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Ultrasonic assisted dyeing. IV. Dyeing of cationised cotton with lac natural dye

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Abstract

The dyeing of cationised cotton fabrics with lac natural dye has been studied using both conventional and ultrasonic techniques. The effects of dye bath pH, salt concentration, ultrasonic power, dyeing time and temperature were studied and the resulting shades obtained by dyeing with ultrasonic and conventional techniques were compared. Colour strength values obtained were found to be higher with ultrasonic than with conventional heating. The results of fastness properties of the dyed fabrics were fair to good. Dyeing kinetics of cationised cotton fibre with lac dye using conventional and ultrasonic conditions were compared. The values of dyeing rate constant, half-time of dyeing and standard affinity and ultrasonic efficiency have been calculated and discussed.

Keywords: Ultrasound; Sonochemistry; Cationisation; Cotton; Natural dye; Dyeing; Kinetic

1. Introduction

Conventional wisdom leads to the belief that natural dyes are friendlier to the environment than their synthetic counterparts. Natural dyes can exhibit better biodegradability and generally have a higher compatibility with the environment. Recently, the potentiality of using natural dyes in textile colouration as anti-UV and anti-microbial has been reported [1–3]. Reviews on the use of natural dyes in food and in textile colouration have been published [4,5]. Lac dye (C.I. Natural Red 25; C.I. 75450) [6] is obtained from the dried bodies of an insect, *Coccus laccae* (*Laccifer lacca* Kerr), found growing on the twigs of certain tree native to southeast Asia. The use of lac dye in the dyeing of silk and leather seems to have been known to the Chinese some 4000 years ago. Lac is a mixture of at least five closely related lacciac acids (Fig. 1), which are water-soluble red dyes of anthraquinoid type structure [7,8].

Cotton, a natural cellulosic fibre, is the most common textile fibre in the world as it possesses many useful characteristics such as comfort, it is soft to the hand, has good absorbency, colour retention, good strength and machine-washable. Natural cellulose fibres are negatively charged due to the presence of carboxyl and hydroxyl groups [9]. Cotton can be easily dyed but the cellulose–dye bond is not very strong. The pretreatment of cotton to enhance its dye adsorption using commercial cationic agents such as Matexil FC-PN, Matexil FC-ER and Solfix E has been explored; it was found that such pretreatment increased the colour strength of the dyeing and improved wash fastness [10,11]. Courtaulds and Clariant (formally Sandoz) have developed the Sandene process using "Sandene 8425" in which the cellulosic fibres are modified with a cationic polymer under basic conditions to enhance cotton dyeability with anionic dyes [12,13]. In this interest, it has been recently reported that polyethylene (imine) has acted as non-metal mordanting agent to link lac dye with cotton via ion–ion interactions [14].

In the previous part of this paper [15], which examined the enhancement effect of ultrasonic power on both lac dye extractability and wool fibres dyeability with the extracts, it

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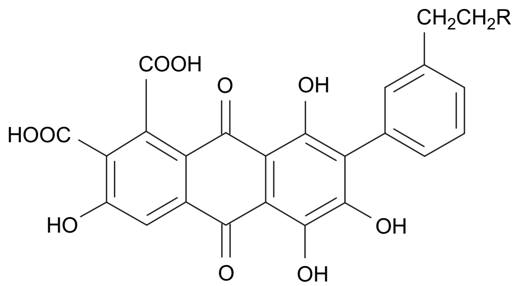

Lacciac acid

R=OH (lacciac acid B)
R=NHCOMe (lacciac acid A)
λ_{max} and molar extinction coefficient in water are 535 nm and 0.0009 l/mg cm, respectively.

Fig. 1. Main colourant species present in aqueous extract of lac.

was found that ultrasonic power substantially enhanced both processes in comparison with the conventional heating as a result of ultrasonic cavitation effect [16,17]. In continuation of our interest in using power ultrasonic in dyeing [15,18,19], we wish to report in this work the dyeing behaviour of cationised cotton with lac dye using power ultrasonic and conventional heating. Different factors affecting dyeability and fastness properties were thoroughly investigated. Comparative results of the dyeing kinetics of cationised cotton fibres using both ultrasonic and conventional dyeing methods are also presented.

2. Experimental

2.1. Materials

A commercial material of lac dye (Fig. 1) was used. Scoured and bleached cotton fabric (142 g/m^2) was purchased from Misr Spinning and Weaving Company, Mahalla El-Kobra, Egypt. Before using, the fabric was treated with a solution containing 5 g/l non-ionic detergent (Hostapal CV, Clariant), at 95 °C for 4 h. Then, the fabric was thoroughly washed with water and air dried at room temperature.

Thermostated CREST benchtop 575 HT ultrasonic cleaner of capacity 5.75 l, frequency 38.5 kHz and with a maximum 500 W output was used. The output power levels are from 100 to 500 W.

2.2. Methods

2.2.1. Conventional and ultrasonic extractions

Conventional and ultrasonic extractions were carried out as described in the previous part of this work [15].

2.2.2. Cationisation of cotton with Sandene 8425

Cotton fabric was cationised according to Clariant's (formally Sandoz) published method [20] to get treated fibres with 0.62 N%.

2.2.3. Dyeing procedure

In a dye bath containing different amounts of sodium chloride (0–20 g/l) and 8% lac dye with liquor ratio 40:1, cationised cotton fabric was dyed using conventional heating (CH) at different pH values (1.5–10) for different duration 12–120 min and at different temperatures (30–80 °C). For comparison, the same condition of dyeing was carried out using ultrasonic dyeing (US) with sonic power of 500 W. The optimum value of sonic power was obtained after studying the effect of sonic power on the dyeability of cationised cotton. Thus, in a dye bath containing 8% lac dye with liquor ratio 40:1 and pH 2.5, cationised fabric was dyed at 80 °C for 60 min using different sonic power levels (100–500 W). The effect of the number (1–5) of dye bath reuse was also conducted in a comparative manner for both US and CH methods.

The dyed samples were rinsed with cold water, washed in a bath of liquor ratio 40:1 using 3 g/l non-ionic detergent (Hostapal CV, Clariant) at 95 °C for 30 min, then rinsed and finally dried at ambient temperature.

The pH values were recorded with Hanna pH meter and adjusted with dilute solutions of sodium carbonate, as the dye extract was acidic (pH 1).

2.2.4. Dyeing rate

The cationised cotton fabric samples were cut into pieces approximately 1 cm^2 and dyed at pH 2.5 in a beaker with 160 ml aqueous solution composed of 1 g/l non-ionic wetting agent (Hostapal CV, Clariant) and 8 g/l lac dye with liquor ratio 40:1 at 80 °C with frequent shaking. Dyeing was conducted using both ultrasonic power at 500 W and conventional heating conditions. After selected time intervals, 0.5 ml of the dye bath was pipetted into test tubes and diluted with water to 5 ml to measure its absorbance at 535 nm.

2.3. Colour strength

The reflectance of the soaped samples was measured on a Perkin–Elmer Lambda 3B UV/Vis spectrophotometer. Relative colour strengths (K/S values) were determined using the Kubelka–Munk equation [21]:

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

2.4. UV/vis absorption spectra

The UV/vis absorption spectra in water were recorded using a Shimadzu UV/vis spectrophotometer. The quantity of dye-uptake was estimated using the following equation:

$$Q = (C_0 - C_f)V/W \tag{2}$$

where Q is the quantity of dye-uptake (mg/g), C_0 and C_f are the initial and the final concentrations of dye in solution (mg/l), respectively, V is the volume of dye bath (l) and W is the weight of fibre (g). The concentration of dye solutions was determined after reference to the respective calibration curve of the lac dye using Lambert–Beer law.

2.5. Nitrogen percentage

Nitrogen was determined by the Cole and Parks modification of the semimicro Kjeldahl method [22].

2.6. Fastness testing

The dyed samples were tested according to ISO standard methods. The specific tests were ISO 105-X12 (1987), colour fastness to rubbing; ISO 105-C02 (1989), colour fastness to washing and ISO 105-E04 (1989), colour fastness to perspiration.

3. Results and discussion

It has been recognised for many years that power ultrasound has great potential for application in a wide variety of industrial processes as it offers potential cost savings in time, chemicals, energy and reduced effluent [23–25]. In this context applying power ultrasound in textile colouration was of interest. In the same interest of better dyeing and less dye effluent, and based on the negative nature of both dye and substrate, it was necessary to use cationised cotton to enhance its dyeability with lac dye. Thus, exploiting power ultrasonic in the dyeing of cationised cotton fabrics using lac as a natural dye was made in two steps, i.e. ultrasonic extraction of the dye followed by ultrasonic dyeing. Therefore, comparative study between CH and US as well as the different factors that may affect these processes are investigated.

3.1. Dye extraction

CH and US extractions of lac dye were reported previously to reveal the effectiveness of US over CH by about 41% enhancement [15].

3.2. Dyeing

3.2.1. Effect of dye bath pH

Fig. 2 shows that the pH values of the dye bath have a considerable effect on the dyeability of cationised cotton fabrics with lac dye under both US and CH conditions. It is clear that US has improved the dyeability of the fabrics at pH 1.5 and 2.5 values. As the pH increases the dyeability, under both CH and US conditions, decreases. The effect of dye bath pH can be attributed to the correlation between dye structure and cationised cotton fibres. Since the lac dye used is a water-soluble dye containing carboxyl groups, it would interact ionically with the protonated terminal amino groups of cationised cotton fibres at acidic pH via ion exchange reaction. The anion of the dye has a complex character, and when it is bound on fibre, further kinds of interactions take place together with ionic forces. This ionic attraction would increase the dyeability of the fibre as clearly observed in Fig. 2.

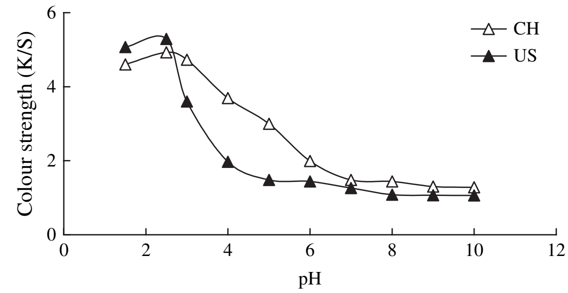

Fig. 2. Effect of dye bath pH on the colour strength of dyed cationised cotton fabrics. Dyeing conditions: 500 W, LR 40:1, 40 ml aqueous dye extract (8% w/v), 10 g/l sodium chloride, 1 h, at 80 °C.

At pH > 2.5, however, the ionic interaction between the carboxylate anion of the dye and cationised cotton fibres decreases due to the decreasing number of protonated terminal amino groups of cationised cotton fibres and thus lowering its dyeability. It is to be mentioned that the lower dyeability in the case of US method than in the case of CH method at pH > 2.5 may be attributed to the enhanced desorption of the dye as its ionic bond is getting decreased.

3.2.2. Effect of salt addition

Dyeing of proteinic fibres with high affinity anionic dyes necessitates the use of salt in the dye bath for obtaining level dyeings. Cationised cotton (aminated fibres) is considered to behave similarly with those of proteinic fibres in its dyeability with anionic dyes. Fig. 3 shows the effect of salt concentration on the colour strength obtained for the dyed fabrics under both US and CH methods. Expectedly, the colour strength was better in the absence than in the presence of salt, and at all concentrations of salt the dyeability under US condition was better than that obtained under CH method.

3.2.3. Effect of temperature

The effect of temperature on the dyeability of the cationised cotton fabrics with lac dye was conducted under US and CH conditions at different temperatures (30–80 °C). As shown in Fig. 4, it is clear that the colour strength increases with increase in dyeing temperature in both cases of US and CH methods with pronounced increase in the US case than the CH. At 60 °C or above a plateau value of *K/S* was observed

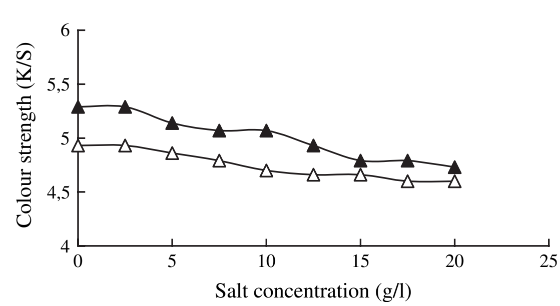

Fig. 3. Effect of salt addition to the dye bath on the colour strength of dyed cationised cotton fabrics. Dyeing conditions: 500 W, LR 40:1, 40 ml aqueous dye extract (8% w/v), pH 2.5, 1 h, at 80 °C. For legend see Fig. 2.

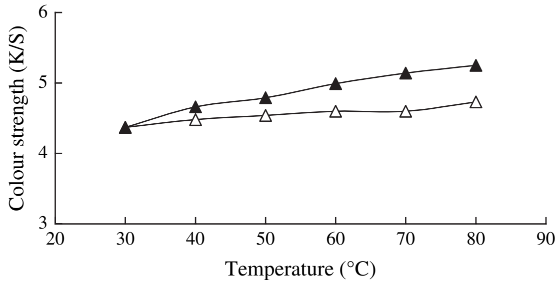

Fig. 4. Effect of dyeing temperature on the colour strength of dyed cationised cotton fabrics. Dyeing conditions: 500 W, LR 40:1, 40 ml aqueous dye extract (8% w/v), pH 2.5, 1 h. For legend see Fig. 2.

in CH, the case that was absent in US method. Generally, the increase in dye-uptake can be explained by fibre swelling and hence, enhanced dye diffusion. Also, the ultrasonic power provides other additional factor of de-aggregation of dye molecules and thus leading to further enhancement of dye diffusion and better dyeability than CH.

3.2.4. *Effect of dyeing time*

The effect of dyeing time was conducted at high concentration of the dye, i.e. 8 g/100 ml water to reveal the effect of power ultrasonic on the de-aggregation of dye molecules in the dye bath as indicated by higher dye-uptake. As shown in Fig. 5, the colour strength obtained increased as the time increased in both US and CH methods with much higher colour strength at all points in the US case. In case of US method, a plateau is attained after 60 up to 75 min and then started to decline slightly with prolongation of the time. Whereas in the case of CH, the decline in colour strength started after 60 min ahead. The decline in the dyeability may be attributed to the desorption of the dye molecules as a consequence of long dyeing time.

3.2.5. *Effect of ultrasonic power*

The effect of ultrasonic power on the dyeability of cationised cotton fabrics with lac dye was conducted at different power levels (100–500 W). As shown in Fig. 6, the colour strength of dyed fabrics seemed to be directly proportional with the power supplied. This behaviour emphasizes again

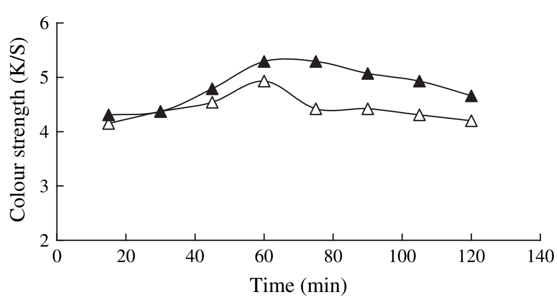

Fig. 5. Effect of dyeing time on the colour strength of dyed cationised cotton fabrics. Dyeing conditions: 500 W, LR 40:1, 40 ml aqueous dye extract (8% w/v), pH 2.5, at 80 °C. For legend see Fig. 2.

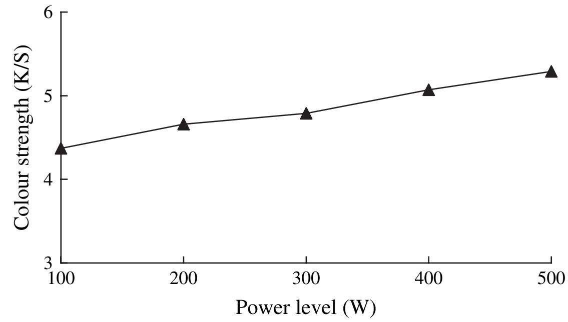

Fig. 6. Effect of power level on the colour strength of dyed cationised cotton fabrics. Dyeing conditions: LR 40:1, 40 ml aqueous dye extract (8% w/v), pH 2.5, at 80 °C, 1 h.

the assisting effect of power ultrasonic on the dyeability of cationised cotton fabrics with the lac dye.

This assistance can be explained as suggested before [26] to dispersion (breaking up of micelles and high molecular weight aggregates into uniform dispersions in the dye bath), degassing (expulsion of dissolved or entrapped gas or air molecules from fibre into liquid and removal by cavitation, thus facilitating dye–fibre contact) and diffusion (accelerating the rate of dye diffusion inside the fibre by piercing the insulating layer covering the fibre if any and accelerating the interaction or chemical reaction, if any, between dye and fibre).

3.2.6. *Effect of reuse number of the dye bath*

Fig. 7 shows the effect of reuse number on the colour strength obtained. It is clear that US reuse is more effective than in the case of CH and as expected, repeating the reuse of the dye bath always leads to different coloured samples from one batch to another until complete exhaustion of the dye bath.

Fastness properties of the US and CH dyed fabrics are shown in Table 1. The results indicate fair to good fastness properties of the dyed samples using both ultrasonic and conventional techniques.

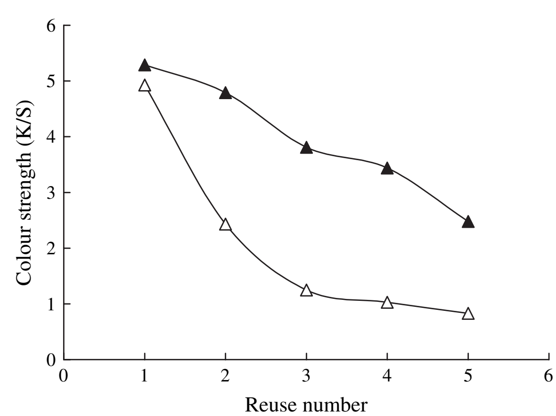

Fig. 7. Effect of reuse number on the colour strength of dyed cationised cotton fabrics. Dyeing conditions: 500 W, LR 40:1, 40 ml aqueous dye extract (8% w/v), pH 2.5, at 80 °C, 1 h. For legend see Fig. 2.

Table 1
Fastness properties of dyed cationised cotton fabrics under conventional heating and ultrasonic conditions

Dyeing methods	Wash–perspiration–rubbing[a]										
	A	C	W	A_a	C_a	W_a	A_b	C_b	W_b	R_d	R_w
CH	4	3–4	4	3–4	3–4	4	3–4	3	3	3–4	2–3
US	4	3–4	4	3–4	3–4	3	3–4	3	3–4	3–4	3

[a] A = change in colour, C = staining on cotton, W = staining on wool, R_d = dry rubbing, R_w = wet rubbing, subscript a = acidic, subscript b = alkaline.

3.3. Kinetics of dyeing

Time–dye-uptake isotherms of cationised cotton fabrics ultrasonically and conventionally dyed with lac dye are shown in Fig. 8. The figure shows that the dye-uptake values of ultrasonically dyed samples are generally better than those of the conventional heating method. Generally, the dyeing process is a solid/liquid phase process, which proceeds by the movement of the dye molecules from liquid phase to the solid surface of the fibre by virtue of their affinity, and then diffusion takes place inside the fibre. Therefore, the first process would be a fast adsorption controlled process, once the dye molecules get into the fibre, the second slow process, which is diffusion controlled, starts to take place. Accordingly, the influence of ultrasonic power on the rate of dyeing process would become clear in the diffusion process to reveal higher dye-uptake in short time for ultrasonically dyed samples in comparison with conventionally dyed ones. This enhancement effect of ultrasonic power may be due to the cavitation effect. Similar indication for the enhancement effect of ultrasonic power on the diffusion rate of wool and nylon dyeing has been recently reported [15,19].

The data in Fig. 8 can be analysed by using the derivable general form of the first order rate Eq. (3) [27,28]:

$$\frac{A_t - A_f}{A_0 - A_f} = e^{-kt} \tag{3}$$

where A_t is the absorbance at time t, A_0 is the initial absorbance, A_f is the final absorbance, t is the reaction time and k is the reaction rate. Since the absorbance of solution is directly

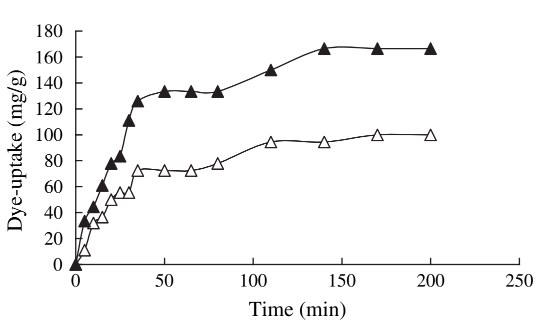

Fig. 8. Ultrasonic and conventional dyeing rates of cationised cotton fabrics. Dyeing conditions: 500 W, LR 40:1, 40 ml aqueous dye extract (8 g/l), pH 2.5, at 80 °C. For legend see Fig. 2.

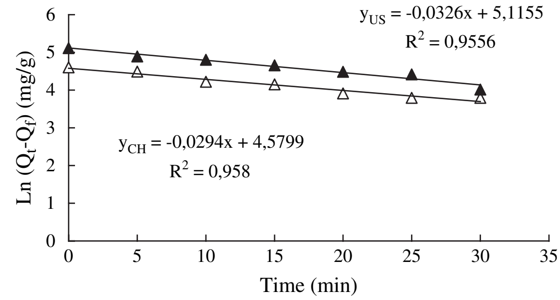

Fig. 9. Plots of $\ln|Q_t - Q_f|$ versus time of dyed cationised cotton fabrics under conventional and ultrasonic methods. For legend see Fig. 2.

related to the concentration by Lambert–Beer law, Eq. (3) can be rewritten in terms of dye-uptake to give Eq. (4):

$$\frac{Q_t - Q_f}{Q_0 - Q_f} = e^{-kt} \tag{4}$$

where Q_t is the dye-uptake at time t, Q_0 is the dye-uptake at zero time, Q_f is the final dye-uptake, t is the dyeing time and k is the dyeing rate. Taking the logarithm of Eq. (4) would lead to Eq. (5), and since Q_f is known, $Q_t - Q_f$ can be calculated as follows:

$$\ln|Q_t - Q_f| = \ln|Q_0 - Q_f| - kt \tag{5}$$

A plot of $\ln|Q_t - Q_f|$ versus time is expected to be linear with a slope of $-k$ and an intercept of $\ln|Q_0 - Q_f|$ if the reaction is first order. Fig. 9 shows the plot of $\ln|Q_t - Q_f|$ as a function of time for dyeing of cationised cotton fabrics with lac dye using both ultrasonic and conventional heating methods. As can be seen in this figure, the linear fitting of Eq. (5) holds indeed and the values of dyeing rate constants could be obtained as listed in Table 2.

The time of half dyeing $t_{1/2}$, which is the time required for the fabric to take up half of the amount of dye taken at equilibrium, is estimated either from each isotherm directly (Fig. 8) or from the following equation:

$$t_{1/2} = \ln 2/k \tag{6}$$

The values of half dyeing $t_{1/2}$ are given in Table 2. The rate constant of dyeing cationised cotton fabrics with lac dye is clearly increased with ultrasonic treatment in comparison with conventional heating. Also, the values of $t_{1/2}$ of dyeing are clearly less for those samples dyed with ultrasonic in comparison with those dyed conventionally.

Table 2
Dyeing rate constant k, efficiency of ultrasonic Δk, times of half dyeing $t_{1/2}$, standard affinity $-\Delta\mu$ and amount of final dye-uptake by cationised cotton fabrics using lac dye

$k \times 100$ (min^{-1})		Δk (%)	$-\Delta\mu$ (kJ/mol)		$t_{1/2}$ (min)		Q_f (mg/g)	
US	CH		US	CH	US	CH	US	CH
3.26	2.94	10.88	12.98	9.98	21.26	23.58	166.5	100

3.4. Standard affinity

The data for dyeing equilibrium are generally reported as the standard affinity of dyeing, $-\Delta\mu$ [29]. As mentioned above, the dyeability of cationised cotton is mainly attributed to ion–ion interactions between the negative carboxylate anions and the positive cationic amino groups present in the cationised cellulose macromolecules. This dyeing mechanism is similar to that of dyeing wool with lac dye as reported previously [15]. Therefore, the standard affinity can be calculated using Eq. (7):

$$-\Delta\mu = \mathrm{R}T\ \ln\frac{[C]_\mathrm{f}}{[C]_\mathrm{s}} \qquad (7)$$

where R is the gas constant, T is the absolute temperature (K), $[C]_\mathrm{f}$ and $[C]_\mathrm{s}$ are dye concentrations in the fibre and the dye bath, respectively. From Table 2, it can be seen that the standard affinity of cationised cotton fibre in the case of US method is higher than in the case of CH method. This is another evidence for the enhancement effect of ultrasonic power, increasing the affinity of lac dye toward cationised cotton fibres in comparison with conventional heating.

3.5. Ultrasonic efficiency

Ultrasonic efficiency $(\Delta k\%)$ in accelerating the dyeing rate was examined by introducing the following equation:

$$\Delta k\% = \frac{(k_\mathrm{US} - k_\mathrm{CH})}{k_\mathrm{CH}} \times 100 \qquad (8)$$

where k_US and k_CH are the rate constants of dyeing with ultrasonic and conventional heating, respectively. As shown in Table 2, the value of ultrasonic efficiency is positive indicating a favorable effect of ultrasonic power on the dyeing process [15,19].

4. Conclusion

Ultrasonic proved effectiveness in dye-uptake of cationised cotton fabric with lac dye, and the enhanced effect after equilibrium dyeing was about 66.5% more than the conventional heating. This technique in addition to its advantage of saving the processing time and energy offers better environmental impact as it helps to obtain higher dye-uptake and also efficient dye bath reuse.

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