The mathematical model of dye diffusion and adsorption on modified cellulose with triazine derivatives containing cationic and anionic groups

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Abstract. Cellulose fabric is chemically modified with the compounds containing cationic and anionic groups. The molecular chains of modified cellulose have both cationic and anionic groups. Dye diffusion properties on modified cellulose are discussed. The dye adsorption and diffusion on modified cellulose are higher than those on unmodified cellulose. The diffusion properties of dyes at different temperature are discussed. Compared with unmodified cellulose, the diffusion processing of dyes in the modified cotton cellulose shows significant change.

1. Introduction
It is well-known that cotton cellulose is highly appreciated for its outstanding characteristics such as comfortable hand, excellent softness for garment industry. Besides the traditional use as textile materials, cotton cellulose has been explored as a substrate for composite materials because of the presence of several functional groups that may be employed in various activation processes [1-3]. Reactive dyes occupy an important position for dyeing cellulose fibers. However, the cellulose fibers dye systems pose environmental question due to their current high salt requirement and colored effluent discharge. The reactive dyes used low salt containing fluorotriazine have been developed [4,5]. The success of the reactive dyes containing fluorotriazine is due to the high ratio of covalently bonded to total dye present on the fiber. The reactive group fluorotriazine is high active. In the other hand, in order to reduce the usage of salt and increase dyebath exhaustion, a number of attempts have been made to modify the cotton fiber using the compounds containing the certain groups and some polymers. It is one of important methods to modify cotton fabric with chemical method in order to improve some properties of cotton cellulose and change its surface chemical structure [6-10]. They are also widely used in preparing for nanofibers by electrospinning[11-14]. This will be of great benefit, as it will enable a reduction in the salt present in dyehouse effluent. Not surprisingly, this is particularly true of their dyeing characteristics. In our recent research work, net modified cellulose fabric with a 1,3,5-triazine derivative containing the multi reactive groups has been investigated [15]. However, molecular chains of modified cellulose fabric with Tri-HTAC (2,4,6-tri [(2-hydroxy-3-...
trimethyl-ammonium) propyl]-1,3,5-triazine chloride) only have cationic groups. Its application and product processing in the composite materials field can be limited. After cellulose fabric is chemically modified with compounds containing cationic and anionic groups, the molecular chains of modified cellulose have both cationic and anionic groups (shown in Scheme 1). They form new structure like silk protein and change the surface chemical structure and property of cellulose.

\[
\begin{align*}
\text{SO}_3\text{Na} \\
\text{Cell} \quad \text{OH} \\
N^+ (\text{CH}_3)_3
\end{align*}
\]

Scheme 1

In this paper, the compounds containing cationic and anionic compounds (Tri-HTAC-Bi-CSAT) are applied to modify cellulose. After modified with Tri-HTAC-Bi-CSAT compounds, the chemical structure and surface properties of cotton are changed. The dye diffusion and adsorption properties on modified cotton fiber are quite different from those of conventional cotton fabric. The dye diffusion and adsorption are nonlinear relationship with time. The mathematical model of dye diffusion and adsorption on modified and unmodified cellulose are investigated. The dyeing behavior of the modified cotton is analyzed and compared with the unmodified cotton.

2. Modification to cellulose fabric with the composition

2.1. Modification method

The 1,3,5-triazine derivative containing the reactive groups, 2,4,6-tri[(2-hydroxy-3-trimethylammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC) was dissolved in distilled water to give the certain concentration solution. 2,4-bichloro [(6-sulfanilic acid anhydrous)-1,3,5-triazine (Bi-CSAT) was added in the Tri-HTAC solution to give the certain quantity solution (Tri-HTAC:Bi-CSAT=5:1 w/w).

Tri-HTAC-Bi-CSAT solution was diluted in distilled water to give 8% solution by weight. To the solution was added 1.5% sodium hydroxide as catalyst. Samples of cellulose were treated with the solutions in the dyeing machine. The samples were kept at room temperature for 4 hr. The treated fabrics were then washed with tap water until neutral and again washed in warm water using a domestic washing machine to remove unfixed compounds. The fabrics were dried at ambient conditions.

2.2. Molecular structure of modified cellulose

The molecular structure of cellulose has a lot of hydroxyl. The compounds (Tri-HTAC-Bi-CSAT) are able to form covalent bonds with cellulose under alkaline conditions (shown in Scheme 2). The modified cellulose fibers formed new molecular structures containing not only cationic but also anionic groups (Scheme 1).
3. Mathematical model of dye diffusion and adsorption

3.1. Experimental method
The unmodified and modified cotton fabrics were dyed in an IR dyeing machine, dye concentration 2g/l, the liquor ratio being 1:500, pH 7. After dyeing, the fabrics were removed, rinsed thoroughly in hot tap water until the rinsing water was clear and air-dried. To determine the diffusion properties, isotherms were carried out at 25, 35, 45, and 65°C on the unmodified and modified cotton fabrics. The dye absorption at each time was determined using a Shanghai 723 Spectrophotometer. The K/S of dyed samples were determined using Datacolor Spectraflash SF600 Computer Color-Matching System in order to monitor the dyebath concentration. The dye up-takes on dyed samples were calculated through standard curves of K/S value.

After cotton fabric was chemically modified with Tri-HTAC-Bi-CSAT compounds, the chemical and morphological structure of the modified cotton cellulose could be changed. The modified cotton cellulose exhibited different behavior towards dye exhaustion and diffusion due to present a lot of cationic and anionic groups on modified cotton. In order to investigate the diffusion processing of the reactive dyes into modified cotton cellulose, Reactive Blue BF-RN was used to dye (the structure of Reactive Blue BF-RN shown in Scheme 3). Figures 1, 2 show the diffusion and exhaustion processing on unmodified cotton and modified cotton at different temperature 25, 35, 45, 65°C, respectively.
3.2. Mathematical model

By comparing Figures 1, 2, it is clear that the dye uptakes were higher on the modified cotton than those on unmodified cotton at any dyeing time. The transfer of a dye molecule from the dye solution into a fiber is usually considered to involve the initial mass transfer from the bulk solution to the fiber surface, adsorption of the dye on the surface, followed by diffusion of the dye into the fiber. The diffusion in a fabric is much more difficult than in solution because of dye-fiber interactions and mechanical obstruction by the fiber molecules in the pores. The diffusion of the dye within the fiber is rate controlling. Diffusion of dyes into fibers during dyeing can take place under either finite or infinite dyebath conditions. In a finite dyebath, the dye concentration at the fiber surface continuously decreases during the sorption process. In an infinite dyebath, the dye concentration does not change during the sorption process. If the initial dye concentration is high, infinite dyebath conditions are maintained throughout the dyeing process. In the present paper, the diffusion properties are analyzed for infinite dyebath condition.

The mathematical model of dye diffusion and adsorption on cellulose can be described as equation $E = at^2 + bt + c$. When $t=0$, values of $c$ means surface adsorption on cellulose in beginning step. The higher the values of $c$ in the beginning step are, the more the dyes sorbed by the fiber are. The $at^2$ may be neglected when time is very shot (for example in 30min). The values of $b$ means...
diffusion rate of a dye molecule from the dye solution into a fiber. With time increasing, $at^2$ will not be neglected and the dye diffusion and adsorption on cellulose reached equilibrium. The experimental results of non-line relationships are achieved by the use of a different dyeing times and temperatures (the equations see 1-8).

![Figure 2 Diffusion processing of Reactive Blue BF](image)

$$E_{u1} = -0.0012t^2 + 0.1888t + 1.9800 \quad (1)$$

$$E_{u2} = -0.0006t^2 + 0.1182t + 1.0789 \quad (2)$$

$$E_{u3} = -0.0005t^2 + 0.0988t + 0.7781 \quad (3)$$

$$E_{u4} = -0.0002t^2 + 0.0609t + 0.7973 \quad (4)$$

$$E_{m1} = -0.0018t^2 + 0.2841t + 8.8717 \quad (5)$$

$$E_{m2} = -0.0016t^2 + 0.2613t + 5.9296 \quad (6)$$

$$E_{m3} = -0.0009t^2 + 0.1897t + 4.9370 \quad (7)$$

$$E_{m4} = -0.0012t^2 + 0.2055t + 3.4246 \quad (8)$$

$E_{u1}$, $E_{u2}$, $E_{u3}$, $E_{u4}$ are the dye uptakes on unmodified cotton at different temperature, respectively. $E_{m1}$, $E_{m2}$, $E_{m3}$, $E_{m4}$ are the dye uptakes on modified cotton at different temperature respectively. The $t$ is dyeing time.

The values of $c$ show the dye adsorptions are higher on the modified cotton than those on unmodified cotton at any dyeing temperatures. The values of $b$ show the dye diffusion rates are faster on the modified cotton than those on unmodified cotton. It can be seen that the values of diffusion coefficient are higher 2-3 times on modified cotton than those on unmodified cotton. This conclusion is valid for each temperature and can be explained by more quaternary ammonium groups on modified cotton exposed to the dye molecules than those on unmodified cotton. Because there are more sites in the modified cotton capable of attracting the dye molecules, the absorption rates of dyes on modified
cotton are significant improved. The dyeing temperature has a significant influence on diffusion and adsorption. The higher the temperature is, the more the dye absorption by the fiber is. The diffusion rates increase as temperature rising. The dye uptake increase initially with the dyeing time, then slow down after 60min, and reach equilibrium after 60min. They demonstrate that diffusion rate of the reactive dyes into modified cotton cellulose is faster than those of them into unmodified cotton.

4. Conclusions
Cotton fabric is chemically modified with Tri-HTAC-Bi-CSAT composition. The modified cotton fabrics exhibit different behavior towards dyeing compared with unmodified cellulose. The mathematical model of dye diffusion and adsorption on modified cellulose can be describes as the equation $E = at^2 + bt + c$. The values of $c$ show the dye adsorptions are higher on the modified cotton than those on unmodified cotton at any dyeing temperatures. The values of $b$ show the dye diffusion rates are faster on the modified cotton than those on unmodified cotton. This will be of great benefit, as it will enable a reduction dyes effluent discharge and salt present in dyehouse effluent.

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