



Research article

High sorption of reactive dyes onto cotton controlled by chemical potential gradient for reduction of dyeing effluents

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ABSTRACT

This research uses soybean oil/water dual-phase solvents system (SWDS) to achieve high dye fixation as well as minimal discharge of waste effluents. Reactive dyeings are one of the most serious pollution sources and few dyeing technologies developed could successfully reduce the generation of toxic substances without decreasing dyeing qualities. Through a remarkable increase in chemical potential of dyes in dyeing medium, SWDS remarkably increased the dye concentration in the internal solvent phase. As a result, % exhaustion of dye was 100%, and % fixation of dye was up to 92% in SWDS. Final discharges of dyes and salts from SWDS were decreased by 85% and 100%, respectively, compared to that from the conventional aqueous system. More than 99.5% of initially added biodegradable soybean oil could be recycled for reactive dyeing without treatments. Furthermore, SWDS could be readily applied in jet-dyeing machines on a pilot scale. Via the reuse of soybean oil, SWDS could save up to \$0.26 per kg of fabric compared to aqueous dyeings in terms of materials cost.

1. Introduction

Large quantities of wastewater containing high concentrations of refractory hydrolyzed dyes and salts are generated in conventional aqueous reactive dyeing (Li et al., 2018b). Every year, more than 400,000 tons of reactive dyes are used to dye cellulosic fibers, mainly cotton (Khatri et al., 2015). In addition to tendering problems (Mu et al., 2015, 2018b), dyeing 1 kg of cotton could generate 200 kg of wastewater containing up to 50% of initial input of dyes in the dyebath and up to 100 g/L of salts, (Ghaly et al., 2014; Rosa et al., 2015). The dyeing effluent has serious carcinogenic effects on aquatic lives and humans (Ayadi et al., 2016; Chequer et al., 2013; Lu et al., 2018) and account for one of the major pollution sources worldwide (Carmen and Daniela, 2012).

Numerous technologies have been developed to tackle the dyeing effluent. Removal of dyes from wastewater is gaining popularities recently. It is reported that ultrafiltration (Jiang et al., 2018; Zhang et al., 2014), and sorption (Gu et al., 2018; Li et al., 2018a; Mu et al., 2018a) could remove nearly 100% of dyes from textile effluents. However, the cost for the wastewater treatments is always high, accounting for half of the current cost of textile wet processing (Wang, 2006). It is reported

that due to the high pollution, 30% of global denim-dyeing chemical capacity has been shuttered (Bomgardner, 2018). Therefore, reduction in waste generation is a fundamental approach to solve the environmental problems of reactive dyeing.

Though new dyeing technologies have been developed to solve the problems of pollution, few could be industrialized to reduce or eliminate the environmental problems. Supercritical CO₂ (ScCO₂) cotton dyeing technology has challenges (Fernandez Cid et al., 2007). Cellulose with high polarity and reactive dyes does not swell and dissolve in non-polar ScCO₂, respectively, leading to little surface areas available for dye sorption, and thus light shades on cotton. The organic solvent system has been developed for reactive dyeing recently (Chen et al., 2015; Wang et al., 2014). However, the dyeing approach requires complicated recycling system, preventing the commercialization in short term. Research on reactive dyeing has been done using water/organic solvent (hexane or decamethylcyclopentasiloxane (D5)) system to reduce the hydrolysis of reactive dyes (Fu et al., 2015; Sawada et al., 2004). However, like organic solvent system, water/organic solvents have safety and environmental concerns due to low flash point (Abu-Arabi et al., 2000) and non-biodegradability (Brooke et al., 2009; Sparham et al., 2008). In summary, current novel reactive dyeing

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technologies fail to completely solve problems of conventional aqueous dyeings.

The highlights in soybean oil/water dual-phase dyeing system (SWDS) are that the chemical potential of reactive dyes, physically dispersed in soybean oil without using any dispersants, is remarkably increased in dyeing medium. Thus, 100% of dyes could migrate into water within the fabric, resulting in a dramatical increase in dye concentration in water within fabrics when the same amounts of dyes are added as conventional aqueous dyeing. As a result, dyeing fixation is remarkably increased. Because of the high chemical potential of dyes in soybean oil, no salts are needed in the SWDS. Besides, a remarkable reduction in generation of dyeing wastewater will be achieved. Because of the high flash point, low flammability (In Table S1) and good biodegradability of soybean oil (Baker and Grant, 2018), the SWDS is safe and discharge of soybean oil would not cause environmental problems. Furthermore, SWDS could be readily applied in current jet dyeing equipments. Though dyeing in full organic solvents could reduce the use of salts, the dye fixations are limited due to low equilibrium conversion ratio of dyes dyeing medium to internal solvent phase in fibers. As result, discharge could not be remarkably reduced. Continuous dyeing in thermosol range could use less water and increase dye concentration in internal phase. However, it is difficult for continuous dyeing to change colors between two dyeing cycles. Also, continuous dyeing always makes fabrics with a harsh hand due to a high degree of stretch on fabrics during the dyeing process. In addition, continuous dyeing consumes large quantities of fabrics for shade adjustment. SWDS dyeing does not have above problems.

2. Material and methods

2.1. Materials

Soybean oil is used as the external phase and purchased from by Walmart. Soybean oil is largely available and widely used in food and other industries with cheap prices. Applied in dyeing field will be a valuable addition to soybean oil industry. Other chemicals such as Na_2SO_4 , Na_2CO_3 (Analytical grade) was purchased from VWR company. Reactive Red 120 (RR 120) was kindly provided by Filo colors (Wuxi, China) and purified to remove salts.

2.2. Dyeing process

The dyeing process for SWDS is illustrated in Fig. 1. First, a swollen cotton fabric by Na_2CO_3 aqueous solution was dipped into a dye/soybean oil suspension bath containing various dye concentrations. The

swollen fabrics were got by dipping the fabrics in Na_2CO_3 aqueous solution and padding to get proper liquor pick-ups. The dye (RR120)/soybean oil suspension was achieved by simply milling dyes in soybean oil without adding any surfactants or dispersants (final particle sizes were within 10–20 μm). The dyeing began with 50 °C and vigorous agitation for 1 h to get dyes in external phase (soybean oil) completely move to internal phase (water) in the fabric. Then the bath was heated to 80 °C for 0.5 h to diffuse and fix dyes in fabric. After dyeing, the sample was undergone vacuum slot to remove oil from the fabric. The oil from the spent bath and vacuum slot would be reused for future dyeings. The fabric after vacuum slot was washed using one cycle of 4-step washing including cold wash, soaping at 95 °C, hot wash at 95 °C and cold wash. Soaping solution contained 1 g/L sodium bicarbonate and 1 g/L AATCC standard detergent. The important parameters such as alkali solution pick-up, alkali concentration, bath ratio (fabric: soybean oil), and dyeing duration were optimized through experiments according to the dyeing results. Detailed optimization is shown in supporting information (Fig. S1 to S3). For comparison, cotton fabrics were dyed in a conventional aqueous system at a fabric-to-liquor ratio of 1:20 using RR 120 with same concentrations as SWDS. For conventional aqueous reactive dyeing, concentrations of Na_2SO_4 and Na_2CO_3 were 100 g/L and 20 g/L, respectively. Visualized procedures are shown in supplementary video.

2.3. Dyeing evaluations

2.3.1. Dye fixation

RR120 was stripped from cotton fabrics using 70% sulfuric acid. The concentration of RR 120 in cotton was measured at a wavelength of 535 nm based on Beer-Lambert law using a Beckman Coulter DU 720 spectrophotometer (Beckman Coulter, United States). The calibration curve had $R^2 > 0.999$.

2.3.2. Color and colorfastness of the dyed cotton fabrics

The color depths of dyed fabrics in terms of K/S value were determined according to the Kubelka–Munk equation based on the reflectance of the dyed fiber mass measured with the iColor spectrophotometer. Colorfastness to washing, light, and rubbing were performed according to AATCC methods 61-2A, 16 option 3, and 8, respectively.

2.3.3. Levelness measurement of dyed fabric

For levelness assessment of a dyed fabric, values of L a and b were measured using an iColor spectrophotometer from at least 20 points on one fabric and largest ΔE should be less than 1.

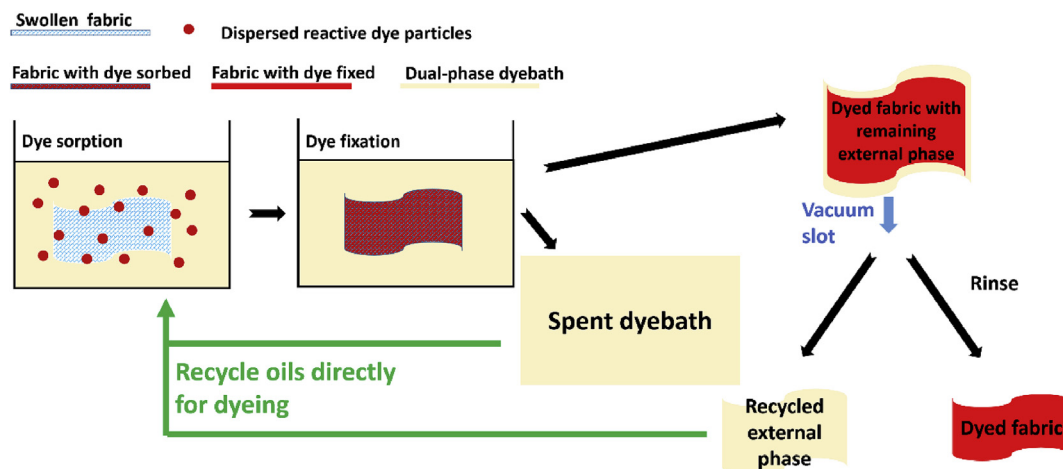


Fig. 1. Flowchart of reactive dyeing in SWDS. [color should be used]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

2.4. Oil removal efficiency from fabrics

High-speed centrifugation was conducted to evaluate the oil removal efficiency (Conditions 9800 rcf, 10 min, 25 °C). To investigate the effect of water content of fabrics on removal efficiencies of oil, water contents of cotton fabrics were controlled to 91%, 54%, and 0% (bone-dry cotton). All the fabrics were soaked in soybean oil at a fabric-to-oil weight ratio of 1:20 and sealed in canisters individually. The canisters were heated under 50 °C for 1 h and then 80 °C for 0.5 h to simulate actual dyeing condition. Subsequently, fabrics were removed from oil using vacuum and centrifuge treatments, as described before and washed using different cycles of 4-step washing, described previously, to remove oil. To determine the oil content in fabrics, oil in fabrics was extracted using acetonitrile-isopropanol. High-performance liquid chromatography (HPLC, UltiMate 3000 series, USA) equipped with a C-18 column (Acclaim 120, 120 Å, 4.6 × 250 mm, 5 µm) was used to quantify the extracted oil. The lower detection limit of HPLC was 0.007% owf of soybean oil in cotton fabric. The mobile phase is acetonitrile and isopropanol with 1 ml/min flow rate at 30 °C. The wavelength for detection is 210 nm.

2.5. Dye fixation isotherm determination in internal phase for SWDS and aqueous systems

For the fixation isotherm study, cotton fabrics were dyed with different concentrations of RR120 and a fixed liquor-to-goods ratio of 20:1 (in SWDS, liquor mentioned was soybean oil and internal phase pick up was 100%). Dyeing was performed at 50 °C for 1 h followed by heating at 80 °C for 3 h to ensure the fixation reached equilibrium. The data were evaluated for compliance with Langmuir and Freundlich isotherm models. In SWDS, since 100% dyes migrated into internal phase, the dye concentration at equilibrium in internal phase $[D]_s$ was calculated based on dye concentration on fabric $[D]_f$, initial dye input and pick up ratio of the internal phase in fabric. In aqueous dyeing system, the dye concentration at equilibrium in internal phase $[D]_s$ was obtained as below. After dyeing, the fabric was dipped out immediately and padded to have 100% liquor ratio. Then certain amounts of water were added to the fabric and the mixture was centrifuged at 8000 rpm for 20 min before the absorbance of the obtained dye solution was measured. The dye concentration in internal phase $[D]_s$ was obtained based on such absorbance results.

2.6. Dye fixation kinetics for SWDS and aqueous systems

The fixation kinetics of RR120 on cotton fabrics for SWDS and aqueous dyeing systems were compared. After dyeing at 50 °C for 1 h, the fixation of RR120 onto cotton was performed at 70–90 °C with a fabric to bath ratio of 1:20 for 5–120 min. The dye concentration on fabric $[D]_f$ at time t was obtained by color stripping, which was shown previously. The pseudo-first-order model and pseudo-second-order model were used to illustrate the fixation kinetics.

2.7. Determination of chemical structures of soybean oil after dyeing cycles

Nuclear magnetic resonance studies were conducted to study the structural changes of oil during dyeings. Before the analysis, soybean oil was acidified using HCl to convert fatty acid sodium to fatty acid in oil phase and centrifuged to remove water content. For the NMR analysis, samples were dissolved in deuterated DMSO (1 wt %) and scanned on an Avance 600 MHz Digital NMR spectrometer (Bruker Co. Ltd. Switzerland). A basic proton pulse sequence (zg30) was used with a relaxation delay of 1 s and acquisition time of 3 s and operated at 400 MHz. Spectra were phase corrected interactively using TOPSPIN. Baseline correction was carried out manually using the appropriate factors.

2.8. Removal of fatty acids from soybean oil

Used soybean oil was washed using an aqueous NaOH solution to remove the acid. After washing, the oil was recollected by centrifuge.

2.9. Degradation of dyeing effluent

To determine the biodegradation of the dyeing effluents from SWDS and aqueous dyeing systems, wastewater sludge from Lincoln Wastewater System, Nebraska, US, was used. The concentration of effluent in wastewater sludge was 300 mg/L. COD was measured according to U.S. Environmental Protection Agency method 8000 using digital reactor block DRB 200 (HACH, DE). Five-day biochemical oxygen demand (BOD₅) was determined according to American Public Health Association guidelines in the standard methods for the examination of wastewater using optical dissolved oxygen meter HQ440d (HACH, DE).

2.10. Jet-dyeing using SWDS on a pilot scale

1 kg cotton fabric with a width of 0.35 m and length of 25 m were dyed in a jet-dyeing machine (ALLFIT-5, China). The dyeing procedures were based on those developed on lab-scale.

3. Results and discussion

3.1. The remarkable increase in dye concentration in internal phase

Fig. 2 shows the dyes in external phase for SWDS and aqueous systems. In SWDS system, 100% of dyes could move into internal phase from soybean oil, the external phase. However, there are still large quantities of dyes in external solution after dyeing for the aqueous system. This is because that dye has notably high chemical potential in external phase due to insolubility of dyes in the external phase. As a result, the difference in chemical potential of dyes between external and internal phases is very large. Therefore, all dyes in external phase could move into internal phase. In contrast to SWDS system, dyes have very high solubilities in water in the aqueous system, resulting in low chemical potential of dyes in an external solvent, so is the difference in chemical potential of dyes between external and internal solvents. To increase the proportion of dyes in an internal solvent, a large quantity of salts are added into dyeing medium for aqueous dyeing system. Even though, the chemical potential of dyes in external phase for aqueous dyeing system is still lower than that for SWDS system. Concentration of dyes in external solvent in the presence of salts is still high for aqueous dyeing system.

Aqueous system: 20 g/L Na₂CO₃ and 20 g/L Na₂SO₄ added to water.

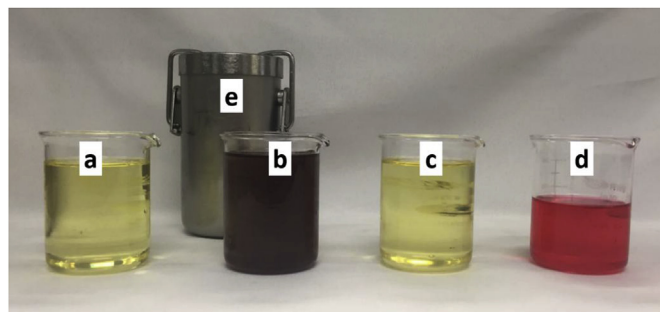


Fig. 2. a) External phase (soybean oil) before dyeing; b) Dyebath of soybean oil containing 3% (owf) of RR 120; c) Spent dyebath of the soybean oil/water system using 3% (owf) of RR 120; d) Spent dyebath of conventional aqueous system using 3% (owf) of RR 120; e) A canister used for both dyeing systems. [color should be used]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1

Comparison of dye concentration in internal phase between aqueous and SWDS systems.

Initial dye concentration (% owf)	Equilibrium concentration in internal phase (g/L)	
	Aqueous dyeing system	SWDS system
1	0.45	0.54
3	1.24	1.75
9	11.05	28.45
15	16.24	64.50

SWDS system: 40 g/L Na_2CO_3 in internal phase. Dyeing procedures for both dyeing systems: 50 °C for 1 h and 80 °C for 0.5 h. Dyeing procedures for both dyeing systems: 50 °C for 1 h and 80 °C for 0.5 h

Table 1 compares concentrations of dyes in internal phase for aqueous dyeing and SWDS systems. The results demonstrate higher dye concentration in internal phase for SWDS than that for the aqueous system when same amounts of dyes are added. This is because that not all dyes could move into internal phase due to strong repulsion between dyes in water and cotton fabrics. In SWDS system, all dyes had to stay in internal phase because of little solubilities of dyes in the external phase. As a result, dye concentration in internal phase for SWDS system notably increased. Both Fig. 2 and Table 1 prove that remarkably high concentration of dye in internal phase was achieved for SWDS system. Higher concentration of dyes in internal phase could help more dyes fixed onto fabrics.

3.2. Same dye sorption behaviors in internal phase for SWDS and aqueous systems

Fig. 3a compares the dye fixation on fabric between SWDS and aqueous systems. The two dyeing systems were Langmuir sorption. There is no significant difference in fixation behaviors in internal solvent phase between SWDS and aqueous dyeing systems (Table S2). The affinity between reactive dyes and fabrics was 2.8 kcal/mol for aqueous dyeing and SWDS systems. Based on the fixation isotherms, subtle differences in internal solvent phase led to large disparity of dye fixations on fabrics when an equilibrium concentration of dyes in internal phase was less than 7 g/L. For instance, increase in equilibrium concentration of dyes in internal phase from 1.2 to 1.7 g/L resulted in a gain of dye fixation from 18 to 27 mg/L.

Based on results of Table 1, dye concentration in internal phase for SWDS is higher than that for the aqueous system at the same initial dye concentrations. Therefore, SWDS system could achieve higher sorption and fixation amounts of dyes onto fabrics than the aqueous system. As shown in Fig. 3b, SWDS system needs much less dye input than aqueous dyeing system to get same fixation amount of dyes on fabrics. For

Table 2

Half fixation time ($t_{1/2}$), fixation rate constants (k) and equilibrium sorption ($[D]_f$) at 70, 80 and 90 °C based on the pseudo-second-order kinetic for aqueous and SWDS systems (3% owf RR 120).

Dyeing System	T (°C)	$t_{1/2}$ (min)	k ($\text{min}^*\text{g}/\text{mg}$)	R^2	Equilibrium sorption $[D]_f$ (mg/g)
Aqueous dyeing	70	19.7	0.002	0.9910	18.4
	80	6.7	0.007	0.9918	19.4
	90	3.3	0.015	0.9981	21.2
SWDS	70	35.3	0.001	0.9921	24.1
	80	9.9	0.005	0.9932	27.4
	90	4.1	0.012	0.9965	27.3

example, based on isotherms and calculation, to get approximate 20 mg/g RR 120 on fabrics, the concentration of RR 120 in SWDS system was around 3% owf while the concentration of RR 120 in the aqueous system was around 5%. To get saturated dye sorption, the concentration of RR 120 in SWDS system was around 13% owf while the dye concentration in the aqueous system was around 20%. Overall, to get the same depth of shade on cotton fabric, SWDS system need 35–40% less amount of dyes. Fig. 3c summarizes the similarities and differences between SWDS and aqueous dyeing systems. SWDS could remarkably increase the chemical potential of dyes in external phase, resulting in migration of 100% dyes into internal phase. There is no significant difference in the process which dyes move from internal phase to fabrics between these two systems. Such difference and similarities make SWDS system not only take the advantages of, but also avoid the problems of aqueous dyeing system.

3.3. Formation of dye aggregates in internal phase for SWDS at low temperatures

Table 2 studies the fixation kinetics for the two dyeing systems and demonstrates that pseudo-second-order kinetic could better describe the fixation for these two dyeing systems. As the temperature rose, fixation rate increased and $t_{1/2}$ decreased. The difference in fixation rates between SWDS and aqueous systems became smaller as the increase in dyeing temperatures. The reason is that dye powders, insoluble in soybean oil, would migrate into internal phase within fabrics, resulting in a dramatic increase in dye concentration in the internal phase. As a result, a large number of dye aggregates were formed in the internal phase. Due to the large size of aggregates, the diffusion rate of these aggregates from surface to interior of fabrics was slower than that of dyes in single molecular form (Mu et al., 2017). Even though these aggregates entered into the interior of fabrics, these aggregates could not react with cellulose in time because large amounts of reactive groups in aggregates exposed insufficiently. Therefore, the fixation rate

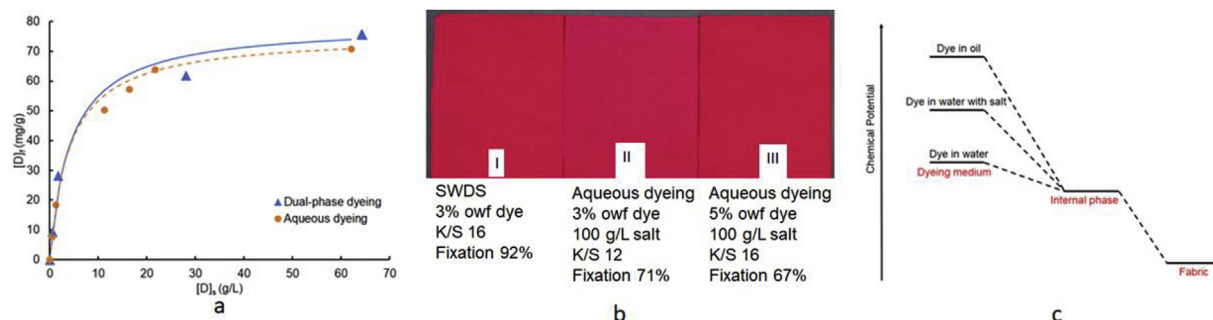


Fig. 3. a) Fixation isotherm of RR 120 onto cotton fabrics in internal phases for SWDS and aqueous dyeing systems. Solid and dash lines are the Langmuir regression fit for SWDS ($R^2 = 0.9944$) and aqueous dyeing ($R^2 = 0.9934$), respectively. Aqueous system: 20 g/L Na_2CO_3 and 20 g/L Na_2SO_4 added to water. SWDS system: 40 g/L Na_2CO_3 added to internal phase. b) Dye fixation between SWDS and aqueous dyeing systems. Aqueous system: 20 g/L Na_2CO_3 . SWDS system: 40 g/L Na_2CO_3 in the internal phase. Dyeing procedures for both dyeing systems: 50 °C for 1 h and 80 °C for 0.5 h c) Principle of SWDS system. [color should be used]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 3

Comparison of colorfastness between cotton fabrics dyed in SWDS and aqueous dyeing systems.

Dyeing system	Dye used	Colorfastness to laundering	Colorfastness to light	Colorfastness to crocking	
				Dry	Wet
Aqueous dyeing	RR 120	4–5	L5	5	3.5
SWDS		4–5	L5	5	3.5

Note: K/S values from two solvent systems for each dye was 16.

for SWDS system was lower than that for the aqueous system. However, increase in temperature, e.g. from 70 to 90 °C, would increase the solubility of dyes in the internal phase. Therefore, the difference in values of fixation rates between SWDS and aqueous systems decreased. Since the internal concentration of dyes for SWDS system was higher, larger equilibrium dye fixation amounts were obtained, as shown in the third column of Table 2. This is consistent with previous results. Aggregates in internal phase within fabric would have side effects on levelness of dyed fabrics. However, such effect would be eliminated by increasing the dyeing temperature. Finally, same levelness as aqueous system for SWDS system could be achieved, as shown in Table S3.

3.4. Same colorfastness as those from aqueous dyeing

Table 3 shows that, with the same K/S value, cotton fabrics dyed in SWDS had colorfastness to laundering, dry/wet crocking and light as good as those dyed in a conventional aqueous system. These results demonstrate that colorfastness from SWDS system meets the actual use requirements.

3.5. High oil removal efficiency

Fig. 4a shows that higher initial water content (WC) could facilitate removal of soybean oil from dyed fabrics via centrifuge. As shown in Fig. 4a, after treatment of centrifugation, oil on the cotton fabric with higher initial WC was more easily to be removed. For example, oil contents of both fabrics with WC of 91% and 54% were reduced to less than 5% owf, while that of fabrics with WC 0% were only reduced to 20% owf after centrifuge. Soybean oil could be easily removed from wet dyed cotton fabrics, as it could only loosely attach to wet cotton fibers due to its low polarity and high surface tension (32 mN/m) (Esteban

et al., 2012). The cellulose molecules in wet fibers could combine tightly with polar water molecules via forming hydrogen bonds, and thus are not available to form hydrogen bonds, van der Waals interaction or any other strong bonds with oil molecules. In Fig. 4b, for cotton fabrics with initial WCs of 91%, one cycle of 4-step washing was sufficient to completely remove soybean oil even after oil removal treatment with least efficiency.

3.6. Recyclable dyeings

Fig. 5a shows the depth of shade (K/S) on fabrics in hot dyeing after each dyeing cycle using the same external phase, the soybean oil. Results demonstrate that dyeing medium in SWDS system had good recyclability. After 5th cycle of dyeing, the K/S value decreased slightly but significantly. This is because that saponification of soybean oil at the oil/water interface consumed the alkali in the internal phase. As a result, there was no enough alkalinity to fix all dyes onto fabrics. ¹H NMR results in Fig. 5b demonstrate the formation of fatty acids (11–12 ppm) after 5 cycles of dyeings. Besides that, structures of soybean oil did not show any other significant structural changes during the dyeing cycles. 2.50 and 3.33 ppm in the spectrum refer to DMSO and trace water in oil. Fig. 5a also shows the depth of shade on fabric could be increased via the decrease in fatty acids in soybean oil. After 5th cycle of dyeing, the soybean oil was treated to remove the fatty acids inside before 6th cycle of dyeing. The K/S after 6th cycle dyeing had no significant difference from that after 1st cycle of dyeing. In dual-phase dyeing system, soybean oil, accounting more than 90 wt% of dyeing materials, could be reused for future dyeings. Furthermore, some products generated during the dyeing via saponification of soybean oil could be applied in other fields. For example, sodium fatty acid and glycerol from saponification could be separated and used in other fields such as cosmetics and pharmaceutical industry. Also, glycerol and fatty acids could be as surfactants for dispersion of dyes in soybean oil. As a result, dyeing levelness could be further improved.

3.7. Good biodegradability

Fig. 6 compares the biodegradability of dyeing medium between SWDS and aqueous dyeing systems and demonstrates dyeing effluent from SWDS system had very good biodegradability. As shown in Fig. 5a, at 0 days, samples from SWDS had higher COD than those from aqueous dyeing systems. After 3 days, COD of dyeing effluents from SWDS system decreased to allowable concentration. Besides, the values

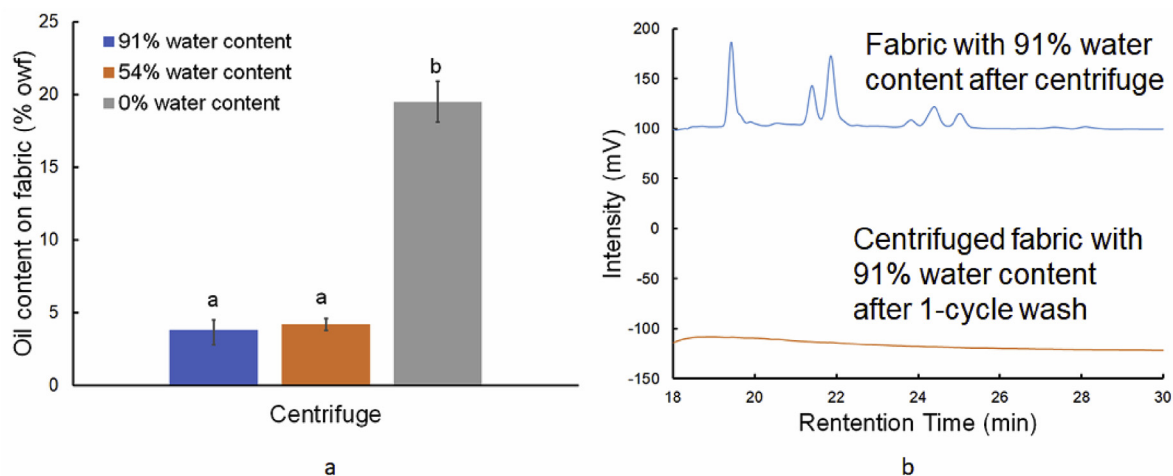


Fig. 4. a) Centrifuge treatments on oil removal efficiencies from cotton fabrics with different initial water contents. b) HPLC analysis on oil residuals on vacuumed fabric with 83% water content before and after one-cycle washing. [color should be used]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

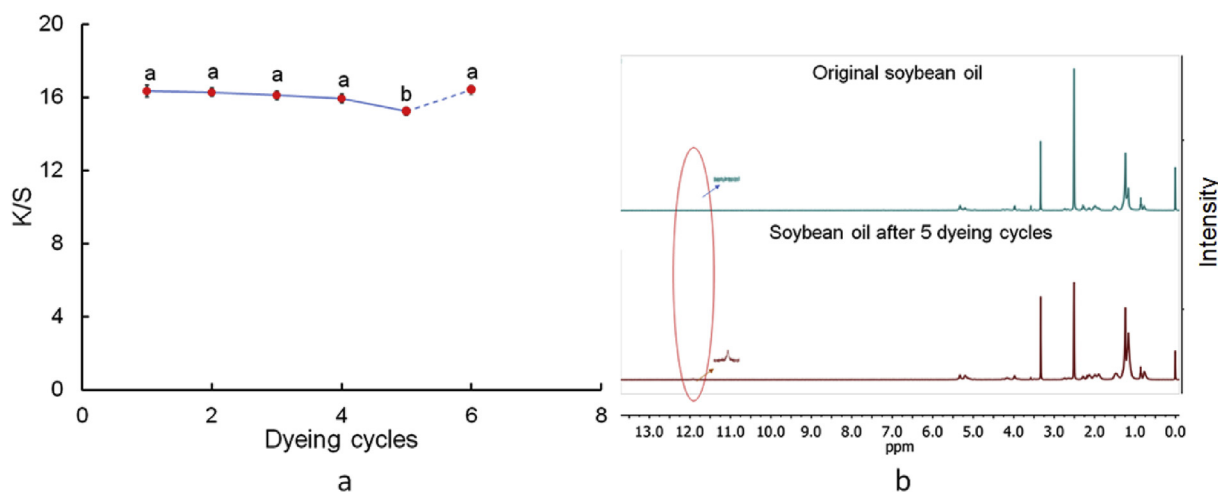


Fig. 5. a) K/S results after each dyeing cycle (cycle 1–5) using the same external dyeing medium and using dyeing medium with fatty acid removed (cycle 6). b) ¹H NMR analysis of soybean oil after 5 dyeing cycles. Each dyeing cycle: 50 °C for 1 h and then 80 °C for 0.5 h (using 3% owf RR120). [color should be used]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

continued to decrease to 70 mg/L under continuous sludge treatment. Nevertheless, COD of dyeing effluents from aqueous system did not change significantly even after 20 days of treatment. These results demonstrate good biodegradability of dyeing medium from SWDS system. Good biodegradability of dyeing effluent from SWDS system is due to high value of BOD₅ of soybean oil, as shown in Fig. 6b. In SWDS system, dye uptake was up to 100%, which means that dyeing medium only contained soybean oil, fatty acid salts and glycerol from saponification. All these compounds are well biodegradable. The BOD₅ value of dyeing effluent after 5 cycles of dyeing for SWDS system was up to 150 mg/L whereas the BOD₅ value of dyeing effluent for the aqueous system was as low as 9 mg/L. After 5 days of treatment, BOD₅ value for SWDS system decreased dramatically, further demonstrating good biodegradability of dyeing medium. Furthermore, the value of BOD₅/COD (0.33) also shows the dyeing effluent from SWDS system would not cause environmental problems. In SWDS system, soybean oil, as a new dyeing medium, is used in the dyeings. Compared to materials such as salts, in conventional dyeings, soybean oil is readily biodegradable. Discharge of soybean oil into environment will not cause concerns. On the contrary, salts, used in traditional dyeings, are toxic to aquatic life and impacts vegetation and wildlife. There is no natural process by which inorganic salts are broken down, metabolized, taken up, or removed from the environment. Use of soybean oil could have dyeing occur without using of salts. Furthermore, SWDS dyeing also allows for using a small water-to-fabric ratio and thus greatly reduces the use of

dyes and alkalis. Besides, soybean oil does not react with reactive dyes, indirectly leading to high dye fixations when dyes enter into internal phase. Nevertheless, a portion of dyes would be hydrolyzed in aqueous dyeing system, resulting in low dye fixation on some extent.

3.8. Pilot-scale jet dyeing using the SWDS system

Jet dyeing on pilot scale was also developed. After the dyeing, the K/S of dyed fabric was 16 and ΔE was 0.15 ± 0.1 . The dyeing quality had no significant difference from that from lab-scale dyeing. Detailed characterizations on dyed fabrics are shown in Table S4. These results validate the potential of industrialization using SWDS system. Table 4 summarizes the results from recent dyeing technologies. From the table, it is obvious to see SWDS system developed in this paper has high dye fixation and low discharge. Furthermore, the effluent of discharges is biodegradable. SWDS system has considerable advantages over dyeing methods listed in the table.

3.9. Economic advantages

The SWDS system needs less dye, no salt and very limited amounts of alkali to obtain the same dyeing quality as the aqueous system. In addition, more than 99% of oil could be reused for subsequent dyeing. Thus, the materials consumption and cost for the dyeing system is low. Besides, soybean oil has high production, is less widely used and has

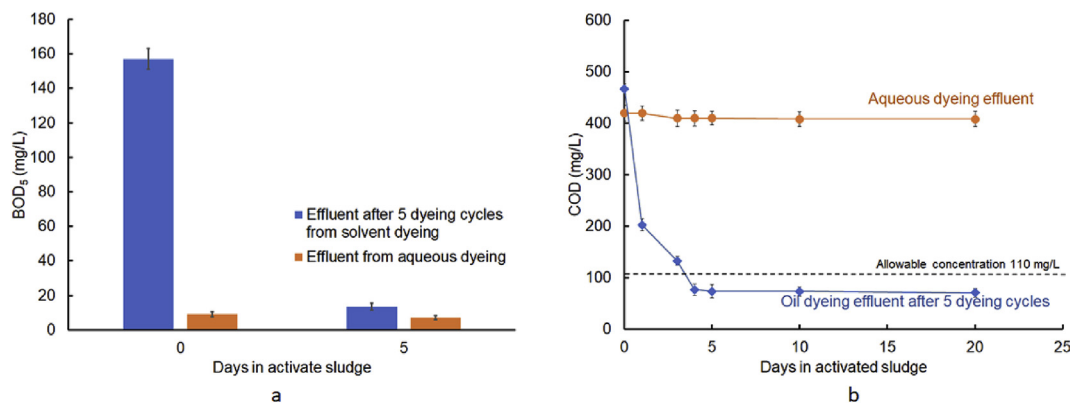


Fig. 6. Changes in a) the chemical oxygen demand (COD) and b) five-day biochemical oxygen demand (BOD₅) of dyeing medium from SWDS and aqueous dyeing systems in activated sludge. (dye: RR 120, concentration: 3% owf). [color could not be used]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 4
Comparison between reported reactive dyeing methods and this work.

Dyeing systems ^a	Dyeing results	Biodegradability/Safety	Reference
Super critical CO ₂	Fixation: 2–60% with co-solvents such as DMSO	Co-solvents always not biodegradable Need specific equipment enduring high pressure	Fernandez Cid et al. (2007)
Non-nucleophilic organic solvents	Fixation less than 70% using DMSO, DMAc etc.	Non-biodegradable Low flash point, unsafe	Chen et al. (2015)
Reversed micellar system	Fixation less than 60%	Use of non-biodegradable organic solvents and surfactants Low flash point of solvents, unsafe	Sawada and Ueda (2003)
D5 solvents with water	Fixation 90+ %	Use of non-biodegradable solvent and surfactants Low flash point, unsafe	Deng et al. (2015)
Our work	Fixation up to 93%	Dyeing medium is totally biodegradable High flash point, safe to use	–

price lower than other edible plant oils, such as soybean oil, canola oil, peanut oil, etc. Therefore, it is feasible for the US industry to use soybean oil for trial. Calculation of cost saving on materials based on current research is listed in Table S5. For example, using soybean oil to dye 1 kg of cotton into K/S of 16 (about 20 mg/g dye on fabric) with RR 120, the material cost of the oil system equals to or is lower than that of the conventional aqueous system if oil is reused. The more cycles of reuse, the less cost of dyeing. If the soybean oil is reused for 12 times, the materials cost in each of the dyeing is roughly the same as that in the aqueous system. If oil is reused for 20 cycles of dyeing, the oil dyeing system is \$0.14 cheaper than the conventional aqueous system in materials cost. If oil is reused for 50 times, the oil system could save up to \$ 0.26. Furthermore, the cost of oil could also be saved, as the collected used oil could still be sold to biodiesel industry as feedstock. Treatment of dyeing wastewater accounts for half of the current cost of textile wet processing. This cost will continue to increase as the regulations become increasingly strict. Since effluent from solvent dyeing system is biodegradable, the cost of waste treatment is substantially lower than the conventional aqueous system and other untraditional systems such as all-organic solvent system. The specific heat capacity value of soybean oil is 0.45–0.67 cal/g/°C (Clark et al., 1946), substantially lower than that of water (1 cal/g/°C). This means heating the dyeing medium to the same temperature, solvent dyeing system could save 33–55% energy. There is no need to build new dyeing equipment except a vacuum slot, which is widely used in textile wet processing mills, especially in front of many of the tenter frames. The vacuum slot is for the removal of residue soybean oil from fabrics after dyeing. The facility cost of solvent dyeing is much lower than that of current unconventional dyeing technologies.

4. Conclusion

Via remarkably increasing the chemical potential of reactive dyes in soybean oil, dye fixation in SWDS increased by up to 30% compared to aqueous dyeing system without using any salts. In addition, use of dyes and alkalis could also be remarkably reduced. Soybean oil, the external phase is safe, recyclable and biodegradable. Furthermore, successful application of SWDS in jet-dyeing machines on a pilot scale demonstrates high potential for industrialization of the dyeing technology. Besides, the materials and energy costs of SWDS are lower than those of aqueous dyeings.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2019.03.062>.

Declarations of interest

None.

References

- Abu-Arabi, M., Allawzi, M., Al-Zoubi, H., Tamimi, A., 2000. Extraction of jojoba oil by pressing and leaching. *Chem. Eng. J.* 76, 61–65.
- Ayadi, I., Souissi, Y., Jlassi, I., Peixoto, F., Mnif, W., 2016. Chemical synonyms, molecular structure and toxicological risk assessment of synthetic textile dyes: a critical review. *J. Develop. Drugs* 5, 2.
- Baker, B.P., Grant, J.A., 2018. Cottonseed Oil Profile.
- Bongardner, M.M., 2018. These new textile dyeing methods could make fashion more sustainable, c&en.
- Brooke, D., Crookes, M., Gray, D., Robertson, S., 2009. Environmental Risk Assessment Report: Decamethylcyclotrisiloxane. Environment Agency of England and Wales, Bristol, UK.
- Carmen, Z., Daniela, S., 2012. Textile Organic Dyes—Characteristics, Polluting Effects and Separation/elimination Procedures from Industrial Effluents—A Critical Overview, Organic Pollutants Ten Years after the Stockholm Convention—Environmental and Analytical Update. InTech.
- Chen, L., Wang, B., Chen, J., Ruan, X., Yang, Y., 2015. Comprehensive study on cellulose swelling for completely recyclable nonaqueous reactive dyeing. *Ind. Eng. Chem. Res.* 54, 2439–2446.
- Chequer, F.M.D., de Oliveira, G.A.R., Ferraz, E.R.A., Cardoso, J.C., Zanoni, M.V.B., de Oliveira, D.P., 2013. Textile Dyes: Dyeing Process and Environmental Impact, Eco-Friendly Textile Dyeing and Finishing. InTech.
- Clark, P.E., Waldeland, C., Cross, R.P., 1946. Specific heats of vegetable oils from 0 to 280 C. *Ind. Eng. Chem.* 38, 350–353.
- Deng, Y., Zhang, Y., Qiu, X., 2015. Non-aqueous Solvent Textile Dyeing Method with Reactive Dye in High Fixation Ratio. Guangdong Esquel Textiles Co., Ltd., Peop. Rep. China, pp. 9pp.
- Esteban, B., Riba, J.-R., Baquero, G., Puig, R., Rius, A., 2012. Characterization of the surface tension of vegetable oils to be used as fuel in diesel engines. *Fuel* 102, 231–238.
- Fernandez Cid, M., Gerstner, K., Van Spronsen, J., Van der Kraan, M., Veugelaers, W., Woerlee, G., Witkamp, G., 2007. Novel process to enhance the dyeability of cotton in supercritical carbon dioxide. *Textil. Res. J.* 77, 38–46.
- Fu, C., Wang, J., Shao, J., Pu, D., Chen, J., Liu, J., 2015. A non-aqueous dyeing process of reactive dye on cotton. *J. Text. Inst.* 106, 152–161.
- Ghaly, A., Ananthashankar, R., Alhattab, M., Ramakrishnan, V., 2014. Production, characterization and treatment of textile effluents: a critical review. *J. Chem. Eng. Process Technol.* 5, 1–19.
- Gu, P., Zhang, S., Li, X., Wang, X., Wen, T., Jehan, R., Alsaedi, A., Hayat, T., Wang, X., 2018. Recent advances in layered double hydroxide-based nanomaterials for the removal of radionuclides from aqueous solution. *Environ. Pollut.* 240, 493–505.
- Jiang, M., Ye, K., Deng, J., Lin, J., Ye, W., Zhao, S., Van der Bruggen, B., 2018. Conventional ultrafiltration as effective strategy for dye/salt fractionation in textile

- wastewater treatment. *Environ. Sci. Technol.* 52 (18), 10698–10708.
- Khatri, A., Peerzada, M.H., Mohsin, M., White, M., 2015. A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution. *J. Clean. Prod.* 87, 50–57.
- Li, J., Wang, X., Zhao, G., Chen, C., Chai, Z., Alsaedi, A., Hayat, T., Wang, X., 2018a. Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions. *Chem. Soc. Rev.* 47, 2322–2356.
- Li, Y., Shen, J., Lu, L., Luo, Y., Wang, L., Shen, M., 2018b. Water environmental stress, rebound effect, and economic growth of China's textile industry. *PeerJ* 6, e5112.
- Lu, L., Zhan, T., Ma, M., Xu, C., Wang, J., Zhang, C., Liu, W., Zhuang, S., 2018. Thyroid Disruption by Bisphenol S Analogues Via Thyroid Hormone Receptor β : In Vitro, In Vivo and Molecular Dynamics Simulation Study. *Environmental Science & Technology*.
- Mu, B., Li, W., Xu, H., Xu, L., Yang, Y., 2018a. Freeze-extrusion for controllable assembly of 3-dimensional ultra-fine and amorphous fibrous matrices: potential applications in sorption. *J. Mater. Chem.* 6 (22), 10320–10330.
- Mu, B., Xu, H., Li, W., Yang, Y., 2018b. Fast Hydrolysis of Cellulose Catalyzed by its Substituents for Potential Biomass Conversion. *Bioresource Technology*.
- Mu, B., Xu, H., Yang, Y., 2015. Accelerated hydrolysis of substituted cellulose for potential biofuel production: kinetic study and modeling. *Bioresour. Technol.* 196, 332–338.
- Mu, B., Xu, H., Yang, Y., 2017. Improved mechanism of polyester dyeing with disperse dyes in finite dye bath. *Color. Technol.* 133, 415–422.
- Rosa, J.M., Fileti, A.M., Tambourgi, E.B., Santana, J.C., 2015. Dyeing of cotton with reactive dyestuffs: the continuous reuse of textile wastewater effluent treated by Ultraviolet/Hydrogen peroxide homogeneous photocatalysis. *J. Clean. Prod.* 90, 60–65.
- Sawada, K., Ueda, M., 2003. Dyeing of protein fiber in a reverse micellar system. *Dyes Pigments* 58, 99–103.
- Sawada, K., Ueda, M., Kajiura, K., 2004. Simultaneous dyeing and enzyme processing of fabrics in a non-ionic surfactant reverse micellar system. *Dyes Pigments* 63, 251–258.
- Sparham, C., Van Egmond, R., O'Connor, S., Hastie, C., Whelan, M., Kanda, R., Franklin, O., 2008. Determination of decamethylcyclopentasiloxane in river water and final effluent by headspace gas chromatography/mass spectrometry. *J. Chromatogr. A* 1212, 124–129.
- Wang, B., Ruan, X., Chen, L., Chen, J., Yang, Y., 2014. Heterogeneous chemical modification of cotton cellulose with vinyl sulfone dyes in non-nucleophilic organic solvents. *Ind. Eng. Chem. Res.* 53, 15802–15810.
- Wang, Y., 2006. *Recycling in Textiles*. Woodhead publishing.
- Zhang, W., Xu, Y., Yu, Z., Lu, S., Wang, X., 2014. Separation of acetic acid/water mixtures by pervaporation with composite membranes of sodium alginate active layer and microporous polypropylene substrate. *J. Membr. Sci.* 451, 135–147.