

Dye Behavior of Cationically Treated Silk

Wei Xiang, Zai-Sheng Cai

Key Laboratory of Textile Science and Technology (Ministry of Education), College of Chemistry and Chemical Engineering, Donghua University, Shanghai 201620, China

Received 13 January 2007; accepted 27 March 2007

DOI 10.1002/app.26990

Published online 22 January 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To increase the performance of silk fabrics, especially their dyeability, a cationic modifying agent, 3-(trimethoxysilyl) propyl dodecyl dimethyl ammonium chloride (HSQA), was prepared in our laboratory. The dye behavior of the cationized silk was examined with five leveling-type acid dyes. Better color shades and good washing fastness were achieved after silk was cationized by HSQA, and it was possible to dye silk under neutral conditions at 70°C. The equilibrium adsorption isotherm and kinetic properties of the cationized silk dyed with CI Acid Orange 7 were investigated. The adsorption of CI Acid Orange 7 onto the HSQA-cationized

silk was also in good agreement with the Langmuir isotherm, with an enthalpy and an entropy of -20.13 kJ/mol and -30.06 J/mol K respectively. A pseudo-second-order kinetic model agreed well with the dynamic behaviors for the adsorption of CI Acid Orange 7 onto the cationized silk under neutral conditions, with the activation energy decreasing from 61.87 to 53.32 kJ/mol. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1005–1012, 2008

Key words: dyes/pigments; fibers; proteins; thermodynamics

INTRODUCTION

Silk is highly appreciated for its outstanding characteristics, such as gentle luster, exceptional handle, excellent softness, and good drape.^{1,2} However, some problems are brought about when acid dyes are applied to silk fabrics. At the beginning of the dyeing process, a great deal of acid (hydrochloric acid or acetic acid) is added to the bath to adjust the value of the pH below the isoelectric point of the fibers, and this finally produces effluent.³ In addition, there are other problems during the dyeing process, that is, the weak color shade and wet fastness properties. At the same time, traditional dyeing techniques for silk with acid dyes operate at a high temperature (90°C), which results in damage to the physical properties of silk to some degree.

The cationization techniques mainly focus on enhancing the dyeability of cotton with direct and reactive dyes through a pretreatment of the fibers with cationic products.^{4–11} Essentially, the pretreatment of cellulose fibers before their dyeing with direct and reactive dyes can improve the substantivity of the

anionic dyes for the substrate through the operation of ion–ion forces of interaction between the anionic (commonly sulfonate) groups in the dye and the cationic groups in the pretreated fibers.^{12,13} The most common approach is to reduce the amount of salt required (or to eliminate salt altogether) and to increase the efficiency of the dye–fiber covalent bonding reaction via reactions of various types of amino compounds with cotton. Improvements in dye fixation and a reduction of the impact of the effluent on the environment have been principal areas of attention.^{14–16}

In this investigation, 3-(trimethoxysilyl) propyl dodecyl dimethyl ammonium chloride (HSQA; Figure 1) was synthesized in our laboratory and used to cationize silk fabrics. HSQA, the cationic modifying agent, contains long hydrophobic alkyl chains and quaternary ammonium groups.

This article mainly examines the dye behavior of HSQA-cationized silk with some acid dyes. Different factors affecting the dyeability and fastness properties are thoroughly investigated. The equilibrium adsorption and kinetics of cationized silk dyed with acid dyes are also presented.

Correspondence to: Z.-S. Cai (zshcai@dhu.edu.cn).

Contract grant sponsor: Program for Changjiang Scholars and Innovative Research Team in University; contract grant number: IRT0526.

Contract grant sponsor: Specialized Research Project for the North-West Science and Technology Combination of the Committee of Shanghai Municipal Science-Technology; contract grant number: 065458209.

EXPERIMENTAL

Materials

Silk fabrics

The degummed and bleached silk fabric (35 g/m²) was purchased from Jiaying Silk Factory (Zhejiang, China).

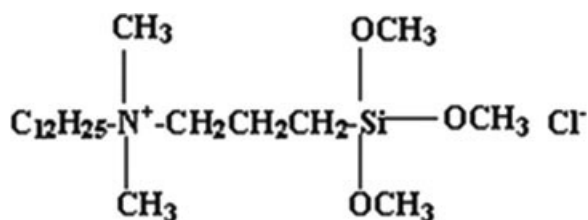


Figure 1 Cationic agent HSQA.

Acid dyes

CI Acid Red 18, CI Acid Orange 7, CI Acid Red 1, CI Acid Red 14, and CI Acid Red 73 were used in these experiments. They were obtained from Baoying Dyestuff and Chemical Co. (Zhejiang, China), except for CI Acid Orange 7, which was supplied by Ciba Co. (Shanghai, China) Their structures are shown in Figure 2.

Reagent

The cationic modifying agent, HSQA, was synthesized in our laboratory. NaHCO_3 , glacial acetic acid, and Na_2SO_4 were obtained from the Guangjiang Chemical Industrial Mill (Zhejiang, China).

Methods

Cationization of silk with HSQA

The silk fabrics were dipped into an aqueous solution with HSQA (15 g/L) and NaHCO_3 (10 g/L). The exhaustion process was carried out at 60°C for

30 min (liquor ratio = 1 : 40). The fabrics were then thoroughly rinsed in water to remove any unreacted HSQA. The samples were finally air-dried.

Dyeing procedure

Dyeing was begun at 40°C for 10 min with an acid dye (2% owf) and a liquor ratio of 1 : 100; the temperature was raised to the desired temperature at a rate of $1^\circ\text{C}/\text{min}$ and held at that temperature for 60 min. Then, the bath was allowed to cool, and the dyed silk was rinsed in water, soaped with a 2 g/L soap solution at 60°C for 10 min, and rinsed in water. It was finally air-dried.

Color measurements

The dyed samples were assessed with an SF600 color meter (Datacolour Co.) (Melbourne, Australia). From the reflectance (R) values at a given wavelength (λ), the color strength (K/S) of the dyed samples was calculated with the Kubelka–Munk equation:

$$K/S = (1 - R_\lambda)^2 / 2R_\lambda \quad (1)$$

Fastness testing

Color fastness to washing was determined according to ISO 105-C01:1989 at 40°C for 30 min in a soaping tester (Washwheel, Roaches) (Jiangsu, China).

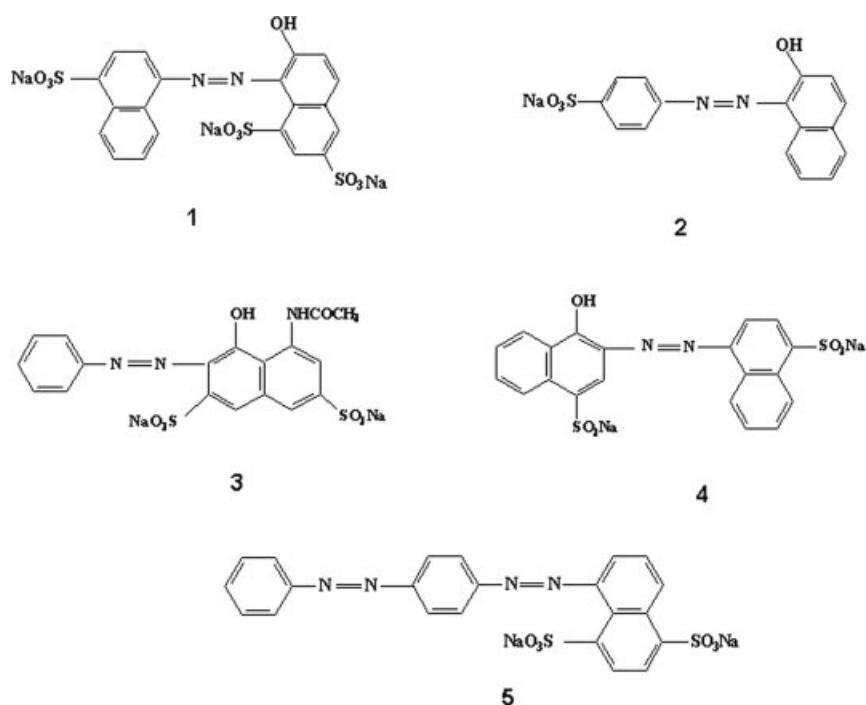


Figure 2 Structures of the acid dyes: (1) CI Acid Red 18, (2) CI Acid Orange 7, (3) CI Acid Red 1, (4) CI Acid Red 14, and (5) CI Acid Red 73.

TABLE I
Four Dye Baths

Dye bath	Recipe
1	1 g/L Na ₂ SO ₄ , pH 3.0
2	No salt, pH 3.0
3	1 g/L Na ₂ SO ₄ , pH 7.0
4	No acid, no salt, pH 7.0

For untreated and cationized samples, a dye concentration of 2% owf and 1 : 100 liquid ratio. pH 3.0, 1 : 100 liquid ratio and 90 were used (Table I).

Equilibrium experiments

CI Acid Orange 7 was dissolved in pyridine, then filtered and crystallized in acetone, and finally dried at 60°C to obtain the purified dye, which was used in equilibrium and kinetic experiments.

Different dye concentrations were freshly prepared through the dissolution of the mentioned refined dyestuff in deionized water. For untreated silk, the pH of the dye solution was adjusted to 3.0 with glacial acid and the addition of 1 g/L Na₂SO₄. For cationized silk, the pH value of the dyeing bath was about 7.0 without the addition of any acid or salt.

The experiments were carried out through the shaking of the silk fabric with acid dye solutions of different concentrations in conical flasks at 70, 80, and 90°C in a thermostat shaker bath operated at 75 rpm. The dye concentrations were determined at different times with a calibration curve based on the absorbance at a maximum λ value of 485 nm (2100 visible spectrophotometer, WFI) (Shanghai, China) versus the dye concentration in standard CI Acid Orange 7 solutions. Equation (2) was used to calculate the amount of dye absorbed per gram of silk at some definite time t [q_t (mg/g of silk)]:^{17,18}

$$q_t = (C_0 - C_t)(V/W) \quad (2)$$

where C_0 and C_t are the initial dye concentration and dye concentration at time t (mg/L), respectively; V is the volume of the dye solution (mL); and W is the weight of the silk fabric (g) used.

When the dyeing reaches equilibrium, C_t is represented by the equilibrium dye concentration (C_e). The amount of dye absorbed per gram of silk at equilibrium (q_e) (mg/g of silk) was also calculated with eq. (2).

Kinetic experiments

CI Acid Orange 7 dyestuff was dissolved in deionized water to the required concentration (200 mg/L). Also, for untreated silk, the pH of the dye solution was adjusted to 3.0 with glacial acid and the addition of 1 g/L Na₂SO₄; for cationized silk, the pH

value of the dyeing bath was about 7.0 without the addition of any acid or salt.

Each silk sample was dipped into the acid dye solution and stirred with a thermostat shaker at 75 rpm. q_t and q_e were calculated with eq. (2).

Fourier transform infrared (FTIR)

IR spectra were recorded with a PerkinElmer 1700 FTIR spectrophotometer under dried air in the spectral region of 2000–400 cm⁻¹.

RESULTS AND DISCUSSION

Dyeability comparison between the untreated and cationized silk

Effect of the dyeing temperature

The color shades of silk dyed with CI Acid Red 18 and CI Acid Orange 7 at different temperatures (70–90°C) were investigated, and the results are shown in Figure 3. For both acid dyes, the K/S values increased with an increase in the dyeing temperature for both untreated and cationized silk. The color shades of the cationized silk dyed with both acid dyes under neutral conditions at 70°C were deeper than those of the untreated samples dyed at 90°C. In addition, the exhaustion percentages of the cationized silk were almost 100% at 70°C.

In addition, the cationized silk was dyed with the three other acid dyes in a neutral dye bath at 70°C, and its dyeability was compared with that of the untreated silk under normal dye conditions at 90°C. The results, shown in Figure 4, indicate that the cationized samples achieved deeper color shades. This

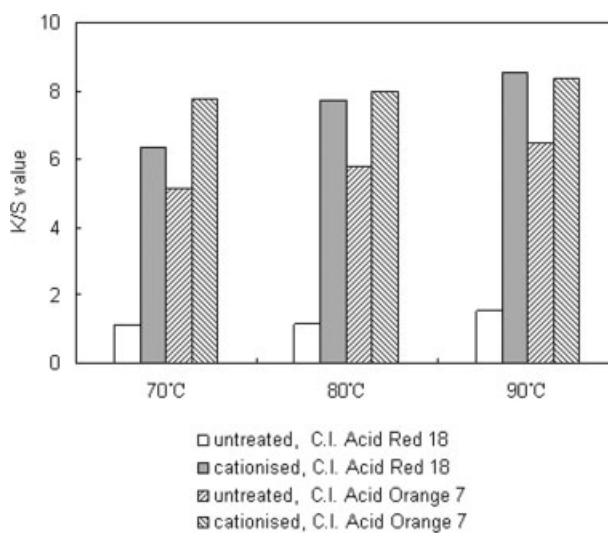


Figure 3 Effect of the dyeing temperature on the K/S values of untreated and cationized silk (untreated samples: dye concentration of 2% owf, 1 g/L Na₂SO₄, pH 3.0, and 1 : 100 liquid ratio; cationized samples: dye concentration of 2% owf, pH 7.0, and 1 : 100 liquid ratio).

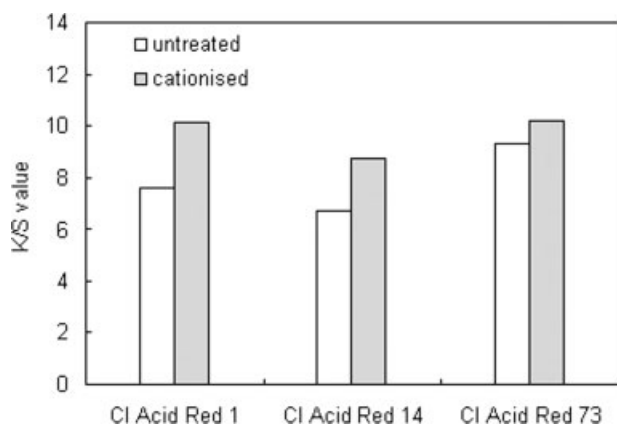


Figure 4 K/S values of untreated and cationized silk dyed with three acid dyes (untreated samples: dye concentration of 2% owf, 1 g/L Na_2SO_4 , pH 3.0, 90°C, and 1 : 100 liquid ratio; cationized samples: dye concentration of 2% owf; pH 7.0, 70°C, and 1 : 100 liquid ratio).

confirmed that the HSQA-cationized silk was also suited for other types of acid dyes.

In conclusion, HSQA-cationized silk can be dyed at a neutral pH and a low temperature (70°C) with leveling acid dyes. This result is very significant, in that it will contribute to diminishing pollution, saving energy, and reducing damage to silk.

Washing-fastness properties

The washing-fastness properties of the untreated and cationized silk dyed with the acid dyes were determined, and the results are given in Table II. The properties of the cationized samples were the same as those of the untreated ones with respect to the staining of silk and the staining of cotton. However, the property of the color change of the cationized silk was improved to some degree. This

TABLE II
Washing Fastness of the Untreated and Cationized Silk Fabrics Dyed with Acid Dyes

Dye	Untreated silk			Cationized silk with HSQA		
	Ch	S	C	Ch	S	C
CI Acid Red 18	3	3-4	4-5	4	3-4	4-5
CI Acid Orange 7	2	2-3	4-5	4	3-4	4-5
CI Acid Red 1	2-3	2	4-5	5	3-4	4-5
CI Acid Red 14	2-3	2	4-5	4	3-4	4-5
CI Acid Red 73	4	2-3	4-5	4	3-4	4-5

For the untreated samples, a dye concentration of 2% owf, 1 g/L Na_2SO_4 , pH 3.0, 1 : 100 liquid ratio, and 90°C were used. For the cationized samples, a dye concentration of 2% owf, pH 7.0, 1 : 100 liquid ratio, and 70°C were used. Ch = color change; S = staining of silk; C = staining of cotton.

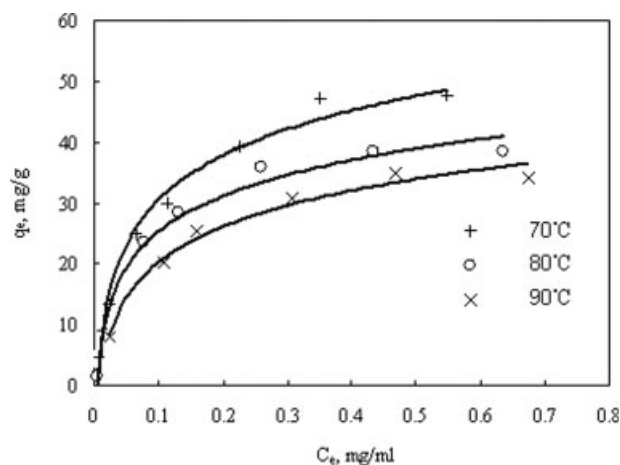


Figure 5 Adsorption isotherms of untreated silk dyed with CI Acid Orange 7 (initial dye concentration of 50–1000 mg/L, 1 g/L Na_2SO_4 , pH 3.0, 1 : 100 liquid ratio, and 3 h).

indicated that the cationized silk samples had good washing-fastness properties.

Adsorption isotherms

Figures 5 and 6 shows the adsorption isotherms of untreated and cationized silk dyed with CI Acid Orange 7 at different temperatures. The Langmuir equation is used to study the experimental data, and it can be expressed at a low concentration as follows:^{19,20,21}

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QbC_e} \quad (3)$$

where Q is the maximum amount of the dye absorbed per unit of weight of the fiber to form

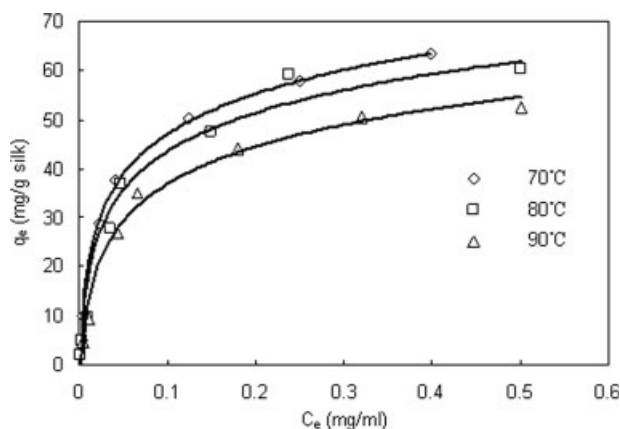


Figure 6 Adsorption isotherms of cationized silk dyed with CI Acid Orange 7 (initial dye concentration of 50–1000 mg/L, pH 7.0, 1 : 100 liquid ratio, and 3 h).

TABLE III
Langmuir Isotherm Constants of Untreated Silk and Cationized Silk Dyed with CI Acid Orange 7

	Temperature (°C)	Q (mg/g of silk)	b (mL/mg)	R ²
Untreated silk ^a	70	53.76	14.31	0.9979
	80	44.05	11.95	0.9991
	90	40.65	9.84	0.9989
Cationized silk ^b	70	64.96	30.70	0.9998
	80	62.50	22.86	0.9986

^a A dye concentration of 50–1000 mg/L, 1 g/L Na₂SO₄, 1 : 100 liquid ratio, and pH 3.0 were used.

^b A dye concentration of 50–1000 mg/L, 1 : 100 liquid ratio, and pH 7.0 were used.

complete monolayer coverage on a surface bound at high C_e and b is the Langmuir constant related to the affinity of the binding sites.

The values of Q and b were calculated from the intercepts and slopes of the straight lines of a plot of $1/q_e$ versus $1/C_e$. A comparison of the untreated silk and cationized silk is presented in Table III. When $1/q_e$ was plotted against $1/C_e$ according to eq. (3), the Langmuir model fitted the experimental data very well, with high correlation coefficients (R^2) for untreated samples (>0.98). The Q values decreased with increasing temperature. Similar observations were attained for cationized silk. These results were in good agreement with the literature.^{14,18} In a neutral dye bath, the maximum amount of the dye adsorbed onto the HSQA-cationized silk was higher than that adsorbed onto the untreated silk under normal dyeing conditions, as shown in Table III.

b is related to the enthalpy of adsorption.²² Therefore, the thermodynamic parameters, including the free-energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0), were also evaluated with the following equations:^{23,24,25}

$$\Delta G^0 = -RT \ln b \quad (4)$$

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (5)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6)$$

T is temperature (K)

ΔG^0 was calculated with eq. (4), whereas ΔH^0 and ΔS^0 of the adsorption were evaluated [eq. (5)] from the slope and intercept of the straight line of a graph of $\ln b$ versus $1/T$. The results are listed in Table IV.

It is well known that the negative values of ΔG^0 indicate the spontaneous nature of acid dyestuff adsorption onto silk. The results in Table IV show that the ΔG^0 values of both the untreated and cationized silk samples were under zero, indicating that the adsorption of CI Acid Orange 7 onto the two silk samples was consistent with spontaneous processes. The enthalpy and entropy values obtained from the adsorption of CI Acid Orange 7 onto cationized silk were -20.13 and -30.06 kJ/mol, respectively, whereas they were -15.55 and -22.95 kJ/mol for the untreated silk, respectively. Therefore, HSQA, CATIONIZATION, could enhance the silk adsorption capacity for CI Acid Orange 7.

Kinetics of adsorption

The cationic modification of silk can enhance its dyeability to acid dyes, and the kinetics of CI Acid Orange 7 adsorption onto untreated and cationized silk fabrics was investigated. The pseudo-first-order and pseudo-second-order equations were used to test the experimental data.

The pseudo-first-order equation can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

where t is the dyeing time (min) and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}).^{26–28}

k_1 and q_e at different temperatures were calculated with eq. (7) and are listed in Table V. A comparison

TABLE IV
Thermodynamic Parameters of Untreated Silk and Cationized Silk Dyed with CI Acid Orange 7

Sample	Temperature (°C)	b (mL/mg)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)	R ²
Untreated ^a	70	14.31	-7.6	-15.55	-22.95	0.9994
	80	11.95	-7.3			
	90	9.84	-6.9			
Cationized ^b	70	30.70	-9.77	-20.13	-30.06	0.9844
	80	22.86	-9.18			
	90	18.99	-8.89			

^a A dye concentration of 50–1000 mg/L, 1 g/L Na₂SO₄, 1 : 100 liquid ratio, and pH 3.0 were used.

^b A dye concentration of 50–1000 mg/L, 1 : 100 liquid ratio, and pH 7.0 were used.

TABLE V
Comparison of k_1 and k_2 for Untreated and Cationized Silk and Calculated q_e Values for CI Acid Orange 7

	Temperature (°C)	$q_{e,exp}$ (mg/g of silk)	Pseudo-first-order equation		Pseudo-second-order equation			
			$k_1 \times 100$ (min ⁻¹)	R^2	$k_2 \times 100$ (g of silk/mg min)	$q_{e,cal}$ (mg/g of silk)	h_i (mg/g of silk min)	R^2
Untreated ^a	70	15.67	1.68	0.9755	1.51	15.73	3.72	0.9986
	80	15.42	1.82	0.9541	2.97	14.95	7.06	0.9982
	90	14.32	2.87	0.8317	5.33	14.00	10.46	0.9997
Cationized ^b	70	18.01	1.58	0.9341	2.29	17.69	7.16	0.9995
	80	17.58	4.12	0.9657	3.83	17.57	11.83	0.9996
	90	16.92	6.16	0.9634	6.86	17.04	18.05	0.9998

^a An initial dye concentration of 200 mg/L, 1 g/L Na₂SO₄, a 1 : 100 liquid ratio, 3 h, and pH 3.0 were used.

^b An initial dye concentration of 200 mg/L, 1 : 100 liquid ratio, 3 h, and pH 7.0 were used.

of the results with R^2 is also shown in Table V. The R^2 values (<0.97) for the pseudo-first-order kinetic model are very low, indicating a poor pseudo-first-order fit to the experimental data.

The pseudo-second-order kinetic model is based on the adsorption equilibrium capacity and can be expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (8)$$

where k_2 (g of silk/mg min) is the rate constant for pseudo-second-order adsorption.²⁶⁻²⁸ Integrating eq. (8) and applying the initial conditions, we have

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (9)$$

or, equivalently,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

$$h_i = k_2 q_e^2 \quad (11)$$

where h_i is the initial dye adsorption rate (mg/g of silk min). A straight line of t/q_t versus t suggests the applicability of this kinetic model to the experimental data. k_2 and q_e were calculated from the slope and intercept of this line, as shown in Figures 7 and 8. The k_2 values of the untreated and cationized silk fabrics and the R^2 values at different temperatures are listed in Table V. It is likely that the behavior over the whole range of adsorption was in agreement with the chemisorption mechanism being the rate-controlling step.^{14,28,29} On the basis of Table V, the adsorption of CI Acid Orange 7 onto the untreated and cationized silk was considered to be pseudo-second-order with high R^2 values above 0.99. In addition, q_e , which is the adsorption capacity, agreed very well with both the experimental and calculated values, as listed in Table V.

The results indicated that the rate constant of the silk fabrics increased with an increase in the temperature, and the R^2 values were all above 0.98. Cationized silk had a higher rate constant even with dyeing at 70°C and under neutral conditions.

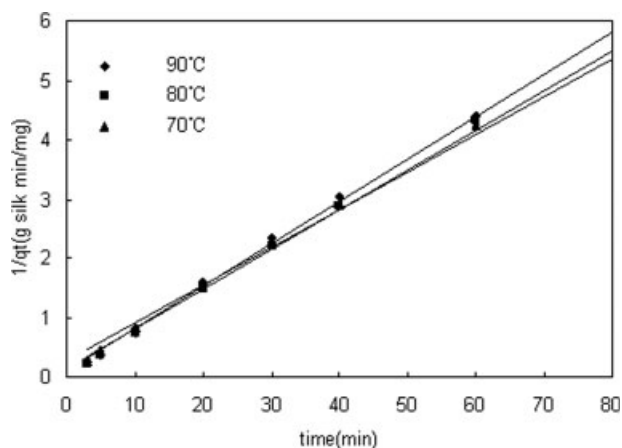


Figure 7 Plot of the pseudo-second-order equation of untreated silk dyed with CI Acid Orange 7 (initial dye concentration of 200 mg/L, 1 g/L Na₂SO₄, pH 3.0, 1 : 100 liquid ratio, and 3 h).

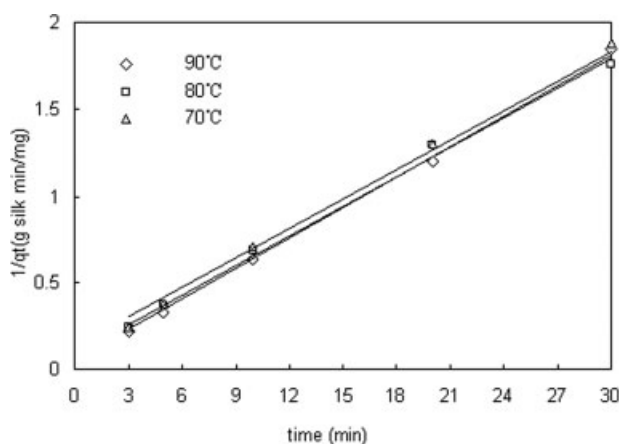


Figure 8 Plot of the pseudo-second-order equation of cationized silk dyed with CI Acid Orange 7 (initial dye concentration of 200 mg/L, pH 7.0, 1 : 100 liquid ratio, and 3 h).

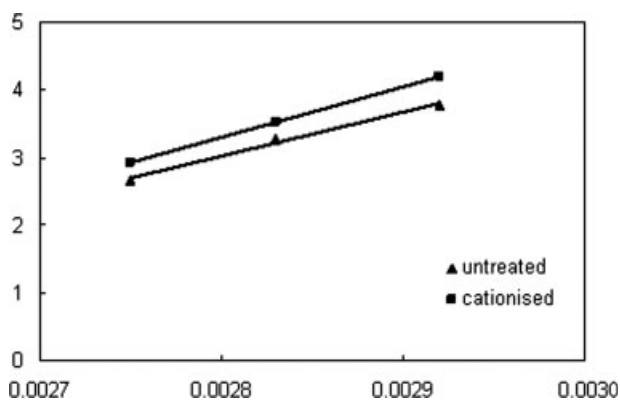


Figure 9 Plot of the Arrhenius equation of silk dyed with CI Acid Orange 7.

Activation energy

The rate constants at different temperatures (listed in Table V) were applied to estimate the activation energy of the adsorption of CI Acid Orange 7 onto silk by the Arrhenius equation:

$$\ln k = \ln A - \frac{E}{RT} \quad (12)$$

k is the rate constant of pseudo-second order adsorption.

where E , R , and A refer to the Arrhenius activation energy, the gas constant, and the Arrhenius factor, respectively.²⁶ The slope of the plot of $\ln k$ versus $1/T$ was used to evaluate E , as presented in Figure 9 and Table VI. The activation energy of the cationized silk decreased from 61.87 to 53.32 kJ/mol, and this indicated that cationization decreased the energy barrier of dye diffusion. Thereafter, the dyeing process could be realized easily.

FTIR

The FTIR spectra of cationic modifying agent HSQA, untreated silk fabric, and cationized samples are presented in Figure 10(a–c), respectively. As shown in Figure 10(a), the absorption bands at 1191.33, 2853.50, and 2924.94 cm^{-1} have been attributed to Si–OCH₃ stretching. The nitrogen atom stretching of the quaternary ammonium group can be observed at 952.77 cm^{-1} .

TABLE VI
Activation Energy of Adsorption of CI Acid Orange 7 for Untreated and Cationized Silk

Sample	Activation energy (kJ/mol)	R^2
Untreated	61.87	0.9999
Cationized	53.32	0.9936

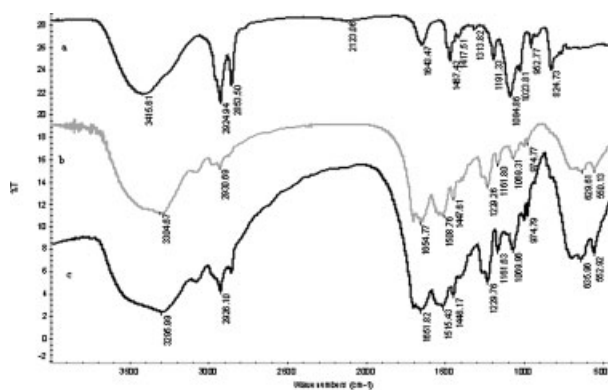


Figure 10 FTIR spectra of (a) HSQA, (b) untreated silk, and (c) a cationized sample.

Figure 10(b,c) illustrates the fibroin absorption bands around 1508.76 and 1654.77 cm^{-1} , which have been assigned to C=O stretching and N–H stretching of amide I and amide II, respectively. It is evident that the FTIR spectrum of cationized silk is almost identical to that of the untreated sample, except that the absorption increased at wave numbers of 974.79 and 2926.10 cm^{-1} . Hence, the FTIR spectra of the cationized silk indicated a crosslinking reaction between the silk and modifying agent HSQA.

CONCLUSIONS

The cationic modification of silk enhanced the dyeability of acid dyes and made it possible to dye silk under neutral conditions at 70°C.

The dye adsorption behavior of HSQA-cationized silk dyed with acid dyestuff still followed the Langmuir adsorption isotherm model. The maximum adsorbed amount of the cationized silk dyed with CI Acid Orange 7 in a neutral dye bath was higher than that of the untreated silk under normal dyeing conditions.

The values of ΔG^0 for both the untreated and cationized silk samples were under zero, showing that acid dyestuff adsorption on both the untreated and cationized silk samples was a spontaneous process. ΔH^0 and ΔS^0 of the adsorption of CI Acid Orange 7 onto cationized silk were –20.13 kJ/mol and –30.06 J/mol K, respectively, whereas those for the untreated silk were –15.55 and –22.95 kJ/mol, respectively.

A pseudo-second-order kinetic model agreed well with the dynamic behaviors for the adsorption of CI Acid Orange 7 onto the cationized silk under neutral conditions. The rate constant of the cationized silk was higher than that of the untreated silk. The activation energy of the cationized silk dropped from 61.87 to 53.32 kJ/mol.

The authors thank Honglin Yang for his help with the experiment.

References

1. Hofstetter, R. *Melliand Textilber, Eng.* 1991, 5, E148.
2. Cai, Z.; Qiu, Y. *Text Res J* 2003, 73, 42.
3. Perkins, W. S. *Textile Coloration and Finishing; China Textile: Beijing*, 2004; p 152.
4. Burkinshaw, S. M.; Gotsopoulos, A. *Dyes Pigments* 1996, 32, 209.
5. Burkinshaw, S. M.; Gotsopoulos, A. *Dyes Pigments* 1999, 42, 179.
6. Burkinshaw, S. M.; Lei, X. P.; Lewis, D. M. *J Soc Dyers Colourists* 1989, 105, 391.
7. Burkinshaw, S. M.; Lei, X. P.; Lewis, D. M. *J Soc Dyers Colourists* 1990, 106, 307.
8. Lewis, D. M. *J Soc Dyers Colourists* 1993, 109, 357.
9. Lewis, D. M.; Lei, X. P. *Text Chem Colorist* 1989, 21, 23.
10. Galafassi, P. V.; Luttringer, J. P.; Tzikas, A. *Book Pap AATCC Int Dyeing Symp* 1995, 115.
11. Lei, X. P.; Lewis, D. M. *J Soc Dyers Colourists* 1990, 106, 352.
12. Lewis, D. M.; Lei, X. P. *J Soc Dyers Colourists* 1991, 107, 102.
13. Ballard, J. U.S. Pat.3,853,460 (1974).
14. Chairat, M.; Rattanaphani, S. *Dyes Pigments* 2005, 64, 231.
15. Kamel, M. M.; El-Shishtawy, R. M. *Dyes Pigments* 2006, 69, 1.
16. Cid, M. V. F.; van der Kraan, M. *J Supercrit Fluids* 2004, 32, 147.
17. Rattanaphani, S.; Chairat, M.; Bremner, J. B.; Rattanaphani, V. *Dyes Pigments* 2007, 72, 88.
18. Kongkachuichay, P.; Shitangkoon, A.; Chinwongamorn, N. *Dyes Pigments* 2002, 53, 179.
19. Choi, J.-H.; Kang, M.-J.; Yoon, C. *Coloration Technol* 2005, 121, 81.
20. Langmuir, I. *J Am Chem Soc* 1918, 40, 1361.
21. McKay, G. *J Chem Tech Biotechnol* 1982, 32, 759.
22. Gupta, V. K.; Ali, I.; Suhas; Mohan, D. *J Colloid Interface Sci* 2003, 265, 257.
23. Sharma, Y. C.; Prasad, G.; Rupainwar, D. C. *Int J Environ Stud* 1991, 37, 183.
24. Jain, A. K.; Gupta, V. K.; Bhatnagar, A.; Suhas. *J Hazard Mater B* 2003, 101, 31.
25. Chiou, M. S.; Li, H. Y. *J Hazard Mater* 2002, 93, 233.
26. Dogan, M.; Alkan, M. *Chemosphere* 2003, 50, 517.
27. Wu, F. C.; Tseng, R. L.; Juang, R. S. *Water Res* 2001, 35, 613.
28. Chiou, M. S.; Li, H. Y. *Chemosphere* 2003, 50, 1095.
29. Chiou, M. S.; Ho, P. Y.; Li, H. Y. *Dyes Pigments* 2004, 60, 69.