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# The performances of carboxymethyl chitosan in wash-off reactive dyeings

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ABSTRACT

Carboxymethyl chitosan (NOCC) with different molecular weight (Mw) and degree of substitution (DS) was synthesized under heterogeneous conditions. The synthesized NOCC was employed as builders in removing unfixed dyes from reactive cotton dyeings. The factors influencing wash-off effectiveness, including the achievable Mw and DS of NOCC and the initial pH value of washing liquor, were investigated. NOCC with the Mw of 25.0 kDa and the DS of approximately 1.0 has achieved the best wash-off effectiveness at the same wash-off conditions. The wash-off effectiveness of NOCC increases with the increase of pH values of washing liquor. The wash-off mechanism was also discussed by spectroscopic study. This study concludes that NOCC is a potential candidate for removing the unfixed reactive dyes on cotton fabrics.



## 1. Introduction

Polymers have found wide utilization in washing procedure recently (Bertleff, Neumann, Baur, & Kiessling, 1998). They play an important role in removing unfixed dyes from reactive cotton dyeings, with the aid of water and by keeping them in the form of colloid, emulsion, or dispersion in the washing liquor (Heissler, Siemensmeyer, Bastian, & Richter, 2004). So the released dyes from the dyed fabrics during wash-off can form complex compound with polymers, which retard the movement of the released dyes in washing liquor and prevent the fabric from restaining.

Carboxymethyl chitosan, an important water-soluble chitosan derivative, has many attractive chemical, physical and biological properties such as gel-forming capability, low toxicity, and good biocompatibility, all of which make it a promising biomaterial (Chen, Wang, Chen, Ho, & Sheu, 2006; Chen, Wang, Liu, & Park, 2002; Zhu & Fang, 2005). Due to its unique properties, particularly its biocompatibility, carboxymethyl chitosan has been extensively used in the biomedical field as moisture-retention agent and bactericide, in wound dressings as artificial bone and skin, and in blood anticoagulants as an element in drug delivery systems (Hirano, 1996; Muzzarelli, 1988; Muzzarelli, Tanfani, Emanuelli, & Mariotti, 1982; Muzzarelli et al., 1998; Zhang, Guo, Zhou, Yang, & Du, 2000). Besides, carboxymethyl chitosan is an efficient metal chelater and exhibits high adsorption capacity for dyes (Gupta & Haile, 2007; Sun & Wang, 2006). Since it has been shown to possess a variety of unique properties, the compound has attracted worldwide attention. Most of the related literatures concern their applicability in biomedical field. There are few literatures about the application of water-soluble NOCC in textile industry and its interaction mechanism with anionic dyes.

The purpose of this work is to apply NOCC to wash-off process of reactive cotton dyeings and determine the effectiveness of NOCC in removing unfixed reactive dyes. At the same time, the influences of the DS and Mw of NOCC and initial pH values of the washing liquor on the wash-off effectiveness have been studied. The working mechanism of NOCC for the dyes has also been discussed by means of absorption spectra.

## 2. Experimental

### 2.1. Materials

Chitosan sample (Mw = 100 kDa) with a degree of deacetylation of approximately 96.2% was acquired from Yongyue Ocean Biology Co., Ltd, China. In this work, the desized and bleached plain woven cotton fabric (121.8 g/m$^2$) was prepared for dyeing. The reactive dyes (C.I. Reactive Blue 21 and C.I. Reactive Red 2) were obtained from Shanghai Dyestuff Co., and used as received. All other chemicals and reagents used were of analytical grade.

### 2.2. Preparation and characterization of NOCC

NOCC was synthesized according to the preparation described in the literature with slight modifications (Chen et al., 2004). Chitosan powder (10 g) with definite Mw prepared according to

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the method described by Peniston and Johnson (1975) was suspended in 100 ml of isopropyl alcohol at 40 °C. Twelve milliliters of 10 N sodium hydroxide solution was added to the stirred slurry over 30 min, and then stirred for an additional 90 min. Subsequently, the stated monochloroacetic acid (20–60 g) was added in four equal portions at 5 min interval. The reaction mixture was heated to 60 °C and the reaction was held for 4 h. Afterward, the product was filtered out and rinsed with 80% (v/v) methanol and vacuum dried at 60 °C.

NOCC samples were confirmed in the form of potassium bromide pellets by a Nicolet NEXUS-670 FT-IR spectrometer. The Mw of the NOCC was measured by a Waters GPC instrument (USA) at 30 °C. The DS of NOCC was determined by using potentiometric titration (Lu, Song, & Cao, 2004).

### 2.3. Dyeing and wash-off procedure

The dyebath (300 ml) was prepared with the reactive dyes (2% o.w.f) and sodium chloride (18 g) at 40 °C, and then cotton fabric (10 g) was immersed in the dyebath and dyed for 30 min with stirring. For C.I. Reactive Red 2, sodium carbonate (3 g) was added and the dyeing was carried out at 40 °C for a further 60 min. For C.I. Reactive Blue 21, the dyeing temperature was raised to 60 °C and then sodium carbonate (3 g) was added to aid fixation and the dyeing followed at 60 °C for a further 60 min.

At the end of reactive dyeing, the dyed fabrics were subjected to rinsing twice with cold tap water for 10 min and then underwent wash-off process using NOCC at 95 °C for 15 min, rinsing with tap water at 50 °C for 10 min and final rinsing with cold tap water. Additionally, wash-off process was also performed just with water in the same conditions at liquor ratio 30:1 to compare the efficiency of removing unfixed dyes. The pH of the washing liquor was not regulated if there was no special demonstration.

### 2.4. Evaluation of washing results

The color strength values ($K/S$) at the maximum wavelength (C.I. Reactive Red 2, $\lambda_{max} = 530$ nm; C.I. Reactive Blue 21, $\lambda_{max} = 660$ nm) of the dyed samples, $K_1/S_1$ before and $K_2/S_2$ after wash-off, were measured on a Datacolor SF 600 Color Measurement Spectrophotometer (USA). The wash-off behavior was studied by comparing the $\Delta K/S$ values, which was calculated according to the following equation:

$$\Delta K/S = K_1/S_1 - K_2/S_2 \quad (1)$$

### 2.5. Spectroscopic investigation of NOCC/dye

Dye solution prepared with 0.1 g/l reactive dye in borax buffer (pH 9.0) was boiled at 95 °C for 1 h to form hydrolyzed dye. Subsequently, NOCC was introduced to keep the mixed solution at 95 °C for 1 h and the absorption spectra were recorded by U-3310 UV–Vis spectrometer to study the influence of varying NOCC concentrations on the UV–Vis spectrum of the dyes. The changes in the spectrum of the dyes after addition of NOCC can indicate the interactions of NOCC/dye.

## 3. Results and discussion

### 3.1. Characterization of NOCC

Fig. 1 shows the FT-IR spectrum of chitosan and NOCC. As shown in the spectrum of chitosan, the peaks observed at 1654 and 1323 cm$^{-1}$ are assigned to amide ($-NH_2$ deformation) and α (−NH-deformation). As for NOCC, the absorption peak at

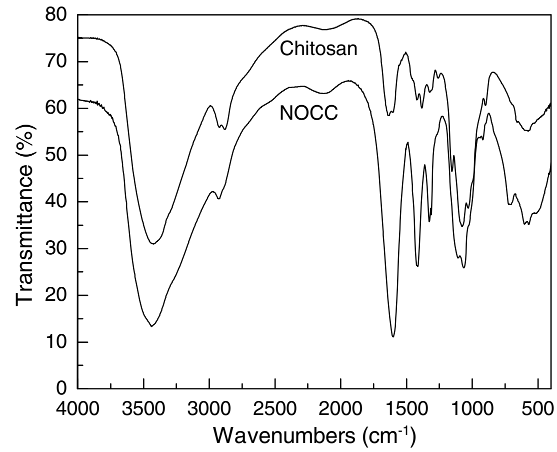


**Fig. 1.** IR spectra of chitosan and NOCC with a DS of 1.04 and Mw of 25.0 kDa.

1654 cm$^{-1}$ has disappeared and the peak at 1323 cm$^{-1}$ has become stronger. Furthermore, the characteristic peaks of NOCC at 1601 ($\nu_{as}$) and 1415 cm$^{-1}$ ($\nu_s$) should be assigned to the carboxylic acid salt ($COO^-$), which confirms that the carboxymethylation has occurred at the amino group of chitosan. In addition, extending vibration of ether bond at 1076 cm$^{-1}$ has become stronger, and the peak of primary alcohol at 1031 cm$^{-1}$ has not been so significant in contrast to the counter part of chitosan, which implies that carboxymethylation has also occurred at primary hydroxyl group of the chitosan. This IR spectrum is consistent with the reported spectra (Chen et al., 2004; Fan et al., 2006). Based on the IR, it can be concluded that carboxymethylation has occurred on both the amino and hydroxyl groups of chitosan. The Mw and DS values of NOCC samples have been listed in Table 1.

### 3.2. Effect of the DS of NOCC on Wash-off

The introduction of carboxylic groups to the repeated unit of chitosan can greatly improve the flocculation capacity (Wang & Wang, 2008). This can not only improve the water solubility of NOCC but also facilitate the removing of the unfixed dyes from cotton fabrics. The influence of the DS on the effectiveness of NOCC for removing the unfixed dyes was investigated at constant Mw of 89.0 kDa and the concentration of 1.0 g/l. The results have been depicted in Fig. 2.

A comparison of the $\Delta K/S$ values in Fig. 2 reveals that the color strength of the washed-off dyeings decreases with the increase of DS of NOCC. When DS increases from 0.87 to 1.06, the $\Delta K/S$ values of the dyeings increase from 1.82 to 2.07 for C.I. Reactive Blue 21 and from 1.78 to 2.03 for C.I. Reactive Red 2, respectively. Theoretically, the color strength of the dyed fabrics should decrease with increase the removal of dyes. This implies that the DS of NOCC has influence on the removal of unfixed dyes. However, the wash-off effectiveness of NOCC decreases with further in-

**Table 1**
Characteristics of NOCC samples prepared in the study

| NOCC sample | Mw (kDa) | DS |
|---|---|---|
| NOCC1 | 89.0 | 1.62 |
| NOCC2 | 89.0 | 1.06 |
| NOCC3 | 89.0 | 0.87 |
| NOCC4 | 43.0 | 1.08 |
| NOCC5 | 25.0 | 1.04 |
| NOCC6 | 8.60 | 1.05 |

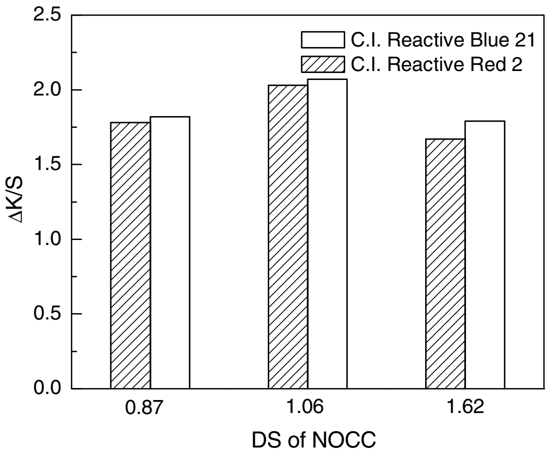


**Fig. 2.** Effect of DS of NOCC on the wash-off (Mw = 89.0 kDa; C.I. Reactive Blue 21, $K_1/S_1 = 11.68$; C.I. Reactive Red 2, $K_1/S_1 = 12.39$).

crease of the DS from 1.06 to 1.62. The results may be attributed to the synergic effect of carboxyl, amino and hydroxyl functional groups of repeated unit of NOCC. On the one hand, NOCC may probably interact with the released dyes through electrostatic, dipolar and hydrogen bonding, etc. This indicates that NOCC can form polyelectrolyte complexes with the released dyes which may protect the released dyes from transfer or restain on the substrate. The appropriate increase of DS of NOCC changes molecular structures of NOCC which may improve the water solubility of the complexes to confer stabilization on the complexes in the washing liquor. On the other hand, excessive carboxylic groups would lead an increase of repulsion between NOCC and the released dyes and cause adverse effects. It can be concluded from the above discussion that the wash-off effectiveness of NOCC is influenced not only by carboxylic groups but also by the amino and hydroxyl groups, and the appropriate ratio of carboxylic, amino and hydroxyl groups can enhance wash-off capacity of NOCC.

### 3.3. Influence of Mw of NOCC upon wash-off

In addition to investigation of the DS of NOCC, it is also of interest to examine the influence of Mw on wash-off effectiveness. Fig. 3 shows the influence of varying Mw of NOCC with constant DS of *ca*. 1.0 and concentration of 1.0 g/l, i.e. the total number of carboxylic groups is approximately constant. Only limited ranges of Mw are available, but the results from wash-off test suggest that increase in Mw of NOCC from *ca*. 8.60 to 25.0 kDa can increase the wash-off effectiveness. This result indicates that the higher Mw of NOCC with longer molecular chain facilitates the hydrophobic interaction with the released dyes. However, this figure also shows that the increase of Mw of NOCC above 25.0 kDa produces a sharp reduction in wash-off effectiveness. Since the total carboxylic group concentration is constant, the result implies that a minimum number of carboxylic groups in NOCC are required to permit the binding of the released dyes. Obviously, not all these carboxylic groups are directly involved in binding with released dyes but are required to allow NOCC to adopt a conformation in which it can bind or wrap around the dyes. The results also imply that there should be other interactions such as electrostatic, dipolar and hydrogen bonding et al. to confer additional stabilization on the complexes. Additionally, it has recently been reported that aromatic rings interact with sugar rings (Paul, 2002) and it can be speculated that the spacing between the aromatics in the dyes, if commensurate to spacing between rings of NOCC, could be beneficial to stabilize the complexes due to a combination of dispersive and multiple hydrogen bonding interactions.

### 3.4. Effect of concentration of NOCC on washing effectiveness

The influence of NOCC level with constant Mw (25.0 kDa) and DS (1.04) on removing unfixed dyes is depicted in Fig. 4. It can be seen from Fig. 4 that the $\Delta K/S$ values increase sharply as the applied concentration of NOCC increase, but gradually level off at NOCC concentration higher than 1.0 g/l. This implies that for the dye used, the existence of NOCC in washing liquor generally has a positive effect on removal of unfixed dyes.

Under the condition of lower concentration in which NOCC molecules are in an unfolded conformation with weaker intermolecular hydrogen bond, this increases probability for NOCC to interact with the released dyes. As a result, the increase concentration of NOCC can increase the wash-off effectiveness. However, the intermolecular hydrogen bonding strengthens with the increase of NOCC concentration which induces the assembly of NOCC (Pang, Chen, Park, Cha, & Kennedy, 2007) and reduces probability for NOCC to interact with the released dyes. The highest wash-off effectiveness for C.I. Reactive Blue 21 and C.I. Reactive Red 2 has been realized at the corresponding concentration of NOCC of 1.0 g/l.

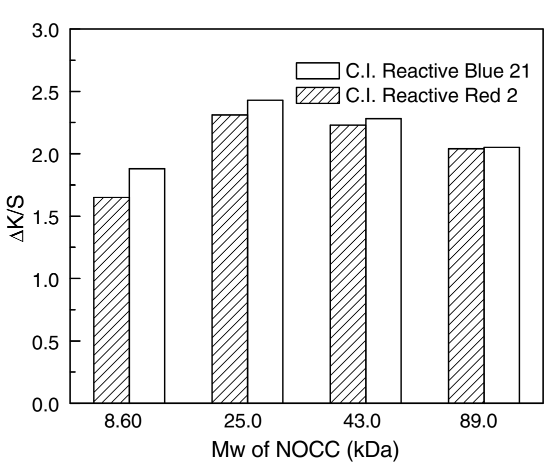


**Fig. 3.** Effect of Mw of NOCC on the wash-off (the corresponding DS are 1.05, 1.04, 1.08, and 1.06; C.I. Reactive Blue 21, $K_1/S_1 = 11.68$; C.I. Reactive Red 2, $K_1/S_1 = 12.39$).

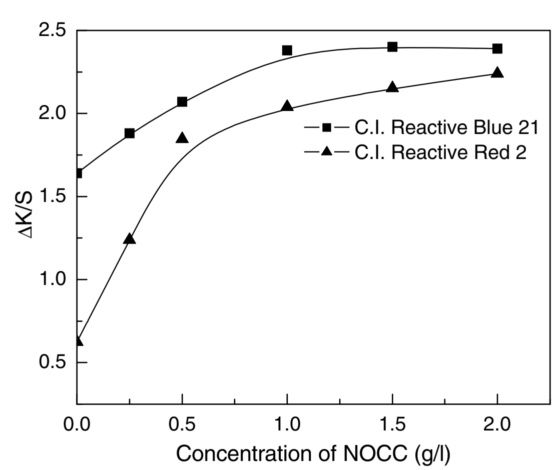


**Fig. 4.** Effect of NOCC concentration on the wash-off (DS = 1.04; Mw = 25.0 kDa; C.I. Reactive Blue 21, $K_1/S_1 = 11.68$; C.I. Reactive Red 2, $K_1/S_1 = 12.39$).

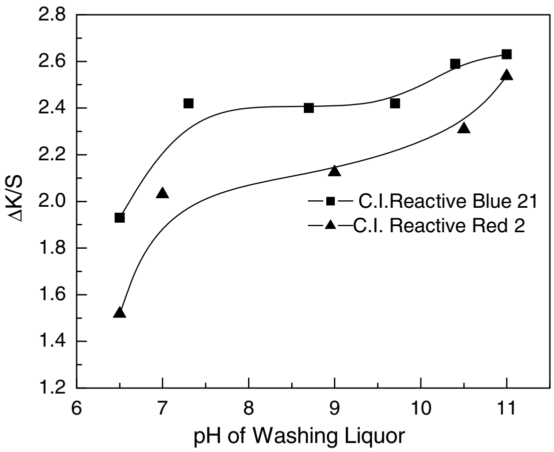


**Fig. 5.** Effect of the pH values on the wash-off (DS = 1.04; Mw = 25.0 kDa; C.I. Reactive Blue 21, $K_1/S_1 = 11.68$; C.I. Reactive Red 2, $K_1/S_1 = 12.39$).

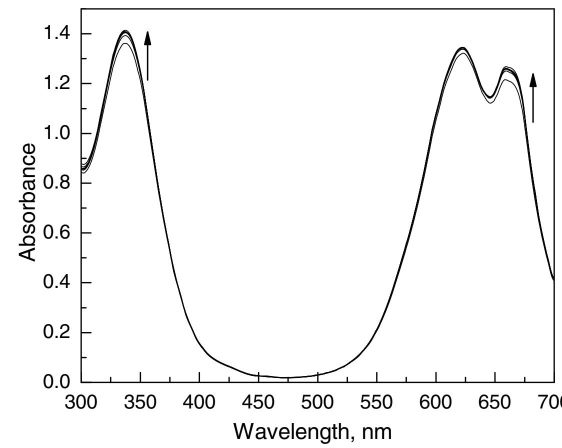


**Fig. 6.** Changes in the spectrum of C.I. Reactive Blue 21 on addition of increasing amounts of NOCC (indicated by arrow) at pH 9.0, borax buffer, 20 °C, (DS = 1.04; Mw = 25.0 kDa).

### 3.5. Effect of pH on washing effectiveness

The pH value of the washing liquor is an important factor influencing wash-off effectiveness of NOCC. Fig. 5 shows the influence of pH values of washing liquor on the wash-off effectiveness of NOCC (DS = 1.04, Mw = 25.0 kDa). The range of pH selected for washing test in this study is between 6.0 and 11.0. As can be seen from Fig. 5, the $\Delta K/S$ values increase rapidly when pH of the liquor increase up to 7.5, and then approaches constant values at $7.5 < \text{pH} < 10.0$. A further increase in pH value from 10.0 shows slightly increases in the $\Delta K/S$ value.

Under acidic conditions, the cotton fiber has more positive charges and has higher dyes adsorption ability (Wang & Lewis, 2002). Desorption of unfixed dyes from the cotton fiber becomes difficult. On the other hand, taking into account that the released dyes exists in the anionic form, NOCC as a cationic polyelectrolyte can bind with the released dyes to form precipitate and restain onto cotton fiber.

Under alkaline conditions, the ionization of the hydroxyl and carboxylic groups in the cotton is increased (Rattanaphani, Chairat, Bremner, & Rattanaphani, 2007), and in turn the increase of repulsion between the anionic dyes and anionic groups on the substrate will result in an increase of dye desorption. The rise of pH during wash-off process confirms this mechanism. On the other hand, the quaternary groups of NOCC are partly neutralized and its dye bonding compatibility is lessened. Nevertheless, the significant binding of NOCC to the released dyes still occurs due to other interactions between NOCC and dyes. This can be further proved in the following. The further increase of the $\Delta K/S$ value at pH >10.0 can be attributed to the increase of the repulsion between the unfixed dyes and cotton substrate. However, hydrolysis of the fixed dyes on the cotton fiber may also occur when the pH of washing liquor increase above 10.0.

### 3.6. The working mechanism of NOCC in wash-off

Fig. 6 shows the influence of varying NOCC (DS = 1.04, Mw = 25.0 kDa) concentrations at pH 9.0 borax buffer on the UV–Vis spectrum of hydrolyzed C.I. Reactive Blue 21. The main spectra increase in intensity as the concentration of NOCC is successively increased. The changes of the absorbance at the maximum wavelength prove that the chromophore of reactive dye interacts with NOCC through polarity force in water (Heissler et al., 2004). A plot showing the increase of absorbance of the dyes in the bulk solution with the addition of NOCC is depicted in Fig. 7. Evidently, the

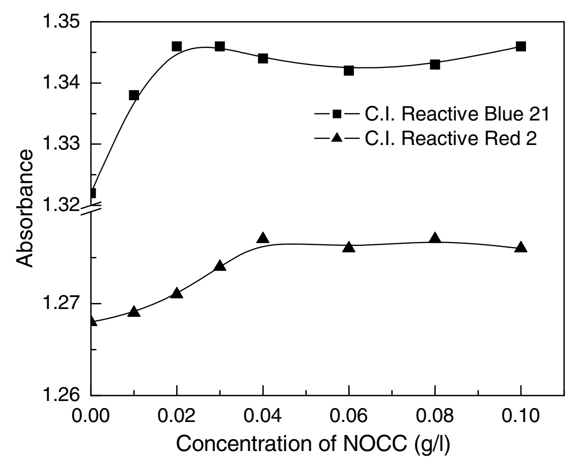


**Fig. 7.** Relationship between absorbance and concentration of NOCC for C.I. Reactive Blue 21 ($\lambda_{max} = 660$ nm) and C.I. Reactive Red 2 ($\lambda_{max} = 530$ nm) at pH 9.0, borax buffer, 20 °C, (DS = 1.04; Mw = 25.0 kDa).

changes in spectra due to the binding of the parent dyes to NOCC require much low concentration of NOCC for the selected dyes (C.I. Reactive Blue 21, 0.3 g/l; C.I. Reactive Red 2, 0.4 g/l). Compared with the effective concentration of NOCC used in wash-off procedure, the binding with the equimolar dyes needs much smaller dosage. It demonstrates that NOCC in wash-off may follow other mechanisms besides binding with the chromophore of the dyes. The related studies will be carried out in future work.

The pH value is known to affect the interactions between the dyes and NOCC. The further investigation of the influence of NOCC has undergone at low and high pH to examine the binding form. The blank dye solution of 0.1 g/l has been boiled for 1 h at 95 °C after the pH adjustment to hydrolyze the dyes and, thereafter, 0.06 g/l NOCC has been added to keep for 1 h and the absorbance of the solution at the maximum wavelength has been measured.

At low pH, NOCC becomes more effective in binding the dyes (Fig. 8); this may be due to the increase of cationic sites on the NOCC (Wang and Wang, 2008). There is also evident aggregate of cationic NOCC with dyes which results in an increase in the spectra yield. However, most of the carboxylic groups do not ionize to assist solubilization in water, which may result in a redeposit of the complexes of NOCC/dye onto the substrate. With the increase of the pH value, the carboxylic groups begin to ionize and extend into

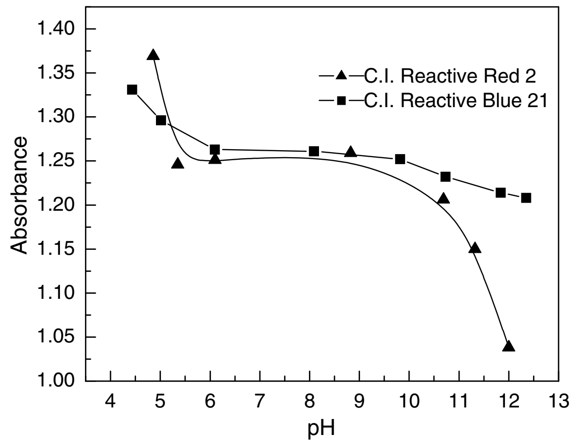


**Fig. 8.** The influence of pH on the absorbance of 0.1 g/l reactive dyes with 0.06 g/l NOCC (C.I. Reactive Blue 21 measured at 660 nm and C.I. Reactive Red 2 measured at 530 nm).

the water phase to stabilize the complexes solution of NOCC and released dyes. At the same time, the repulsion force between NOCC and dyes increased. Nevertheless, the absorbance values level off with the increase of pH from 6.0 to 10.0. It demonstrates that the binding of the anionic dyes with NOCC still occurs due to other interactions between the dyes and NOCC. At high pH, most of the carboxylic groups ionize and the interactions with the dyes decrease. This result can be illustrated by the decrease of the absorbance when the pH value above 10.0 in Fig. 8.

These results can be explained based on the forces of repulsion and attraction expected to occur during the wash-off process. When NOCC is dissolved in water, the solution is an alkalescent system, NOCC behaved as a relatively weak anionic polyelectrolyte. The forces arise due to the presence of negative charge on reactive dyed cotton fabrics, anionic groups of the released dyes and amino and carboxylic ions in NOCC, besides other factors as mentioned before. In the wash-off process, the presence of amino groups in NOCC enhances the attraction between NOCC and the anionic dyes. Besides, the carboxylic groups in NOCC repel the complexes of NOCC and the released dyes from the negative charged reactive dyeings, which inhibit the restain of released dyes onto cotton fabric.

## 4. Conclusions

NOCC with different DS and Mw can in evidence influence the washing effectiveness of reactive dyeings. NOCC with the DS of *ca*. 1.0 and Mw of 25 kDa exhibit the much higher effectiveness for removing the unfixed reactive dyes at the same wash-off conditions. Results obtained from this study show that the wash-off effectiveness of NOCC for the selected dyes increased with increase of pH. The binding of NOCC with anion dyes plays an important role in the wash-off but it is not the unique means. Although the presence of carboxylic groups in NOCC is critical for wash-off, there is a limit, i.e. incorporation of too many negatively charged groups may be counterproductive.

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