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Ultrasound-assisted adsorption of anionic nanoscale pigment on cationised cotton fabrics

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ABSTRACT

Application of pigments in textile coloring has many advantages such as less water and energy consumption, less effluent load and higher efficiency, so the pigments are perfect alternatives to dyes for eco-friendly coloring. In this work, a stable anionic nanoscale pigment suspension was prepared using a polymeric dispersant to color the cationised cotton with the exhaust method. Meanwhile, ultrasound was carried out during the adsorption to evaluate the ultrasonic influences on the uptake of pigment, adsorption efficiency and final product quality. The uptake of pigment is found to be higher with ultrasonic method than that with conventional technique because of the good dispersing capacity of ultrasound to pigment particles. Besides, it is found that nanoscale pigment has higher adsorption rate when using ultrasonic method because the ultrasound promotes the diffusion of pigment through the fiber–liquid boundary layer. Lastly, the color difference (ΔE) reveals the nanoscale pigment can be deposited on cotton surface more uniformly under ultrasonic condition, improving the product quality obviously.

1. Introduction

Reactive dyes are widely used to color cellulosic substances such as cotton, rayon or linen owing to their wide gamut of hues and good wet fastness (Ahmed, 2005; Ibrahim, Abdel Moneim Nabil, Abdel Halim, & Hosni, 2008; Oner & Sahinbaskan, 2011). Exhaust coloring of cotton with reactive dyes needs the presence of large quantities of electrolytes (e.g. sodium chloride or sulfate), which can suppress negative charges build-up at the fiber surface and promote dye uptake (Bhattacharya & Iyanger, 2001; Tutak & Oktay zdemir, 2011). The concentration of electrolytes can be regulated at the range of 30–100 g/l, depending on the depth of color, dye structure or coloring recipe. However, the high concentration of electrolytes inevitably leads to serious environmental pollution (Xie, Cheng, Zhao, & Xu, 2011). Therefore, various alternative methods have been explored to achieve cleaner coloring technology. Cationisation of cotton is an effective means to tackle this issue because cationisation could alter electric properties of cotton surface and increase the substantivity between reactive dyes and cotton. Many researches have been carried out in this area. Teng, Ma, and Zhang (2010) pretreated cotton with cationic polyacrylamide using a dip-pad-bake method and explored its coloring performance without electrolyte. They found the fixation and K/S values of the reactive dyes on cationised cotton were significantly improved in comparison with those on untreated ones in the presence of salt. Wang, Ma, Zhang, Teng, and Yang, (2009) treated cotton with 3-chloro-2-hydroxypropyltrimethyl ammonium chloride using a designed two-bath pad procedure to realize continuous cotton cationisation. They found the gained cationic cotton was suitable for application in salt-free dyeing.

Although cationisation is an effective way to reduce salt consumption in reactive coloring, there are still other issues that cannot be ignored. Under alkaline fixation condition (pH over 10.5), the reactive dyes can react not only with the hydroxyl groups in cotton but also with water to form hydrolyzed dyes as well. Undoubtedly, this competitive process will significantly compromise the coloring efficiency of cotton with reactive dyes. Moreover, the hydrolyzed dyes may be weakly attached to cotton by secondary forces and must be thoroughly washed off at the end of coloring cycle for satisfactory fastness (Burkinshaw & Katsarelias, 1997; Burkinshaw & Paraskevas, 2011). As a result, large volumes of wastewater, containing significant amounts of hydrolyzed dyes and chemicals, have to be discharged from a typical cotton coloring works (Xue, Li, & He, 2009).

Anionic pigments, with many advantages over reactive dyes, are perfect alternatives to color cationised cotton for eco-friendly coloring. First, pigment has faster adsorption rate and shorter coloring cycle on cationised cotton than reactive dyes, which will improve coloring efficiency and reduce the energy consumption. In addition, there is no soaping off procedure needed after pigment coloring, which will then save a large amount of water and reduce coloring cost (Hao, Cai, & Fang, 2009; Hao, Wang, Liu, Cai, & Liu, 2012). By contrast, the nanoscale pigment can provide better coloring quality than the conventional one with large particle size. Fang,

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Wang, Zhang, and Xu, (2005) studied the coloring performance of 100–200 nm nanoscale pigment on cationised cotton using exhaust method and found this nanoscale pigment could provide much higher color yield, softer hand and more brilliant shade than coarse pigment over 1 μm in size. For the coloring with nanoscale pigment, how to keep the nanoscale particles in good stability is the key for success.

Sound wave with a frequency beyond human audible range of 20 kHz is defined as ultrasound wave. Ultrasound can improve a wide variety of chemical and physical processes mainly because of the cavitation effect in liquid medium. Acoustic cavitation is the growth and explosive collapse of microscopic bubbles, which causes drastic increase in the pressure and temperature (Merdan, Akalin, Kocak, & Usta, 2004). The use of ultrasound energy in textile coloring is well documented in many literatures, in which it is reported the use of ultrasound can result in increased color yield, lower dyeing temperatures, reduced dyeing time and consumption of dyeing auxiliaries. In the previous studies, researchers have focused their interests on the dyeing of various dyes at different textile substrates with ultrasound, including reactive dyes (Kan & Yuen, 2005; Merdan et al., 2004), acid dyes (Ferrero & Periolatto, 2012; McNeil & McCall, 2011), disperse dyes (Burkinshaw & Jeong, 2012a), natural dyes (Kamel, El-Shishtawy Reda, Yussef, & Mashaly, 2005, 2007; Vankar & Shanker, 2008; Vankar, Shanker, & Srivastava, 2007) and basic dyes (Kamel, Helmy, Mashaly, & Kafafy, 2010). Hitherto, the effect of ultrasound on the dyeing of pigments on textile has not received attention.

In this work, a stable nanoscale pigment dispersion was prepared by a polymeric dispersant using a micro-jet milling machine, and then its physical properties such as the particle size, zeta potential and viscosity were analyzed. The main purpose of this work was to color the cationised cotton with above nanoscale pigment, using both ultrasonic (US) and conventional (CV) methods, to show the effect of ultrasound on adsorption efficiency and quality of nanoscale pigment at different coloring conditions.

2. Experimental

2.1. Pigment and fabrics

The phthalocyanine blue pigment (Fig. 1a) was provided by Hangzhou Hongyan Co. Ltd., China. Scoured and bleached pure cotton knit fabrics (180 g/m^2, 20 tex single yarn) were offered by Xinrong Textile Factory, China. The fabric was treated with a solution containing 2 g/l nonionic detergent (DNS, Haiyi chemical company) at 90 °C for 30 min prior to utilization. At last, the fabric was taken from the bath and thoroughly rinsed with tap water, and then dried at room temperature.

2.2. Auxiliaries

A polymeric dispersant SMA was kindly provided by NDC lab of China. Cationic agent PNH, a poly-aminochlorohydrin quaternary ammonium polymer with epoxide functionality that can react with cellulose by ether formation in the presence of alkalis, was gained from Haiyi Chemical Co. Ltd., China. Polyacrylate binder FSB was bought from Hongqing Chemical Co. Ltd., China. Other chemical agents were all A.R. grade.

2.3. Ultrasound equipment

A Kudos (Japan) ultrasound cleaner bath was used at a frequency of 59 kHz with maximum about 5 L of water throughout the experiment. The output power was adjusted to the range of 50–300 W and supplied by three transducers at the bottom of the tank. The apparatuses has accurate digital time controller (0–90 min), thermostatically controlled heater and degas functions.

2.4. Preparation of nanoscale pigment dispersion

8 g dispersant SMA and 50 g pigment were added in 192 g aqueous media with the aid of a JY92 (Ningbo, China) ultrasonic crusher for 20 min at 25 kHz, and then the pigment dispersion was treated with an M-110EHI microfluidiser (Microfluidics Int. USA) at a pressure of 22,000 psi for 30 min to afford nanoscale pigment dispersion.

2.5. Cationisation of cotton with exhaust method

10 g scoured and bleached cotton fabrics were immersed in aqueous solutions of cationic agent PNH (15%, on weight of fabric) at a liquor ratio of 30:1 using a SW-2 dyeing instrument. pH of the resulting solution was adjusted to 10.5 with 0.5 M sodium hydroxide. Temperature was raised to 90 °C over 10 min and held

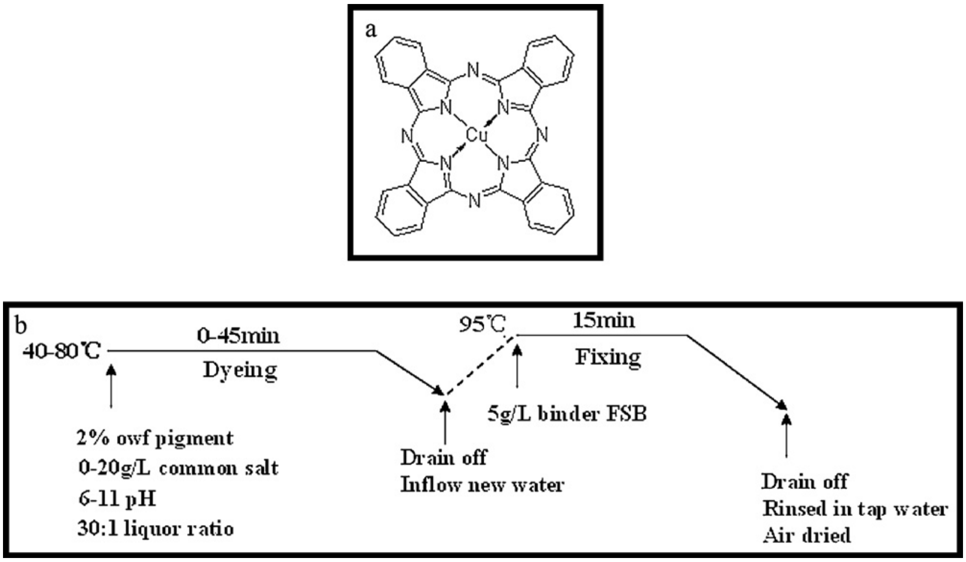

Fig. 1. (a) Pigment structure; and (b) the coloring procedure of nanoscale pigment.

at this temperature for 30 min. The resulted cationised fabrics were rinsed thoroughly using tap water, followed by soaping with 2 g/l nonionic detergent at a boil for 10 min, then rinsed with water and air dried.

2.6. The coloring procedure of nanoscale pigment

The coloring procedure of nanoscale pigment was described in Fig. 1b. 10 g cationised fabrics were conventionally colored in pigment baths (2% pigment, owf) with a liquor ratio 1:30 at different pH values (6–11), concentrations of common salt (0–20 g/l), for different durations (0–45 min) and temperatures (40–80 °C). For comparison, the same conditions of coloring were carried out using ultrasound at different sonic power (50, 100, 200 and 300 W). After dyeing, the fabrics were taken out and treated in the solutions containing 5 g/l binder FSB at 95 °C for 15 min using a liquor ratio 1:30, and then rinsed in tap water and air dried.

2.7. Measurements and analysis

2.7.1. Pigment particle and zeta potential measurement

Particle size distribution of nanoscale pigment was measured by a particle size analyzer (Malvern Instruments Ltd.). The analysis is based on light scattering method, capable of Mie scattering, and covers a wide size range of 0.02–2000 μm. Zeta potential was measured by a Zeta Meter (Malvern Instruments Ltd.), and calibration control of the zeta meter was made daily with standard test colloid. Zeta potential was calculated from mean electrophoretic mobility using Smoluchowski's equation. Each sample was measured three times to give an average particle size and zeta potential.

2.7.2. Rheological analysis of pigment dispersion

The rheological measurements were realized at 25 °C using a Brookfield DV-III rheometer fitted with a concentric cylinder sensor (Brookfield Company, America). The pigment dispersions were sheared at an increasing shear rate from 0 to 60 s^{-1}.

2.7.3. Transmission and scanning electron microscope

The pigment dispersion diluted by distilled water was analyzed using a JEM-1200EX Transmission Electron Microscope (JEOL, Japan) with voltage of 25 kV. The cotton fabrics were analyzed using a JSM-6390LV Scanning Electron Microscope (JEOL, Japan) with accelerating voltage of 15 kV and magnification between 10 and 400,000×. All the samples were coated with gold before SEM testing.

2.7.4. UV/vis absorption spectrum

Absorption spectrum of pigment was recorded using a 722 spectrophotometer. 1 ml of the pigment bath was taken into test tube and diluted with distilled water to 10 ml to measure its absorbance at 621 nm (λ_{max}). The pigment-adsorption percentage was calculated using the following equation:

$$R = \frac{A_0 - A_t}{A_0} \times 100\% \qquad (1)$$

where A_0 is the initial absorbance, A_t is the absorbance at time t.

2.7.5. Color yield, color difference and fastness testing

The color yields (K/S) were determined with Xrite-8400 colorimeter under illuminant D_{65} using the 10° standard observer. The pigment absorbance was measured in the visible spectrum region from 450 nm to 700 nm and the reflectance at the wavelength of maximum absorption (λ_{max}) was used to calculate the color yield of fabrics by the Kubelka–Munk equation:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (2)$$

where K is the coefficient of absorption, S the coefficient of scatter, R the fractional reflectance at λ_{max}.

The sample were folded to realize four thicknesses and three points on the folded line were selected for measuring the color data by a Xrite-8400 colorimeter under illuminant D_{65} using the 10° standard observer. The tristimulus values X, Y and Z of the samples were measured in the visible spectrum region 400–700 nm. The color parameters L, a and b, were also calculated. The color difference (ΔE) was assessed by Eq. (3):

$$\Delta E = \left[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2\right]^{1/2} \qquad (3)$$

where ΔL, Δa and Δb are the difference in the color parameters of the dyed fabrics. Mean values of color differences (ΔE) on three points were calculated to represent the leveling properties of pigment adsorption (Xie et al., 2011).

Washing, rubbing and light fastness of fabrics with pigment were tested according to ISO 105-C06, ISO 105-X12 and ISO 105-B02 standards, respectively.

3. Results and discussion

3.1. Characterization of nanoscale pigment

3.1.1. Dispersion degree

Dispersion degree of nanoscale pigment, which plays an important role in its adsorption performance, can be properly determined by its particle size. The mean pigment size is a. 163 nm according to the particle size measurement by the light scattering method, showing an efficient dispersion of the pigment (Buschle-Diller, Inglesby, & Wu, 2005; Fu & Fang, 2006). The TEM image of nanoscale pigment is shown in Fig. 2a, where stable and well-dispersed pigment can be observed in aqueous medium although the shape of pigment particles is irregular. During the dispersion, large pigment particles were wetted by liquid phase first, and then ground into small ones by mechanical impact. At the same time, molecules of polymeric dispersant were adsorbed onto pigment surface to prevent the re-agglomeration of fine particles by static electricity or steric repulsion (Wijting, Laven, van Benthem, & de With, 2008). Many dispersion equipments have been designed for efficient smashing the oversized pigment particles into small ones. Although different kinds of dispersion tools may adopt different dispersion mechanism, they can offer one of the three types of forces: shear force, impact force and attrition force, with maximum efficiency of transferring mechanical energy from dispersion tools to pigment particles (Lin, 2003).

3.1.2. Zeta potential and stability

The surfaces of pigment particles are negatively charged because of the use of anionic dispersant during the preparation, which can produce static repulsions among dispersed pigment particles and thus keep the dispersion in good condition. Fig. 2b shows the zeta potentials of nanoscale pigment at different pH conditions. It can be seen the zeta potential value increases with the increasing pH, telling that more carboxylic acid groups in polymeric dispersant are deprotonated at higher pH (Baez, Quazi, Ivanov, & Bhattacharya, 2009). As we know, there are two main forces existing between pairs of colloidal particles in solution: electrostatic double layer and van der Waals interaction. Depending on the balance of these two interactions, the net interaction may be either repulsive or attractive. This idea was proposed by Darjaguin, Laundau, Verway

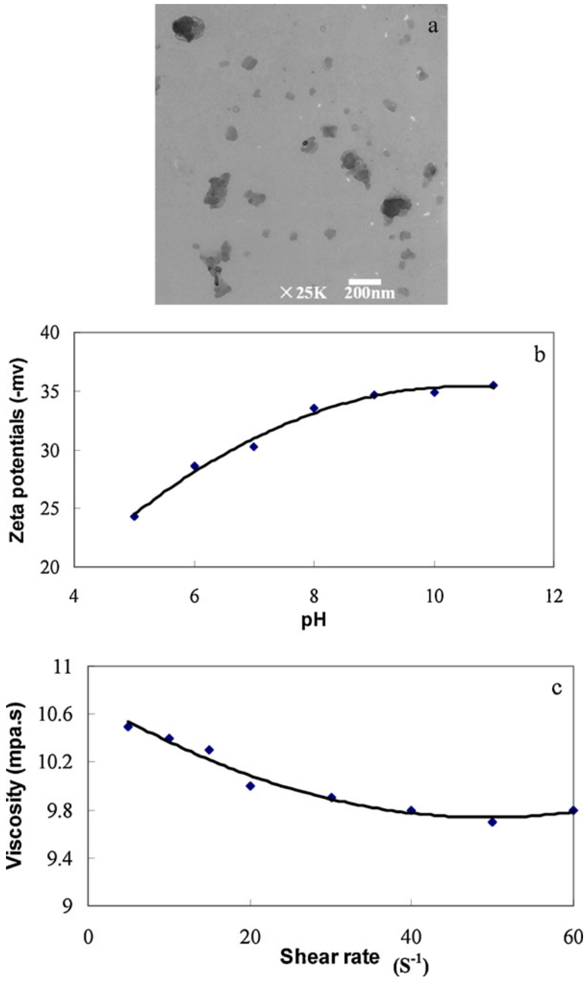

Fig. 2. (a)TEM photograph of nanoscale pigment; (b) effect of pH on zeta potentials of nanoscale pigment; and (c) effect of shear rate on viscosity of nanoscale pigment dispersion.

and Overbeek and therefore referred as the DLVO theory (Ishikawa, Aoki, & Ohshima, 2005; Ishikawa, Katoh, & Ohshima, 2005), which can be expressed with the following equation:

$$V_T = K\varepsilon\phi^2 r \exp(-\kappa H) - \frac{Ar}{12H} \tag{4}$$

where V_T is the total potential energy of interaction between two pigment particles, K is the constant, ε is the permittivity of the medium, φ is the surface potential of the particles, r is the particle radius, κ is the Debye–Huckel parameter, H is the separation distance between two particles and A is the Hamaker constant. So, the pigment dispersion can be in better stability at higher pH because of higher zeta potential.

3.1.3. Dispersion viscosity

Viscosity reflects the inner friction of pigment dispersion and demonstrates the dispersing behaviors of polymeric dispersant. Fig. 2c shows the nanoscale pigment dispersion displays a low and stable viscosity when shear rate is in the range of 5–60 s^{-1}, suggesting the homogeneity of pigment particles in dispersion is excellent and no obvious fluctuation occurs as shear rate increases (Fu & Fang, 2008).

3.2. The adsorption properties of nanoscale pigment

3.2.1. Effect of ultrasonic power

Unlike the dyes, pigments are insoluble in water, so they lack the inherent substantivity for the cotton substrate. Besides, in the preparation, the surfaces of pigment particles are negatively charged because of the use of anionic dispersant, which will produce repulsion force to the similarly charged cotton (Chen et al., 2009). To overcome this repulsion, the cationic reagent PNH was used to introduce cationic sites on the cotton fiber for successful adsorption of pigment. During cationisation, the molecules of cationic agent gradually transfer from the treatment bath to the solid surface of the fabrics and then react with the cellulosic molecular chains by forming ether bond between the epoxide and hydroxyl groups (Hao, Wang, Liu, & Liu, 2012; Kamel, El-Shishtawy Reda, Youssef, & Mashaly, 2007). After cationisation, the cotton surface will hold permanent positive charges and thus the nanoscale pigment can be favorably adsorbed onto it.

Like the soluble dyes, the dyeing of nanoscale pigment can be successfully carried out on cationised cotton using both the CV and US methods. For various dyes, the increment of dye uptake by the ultrasound can be attributed to (1) dispersion – breaking up of micelles or aggregates of dyes into uniform dispersions in the dye bath. (2) Degassing – expulsion of dissolved or entrapped gas or air molecules from fiber. (3) Diffusion – penetrating the insulating layer covering the fibers and accelerate the rate of diffusion of dye molecules inside fiber (Kamel, Ei-Shishtawy, Hanna, & Ahmed, 2003; Sun, Guo, & Liu, 2010). For the insoluble pigment, the increment of pigment adsorption can also be gained with the aid of ultrasound, which can be mainly attributed to the dispersion by the acoustic cavitation effect because the pigment particles can only deposit on the cotton surface or just diffuse into the large intra-yarn pores.

The improvement effect can be manipulated by the ultrasonic power during the pigment adsorption. The effect was explored by adjusting the ultrasonic power at 50, 100, 200 and 300 W and the result shown in Fig. 3. What should be pointed out is the ultrasonic power present is the nominal value quoted by the manufacturer. When an ultrasound wave travels through liquid medium, energy will be absorbed from the wave and conversed into heat. The conversion results in the energy loss between the actual energy input (P_{in}) in the dyeing bath and energy output (P_{out}) quoted by the manufacturer (Lorimer, Mason, & Fiddy, 1991; Sun et al., 2010). It is noted the equilibrium adsorption of pigment increases with the increasing ultrasonic power because of the upgraded acoustic cavitation. Higher equilibrium adsorption of pigment means the pigment particles left in the bath are reduced, which is desirable from both the economic and environmental aspects.

3.2.2. Effect of pH

The bath pH is also an important factor to affect the adsorption of nanoscale pigment. In this study, the pH of pigment bath was

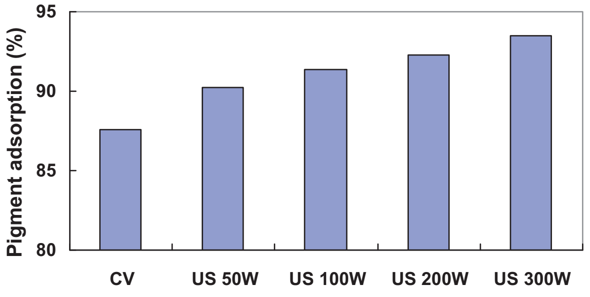

Fig. 3. Effect of ultrasonic power on adsorption of pigment (conditions: pH 7, at 60 °C for 45 min).

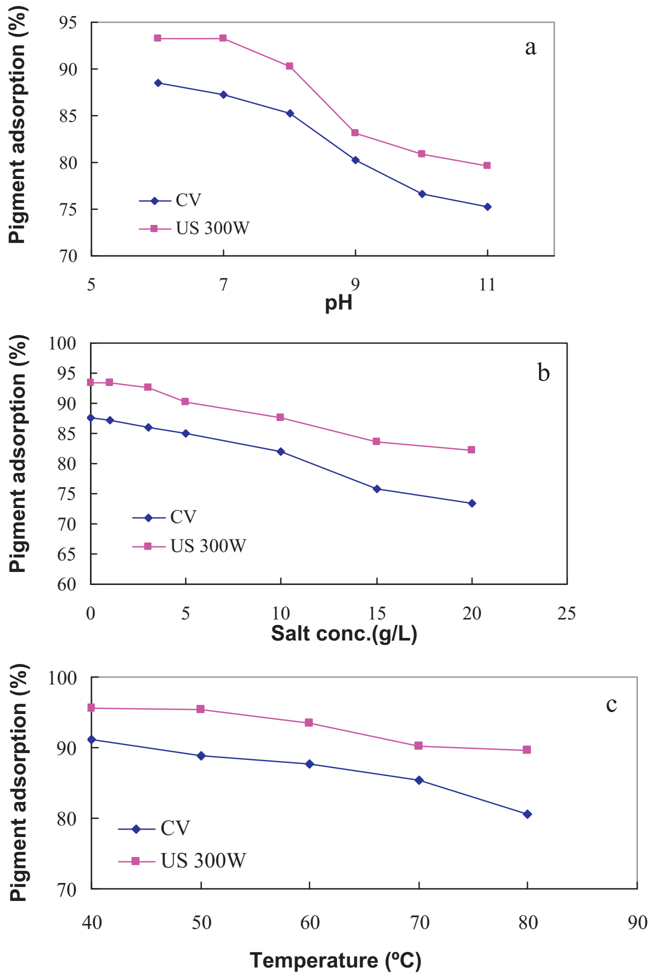

Fig. 4. (a) Effect of bath pH on pigment adsorption at 60 °C for 45 min; (b) effect of electrolyte on pigment adsorption at 60 °C for 45 min; and (c) effect of temperature on pigment adsorption at pH 7 for 45 min.

varied in the range of 6–11. Fig. 4a shows that as the pH increases, the equilibrium adsorption of pigment decreases under both CV and US conditions. As known to all, some pendant hydroxymethyl groups in cotton fiber are naturally oxidized to carboxylic acid groups during growth or following wet processing, and therefore the cotton fibers carry weak negative charges when solution pH higher than 4 (Rattanaphani, Chairat, Bremner, & Rattanaphani, 2007). Once the cotton fiber is fully cationised by cationic agent, its surface will hold permanent positive charges, resulting in strong ionic attraction between cationised cotton and anionic pigment particles. The ionic bond is a salt linkage which is stronger than secondary interactions such as hydrogen bonds and van der Waals forces. As the bath pH increases, carboxyl acid groups will be further deprotonated and some of the hydroxyl groups present on the side chains may also ionize, decreasing the positive charges significantly (Rattanaphani et al., 2007). Therefore, the substantivity between cationised cotton and pigment is reduced with the increasing pH, resulting in lower equilibrium adsorption of pigment.

3.2.3. *Effect of salt addition*

Electrolytes such as sodium chloride or sulfate have always been added into the dye bath to promote the adsorption of anionic dyes on cotton fibers. The effect of sodium chloride on the adsorption of nanoscale pigment was explored under both the CV and US conditions and the results shown in Fig. 4b. It is indicated the equilibrium adsorption of pigment decreases with the increasing electrolyte concentration. Upon addition of sodium chloride to the bath, the Cl^- would distribute between the external and internal solution so that the positive charges on the cationised cotton are partially neutralized or shielded, reducing the ionic attraction between cotton and pigment particles (Hao, Cai, & Wang, 2011). Another reason is the “salting out” effect of electrolyte will speed up the re-agglomeration of nanoscale pigment, undermining the adsorption capacity of pigment obviously.

3.2.4. *Effect of temperature*

The effect of temperature on the adsorption of nanoscale pigment under CV and US conditions is shown in Fig. 4c. It can be seen that fewer amount of pigments are bound on cotton at higher temperatures. This trend can be explained from the perspective of adsorption thermodynamics (El-Shishtawy, Youssef, Ahmed, & Mousa, 2004). The formation of ionic linkage between pigment and cationised cotton is exothermic and the standard affinity of pigment adsorption at different temperatures can be compared from Eq. (5):

$$\Delta H^\circ\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{\Delta\mu_1^0}{T_1}-\frac{\Delta\mu_2^0}{T_2} \qquad (5)$$

where $\Delta\mu_1^0$ and $\Delta\mu_2^0$ are the standard affinity at temperatures T_1 and T_2, respectively, and ΔH° the adsorption enthalpy. It can be concluded that standard affinity of pigment adsorption will decrease with the improving temperature, resulting in lower adsorption percentage of pigment at higher temperature. Another possible reason is the collisions among pigment particles will increase with the increasing temperature to form unstable pigment aggregations in the bath. It is also found the pigment has higher equilibrium adsorption with the aid of ultrasound at various temperatures because of the dispersion by the acoustic cavitation effect.

3.3. *The adsorption rate of nanoscale pigment*

Rate of pigment adsorption isotherms using both the CV and US methods are shown in Fig. 5a. Pigment adsorption will proceed by

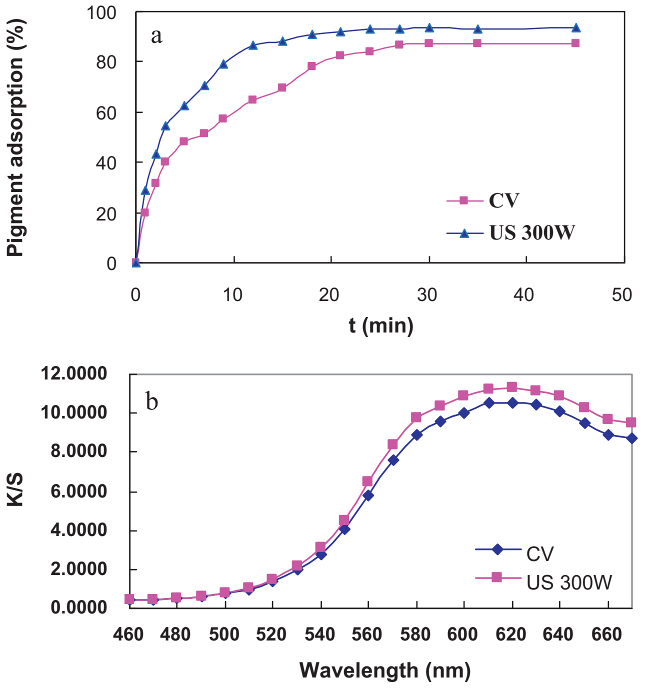

Fig. 5. (a) Effect of time on pigment adsorption; and (b) effect of ultrasound on K/S value of cationised cotton.

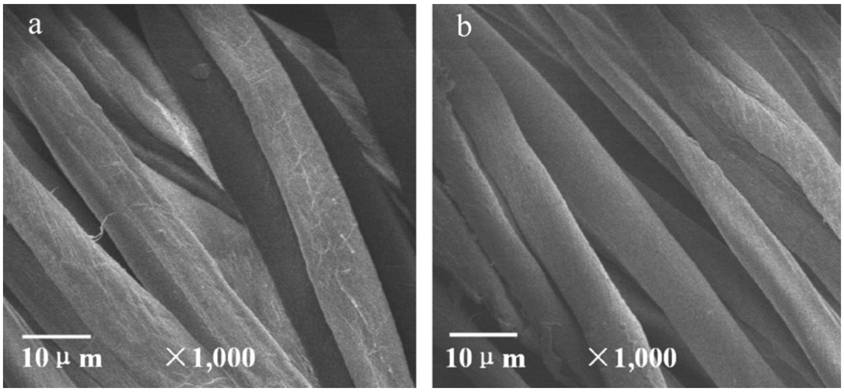

Fig. 6. SEM photographs of cotton fibers (a) with CV and (b) with US method.

the movement of pigment particles from the bath to fabric surface. Nanoscale pigment must pass through the boundary layer to attach on cotton fiber. Once the pigment is attracted onto the cotton surface, it will deposit on-site instead of diffusing into the fiber because its size is larger than the amorphous pores in cotton. Therefore, overall adsorption is fast. The slope of the isotherms becomes flat after some time, telling the system has reached equilibrium. The time needed to reach equilibrium with US method is nearly 10 min shorter than that needed with CV method, suggesting higher coloring efficiency and less energy consumption. The main reason is that ultrasound, with cavitation effect, can boost the pigment particles through the fiber–liquid boundary layer more quickly and easily. This is similar with the adsorption procedure of various dyes on textile substrate, in which the ultrasound can accelerate the diffusion rate of dye molecules through the fiber–liquid boundary layer and inside the fiber (Kamel et al., 2003; Sun et al., 2010).

After adsorption, the pigment particles are initially deposited on the cotton surface or in the large intra-yarn pores of the cotton fabric. Light scattering and light absorption of visible light decide the color of an opaque object. The Kubelka–Munk equation provides for calculation of a ratio, K/S, from measured reflectance values (Kamel, El Zawahry, Ahmed, & Abdelghaffar, 2009). The K/S values of the cotton with nanoscale pigment are shown in Fig. 5b. It is found the K/S value of cotton colored using US method is higher than that using CV method because ultrasound can increase the adsorption of pigment on the substrate. More amount of bound pigment particles on the substrate will decrease the fractional reflectance of the colored substrate resulting in higher K/S value. The improvement in color yield means that we can get the same coloring depth with less pigment consumption.

3.4. Morphological study

The SEM technique was used to explore the change in the surface morphology of the cationised cotton under different conditions. The SEM images are shown in Fig. 6, where typical cotton fibers with twisted, wrinkled surfaces and occasional breaks can be observed (Hebeish et al., 2009). It is shown the fibers treated by the ultrasound are smoother than those under CV condition, proving the slight change of cotton surface from the ultrasound. Some other researchers, by X-ray analysis, found that ultrasound could reduce the crystallinity of cotton fiber from 51.35% to 44% to create a looser structure (Kamel et al., 2009). In brief, the ultrasound can produce morphological and structural changes in cotton. However, these changes created by ultrasound cannot change the adsorption properties of nanoscale pigment on cotton because pigment particles can only be bound and deposited on the cotton surface or in the large intra-yarn pores instead of diffusing inside the fiber.

3.5. Evaluation of product quality

3.5.1. Color evenness

The leveling property of pigment adsorption is an important feature for the dyeing quality. The ultrasound can prevent the nanoscale pigment from aggregating in the dyeing bath because of its strong dispersing ability, which could be clearly shown by Fig. 7a and b. This will result in more even deposition of pigment particles on the fabric surface. The mean color differences (ΔE) on three points were calculated to represent the leveling properties of pigment adsorption on cationised cotton (Xie et al., 2011). The ΔE values for CV and US methods are 0.497 and 0.412, respectively, suggesting the ultrasound could give better leveling property to the nanoscale pigment. More directly, this improvement in leveling of pigment adsorption can be displayed by the SEM of the dyed fabrics in Fig. 7c and d. Fig. 7c shows the dyed fabric using the CV method, where some large pigment aggregates can be found because the fine pigment particles are totally confined within the narrow space on the cotton substrate after abandoning the commodious bath. From Fig. 7d, it can be seen the smaller pigment aggregates are formed and the distribution of these aggregates is more uniformly when using US method because the ultrasound can play a significant role in dispersing the pigment particles not only in the bath but also on the cotton surface.

3.5.2. Fastness properties

The fastness results involving washing, rubbing and light of cationised cotton colored by pigment using the CV and US methods are shown in Table 1. It is obvious the samples gained in the presence of ultrasound display similar washing fastness with corresponding dyeings without ultrasound. The high-level of staining kept for cellulose triacetate (CT), polyester (PET) and polyamide (PA) strip materials can be attributed to the high substantivity of the pigment toward these three types of fibers under the testing condition. The small extent of staining of both the wool (WO) and cotton (CO) multifiber strip materials can be ascribed to their polar and negatively charged nature. The absolute lack of staining of the acrylic strip material is attributable to its negatively charged nature and lack of substantivity for pigment at temperatures below its Tg (Burkinshaw & Jeong, 2012b). Table 1 also shows the wet rubbing fastness is slightly lower when using US method, which can be attributed to the higher adsorption amount of pigment on cotton surface under the same concentration of pigment. The light

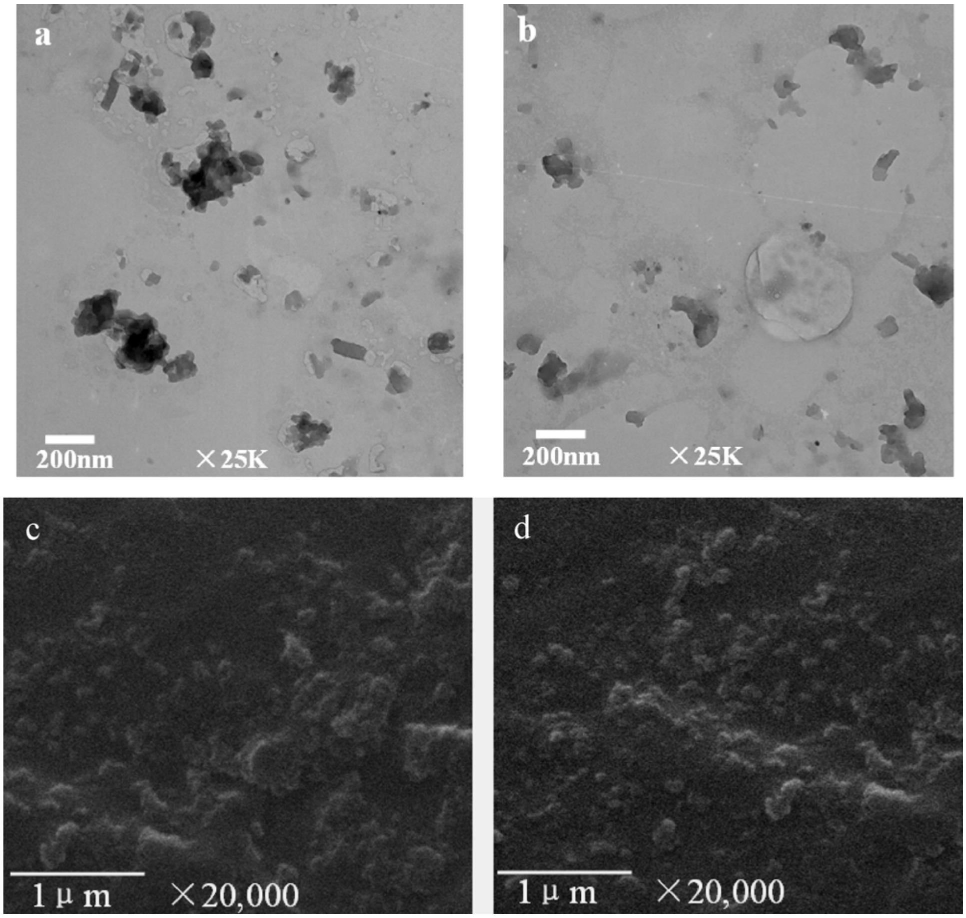

Fig. 7. (a) TEM photographs of pigment with CV method; (b) TEM photographs of pigment with US method; (c) SEM of pigment on cotton surface with CV method; and (d) SEM of pigment on cotton surface with US method.

Table 1
Color properties of nanoscale pigment on cationised cotton (CT: cellulose triacetate; CO: cotton; PA: polyamide; PET: polyester; PAC: polyacrylic; WO: wool).

Methods		Washing fastness						Rubbing fastness		Light
	Change	Staining on multifiber						Dry	Wet	
		CT	CO	PA	PET	PAC	WO			
CV	4–5	4	4–5	4	4	5	4–5	3–4	3	6
US 300 W	4–5	4	4–5	4	4	5	4–5	3–4	2–3	6

fastness of the samples is good and does not change after using the ultrasound.

4. Conclusions

A nanoscale pigment suspension was successfully prepared and used in the coloring of cationised cotton using both the CV and US methods. It is found the ultrasound is an effective technique to improve the equilibrium adsorption of this nanoscale pigment. With higher cavitation effect, the higher ultrasonic power can keep the pigment particles in smaller size and thus produce higher equilibrium adsorption. In addition, it is found that ultrasound can boost the adsorption rate of nanoscale pigment by accelerating the movement of nanoscale pigment through the fiber–liquid boundary layer and thus reduce the time needed to reach adsorption equilibrium. The fastness properties are similar under CV and US conditions, but it can be seen from SEM images the nanoscale pigments can be more evenly deposited and distributed on the cotton surface when using ultrasound. From above discussion, we come to conclusion the ultrasound can be used to assist the adsorption of nanoscale pigment with the benefit of less pigment residual, higher coloring efficiency and quality.

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