewater from tanning process for blank, sample 1-containing system, and sample 2-containing system. (c) Wiping test for tanned leather, i.e., blank leather, sample 1-containing leather, and sample 2-containing leather. (d) Determination of thickening rate for tanned leather, i.e., blank leather, sample 1-containing leather, and sample 2-containing leather.

### 3 Conclusions

In this work, a cationic protein with a high quaternary ammonium degree was synthesized; it presented an excellent adsorption ability for direct and acid (anionic) dyes. The  $^1\text{H}$  NMR, IR, DSC, and TGA results revealed the structure of the DEQAS and cationic protein. At concentrations of 3, 7, 11, and 15 wt%, the cationic protein rapidly and completely adsorbed Direct Purple N and Acid Black 24 within 5 min. A remarkable efficiency in removing Acid Red 73, Acid Golden G, Acid Lake Blue A, Acid Green, and Acid Orange II, with >96% removal rates, was achieved. Acid Orange II ( $2000 \text{ mg L}^{-1}$ ) was used in an actual tanning process. The residual concentration of this dye in the wastewater was  $23.1 \text{ mg L}^{-1}$ . This result indicated that the dye was almost entirely adsorbed by the cationic protein. This work can help realize an in-situ, green, and innovative strategy for limiting dye emissions, to replace subsequent waste management.

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