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Salt-free reactive dyeing of betaine-modified cationic cotton fabrics with enhanced dye fixation☆

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ABSTRACT

Novel cationic cotton fabrics were prepared by an efficient and simple one-step pad–dry–bake pretreatment process with betaine as cationic reagent. Ester bonds formed between cotton fibers and betaine hydrochloride were proved by Fourier transformed infrared attenuated total reflection (FTIR-ATR) spectra. Moreover, the properties of the cationic fabrics, including X-ray Diffraction (XRD), tensile strength and whiteness and yellowness index, were investigated in comparison with that of the untreated ones. The cationic fabrics were applied in salt-free dyeing of C.I. Reactive Red 195, C.I. Reactive Yellow 145 and C.I. Reactive Blue 19. Different dye fixation processes were applied and compared for untreated and cationic cotton. Dye fixation and color fastness properties of the dyes were tested, and the results presented that dye fixation on the cationic fabrics in the absence of salt was improved with satisfactory light fastness property and applicable wash and rub fastnesses.

1. Introduction

In recent years, environmental pollution in the dyeing industry has aroused great public concern and substantial researches were focused on solving the problem [1–5]. Reactive dyes are a kind of popular dyes for cotton dyeing due to their excellent properties, such as wide range of hue, brilliancy and good wet fastness. However, owing to the low affinity between the dyes and the fibers, a large amount of salt (30–100 $g\cdot L^{-1}$), such as sodium sulfate or sodium chloride, is added in the dyebath to promote dye adsorption in the exhaust dyeing method [6]. As it is not consumed during dyeing process, the added salt is all released after dyeing. However, the salt-containing dye wastewater is quite difficult to deal with and does great harm to the environment. In order to solve the problem, cationization of cotton has been widely studied in recent years for effective adsorption of reactive dyes in the absence of salt [7–15]. Among the cationic agents used, most of them are synthetic compounds which may present safety problem in application. Although some biopolymers or their derivatives, such as chitosan and its derivative, have been studied, the polymers on cotton may prevent dye penetration into the fibers and influence dye fixation. In addition, the existence of cationic groups on cotton surface easily leads to color staining and results in inferior color fastnesses, especially low light fastness [16–19].

In this study, a novel cationic agent — betaine is designed to be used to modify cotton fibers. Betaine (*N*,*N*,*N*-trimethyl glycine) is a kind of natural product. It was named after its discovery in sugar beets (*Beta vulgaris*) in the 19th century. Betaine shows good biodegradability and biocompatibility. It is even edible for health care, and usually used as additive in food or animal feed. Under acidic condition, betaine partially or totally turns into betaine hydrochloride which contains both a quaternary ammonium group and carboxyl group. Cationization of the fibers can be realized through reaction of the carboxyl group of betaine hydrochloride and the hydroxyl group of cotton to form an ester bond (see Fig. 1). In this study, as-prepared cationic fabrics were for the first time designed to be applied in salt-free dyeing of reactive dyes. Another merit of the betaine-modified fabrics is that the formed ester bonds could hydrolyze under alkaline and high-temperature conditions, which just accords with the dye fixation conditions, thus the cationic groups could be removed from cotton to decrease the influence of color staining.

As known, ester bonds are usually formed in organic solvents and the reaction conditions are severe, which are not suitable for treatment of cotton fabrics. Our previous study showed that with the dry method and dicyandiamide as condensing agent, a kind of novel cationic cellulose — cellulose betainate was successfully prepared [20]. Borrowing the synthesis idea above, a facile pad–dry–bake method was designed for pretreatment of cotton fabrics with betaine as a cationic agent. In addition, to achieve high dye fixation and effective hydrolysis of ester bonds, the steaming dye fixation process was designed for the cationic cotton [21]. The objectives of this study are to characterize the

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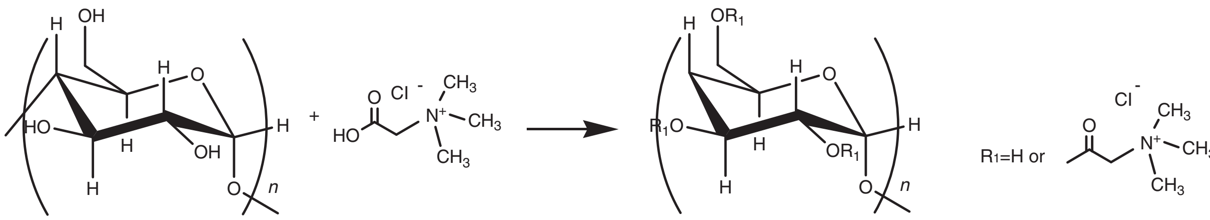


Fig. 1. Preparation of cationic cotton.

betaine-modified cationic fabrics, measure their properties and investigate their dyeing performance with three commercial dyes — C.I. Reactive Red 195, C.I. Reactive Yellow 145 and C.I. Reactive Blue 19 (as shown in Fig. 2).

2. Experimental

2.1. Materials

100% cotton, bleached, desized and mercerized, was purchased from Testfabrics, Inc., Shanghai (China). Anhydrous betaine was purchased from Hangzhou Wan Jing New Materials Co., Ltd. (Zhejiang, China). Dicyandiamide was purchased from Tianjin Bodi Chemical Co., Ltd. (China) and was analytically pure. The reactive dyes in this study were obtained from Shanghai Dyestuff Co. (China) and used as received. The other reagents and solvents were analytically pure.

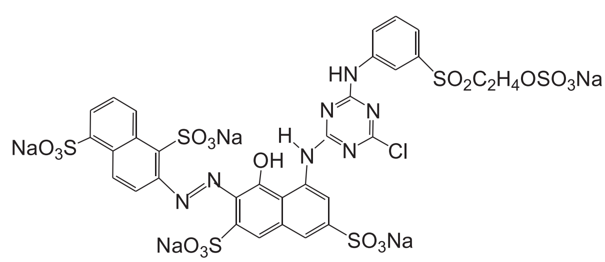
2.2. Pretreatment of cotton fabrics

Anhydrous betaine was dissolved in water to obtain an 8wt% solution and a certain amount of hydrochloric acid was added to yield a molar ratio of it to betaine of 1:1. Then dicyandiamide was added to the above solution to obtain a 5wt% concentration. Cotton fabrics were dipped into the above aqueous solution at a liquor ratio of 10:1 and padded on a mangle to give 90% pickup. The two-dip-two-pad procedure was used. The padded fabrics were dried at 80 °C for 3 min, and then baked at 150 °C for 40 s. In the following, the pretreated fabrics were washed and then dried *in vacuo*. The nitrogen content of the pretreated cotton was 0.027 $mol \cdot g^{-1}$.

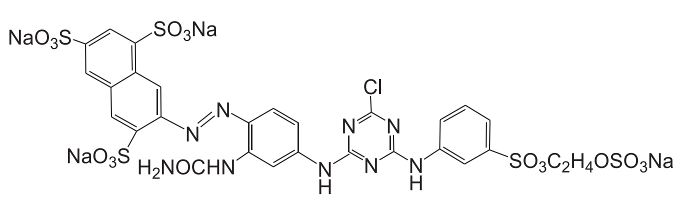
2.3. Dyeing procedure

Dyeing was carried out using a liquor ratio of 20:1. C.I. Reactive Red 195 applied was 2% o.w.f, C.I. Reactive Yellow 145 was 1% o.w.f and C.I. Reactive Blue 19 was 3% o.w.f. Exhaust dyeing was used for both untreated and cationic cotton fabrics, while two different dye fixation procedures — dye-bath fixation and steaming fixation were employed and compared.

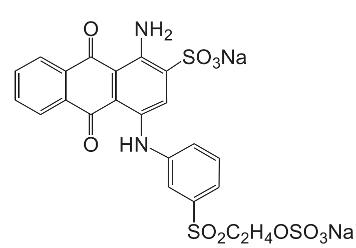
Procedure 1: untreated cotton fabrics were dyed at 30 °C over 40 min in dyebath with the addition of 60 $g \cdot L^{-1}$ anhydrous sodium sulfate, and then the temperature rose to 60 °C with the heating-rate of 2 $°C \cdot min^{-1}$, followed by the addition of 10 $g \cdot L^{-1}$ of sodium carbonate for dye fixation and kept at fixation temperature for 40 min.
Procedure 2: cationic cotton fabrics were dyed at 30 °C over 40 min in dyebath without the addition of sodium sulfate, and then the temperature rose to 60 °C with the heating-rate of 2 $°C \cdot min^{-1}$, followed by the addition of 10 $g \cdot L^{-1}$ of sodium carbonate for dye fixation and kept at fixation temperature for 40 min.
Procedure 3: untreated cotton fabrics were dyed at 30 °C over 40 min in dyebath with the addition of 60 $g \cdot L^{-1}$ anhydrous sodium sulfate. After that, the fabrics were taken out of the dyebath and



C. I. Reactive Red 195



C. I. Reactive Yellow 145



C. I. Reactive Blue 19

Fig. 2. Structures of the dyes applied.