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Kinetics of dyeing natural protein fibers with silver nanoparticles

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ABSTRACT

The kinetics of dyeing silk and wool fibers with silver nanoparticles was investigated by ultraviolet-visible (UV-Vis) absorption spectroscopy at different temperatures. Silver nanoprisms (AgNPrs) acting as novel dyestuffs endowed fibers with blue color because of their localized surface plasmon resonance. Color characteristics of dyed fibers were measured and analyzed. The dyeing rate of fibers with AgNPrs increased with an increase in temperature. Compared with wool, silk exhibited faster dyeing rate with AgNPrs. The pseudo-first-order model described suitably the initial stage of the dyeing process of silk and wool based on AgNPrs. Whereas, the entire dyeing process except for the beginning stage followed the pseudo-second-order model appropriately. Traditional dye (acid blue 199) was used for comparison with AgNPrs. The pseudo-second-order model fitted the entire dyeing process with acid blue 199 better. Activation energy for silk dyeing with AgNPrs was the lowest among the examined dyeing systems, demonstrating that AgNPrs combined most easily with silk fibers. Thermodynamic activation parameters for the adsorption of AgNPrs and acid blue 199 onto fibers were obtained to investigate the involved dyeing process of silk and wool.

1. Introduction

Dyeing of textiles is a complex process, including diffusion of dyes in solution and adsorption of dyes into fibers. Insights into dyeing process are important to the manufacture of colored textiles. Factors that affect textile dyeing include structure of dyestuff, component of fibers, pH value of dyeing solution, and dyeing temperatures [1,2]. Dyeing theory involves many aspects in the area of physical chemistry, relating to the state of dyes, the nature of the interaction between dyes and fibers, mechanisms of dyeing, mass-transfer and diffusion of dyes from the bath solution to fibers, the phenomena occurring at the dye-fiber interface, the thermodynamics and kinetics of dye adsorption [3,4]. Investigations on dyeing theory have been carried out to improve the quality of dyed textiles [5,6] and save water and energy [7,8]. Dying kinetics is concerned with the study of the rate of dye adsorption reactions during dyeing process. Fundamental research on the dyeing kinetics can help understand the dyeing mechanisms and improve the dyeing technology of textiles [6]. For examples, Sribenja and Saikrasun modified bamboo fibers with poly (ethyleneimine) (PEI) and inspected the influences of PEI treatment on dyeability of lac dyeing on bamboo fibers in comparison of controlled (alkali treated) bamboo fibers [6]. The adsorption behavior of lac dye on bamboo fibers was described by pseudo-first-order model well. Wei et al. discussed the adsorption of lac dye on wool, silk and nylon fibers by investigating the adsorption kinetics of lac dye on different fibers [9]. The adsorption process of lac dye on the three fibers agreed with pseudo-second-order kinetic model and followed Langmuir mechanism. Hou et al. used a natural sodium copper chlorophyllin to colorate silk. The kinetic data was collected to examine the effect of pH and sodium chloride on adsorption of dye on silk [10].

Recently, functionalization of textiles has attracted extensive attention of scientists and engineers. The modification based on functional materials imparted various features to textiles [11–17]. Among them, many types of substances including natural extracts and nanomaterials were used as colorants for dyeing textiles [11,17–20]. The coloration of fabric/fiber could be achieved through the combination with noble metal (gold and silver) nanoparticles, by virtue of the optical properties of plasmon nanomaterials, i.e.

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localized surface plasmon resonance (LSPR) [11,21]. In our previous research, diverse fibrous materials such as wool [22,23], silk [24–26], cotton, bamboo [27] and ramie [28] were functionalized using noble metal nanoparticles. Different colors were imparted to textiles *via* a self-assembly or in-situ synthesis methods. With regards to the self-assembly method [22–24], the noble metal nanoparticles were prepared prior to combination of nanoparticles and fibers. Natural protein fibers including wool and silk fibers can adsorb the silver nanoparticles carrying negative charges under acid condition, leading to the coloration of fibers. The amino groups on protein fibers were protonated to carry positive charges in acid solution. The electrostatic interaction gave rise to the combination of fibers and silver nanoparticles. Investigation into the dyeing of textiles with noble metal nanoparticles would facilitate the development of the novel dyeing technology involving noble metal nanoparticle in industry. It is significant to study the kinetic process of dyeing with nanoparticles and explore the theory of nanoparticle-dyeing of textiles.

Noble metal nanoparticles as novel dyes do not only provide textiles with vivid colors, but also render other functions, such as antibacterial and UV-blocking properties. Monitoring the combination of nanoparticles and fibers is essential for modifying textiles using functional nanoparticles. To the best of our knowledge, very little has been report in the literature reported on the kinetics of interaction between nanoparticles and fibers.

Herein, the dyeing process of natural protein fibers (silk and wool) using silver nanoparticles was monitored by recording the evolution of UV-Vis absorption spectra of dyeing solution (silver nanoparticle solution). The influences of dyeing temperature on the adsorption of silver nanoparticles onto fibers were observed. A series of UV-Vis absorption spectra of silver nanoparticle solutions collected under different conditions were used for analysis of dyeing kinetics. Traditional dye was utilized to color silk and wool to compare the dyeing with silver nanoparticles. Pseudo-first-order and pseudo-second-order models were employed to fit the dyeing processes of silk and wool. Activation energies of the corresponding dyeing processes were calculated. The combining ability and adsorption mechanism of dyestuffs on fibers was discussed. The thermodynamic activation parameters were obtained to gain insights into the adsorption of dyestuffs onto silk and wool.

2. Experimental section

2.1. Materials

Silver nitrate ($AgNO_3$, ≥99%), trisodium citrate (≥99%), sodium borohydride (≥98.0%), sodium hydroxide (≥99.0%), acetic acid (≥99.0%) were purchased from Sigma-Aldrich. All chemicals were of analytic grade and used as received. Traditional dye, acid blue 199 (AB199), was purchased from Clariant Co. Ltd. Silk and wool fibers were obtained by a local retailer.

2.2. Instruments

The UV-Vis absorption spectra were recorded using an Ocean Optics USB4000 spectrophotometer. A sodium lamp (Osram China Lighting Co. Ltd., model NAV-T 70) was used for the synthesis of silver nanoparticles. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 with an acceleration voltage of 200 kV. Dyeing procedures were performed in a Stuart SBS40 shaking water bath. A Datacolor 600 SPECTRUM spectrophotometer was used for characterization of colors of dyed fibers.

2.3. Synthesis of silver nanoparticles

Silver nanoprisms (AgNPrs) used for the dyeing of silk and wool were prepared by a photo-induced seed-mediated method [29–31]. Briefly, silver seeds (small silver nanoparticles for growth of AgNPrs) were prepared by dropwise addition of $NaBH_4$ solution (8.0 mM, 1.0 mL) to an aqueous solution of $AgNO_3$ (0.1 mM, 100 mL) in the presence of trisodium citrate (1.0 mM) under vigorous stirring. The yellow silver seed solutions were then irradiated with a sodium lamp. Finally, silver colloidal solutions in blue were obtained through conversion of the yellow silver seeds during the irradiation of sodium lamp (as shown in Fig. 1a). It is supposed that all the silver ions were transformed to silver nanoparticles after the photo-induced reaction. The mass concentration of blue silver nanoparticle solution was 10.79 mg L^{-1}.

2.4. Kinetic monitoring of dyeing processes

Silk and wool fibers were dyed by blue AgNPrs by an assembly method described in our previous reports [23,24]. The pH values of AgNPr solutions were adjusted to 4.0 with acetic acid. Silk and wool fibers were immersed into the AgNPr solutions (dyeing solutions). The weight ratio of dyeing solution to fiber was 100: 1. The solutions containing AgNPrs and fibers were shaken at different temperatures to achieve the coloration of fibers. During dyeing process, the UV-Vis absorption spectra of AgNPr solutions were recorded at different dyeing times. One acid traditional dye (AB199) was used to dye silk and wool fibers at the similar conditions. The dyeing of fibers was implemented in the presence of 200 mg L^{-1} of AB199 aqueous solution with a pH value of 4 at different temperatures in a shaking water bath with a weight ratio of dyeing solution to fiber of 100: 1. A series of UV-Vis absorption spectra of dyeing solution were collected during dyeing process.

2.5. Color measurement

Color characteristics (L^*, a^*, b^*, C^*, h and K/S) of the silk and wool fibers dyed with AgNPrs and AB199 were measured by a Datacolor 600 SPECTRUM spectrophotometer using illuminant D65 and 10° standard observer. L^*, a^*, b^*, C^* and h are the Commission Internationale de l'Éclairage (CIE) Lab color coordinates. L^*, C^* and h represent lightness, chroma and hue angle of color, respectively. a^* represents the degree of redness (positive) or greenness (negative), and b^* represents the degree of yellowness (positive) or blueness (negative). Color strength (K/S) values at the wavelength of maximum absorbance (λ_{max}) were also obtained through the reflectance of samples based on calculation with Kubelka-Munk equation [19,32].

3. Results and discussion

3.1. Dyeing of fibers

The as-synthesized silver nanoparticles were dominated by triangular nanoplates (nanoprisms) (TEM image shown in Fig. 1a). The LSPR optical property leads to the blue color of silver nanoprism (AgNPr) solution [29,30]. The UV-Vis absorption spectrum of the blue silver nanoparticle solution shows three LSPR bands centered at around 333, 510 and 699 nm, which are ascribed to the out-of-plane quadrupole, in-plane quadrupole, and in-plane dipole plasmon resonance modes of AgNPrs, respectively (Fig. 1b) [29]. The intensity of LSPR bands of AgNPr solution during dyeing process decreased gradually, which indicates that silver nanoparticles were assembled on fibers. Fig. 1b displays the UV-Vis absorption spectra before and after dyeing of wool fibers. No visible LSPR