RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Adsorption properties of direct dyes on viscose/chitin bicomponent fiber: evaluation and comparison with viscose fiber

Hongxian Zeng and Ren-Cheng Tang*

National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, 199 Renai Road, Suzhou 215123, China

*Corresponding author:

E-mail address: tangrencheng@suda.edu.cn

Tel: +86 512 6716 4993. Fax: +86 512 6724 6786.

Abstract: Two direct dyes were applied to the dyeing of viscose/chitin bicomponent fiber whose chitin component can provide functionalities and enhanced dyeing properties. The dyeing rates, adsorption isotherms and mechanisms, and electrolyte and dye concentration dependence of dye adsorption as well as the desorption of dyes from the dyed fiber were investigated in comparison with the dyeing system of regular viscose fiber. The higher adsorption and lower desorption of dyes occurred for viscose/chitin fiber. Viscose/chitin fiber showed great dye adsorption capability even at a low salt dosage, providing environmental benefits for dyeing process. The rates of dye uptake by viscose/chitin fiber were faster, and followed the pseudo-second-order kinetic model. The dye adsorption isotherms were most closely correlated to the dual Langmuir-Nernst model consisting of site-specific and non-site-specific interactions between dyes and fibers; the Langmuir adsorption was predominant in total adsorption, and this predominance was more obvious for viscose/chitin fiber. The above dye adsorption characteristics of viscose/chitin fiber resulted mainly from its partially deacetylated chitin component which can reduce the negative charge density of the fiber and provide more site-specific dyeing sites.

Keywords: Viscose; Chitin; Fiber; Adsorption; Dyeing; Direct dyes

1. Introduction

Most of the world's man-made cellulose fibers are produced by the classical viscose process based on deriving cellulose with carbon disulfide.[1] These fibers are called rayons. Although some problems connected with the viscose process such as relatively high production costs and environmental pollution need to be reduced and stimulate the application of alternative production routes, the production of viscose fiber has an accepted importance within the fiber family, not only just the standard fiber but also speciality fibers such as micro-fibers, spun-dyed fibers, functional fibers, fibers for nonwovens, etc.[1] Viscose fiber has no functionality in essence except wear comfort and moisture management, but the functional additives incorporated in the spinning process can endow it with diverse functionalities such as flame retardancy, antibacterial activity, ultraviolet protection capability, water repellency, and combined antibacterial activity and enhanced dyeability, etc.[1-5]

Cellulose is the most abundant natural polymer in the world, followed by chitin. Chitin and its deacetylated product (chitosan) have been extensively applied in many fields because of their outstanding properties such as biocompatibility, non-toxicity, biodegradability and antimicrobial activity.[6, 7] In the fiber industry, chitin, chitosan and their blends with other polymers can be applied to the manufacturing of functional fibers by wet spinning.[6, 8] Nowadays, chitosan fiber and viscose/chitin or chitosan bicomponent fiber have been commercially produced. The manufacturing of viscose/chitin or chitosan bicomponent fiber by wet spinning can be mainly divided into two following approaches: one is the use of cellulose viscose in which a fine chitosan powder is dispersed, and the other is the use of a mixed solution of cellulose viscose and chitin viscose. A typical product prepared by the former technique is *Chitopol*y fiber (Fuji Spinning Co., Japan), and the product examples prepared by the latter technique are *Crabyon* (Ohmikenshi Co., Japan) and *Chitcel* (CHTC Helon Co. Ltd., China) fibers.[9, 10] Viscose/chitin bicomponent (viscose/CH) fiber is a new kind of modified viscose fiber combining the advantages of viscose fiber and chitin polymer. Its merits include no allergenic reaction, low antigenicity, high safety, organism compatibility, gentleness to the body, antibacterial and deodorizing effects, and moisture-retaining.[8-10]

If a new kind of fiber stands a chance of success on the market, its performance is a primary factor. Additionally, a suitable dyeing and finishing process can not be neglected. Viscose/CH fiber contains chitin component which is partially deacetylated in the course of mixing and spinning of chitin viscose and cellulose viscose owing to the strong alkalinity of these viscoses. The deacetylation degree of the chitin in *Crabyon* fiber is about 55%.[10] The inclusion of partially deacetylated chitin in viscose/CH fiber delivers different dyeing and finishing characteristics from regular viscose fiber. Therefore, the research on the wet processing properties of viscose/CH fiber is of great significance both in theory and in practice. Several investigations have been undertaken on the dyeing and functional modification of viscose/CH fiber. Nakajima et al. measured the dyeing rate curves of C.I. Acid Orange 7 with a small molecular size and C.I. Direct Red 28 with a large molecular size for viscose/CH fibers under the conditions of pH 4 and 30 to 50 °C,[11] and found that the dyeing rates of two dyes for viscose/CH fibers were higher than those for silk and viscose fibers, and increased with increasing chitin content. Shimizu et al. observed the sigmoid type adsorption of C.I. Acid Orange 7 on visocose/CH fibers different from the Langmuir type adsorption on silk and wool fibers at pH 4 and temperatures below 50 °C.[10] Shimizu et al. also studied the effect of pH on the fixation of four reactive dyes on viscose/CH fibers in the absence of neutral electrolyte,[12] and noticed that C.I. Reactive Blue 5 with a monochlorotriazinyl group in a weakly acidic solution and C.I. Reactive Blue 19 with a sulfatoethylsulfonyl group in weakly acidic to weakly alkaline solutions showed high fixation on viscose/CH fibers, whereas viscose fiber could not react entirely with Blue 19 at the same pH region. Recently, Kokol and co-workers utilized polyphenol oxidases to graft natural flavonoids onto viscose/CH fiber with the aim of significantly upgrading the antioxidant activity of this fiber.[13, 14] In addition, Vasile et al. carried out the modification of viscose/CH fiber with a variety of monomers under plasma conditions.[9, 15]

Viscose/CH fiber consists of viscose and partially deacetylated chitin, and its most predominant component is viscose. Therefore the dyes (e.g., widely used reactive and direct dyes) suitable for cellulosic fibers can also be applied to the dyeing of the fiber. Although the previous research discussed the adsorption mechanisms and dyeing properties of some dyes on viscose/CH fiber, further studies still deserve to be carried out in order to better understand the adsorption mechanism of various dyes, know the dyeing properties of dyes under the conditions close to those used in practical dyeing process, and provide help for the dyers to control the dyeing process and optimize the application of dyes. In this work, two commercial direct dyes bearing four sulfonate groups were employed to dye viscose/CH fiber, and the rates, equilibrium isotherms and mechanisms of dye adsorption were investigated. The dual Langmuir-Nernst model consisting of site-specific and non-site-specific interactions between dyes and fibers was used to describe the adsorption isotherms of dyes with the aim of providing an insight into the mechanism of the direct dyeing process of viscose/CH fiber. Moreover, the effect of neutral electrolyte on dye adsorption, the building-up properties of dyes, and the desorption properties of dyes from the dyed fiber were also discussed. In these studies, the regular viscose fiber was selected as the reference sample.

2. Experimental

2.1. Materials

The 1.67 dtex×38 mm viscose fiber was kindly supplied by Hebei Jigao Chemical Fiber Co., Ltd., China. The 1.67 dtex×38 mm viscose/chitin bicomponent (abbreviated as viscose/CH) fiber under the trade name of *Chitcel* was purchased from CHTC Helon Co. Ltd., China. According to the previous report, the viscose/CH fiber contains 9-11% wt chitin.[9] To remove the finish oils added to the fibers in post-spinning treatments, the fiber samples were treated in a scouring bath containing 0.5 g/L *Levelling Agent O* and 1 g/L sodium carbonate at 80 °C for 60 min using a 30:1 liquor ratio. The scoured fibers were then rinsed thoroughly in tap water, allowed to dry in the open air and kept in a desiccator with silica gel.

Everdirect Supra Yellow RL (C.I. Direct Yellow 86) and *Everdirect Blue BRR* (C.I. Direct Blue 71) were from Everlight Chemical Industrial Co., and used as received. The dye structures are given in Fig. 1. Acid Orange II (C.I. Acid Orange 7, a sulfonated monoazo dye) was a commercial product, and purified by repeatedly dissolving in N,N-dimethylformamide followed by precipitating in acetone. Sodium carbonate, sodium sulfate, glacial acetic acid, sodium acetate, N,N-dimethylformamide and acetone were of analytical reagent grade. *Levelling Agent O* (a nonionic polyoxyethylene ether surfactant) was provided by Jiangsu Hai'an Petrochemical Plant, China and used as received.

< Insert Fig. 1>

2.2. Adsorption and dyeing methods

All adsorption and dyeing experiments were carried out in the sealed and conical flasks immersed in a XW-ZDR low-noise oscillated dyeing machine (Jiangsu Jingjiang Xingwang Dyeing and Finishing Machinery Factory, China). All of the dye solutions were prepared with direct dyes, sodium sulfate and *Levelling Agent O* (0.3 g/L). The liquor-to-goods ratio was kept at 60:1. At the end of dyeing, the dyed fibers were rinsed thoroughly in distilled water, and allowed to dry in the open air.

2.2.1. Effect of sodium sulfate dosage on the uptake of dyes

To assess the dependence of the uptake of two dyes on sodium sulfate concentration, the fibers were dyed in the solutions including 3% owf (on the weight of fiber) dye and 0-20 g/L sodium sulfate. The dyeing started at 30 ^{o}C, the temperature was raised at a rate of 2 ^{o}C/min up to 90 ^{o}C, and at this temperature the dyeing continued for 60 min.

2.2.2. Adsorption rates of dyes

The fibers were dyed in the dye solution containing 3% owf dye and 10 g/L sodium sulfate for different times at 90 ^{o}C. The fibers were not placed in the dyebath until the dyebath reached the dyeing temperature.

2.2.3. Equilibrium adsorption isotherms of dyes

The adsorption isotherms were measured in a series of dye solutions of various concentrations (0.5-5% owf), which contained 10 g/L sodium sulfate. The fibers were dyed at 90 ^{o}C for 3 h in order to achieve equilibrium adsorption.

2.2.4. Building-up properties of dyes

The building-up properties of dyes on fibers were measured in the dye solutions which were composed of 0.5-5% owf dye, and 10 g/L sodium sulfate. The fibers were immersed into the solutions at 30 ^{o}C, and subsequently the solutions were heated to 90 ^{o}C at a rate of 2 ^{o}C/min and the dyeing continued for 80 min.

2.3. Measurements

2.3.1. Dye uptake

The absorption spectra and the absorbance at the maximum absorption wavelength of the dye solutions were measured using the *Shimadzu* UV-1800 UV-vis spectrophotometer (Shimadzu Co., Japan). The quantity of dyes in solution was calculated using a previously established absorbance/concentration relationship, and the percentage of exhaustion (%*E*) was determined using Eq. 1, where C_0 and C_1 are the quantities of dyes in solution before and after dyeing, respectively. The quantity of dyes on fibers was calculated by taking into account the initial and final quantity of dyes in solution and the weight of fibers.

$$\%E=100\times\frac{C_0\text{-}C_1}{C_0} \tag{1}$$

2.3.2. Desorption of dyes from the dyed fibers

The desorption of Yellow RL and Blue BRR from the dyed fibers in water was tested at 60 ^{o}C using a liquor ratio of 100:1. Prior to the desorption experiments, the viscose/CH and viscose fibers were dyed using the method described in Section 2.2.4. For the desorption of Yellow RL, both the viscose/CH fiber and the viscose fiber were dyed with 2% owf dye; for the desorption of Blue BRR, the viscose/CH and viscose fibers were dyed with 2.5% and 4% owf dye, respectively. For both Yellow RL and Blue BRR, the corresponding dye dosages nearly gave the same quantity of dye adsorption by the viscose/CH and viscose fibers according to the previously evaluation in Section 2.2.4. After dyeing, the fibers were completely rinsed in distilled water, washed at 40 ^{o}C for 5 min, and finally dried in the open air. The desorption rate at different times was calculated by the difference in the concentrations of the dye on the fibers before and after desorption.

2.3.3. Determination of amino groups in viscose/CH fiber

The amount of amino groups in viscose/CH fiber was evaluated by means of the adsorption of C.I. Acid Dye 7 according to a previously reported method.[13] For this adsorption experiment, 0.25 g of the fiber sample was immersed into an acidic dye solution of 4×10^{-4} mol/L; the pH value of the dye solution was adjusted to 3.6 with acetic acid/sodium acetate buffer; the adsorption was conducted at 25 ^{o}C for 6 h in order that the equilibrium was reached. After adsorption, the residual dye solution was analyzed spectrophotometrically, and the amount of the adsorption of C.I. Acid Dye 7 was calculated. This procedure was found to give a 100% stochiometric reaction at dye anionic sites with protonated amino groups along the partially deacetylated chitin chains integrated into a viscose fiber skeleton.[13] The average results of two repetitions were presented as the amount of amino groups per kg of fiber.

2.3.4. FTIR analysis

The infrared spectra of viscose/CH and viscose fibers were recorded with the Nicolet 5700 FT-IR spectrometer (Thermo Fisher Scientific Inc., USA) using potassium bromide pellets. The fibers were cut into powder with a pair of scissors and the fiber powders were then used as samples. All of the IR data were collected from 32 scans with a resolution of 4.0 cm^{-1}.

2.3.5. X-ray diffraction characterization

The wide angle X-ray diffraction (WAXD) measurements of fiber powders were carried out on the X'Pert-Pro MPD X-ray diffractometer (PANalytical B.V., NL) equipped using copper K alpha radiation of wavelength 0.15418 nm at room temperature. The scattering angle range was 5^o–45^o, and scans were collected at 40 kV and 35 mA. The crystallinity degree was determined by corresponding peak separation analysis.

3. Results and Discussion

3.1. Characterization of viscose/CH fiber

The FTIR spectra in the 2000–400 cm^{-1} region of viscose/CH and viscose fibers are shown in Fig. 2. This region contains the largest number of spectral differences which allows for the identification of structural changes in cellulosic fibers.[16] The spectrum of the viscose fiber showed the characteristic peaks of cellulose II at 1419 (δ CH_2 symmetric bending), 1375 (C–H bending), 1317 (CH_2 wagging), and 895 cm^{-1} (γ[COC] in plane, symmetric stretching), in agreement with the literature.[16] Due to the inclusion of partially deacetylated chitin, the viscose/CH fiber displayed the IR spectrum slightly different from that of viscose fiber. For the viscose/CH fiber, the weak bands at 1660 and 1557 cm^{-1} attributable to the C═O stretching of amide I and the N–H bending of amide II from the partially deacetylated chitin component, respectively[17, 18] were found, and these characteristic absorptions became a good evidence for the presence of nitrogen atoms on the surface of this fiber.

< Insert Fig. 2 >

The quantity of amino groups as an indication of the partially deacetylated chitin component present in viscose/CH fiber was detected using the Acid Orange 7 adsorption method.[13] The corresponding values for viscose/CH and viscose fibers were

68.19 and 2.82 mmol/kg, respectively. Actually there is no amino group in viscose fiber. An insignificant amount was detected in viscose fiber due to very weak and non-ionic interaction between the acid dye and this fiber. The presence of amino groups in viscose/CH fiber may affect the adsorption of anionic dyes.

The dyeing properties of one fiber are usually affected by its crystalline structure. Thus the crystalline structure of the viscose/CH and viscose fibers was studied by WAXD. Fig. 3 shows X-ray diffraction traces for these two fibers. Three diffraction peaks were at the angular positions (2θ) of approximately 12.4, 20.4 and 21.8, showing the crystalline structure of cellulose II.[19, 20] The inclusion of partially deacetylated chitin into the viscose/CH fiber had no obvious impact on the crystalline structure of viscose fiber. The crystallinity degrees of the viscose/CH and viscose fibers determined by a peak separation analysis were 41.5% and 34.8%, respectively. The difference of crystallinity degree between these two fibers possibly resulted from the different spinning parameters employed by the corresponding manufacturers. In general, the regenerated cellulosic fibers with a low crystallinity degree would have the great capacities for the adsorption of dyes if their other physical and chemical characteristics are the same.

< Insert Fig. 3 >

3.2. Effect of sodium sulfate dosage on the uptake of dyes

Fig. 4 shows the effect of sodium sulfate dosage on the uptake of two direct dyes, Yellow RL and Blue BRR. The uptake of two dyes by viscose/CH and viscose fibers increased with increasing salt concentration until a plateau was reached when the salt concentration was higher than a certain value. It was found that two dyes exhibited very high uptake by viscose/CH fiber even at a very low dosage of salt. The dye exhaustion of viscose/CH fiber exceeded 90% at a sodium sulfate dosage of 5 g/L, whereas 15-20 g/L sodium sulfate had to be consumed for viscose fiber to acquire the same dye exhaustion. Taking the fact into consideration that viscose/CH fiber had a slightly higher crystallinity degree than viscose fiber, and possessed amino groups as discussed in Section 3.1, the higher dye exhaustion of viscose/CH fiber at a low dosage of salt is preliminarily considered to result from the reduced negative charge density of the fiber caused by the partially protonated amino groups of the partially deacetylated chitin component.[10] Generally, neutral salt is applied in the dyeing of cellulosic fiber to overcome repulsive forces between direct dyes and fibers, and its dosage should be increased as a function of dye concentration. The great dyeability of viscose/CH fiber at a low dosage of salt suggests that the dosage of salt can be saved for the direct dyeing of viscose/CH fiber in comparison with the dyeing of regular viscose fiber, thus providing eco-friendly benefit.

< Insert Fig. 4 >

3.3. Adsorption kinetics of dyes

The adsorption rates of two direct dyes for viscose/CH and viscose fibers are depicted in Fig. 5. As shown in Fig. 5, the adsorption quantity of two dyes increased dramatically in the first 15 min, and then reached equilibrium at 30 to 45 min; two dyes exhibited higher adsorption rates for viscose/CH fiber than for viscose fiber at the initial stage of dyeing. Furthermore, the quantity of dye adsorption at equilibrium on viscose/CH fiber was higher than that on viscose fiber.

< Insert Fig. 5 >

To obtain the kinetic parameters of the dyeing of viscose/CH and viscose fibers, the pseudo-second-order equation (Eq. 2) [21] was used to analyze the experimental data.

$$\frac{t}{C_t} = \frac{1}{kC_\infty^2} + \frac{1}{C_\infty} t \qquad (2)$$

where k (g/[mg min]) is the equilibrium rate constant of pseudo-second-order adsorption, and C_∞ and C_t refer to the amount of dye (mg/g) at equilibrium and at t time (min).

The rate constant (k) and the dye adsorption quantity at equilibrium (C_∞) were able to be calculated by the slope and intercept of the linear plot of t/C_t versus t (Fig. 5), and listed in Table 1. The correlation coefficients (R^2) for the linear plots were very close to 1 for all the experimental data. The C_∞ values obtained also agreed with the experimental data. These results suggest that the pseudo-second-order kinetic model can be used to describe the adsorption process of direct dyes onto viscose/CH and viscose fibers.

< Insert Table 1 >

Based on the pseudo-second-order kinetic model, the initial adsorption rate (h_i) and the half-adsorption time ($t_{1/2}$) were calculated using the following Eqs. 3 and 4, respectively.[22, 23] The half-adsorption time is defined as the time required for the adsorbents to uptake half of the amount adsorbed at equilibrium, and often considered as a measure of the adsorption rate.

$$h_i = kC_\infty^2 \qquad (3)$$

$$t_{1/2} = \frac{1}{k \cdot C_\infty} \qquad (4)$$

As can be seen from Table 1, the kinetic parameters for the adsorption of direct dyes varied according to fiber and dye categories. For viscose/CH fiber, the higher rate constant and initial rate of dye adsorption were found with the shorter half-adsorption time. The higher dye adsorption or dyeing rate of viscose/CH fiber should be ascribed to the additional positive adsorbing sites and the reduced negative charge density which are caused by the partially protonated amino groups of the partially deacetylated chitin in this fiber.

3.4. Adsorption isotherms of dyes

In general, equilibrium adsorption will be reached in longer times when the dye concentrations are high. Therefore the isotherms were determined on the basis of the adsorption for 3 h. The isotherms of the adsorption of direct dyes on viscose/CH and viscose fibers are depicted in Fig. 6.

< Insert Fig. 6 >

To better understand the interactions between direct dyes and viscose/CH fibers, three isothermal models, namely Langmuir, Freundlich, and Langmuir–Nernst (the dual adsorption equation consisting of the partition and Langmuir models), were selected to compare the equilibrium adsorption data.

The expression for the widely used Langmuir isotherm is:[24]

$$C_f = \frac{SK_LC_s}{1 + K_LC_s} \qquad (5)$$

where C_f (mg/g) and C_s (mg/L) are the concentrations of dyes on fibers and in solution at equilibrium, respectively; S (mg/g) is the saturation concentration of dyes on fibers; K_L (L/mg) is the Langmuir affinity constant.

The empirical Freundlich model equation can be written:[25]

$$C_\mathrm{f} = K_F \cdot C_s^{1/n} \tag{6}$$

where K_F (mg/[(g/L)$^{1/n}$ g]) is the Freundlich constant, and $1/n$ stands for heterogeneous factor.

The Langmuir–Nernst model can be described by the expression:[26, 27]

$$C_f = C_P + C_L = K_P C_S + \frac{SK_L C_s}{\mathbf{1} + K_L C_s} \tag{7}$$

where C_P and C_L are the concentrations of dyes on fibers by Nernst type partitioning and Langmuir adsorption, respectively; S is the saturation concentration of dyes on fibers by Langmuir adsorption; K_P (L/g) and K_L (L/mg) are the partition coefficient and the Langmuir affinity constant, respectively.

All the experimental adsorption isotherms in Fig. 6 were fitted to the three isotherm models using the nonlinear least-squares fitting procedure, and thus the parameters in Eqs. 5–7 were obtained. The adsorption parameters for the Langmuir–Nernst model were summarized in Table 2 (the data for other models not shown). For the purpose of assessing the fitting results, the normalized deviations (*ND*) of the experimental values used to estimate the extent of fitting were calculated according to Eq. 8.

$$ND(\%) = 100 \times \frac{1}{N} \sum_{i=1}^{N} \left(\frac{\left| C_{f,\exp,i} - C_{f,calc,i} \right|}{C_{f,\exp,i}} \right) \tag{8}$$

where $C_{f,exp,i}$ and $C_{f,calc,i}$ are the experimental and calculated values (the amount of adsorbed dyes on fibers), respectively; the latter is a result of calculation using Eqs.

5–7 on the basis of the parameters which were obtained by the fitting procedure; the index "*i*" refers to the sequence number of adsorption data; N is the total number of data sets.

The *ND* values for the three adsorption models are presented in Table 3. Evidently, the Langmuir–Nernst model nearly gave the lowest *ND* values, and thereby showed the highest fitting extent. The Langmuir and Freundlich equations did not give a good fit to the experimental data. Thus, the Langmuir–Nernst isotherm is the most appropriate model to describe the adsorption behaviors of direct dyes. Fig. 6 also shows the plots of the fitting of the Langmuir–Nernst model to the experimental data. The fitting curves almost went through all the experimental data exactly, further suggesting the validity of the proposed adsorption mechanism.

< Insert Table 2 >

< Insert Table 3 >

To demonstrate the effect of initial dye concentrations on adsorption clearly, the percent of the contribution of Langmuir or Nernst adsorption to total adsorption[26, 27] was calculated using the parameters in Table 2 and the known C_s according to Eq. 7 at each initial dye concentration, and depicted in Fig. 7. As shown in Fig. 7, the contribution of Langmuir adsorption to total adsorption decreased with increasing initial dye concentration, while the contribution of Nernst adsorption increased. Moreover, the contribution of Langmuir adsorption was always much higher than that of Nernst adsorption; in other words, Langmuir adsorption was predominant in total adsorption. For viscose/CH fiber, this predominance was more obvious.

< Insert Fig. 7 >

In this study, the adsorption equation giving the best correlation of the experimental data was the Langmuir–Nernst equation rather than the Freundlich equation. The traditional equation used to describe direct dye adsorption is the classical Freundlich equation. This was used because the cellulose substrate was considered to be heterogeneous in the accessible regions where the dye is absorbed without having obvious specific dye sites like wool or nylon fibers.[28] However, some researchers have reported that the classical Langmuir model offers a better interpretation of the adsorption of direct dyes,[28-38] and hydrolyzed reactive dyes[37, 38] on cellulose. Porter explained this adsorption phenomenon in terms of limited dye space or sites for dye adsorption,[28] and considered that the interaction of dyes with cellulose substrate is rather specific. Blackburn and co-workers tended to consider that the adsorption of the hydrolyzed reactive dye with a large molecular size on caustic soda treated cellulose II may occur by virtue of a combination of Langmuir (limited) and Freundlich (unlimited) adsorption mechanisms,[38] and that the adsorption in excess of the experimentally determined saturation value occurs as a result of non-site-specific interaction. Bae et al. reported that the saturation values of direct dyes on cellulose depend on the inner surface areas of fibers, the size of dye molecules, and the intermolecular repulsive interaction between the dye anions adsorbed on the inner surface of cellulose (restricting further adsorption).[30] Despite the above findings, how the limited adsorption or the site-specific interaction occurs in theory has been remaining somewhat obscure.

According to the previously reported investigations, it may be concluded that the dual Langmuir-Nernst mechanism of the adsorption of direct dyes on viscose/CH and viscose fibers consists of site-specific and non-site-specific interactions. Because in viscose/CH fiber there exist the partially protonated amino groups of the partially deacetylated chitin, this fiber apparently possesses the more specific dyeing sites for the adsorption of anionic dyes which allow the higher contribution percent of dye adsorption by Langmuir mechanism. Consequently, the affinity of direct dyes to viscose/CH fiber also becomes higher as compared with that to viscose fiber, leading directly to the higher Langmuir affinity constant of dye adsorption and the higher dyeing saturation of the fiber as expressed by the K_L and S values in Table 2. The higher contribution percent of Langmuir adsorption at lower initial dye concentrations shown in Fig. 7 may be explained by the fact that the adsorption is mainly controlled by the specific adsorbing sites in fibers. At higher initial dye concentrations, a number of adsorbed dyes on the exterior and interior surface areas of fibers give rise to the increased negative charge density of fibers, and the decreased quantity of specific adsorbing sites which accordingly reduce the contribution percent of Langmuir adsorption.

3.5. Building-up properties of dyes

The building-up properties of direct dyes on fibers should be related to fiber and dye structures, dye affinity to fibers, dye adsorption mechanisms, dyeing temperature, additives used in dye solution, etc. The dyes having good building-up performance are particularly suitable to dye the fibers required for dark shades. The building-up properties are of great importance for practical application. Viscose/CH fiber contains partially deacetylated chitin, and accordingly possesses positive dyeing sites capable of capturing anionic dyes. It stands to reason that direct dyes have better building-up properties on viscose/CH fiber than on viscose fiber. However, it is still worth exploring how the partially deacetylated chitin in viscose/CH fiber affects the building-up properties of direct dyes.

< Insert Fig. 8 >

In practical dyeing, the processing time is not so long as that employed for thermodynamic studies. Therefore the building-up properties of direct dyes were determined in a temperature-rise process in place of a constant temperature process. The building-up properties expressed by C_f as well as the exhaustion of dyes are depicted in Fig. 8. The quantity of adsorption almost increased linearly with an increase in initial dye concentration, even at a high concentration of dye; the curve slopes of the adsorption quantity versus initial dye concentration for viscose/CH fiber were higher than those for viscose fiber, indicating the better building-up properties of direct dyes on viscose/CH fiber. This was particularly true for the dye Blue BRR. As the applied dye concentration increased, the difference between the adsorption capability of viscose/CH and viscose fibers became greater for Blue BRR. These observations implies that direct dyes have better building-up properties on viscose/CH fiber and higher affinity to viscose/CH fiber, which are consistent with the higher K_L values for viscose/CH fiber as shown in Table 2.

The high dye adsorption capability of viscose/CH fiber in the case of the use of a high dye concentration means that this fiber has the advantage in terms of deep dyeing. At the same time, the dyeing system of viscose/CH fiber exhibited higher dye exhaustion than that of viscose fiber as confirmed by the results of Fig. 8. Even when a dye concentration of 5% was used, the exhaustion of Yellow RL and Blue BRR was able to reach to 90% or so. The high dye exhaustion allows a high utilization of dyes, a reduced cost of dye consumption in the dyeing process and a decrease of wastewater discharge, which becomes another advantage of viscose/CH fiber in the aspect of dyeing.

3.6. Desoprtion of direct dyes from the dyed fibers

The dyed fibers and textiles are subjected to frequent washing during their usage. Hence the resistance of dyes on fibers to washing is very important. The washing resistance can be evaluated using the color fastness to washing, and also characterized using the desorption of dyes from fibers in water. On the other hand, the adsorption of dyes onto fibers and the desorption of dyes from dyed fibers occur simultaneously during the dyeing process, and the desorbed dyes are likely to be again adsorbed by fibers. The adsorption, desorption and re-adsorption performance of dyes is defined as the migration property. The good migration property of dyes allows fibers to obtain a good leveling effect. A certain degree of desorption of dyes from the dyed fibers is the prerequisite for the migration of dyes and the even dyeing of fibers. The low and slow desorption of dyes from fibers usually means their high affinity to fibers and poor migration property, and easily leads to the poor dyeing levelness. Taking the above factors into consider, the performance of the desorption of direct dyes from the dyed viscose/CH and viscose fibers in water was investigated.

< Insert Fig. 9 >

Fig. 9 displays the variation of the dye desorption percent with time. The desorption of dyes increased as a function of time, and showed a trend towards equilibrium as the time was prolonged. As expected, the dye desorption from the dyed viscose/CH fiber was remarkably lower than that from the dyed viscose fiber. The desorption test suggests that the washing resistance of direct dyes on the viscose/CH fiber is very good, indicating that the dyed viscose/CH fiber has better washing color fastness as compared with the viscose fiber. Meanwhile, the very low and slow desorption of dyes from the dyed viscose/CH fiber implies the higher affinity and poor migration of direct dyes towards this fiber, which easily result in the poor dyeing levelness. Virtually, the low desorption of dyes from the dyed viscose/CH fiber has a direct correlation with the rapid rate of dye uptake by the fiber as shown in Fig. 4 and Table 1, and with the high Langmuir affinity constant of dyes as shown in Table 2.

4. Conclusions

The studies on the equilibrium isotherms of dye adsorption indicated that the adsorption of direct dyes on viscose/CH bicomponent fiber occurred via a combination of Langmuir and Nernst model, i.e., site-specific and non-site-specific interactions between dyes and fibers, and that the Langmuir adsorption was predominant in total adsorption. The rates of dye uptake by viscose/CH fiber followed the pseudo-second-order kinetic model. Viscose/CH fiber showed faster dye adsorption rate as well as lower dye desorption and migration as compared with regular viscose fiber, suggesting that some measures should be taken to improve the dyeing levelness of the fiber in the industrial dyeing process. Viscose/CH fiber exhibited higher dye adsorption capability, higher dye exhaustion, and better washing resistance of adsorbed dyes than viscose fiber, indicating that it possesses the advantages of deep dyeing performance, good colorfastness to washing, and environmental benefits of dyeing process. The above dye adsorption and dyeing characteristics of viscose/CH fiber may be primarily ascribed to its partially deacetylated chitin component.

The difference between the dye adsorption and dyeing properties of viscose/CH and viscose fiber was related to dye categories. The comparison between the adsorption properties of two dyes was not carried out in the present work due to the fact that the dyes used were commercial products and not purified dyes. Further studies on the difference between purified dyes in adsorption deserve to be performed in order to obtain the information about the effect of dye structures on the dyeing of viscose/CH fiber, and to achieve a deeper understanding of the fundamental physical chemistry involved in dye adsorption onto viscose/CH fiber.

Acknowledgments

This study was funded by Jiangsu Provincial Natural Science Foundation of China (BK20131178), and the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions.

References

1. K. Bredereck and F. Hermanutz, *Rev. Prog. Color.*, 2005, 35, 59–74.
2. N. Bairagi, M. L. Gulrajani and B. L. Deopura, *Color. Technol.*, 2007, 123, 46–53.
3. B. Müller, M. Gebert-Germ and A. Russler, *Lenzinger Berichte*, 2012, 90, 64–71.
4. W. Roggenstein, *Lenzinger Berichte*, 2011, 89, 72–77.
5. X. Wang, Q. Li, Y. Di and G. Xing, *Fiber. Polym.*, 2012, 13, 718–723.
6. M. N. V. Ravi Kumar, *React. Funct. Polym.*, 2000, 46, 1–27.
7. M. Rinaudo, *Prog. Polym. Sci.*, 2006, 31, 603–632.
8. S. Hirano, *Macromol. Symp.*, 2001, 168, 21–30.
9. A. Sdrobiş, O. Kylian, H. Biederman and C Vasile, *Cellulose*, 2013, 20, 509–524.
10. Y. Shimizu, T. Nakajima, M. Yoshikawa and T Takagishi, *Text. Res. J.*, 2002, 72, 563–567.
11. T. Nakajima, Y. Shimizu and T. Higashimura, *Chitin Chitosan Res.*, 2000, 6(2), 59–65.
12. Y. Shimizu, M. Dohmyou, M. Yoshikawa and T. Takagishi, *Text. Res. J.*, 2004, 74, 34–38.
13. L. Fras-Zemljič, V. Kokol and D. Čakara, *Text. Res. J.*, 2011, 81, 1532–1540.
14. F. Sousa, G. M. Guebitz and V Kokol, *Process Biochem.*, 2009, 44, 749–756.
15. A. Sdrobiş, G. E. Ioanid, T. Stevanovic and C. Vasile. *Polym. Int.*, 2012, 61, 1767–1777.
16. X. Colom and F. Carrillo, *Eur. Polym. J.*, 2002, 38, 2225–2230.
17. L. Li and Y.L. Hsieh, *Carbohyd. Res.*, 2006, 341, 374–381.

18. J. Du and Y.L. Hsieh, *Cellulose*, 2009, 16, 247–260.
19. T. Yamashiki, T. Matsui, K. Kowsaka, M. Saitoh, K. Okajima and K. Kamide. *J. Appl. Polym. Sci.*, 1992, 44, 691–698.
20. M. Lee, T. Wakida, T. Tokuyama, C. Doi, Y. J. Lim and S. K, Jeon, Text. Res. J., 2005, 75, 13–18.
21. Y. S. Ho and G. Mckay, *Process Biochem.*, 1999, 34, 451–465.
22. Y. H. Mao, Y. Guan, Q. K. Zheng, X. N. Feng and X. X. Wang, *Cellulose*, 2011, 18, 271–279.
23. X. Y. Pang and F. Gong, *J. Chem.*, 2008, 5, 802–809.
24. I. Langmuir, *J. Am. Chem. Soc.*, 1918, 40, 1361–1403.
25. H. Freundlich, *Zeitschr f Physik. Chem. A*, 1907, 57, 385–457.
26. R. C. Tang, H. Tang and C. Yang. *Ind. Eng. Chem. Res.*, 2010, 49, 8894–8901.
27. L. Liu, J. Zhang and R. C. Tang, *React. Funct. Polym.*, 2013, 73, 1559–1566.
28. J. J. Porter, *Color. Technol.*, 2002, 118, 238–243.
29. M. E. Amato, S. Fisichella and S. Occhipinti, *Dyes Pigments*, 1986, 7, 1–12.
30. S. H. Bae, H. Motomura and Z. Morita, *Dyes Pigments*, 1997, 34, 37–55.
31. M. K. Inglesby and S. H. Zeronian, *Cellulose*, 1996, 3, 165–181.
32. M. K. Inglesby and S. H. Zeronian, *Cellulose*, 2002, 9, 19–29.
33. T. T. Nge, S. H. Lee and T. Endo, *Cellulose*, 2013, 20, 1841–1852.
34. J. J. Porter and W. S. Perkins, *Text. Res. J.*, 1970, 40, 81–88.
35. J. J. Porter, *Text. Chem. Colorist.*, 1993, 25(2), 27–37.

36. G. Simu, S. Funar-Timofei, L. Kurunczi, S. Hora, W. Schmidt and M. Grad, *Cell. Chem. Technol.*, 2004, 38, 409–416.

37. P. Goswami, R. S. Blackburn, J. Taylor and P. White, *Cellulose*, 2011, 18, 1063–1072.

38. J. Široký, R. S. Blackburn, T. Bechtold, J. Taylor and P. White, *Carbohyd. Polym.*, 2011, 84, 299–307.

Figure Legends

Fig. 1 The chemical structures of direct dyes

Fig. 2 FTIR spectra in the range of 2000 to 400 cm^{-1} of viscose/CH and viscose fibers

Fig. 3 X-ray diffraction patterns of viscose/CH and viscose fibers

Fig. 4 Effect of sodium sulfate dosage on the uptake of direct dyes by viscose/CH and viscose fibers

Fig. 5 Adsorption rates of direct dyes for viscose/CH and viscose fibers

Fig. 6 Adsorption isotherms of direct dyes on viscose/CH and viscose fibers (solid lines present the Langmuir–Nernst plots)

Fig. 7 Contribution of Langmuir and Nernst adsorption to total dye adsorption on viscose/CH and viscose fibers: (a) Yellow RL, and (b) Blue BRR

Fig. 8 Building-up properties of direct dyes on viscose/CH and viscose fibers: (a) Yellow RL; (b) Blue BRR

Fig. 9 Desorption of direct dyes from the dyed viscose/CH and viscose fibers in water

Table 1 Kinetic parameters of the adsorption of direct dyes

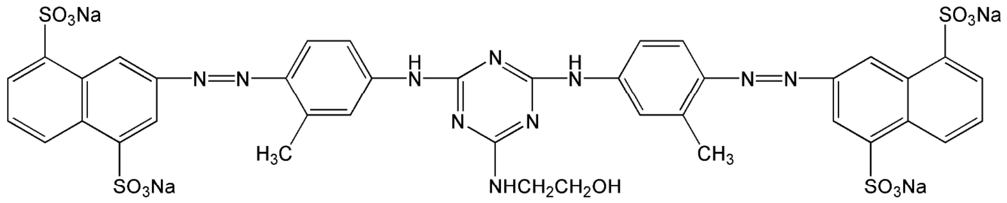
Dyes	Fibers	k (g/[mg min])	h_i (mg/[g min])	$t_{1/2}$ (min)	C_∞ (mg/g)	R^2
Yellow RL	Viscose/CH	0.0998	78.75	0.36	28.09	1.0000
	Viscose	0.0875	60.29	0.44	26.25	1.0000
Blue BRR	Viscose/CH	0.0363	31.04	0.94	29.24	0.9995
	Viscose	0.0271	12.54	1.71	21.51	0.9996

Table 2 Parameters in the Langmuir–Nernst equation

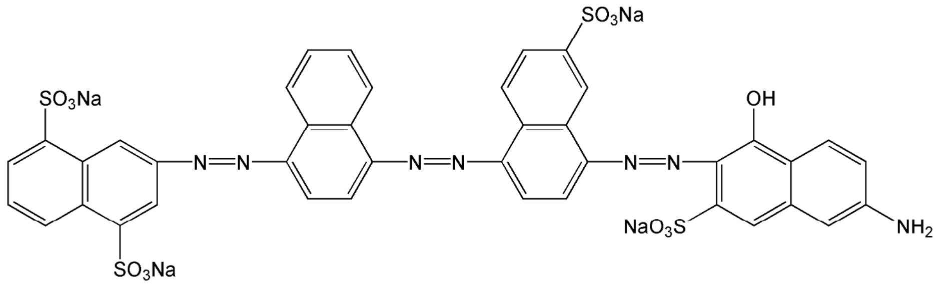
Dyes	Fibers	K_L (L/mg)	S (mg/g)	K_P (L/g)
Yellow RL	Viscose/CH	0.026	60.25	0.081
	Viscose	0.024	33.76	0.099
Blue BRR	Viscose/CH	0.443	30.31	0.144
	Viscose	0.055	18.78	0.027

Table 3 Normalized deviations (%) of the isotherm models

Models	Yellow RL		Blue BRR	
	Viscose/CH	Viscose	Viscose/CH	Viscose
Langmuir	4.17	3.78	16.20	10.37
Freundlich	11.91	7.25	13.11	5.26
Langmuir–Nernst	4.00	0.34	7.13	3.76



C.I. Direct Yellow 86 (MW=1066.9 Da)



C.I. Direct Blue 71 (MW=1029.9 Da)

Fig. 1 The chemical structures of direct dyes
246x134mm (300 x 300 DPI)

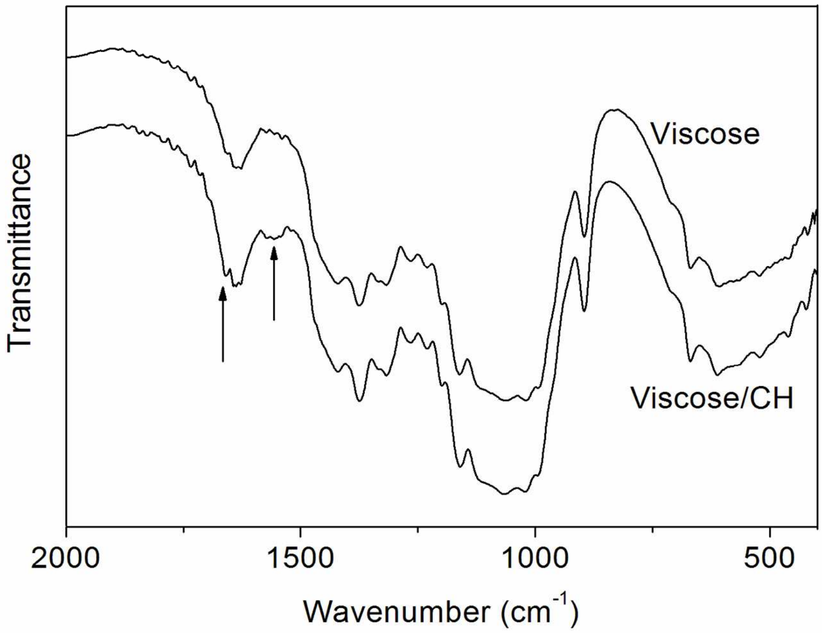


Fig. 2 FTIR spectra in the range of 2000 to 400 cm-1 of viscose/CH and viscose fibers
288x200mm (150 x 150 DPI)

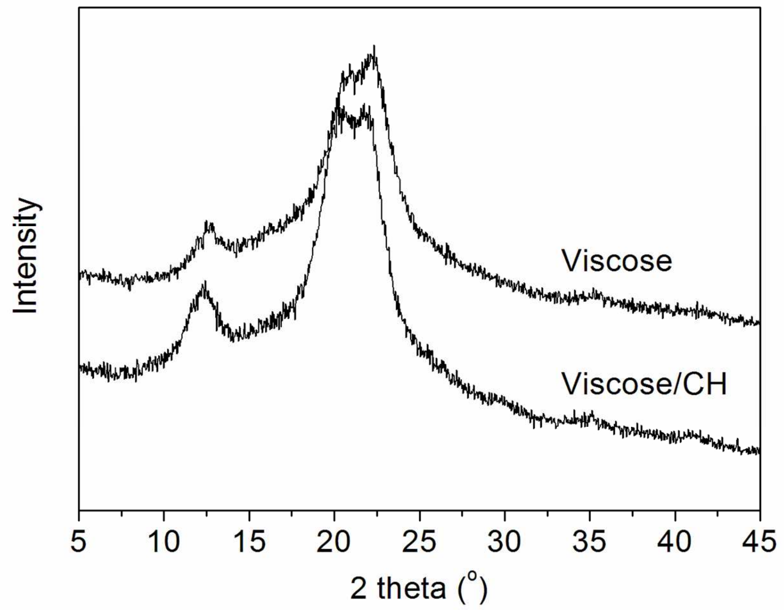


Fig. 3 X-ray diffraction patterns of viscose/CH and viscose fibers
284x199mm (150 x 150 DPI)

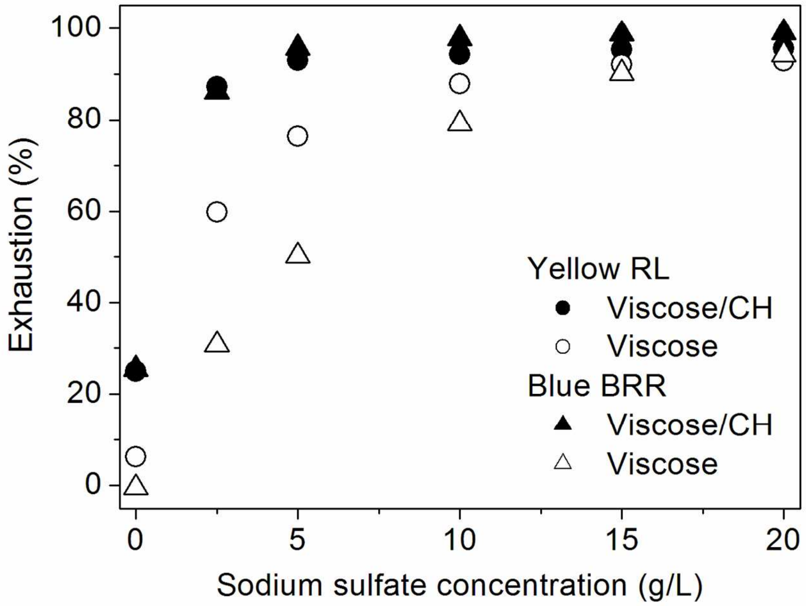


Fig. 4 Effect of sodium sulfate dosage on the uptake of direct dyes by viscose/CH and viscose fibers
284x199mm (150 x 150 DPI)

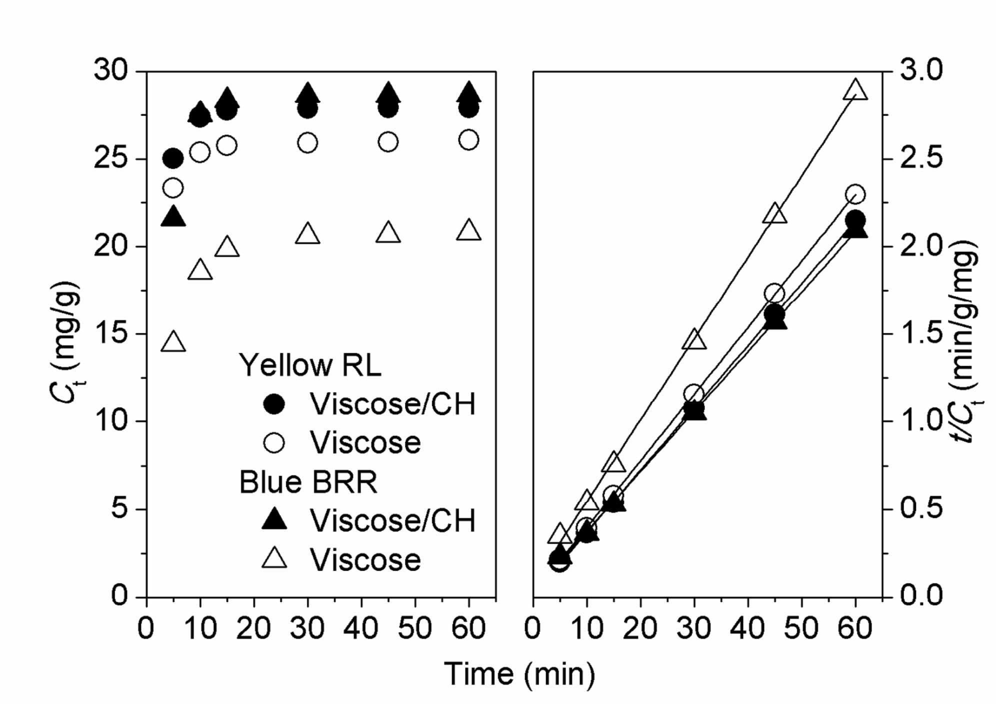


Fig. 5 Adsorption rates of direct dyes for viscose/CH and viscose fibers
289x203mm (150 x 150 DPI)

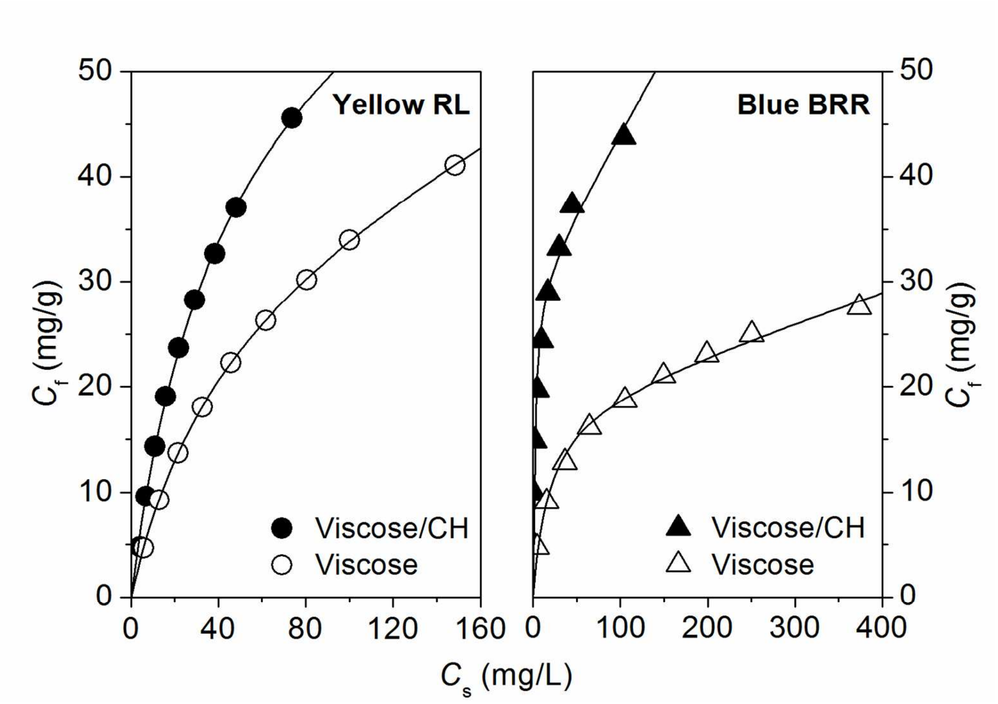


Fig. 6 Adsorption isotherms of direct dyes on viscose/CH and viscose fibers (solid lines present the Langmuir–Nernst plots)
284x199mm (150 x 150 DPI)

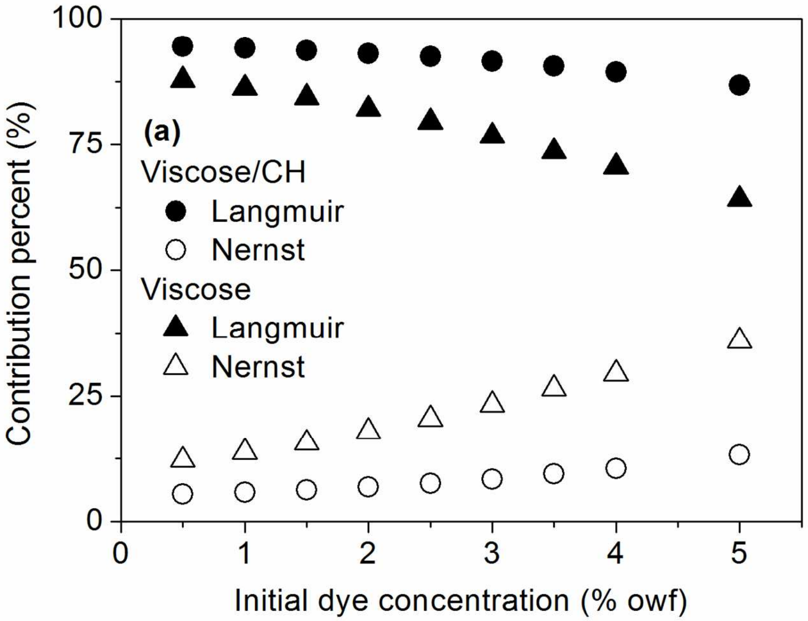


Fig. 7 Contribution of Langmuir and Nernst adsorption to total dye adsorption on viscose/CH and viscose fibers: (a) Yellow RL, and (b) Blue BRR
284x199mm (150 x 150 DPI)

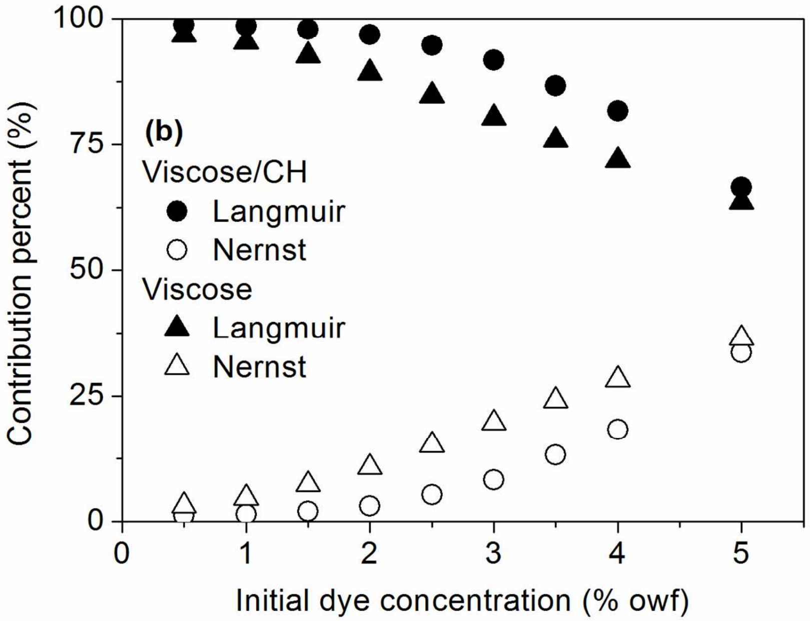


Fig. 7 Contribution of Langmuir and Nernst adsorption to total dye adsorption on viscose/CH and viscose fibers: (a) Yellow RL, and (b) Blue BRR
284x199mm (150 x 150 DPI)

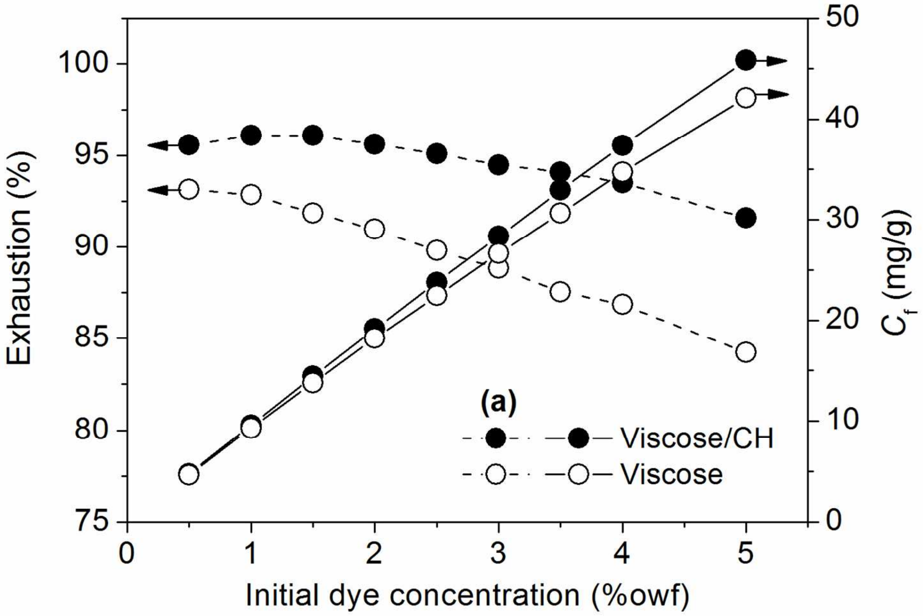


Fig. 8 Building-up properties of direct dyes on viscose/CH and viscose fibers: (a) Yellow RL; (b) Blue BRR
284x199mm (150 x 150 DPI)

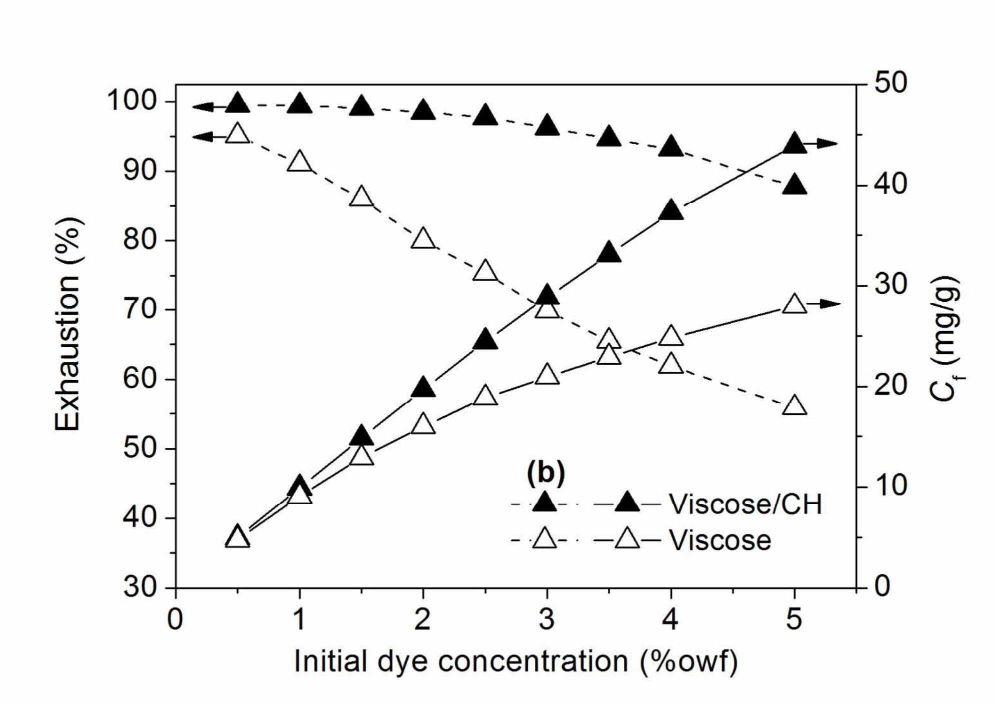


Fig. 8 Building-up properties of direct dyes on viscose/CH and viscose fibers: (a) Yellow RL; (b) Blue BRR
284x199mm (150 x 150 DPI)

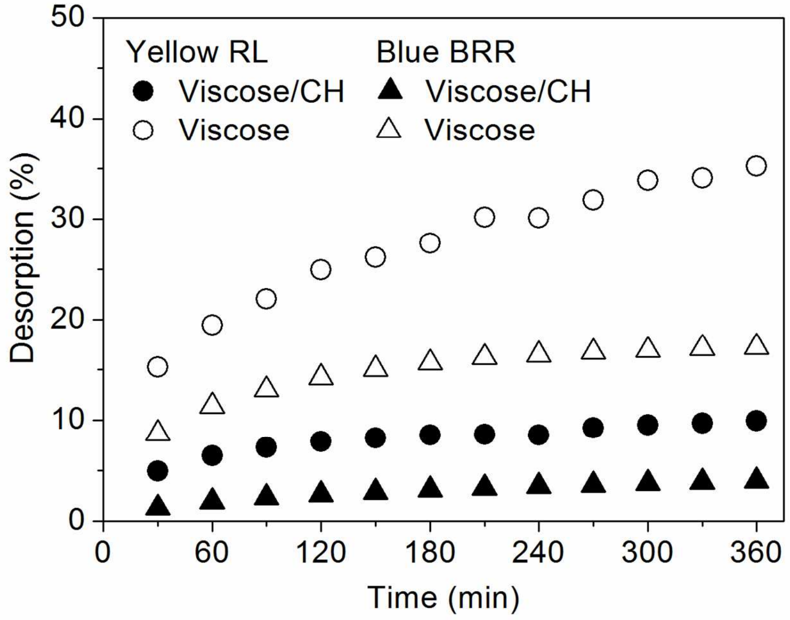


Fig. 9 Desorption of direct dyes from the dyed viscose/CH and viscose fibers in water
284x199mm (150 x 150 DPI)