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ORIGINAL RESEARCH

Solvent-assisted salt-free reactive dyeing of cotton fabric

Aravin Prince Periyasamy · Shubhajit Dutta · Ali R. Tehrani-Bagha

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Abstract The objective of this study was to establish a solvent-assisted salt-free dyeing method for cotton fabric utilizing commercially available reactive dyes. In this study, the feasibility of substituting water as the dyeing medium with environmentally friendly solvents, specifically ethanol (EtOH), isopropyl alcohol (IPA), and propanol (PrOH), was investigated. Eight commercial reactive dyes, each possessing distinct chemical structures, were examined with various dyeing characteristics including exhaustion, fixation, and fastness properties, in the presence of various alcohols. However, solvent-assisted dyeing exhibited comparable or enhanced color strength (K/S) values, exhaustion, and fixation rates compared to conventional aqueous dyeing. For instance, the RR35 dye demonstrated a substantial increase in K/S values with PrOH, EtOH, and IPA, ranging from 115 to 369% improvement. The substitution of alcohol for water did not affect the wash, rub, and light-color fastness properties, as these properties remained consistently excellent. Solvent-assisted salt-free dyeing of cotton fabrics offers a promising solution to address the environmental impacts of traditional water-based dyeing methods by eliminating the requirement for water and salt. Overall, this study presents a solvent-assisted salt-free dyeing technique and contributes to the field by offering detailed insights into its mechanisms and performance. Our research has the potential to reduce water consumption, eliminate salt usage, and mitigate environmental pollution.

Keywords Cellulose coloration · Solvent-assisted dyeing · Salt-free · Reactive dyes · Alcohols · Color strength

Introduction

Cellulose, the most abundant polymer found on our planet, provides the development of textiles composed of cellulosic fibers that exhibit a diverse range of desirable characteristics, including but not limited to softness, hydrophilicity, breathability, and biodegradability. Cellulosic materials are frequently dyed using direct, vat, sulfur, and reactive dyes. Among these options, reactive dyes are the most prevalent due to their exceptional color intensity and superior resistance to fading when exposed to moisture (Kumar et al. 2021). The exceptional wash-fastness

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A. P. Periyasamy · S. Dutta · A. R. Tehrani-Bagha (✉)
Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Espoo 02150, Finland
e-mail: ali.tehrani@aalto.fi

A. P. Periyasamy
Biomaterial processing and products, VTT Technical Research Centre of Finland Ltd, Tietotie 4E, Espoo 02150, Finland

characteristics exhibited by reactive dyes when applied to cellulose textiles can be ascribed to the creation of covalent bonds with the hydroxy groups present in cellulosic fibers, particularly in alkaline environments.

Traditional dyeing processes rely heavily on large amounts of water (10 to 15 times the weight of the textile) and salt (Chattopadhyay 2011; Khatri et al. 2015), variable fixation rates of reactive dyes ranging from 50 to 90% resulting in substantial environmental pollution and resource depletion (Lewis 2014). Consequently, this situation presents notable ecological challenges, and encompassed in this context pertain to the depletion of water resources, the pollution caused by salt and alkali, the adverse impacts of unbound dye on aquatic ecosystems, and the complexities associated with the treatment of saline and alkaline wastewater (Periyasamy et al. 2011; Arivithamani and Giri Dev 2018). In order to tackle these concerns, it is necessary to develop more environmentally friendly dyeing techniques that aim to minimize water consumption, decrease reliance on salt and alkali, and enhance dye fixation rates. The hydrolysis of reactive dyes in aqueous solutions, especially when alkaline salts are present, is a significant contributing factor to the low fixation rate (Lewis 2014; Chen et al. 2015b). To tackle this matter, a viable strategy involves replacing the aqueous dye medium with an environmentally friendly solvent. The utilization of such an alternative solvent presents a feasible approach to mitigate the hydrolysis rate of dyes and augment the rate of dye fixation on cellulose substrates (Lewis 2014).

Reactive dyes refer to a class of anionic dyes that possess water solubility and exhibit varying degrees of affinity towards cellulose fibers. This affinity is influenced by the slightly negative surface charge of the cellulose fibers, which results in electrostatic repulsions. In the dyeing process, it is common practice to employ sodium sulfate (Na_2SO_4) or sodium chloride (NaCl) at significantly elevated concentrations, typically ranging from 10 to 100 g/L. The primary purpose of this practice is to counterbalance the surface charge of cellulose and thereby augment the adsorption of reactive dyes onto cellulose fibers (Lewis 2014). The adsorbed salt anions are replaced by large anionic dye molecules during the dyeing process. Thus, a large amount of salt remains in the dye bath after the process which increases the salinity and alkalinity of the wastewater. The remaining reactive dye molecules in the wastewater are difficult to remove because they are persistent organic species resistant to mild oxidation/reduction and biodegradation. Unfixed or hydrolyzed reactive dyes are adsorbed on cellulose and held by weak intermolecular forces including hydrogen bonds and Van der Waals forces; thus, they are desorbed to the solution during the first washing cycle (Amin and Blackburn 2015). The remaining reactive dyes in the dyeing wastewater are persistent colored organic compounds that increase the color, biological oxygen demand (BOD), chemical oxygen demand (COD), and dissolve solids (Moyo et al. 2022).

To minimize the environmental impact of cellulose dyeing with reactive dyes, several strategies can be employed. Firstly, the amount of water utilized in the process can be reduced through the implementation of techniques such as cold pad batch or pad steam. Secondly, the chemical structures of the dyes themselves can be modified to improve their adsorption and fixation rates on cellulose fibers (Hauser and Tabba 2001; Hashem et al. 2003; Fu et al. 2016). Thirdly, the hydroxy groups of cellulose can be chemically activated or grafted through methods such as plasma treatment or gamma treatment (Gulzar et al. 2015). Additionally, the use of an alternative green solvent as a dyeing medium may reduce dye hydrolysis and improve the overall rate of dye fixation (Capello et al. 2007; Alder et al. 2016; Xia et al. 2018).

The solvent-assisted salt-free reactive dyeing approach, also known as a closed-loop system, offers the advantage of recovering and reusing the solvent continuously throughout the dyeing process (Mu and Yang 2022). This closed-loop system eliminates the need for water, a significant breakthrough in the industry. Moreover, it substantially reduces salt consumption, which not only benefits the environment but also alleviates the burden on wastewater treatment facilities. Extensive research has been conducted to explore the impact of various solvents on dyeing properties, including color strength and fastness properties of cotton fabric dyed with reactive dyes (Mu et al. 2019; Wang et al. 2020). However, there is a lack of sufficient data regarding the optimization of solvent dyeing concerning solvent types, dye chemistry, and other process parameters. Some studies have utilized non-nucleophilic solvents such as dimethyl sulfoxide (DMSO) (Deng et al.

2019) and N, N-dimethylacetamide (DMAc) (Chen et al. 2015a) as dyeing media, yielding superior dyeing outcomes. However, one limitation encountered in these studies was the challenge of recycling and reusing DMSO and DMAc in the dyeing process due to their high boiling points (Chen et al. 2015b). In contrast, the solvent-assisted dyeing system involving ethanol (EtOH), carbon tetrachloride (CCl_4), and water (H_2O) has demonstrated significantly higher color strength values (K/S values) compared to conventional aqueous dyeing systems without the addition of salt (Wang et al. 2020). The previous studies have certain limitations, such as the utilization of hazardous solvents like carbon tetrachloride (CCl_4) that pose significant health risks (Menezes 2022). Additionally some of the work has been conducted used D5 solvents as a dyeing medium (Hossain et al. 2021, 2022; Cai et al. 2023), in somecases, PEG-based reverse micelles are used (Tang et al. 2019). However, in the above studied, the number of reactive dyes utilized in these studies has been limited, thus hindering an in-depth understanding of the solvent-assisted salt-free dyeing process. Additionally, the previous studies neglect to demonstrate the impact of essential variables, including the different organic solvents, different reactive dyes and their chemical structures, and reactivity during the dyeing. As a result, there is a research gap in terms of studying a broader range of dye chemistry and thoroughly examining their impacts on the solvent-assisted salt-free dyeing process, necessitating additional research to address this gap.

This research aims to develop a more environmentally friendly and efficient dyeing process for cotton fabrics. By eliminating the use of salt and introducing solvents, our study helps to reduce the negative impact of traditional dyeing practices on water resources and the environment, also it provide additional insight into the viability of this technique by investigating the effects of various parameters on dyeability results. So, we have incorporates the use of green solvents such as isopropyl alcohol (IPA), propanol (PrOH), and ethanol (EtOH) to test eight widely available reactive dyes with varying chemical structures and reactivity in the dyeing process. Through this investigation, we aim to optimize the solvent-assisted salt-free dyeing process and pave the way for its widespread adoption in the textile industry.

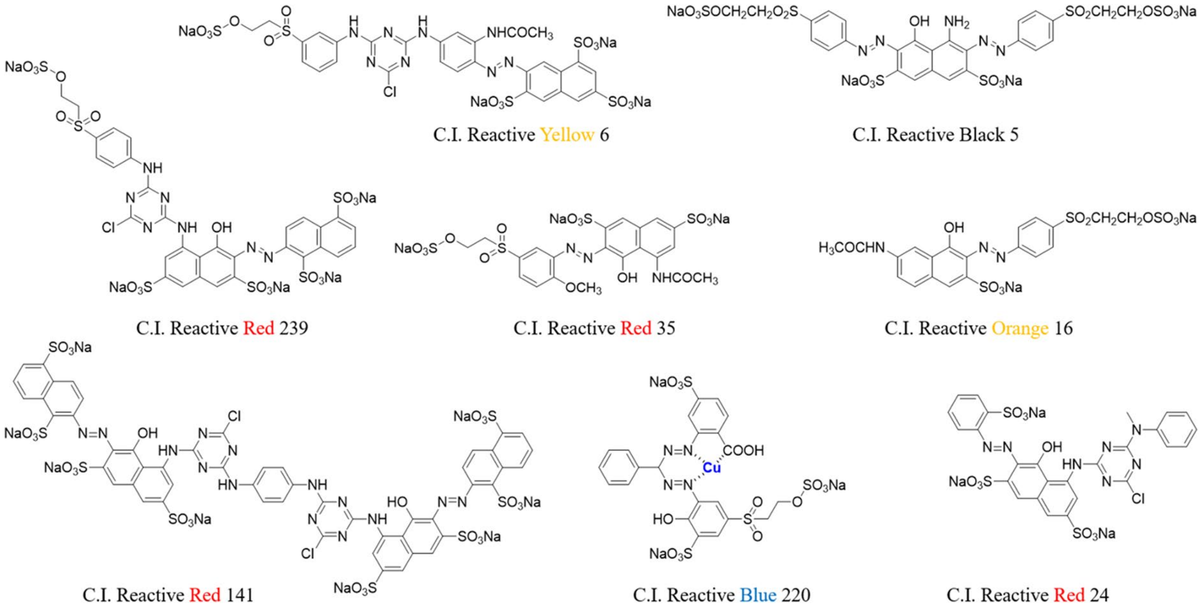
Experiments

Materials

Bleached knitted cotton fabric (single jersey, course-24 Ne, wale-24 Ne, and fabric weight of 150 g/m^2) was purchased from Orneule Knitting Company, Tampere, Finland. Eight commercially available reactive dyes (Fig. 1 and Table 1) were obtained from Colorant Co., India, Huntsman, Switzerland, and Archroma Co., Spain, and used without any purification. In this study, the selection of dyes has been identified as the predominant choice within the dyeing industry. Analytical grade ethanol (EtOH), propanol (PrOH), isopropyl alcohol (IPA), sodium carbonate (Na_2CO_3), and sodium chloride (NaCl) were bought from VWR, Finland. The non-ionic detergent (i.e., SDC standard soap) was purchased from SDC-Germany.

Dyeing procedure

A solution of sodium carbonate (Na_2CO_3) with a concentration of 20 g/L was used to immerse the fabric for 10 min under 60 °C and followed by padding with 80% pick-up. This process was carried out to activate the hydroxy groups present in the cellulose before the dyeing process facilitated by a solvent-assisted dyeing process. Then the fabric samples were dyed using a laboratory dyeing machine (Testex-Hong Kong) while being exposed to various solvents namely ethanol (EtOH), propanol (PrOH), isopropanol (IPA), and an aqueous medium. In order to improve the solubility of dyes, a little amount of water (4.5%) is often added to the dyeing solution in all organic solvent-based dyeing processes, with a ratio of 0.045:0.955. Typically, each dyes exhibit variations in the quantity of sulfonate groups they possess. In a broad sense, a set of eight reactive dyes exhibit varying quantities of sulfonate groups. Furthermore, an examination was conducted to assess their impact on the efficacy of the dyeing process. The concentration of dye used in the experiment was 1% relative to the weight of the fiber (o.w.f). The ratio of liquor to fabric was 20:1, and the dyeing process without the use of salt as alcohol was carried out at a temperature of 60 °C for 60 min. In contrast, the conventional aqueous dyeing process involved the addition of 30 g/L of salt. The process



C.I. Reactive Yellow 6

C.I. Reactive Black 5

C.I. Reactive Red 239

C.I. Reactive Red 35

C.I. Reactive Orange 16

C.I. Reactive Red 141

C.I. Reactive Blue 220

C.I. Reactive Red 24

Fig. 1 The chemical structures of reactive dyes used in this study

Table 1 The characteristic information of the commercial reactive dyes used in this study

Color Index (C.I.)	Molecular formula	Molecular weight (g/mol)	Dye Class	Reactive Group(s)
Reactive Red 35 (RR35)	$C_{12}H_{18}N_3Na_3O_{14}S_4$	732.9	Azo	Vinyl-sulfone
Reactive Blue 220 (RB220)	$C_{23}H_{18}N_3O_{15}S_{43}Na_3$-Cu	740.6	Diazo	Vinyl-sulfone
Reactive Orange 16 (RO16)	$C_{20}H_{17}N_3Na_2O_{11}S_3$	617.5	Azo	Vinyl-sulfone
Reactive Red 239 (RR239)	$C_{31}H_{19}ClN_7Na_5O_{19}S_6$	1136.3	Azo	Monochlorotriazine and vinyl-sulfone Bifunctional
Reactive Black 5 (RB5)	$C_{26}H_{21}N_5Na_4O_{19}S_6$	991.8	Diazo	Two vinyl-sulfone Bifunctional
Reactive Yellow 6 (RY6)	$C_{29}H_{21}ClN_8Na_4O_{16}S_5$	1025.2	Azo	Monochlorotriazine and vinyl-sulfone Bifunctional
Reactive Red 141 (RR141)	$C_{52}H_{26}Cl_2N_{14}Na_8O_{26}S_8$	1774.2	Diazo	Dichlorotriazine
Reactive Red 24 (RR24)	$C_{26}H_{17}ClN_7Na_3O_{10}S_3$	788.1	Azo	Monochlorotriazine

of washing the dyed cotton fabrics was conducted by the washing instructions provided by the manufacturer. This involved a cold rinse, followed by a warm soaping phase using a concentration of 2 g/L of nonionic detergents at a temperature of 60 °C for 20 min. The process concluded with a final cold rinse. Figure 2 illustrates the two different dyeing procedures: the single-bath conventional method and the solvent-assisted salt-free method.

The dyeing conditions presented in our study adhere to established industry norms for reactive dyeing of cotton fabrics with vinyl sulfone reactive dyes. It is worth noting that further optimization may be required for solvent-assisted dyeing processes.

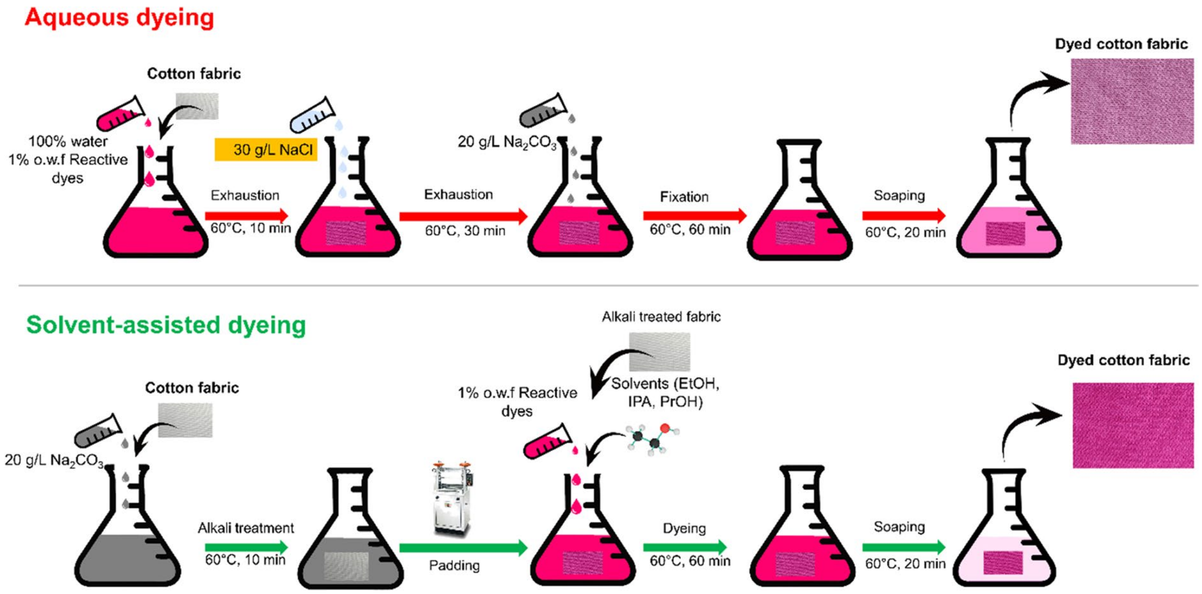


Fig. 2 Scheme showing the dyeing procedure of cotton fabrics with reactive dyes in aqueous and solvent-assisted dyeing processes

Characterization

Particle size and zeta potential

For the particle size analysis, the reactive dye solutions (1 g/L) were prepared by magnetic stirring of the corresponding dye powder in the medium at room temperature. Zetasizer Nano ZS90 (Malvern Instruments Ltd, UK) was used to analyze the average particle size distribution based on the dynamic light scattering (DLS) measurements and mean zeta potential (ZP).

Measurement of dye exhaustion

A Shimadzu UV-1800 UV–Vis spectrophotometer was used to determine the absorbance of the dye solutions at various wavelengths (200-700 nm). In this UV–Vis measurement, the dye solution has been diluted using exactly the same solvent employed in the dyeing process, maintaining a consistent ratio of solvent to water (4.5:95.5; v/v). By using the calibration curves (Absorbance vs. concentration) for each dye, one can calculate the remaining dye concentration in the dye bath to measure the percentage of exhaustion (E%) Eq. 1:

$$E(\%) = \left(1 - \frac{C_\infty}{C_0}\right) \times 100 \tag{1}$$

C_0 and C_∞ are the initial and final dye concentrations in the dye bath, respectively.

Determination of Color Strength Measurements

A reflectance spectrophotometer (Macbeth spectrophotometer under illuminant D65, wavelength 380–700 nm, and the 10° standard observer) was used to determine the color strength (K/S) of the dyed samples. The reflectance measurements were repeated several times for each dyed sample at different parts and angles. By measuring the sample's reflectance (R), the color strength or absorption to scattering coefficient (K/S) values of the dyed samples were calculated using the Kubelka–Munk equation (Eq. 2):

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

The color strength (K/S) is normally reported at the wavelength of maximum dye adsorption (λ_{max}).

Dyeing levelness

A total of ten spots were randomly chosen on the fabric surface, and the K/S values of these sites were measured using a Macbeth spectrophotometer. The level dyeing property was determined by employing the below equation, whereby a smaller value of Sγ(λ) indicates a superior level dyeing property (Wang et al. 2018).

$$S\gamma(\lambda) = \sqrt{\frac{\sum_{i=1}^{n}\left[\frac{\left(\frac{K}{S}\right)_{i\lambda}}{\left(\frac{K}{S}\right)_{i\lambda}} - 1\right]^2}{n-1}} \tag{3}$$

The CIEL*a*b* and ΔE (CIE) 1976 were calculated by computing the Eq. 4:

$$(\Delta E) = \sqrt{\left(L_1 - L_2\right)^2 + \left(a_1 - a_2\right)^2 + \left(b_1 - b_2\right)^2} \tag{4}$$

where ΔE is the color difference; L_1 is the CIE L* value of conventionally dyed fabrics and L_2 is the CIE L* value of solvent-assisted dyed fabrics; a similar method has been considered to compute a and b has been applied.

To assess color uniformity in dyed samples, we randomly measured the CIE L*a*b* values at five distinct points on each sample. The color difference of each point was calculated in reference to the average point, representing the mean of these measurements. Color uniformity was quantified by determining the average of these ΔE values, providing a comprehensive evaluation of color consistency across the sample.

Measurement of dye fixation, relative color strength, and dye intensity

During the soaping process, the dye molecules that are adsorbed on cellulose fabric by non-covalent bonds may be absorbed into the soaping bath. As a result, the color strength of the dyed sample may decrease. The dye fixation percentage (F%) can be estimated using Eq. 5 (Periyasamy 2022):

$$F\% = \left(\frac{\left(\frac{K}{S}\right)_{a.s.}}{\left(\frac{K}{S}\right)_{b.s.}}\right) \times 100 \tag{5}$$

where $(K/S)_{\text{b.s.}}$ and $(K/S)_{\text{a.s.}}$ are the color strength values of the dyed samples before and after soaping, respectively, and the total fixation percentage (TF%) has been calculated as follows,

$$TF\% = \left(\frac{Exhaustion}{Fixation}\right) \times 100 \tag{6}$$

Fastness properties

ISO 105-C06-A1S (2010a) standard test method was used for assessing the color wash-fastness of dyed fabrics by using 2 g/L non-ionic detergent at 40 °C for 30 min (2010a). The rubbing fastness were assessed according to ISO 105-X12 (2010b) standard. The lightfastness testing in this study was conducted by the ISO 105-B02 (2014) standard test, specifically using method 2. The dyed fabric underwent individual exposure for a duration of 96 h at a specific temperature of 47˚C and approximately 40% relative humidity. This exposure occurred under controlled conditions using an artificial light source (2.2 kW continuous wave Xenon Arc Lamp), James Heal apparatus. The apparatus was equipped with both xenon arc and mercury-tungsten fluorescent lamps, which emitted wavelengths comparable to those of natural sunlight. The color change was evaluated with the help of blue wool samples and the ISO grey card (2014).

XRD measurement

XRD patterns of dyed cotton samples in aqueous and solvent-based solutions were analysed using an X-ray diffractometer system (Xenocs Xeuss 3.0; transmission mode; CuK$_\alpha$ radiation; $\lambda = 1.54189$ Å; 50 kV/0.6 mA; 2D Dectris Eiger2 R 1 M detector; 56 mm sample-to-detector distance). The background was corrected by a blank run. A Savitzky-Golay filter with a window size of 29 and a polynomial order of 1was used to smoothen the pattern. Subsequently, the window size was raised to 201 (equivalent to 4° by 2Θ) to calculate the background profile from 4° to 48° 2Θ. The crystallinity index [%] was calculated by determining the ratio of the total intensity to the estimated background intensity by the following equation (Elsayed et al. 2021; Moriam et al. 2021):

$$CI = 100\frac{\int I(\theta)d\theta - \int I_{bkg}(\theta)d\theta}{\int I(\theta)d\theta} \tag{7}$$

Result and discussion

Selection of solvents for cellulose dyeing

Water is the most abundant and eco-friendly solvent for the dyeing process that has been used for thousands of years. Replacing such solvent in the dyeing process can only be justified if we can develop a closed-loop system for recycling and reusing the alternative solvent. The low environmental footprint and low toxicity that includes the waste management, environmental impact, health and safety considerations were among our selection criteria for solvents. According to the GlaxoSmithKline (GSK) solvent selection guide, solvents such as IPA, PrOH, and EtOH are considered green solvents with acceptable environmental health and safety properties (Alder et al. 2016).

The dyeing rate at which dye molecules diffuse from the dye solution to the cotton fabric is influenced by their solubility in the dye bath. The majority of commercial reactive dyes are currently designed to be water-soluble (e.g., by adding sulfonate groups to their chemical structures). The presence of several solubilizing groups in their chemical structures can influence their behavior in other solvents.

Effects of solvents on spectral properties

Figure 3 indicates the ultraviolet–visible (UV–Vis) spectra of the chosen reactive dyes when dissolved in water, ethanol (EtOH), isopropyl alcohol (IPA), and propanol (PrOH), covering the wavelength range of 300–800 nm. To facilitate a more accurate comparison, the UV–Vis measurements were conducted using identical dye concentrations (i.e., 10 g/L) and it has been diluted using exactly the same solvent employed in the dyeing process, maintaining a consistent ratio of solvent to water (4.5:95.5; v/v) to ensure the accuracy of the results. The absorption characteristics of dye solutions and their λ_{max} 0 can be observed through the manipulation of the solvent. The reactive dyes that have been chosen for this study are readily accessible in the market and are widely employed in the dyeing of cellulose during the production of textiles. The chemical structures of these substances have been modified to incorporate sulphonate groups, rendering them capable of dissolving in water. This phenomenon restricts their solubility in solvents with lower polarity, such as isopropyl alcohol (IPA) and propanol (PrOH). Consequently, it is anticipated that the absorbance of the dye solution will be comparatively reduced in solvents such as EtOH, IPA, and PrOH when compared to water, given the same initial dye concentration.

The observation of different dyeing performance of cellulosic fabrics when using the same dyes with different solvents confirms the significant influence of solvents on the dyeing process. The influence on reactive dyes caused by the adsorption of solvent molecules onto dye particles can be attributed to the dielectric constant of the solvents. As a result, reactive dyes can aggregate in the solvent–water mixture, and this aggregation varies depending on the type of solvent used (such as EtOH, PrOH, and IPA). Dye aggregation significantly affects dyeing performance, thereby influencing their adsorption onto and diffusion into cellulose fibers, as well as their dyeing behavior. In additions to that, dye aggregation behavior can be influenced by various physical–chemical properties of solvents, such as surface tension and viscosity (Takahashi et al. 2005). The level of dye aggregation in a solvent increases by increasing the intermolecular attractive forces (e.g., hydrogen bonds and Van der Waals forces) (Qi et al. 2020) and decreases by intermolecular repulsive forces (e.g., electrostatic repulsion and solvation).

The solvation of a dye molecule in a solvent depends on the dye and solvent chemical structures affecting their intermolecular interactions and polarity. The λ_{max} values of the reactive dyes in the chosen solvents are presented in Table 2. For instance, the λ_{max} of RR24 in an aqueous dyeing medium is observed at 540 nm, while in an EtOH medium, it is observed at 520 nm, and in an isopropanol/propanol (IPA/PrOH) medium it is observed at 530 nm. The phenomenon of negative solvatochromism, characterized by a blue shift, is observed when there is an increase in solvent polarity the ground electronic state becomes more stable than the excited state, and vice versa. A positive solvatochromism, characterized by a redshift, will manifest when the

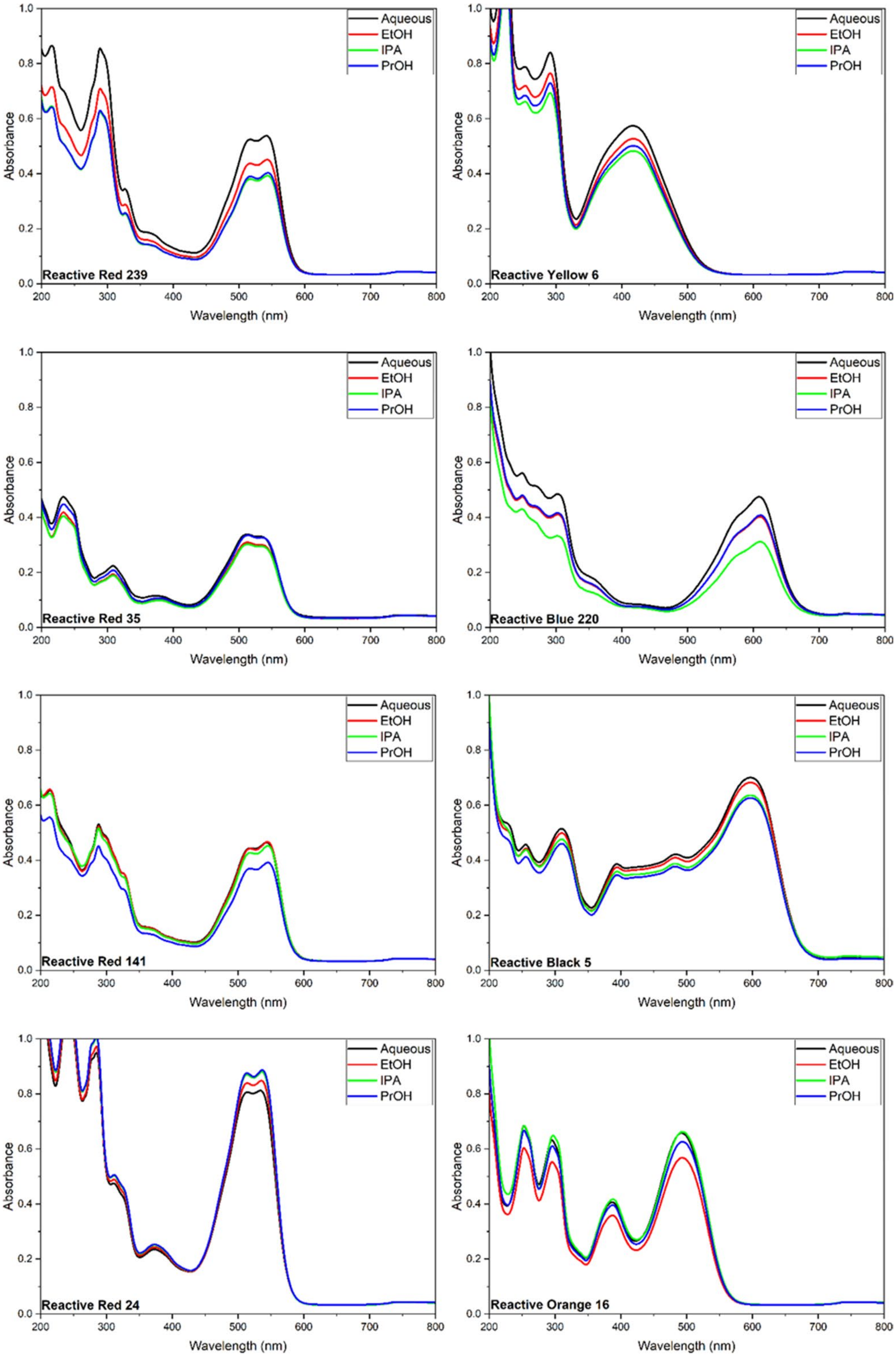


Fig. 3 UV–Vis spectra of used reactive dyes in different solvents (10 g/L)

Table 2 Comparison of reactive dyeing of cotton fabrics with conventional and solvent-assisted salt-free dyeing techniques. (Notes: represents the standard deviation, E- Exhaustion; F-Fixation and TF-Total Fixation)

Dyes (1%)	Medium		λ_{max} (nm)	K/S	σ (K/S)	L*	a*	b*	E (%)	σ(E%)	F (%)	σ(F%)	TF (%)
RR239	Conventional		550	6.71	0.17	48.8	51.74	-9.47	72.57	1.56	90.45	3.98	80.2
	Solvent assisted	EtOH	550	7.41	0.05	47.79	53.41	-7.38	91.02	1.94	89.08	2.89	102.2
		IPA	550	8.01	0.04	47.7	53.64	-8.93	92.69	2.81	94.69	1.99	97.9
		PrOH	550	9.16	0.15	46.28	54.74	-7.39	93.07	4.13	98.14	1.26	94.8
RY6	Conventional		430	10.83	0.33	71.18	26.75	74.46	82.47	2.17	88.52	6.62	93.2
	Solvent assisted	EtOH	430	12.98	0.76	72.8	23.01	70.98	93.05	2.6	74.46	1.19	125.0
		IPA	430	10.18	0.26	70.11	23.43	73.36	91.37	1.71	62.42	3.08	146.4
		PrOH	430	16.21	0.81	71.09	28.33	80.46	95.02	2.75	86.17	10.13	110.3
RR35	Conventional		530	1.31	0.02	66.38	34.23	-7.94	47.39	1.28	93.54	3.34	50.7
	Solvent assisted	EtOH	530	4.57	0.12	52.86	50.88	-7.52	89.92	0.31	94.54	3.29	95.1
		IPA	530	2.81	0.04	53.3	50.21	-8.12	89.04	1.09	78.97	1.6	112.8
		PrOH	530	6.14	0.33	53.3	52.94	-8.36	89.78	1.97	89.44	0.84	100.4
RB220	Conventional		620	4.83	0.26	51.1	-10.3	-27.07	66.02	2.37	85.91	2.89	76.8
	Solvent assisted	EtOH	620	3.58	0.32	55.76	-9.63	-25.27	72.2	4.2	72.3	0.65	99.9
		IPA	620	6.01	0.35	48.04	-10.3	-28.63	89.22	2.15	64.99	2.25	137.3
		PrOH	620	6.51	0.45	47.12	-10.2	-28.24	87.39	1.56	83.19	1.49	105.0
RR141	Conventional		560	8.4	0.16	45.53	54.92	-7.71	86.69	1.55	91.93	3.23	94.3
	Solvent assisted	EtOH	560	6.59	0.98	49.93	54.14	-9.29	93.29	1.78	81.97	2.33	113.8
		IPA	560	2.23	0.63	60.47	42.6	-11.29	91.31	1.81	69.08	10.68	132.2
		PrOH	560	3.02	0.68	56.96	45.97	-11.01	93.16	2.37	66.16	13.24	140.8
RB5	Conventional		610	8.97	0.28	29.85	-0.25	-4.95	66.87	1.07	97.66	0.04	68.5
	Solvent assisted	EtOH	610	7.41	0.62	34.59	-2.8	-11.44	66.92	3.51	79.16	0.65	84.5
		IPA	600	13.83	0.53	25.91	-2.06	-9.6	93.39	0.76	74.85	2.13	124.8
		PrOH	610	19.13	0.52	26.62	-1.74	-9.41	94.17	1.39	86.33	1.86	109.1
RR24	Conventional		540	1.48	0.13	65.45	38.37	-3.76	59.65	5.16	75.32	2.82	79.2
	Solvent assisted	EtOH	520	2.74	0.18	61.75	44.42	-1.75	76.68	3.28	33.9	0.2	226.2
		IPA	530	2.59	0.29	60.32	45.79	-1.8	87.94	2.7	58.18	3.46	151.2
		PrOH	530	3.37	0.32	57.76	48.71	-0.56	92.24	1.57	60.74	2.22	151.9
RO16	Conventional		500	4.69	0.07	61.71	42.53	23.24	56.7	2.8	82.93	4.27	68.4
	Solvent assisted	EtOH	500	2.64	0.05	64.41	41.41	23.05	40.31	3.58	84.73	3.46	47.6
		IPA	500	4.86	0.47	59.04	44.55	24.91	72.46	2.2	64.15	1.43	113.0
		PrOH	500	6.19	0.69	56.75	50.67	29	52.19	3.23	58.99	1.5	88.5

solute-excited state experiences enhanced stabilization (Airinei et al. 2010). Moreover, it is anticipated that the dye molecule would exhibit a higher affinity towards a solvent with greater polarity, leading to a redshift (Reichardt 1994). However, this phenomenon is contingent upon both the dielectric polarization theory and the persistence of dipole moments in the ground and excited states (Thiagarajan et al. 2004). The stabilization of dye molecules in their highest occupied molecular orbital (HUMO) or lowest unoccupied molecular orbital (LOMO) states can be influenced by various parameters, such as the chemical structure of the dye, the polarity of the solvent, the solubility of the dye, and the intermolecular interactions between the dye and the solvent. When the ground state of the dye molecule is stabilized in a solvent, there is a corresponding increase in the energy gap between the HUMO and the LOMO states. Consequently, the maximum wavelength (λ_{max}) of the dye in the solvent undergoes a shift toward lower values, commonly referred to as a redshift.

Comparison of conventional and salt-free dyeing

The average particle size of dyes in various solvents was examined with Zetasizer ZS90 to understand their aggregation behavior. To examine the particle size and zeta potential, 1 g/L of each dye was dissolved in different solvents. The dye average particle size values in EtOH, IPA, and PrOH were relatively higher than those in aqeous medium (Fig. 4a). This is an indirect sign of lower dye solubility and larger dye aggregations in these solvents with less polarity than in aqeous medium. The dielectric constant values of these alcohols are much lower than that of aqeous medium (Akerlof 1932). The reactive dyes are all anionic and polar molecules with several sulfonate groups in their chemical structures. The dye molecules with lower molecular weight and a higher number of sulfonate acid groups have higher polarity and water solubility. These dyes seem to have less solubility in EtOH, IPA, and PrOH probably due to the mismatch of polarity between the dye and solvent molecules.

The rate at which dye molecules diffuse from the dye solution to the cotton fabric, known as the dyeing rate, depends on how well they dissolve in the dye bath. Most commercial reactive dyes are designed to be water-soluble, often by incorporating sulfonate groups into their chemical structures. However, when used in other solvents like alcohols, these dyes tend to have lower solubility, as indicated by the particle size distribution in Fig. 4a. Interestingly, despite their limited solubility in alcohols, we did not observe any color inconsistency issues in the dyed samples. This can be attributed to the continuous nature of the dye solubilization, adsorption, and diffusion processes. Initially, dye molecules that dissolve and disperse in the medium are adsorbed onto the surface of cellulose fibers and then penetrate into the fibers. Subsequently, the medium retains the capacity to dissolve more dye molecules. This constrained dye solubility in alcohol contributes to reduced dye hydrolysis, leading to higher dye exhaustion and fixation.

The zeta potential (ZP) determines the electrophoretic mobility of particles in an electric field. The ZP values for all of these dyes in alcohols are lower than those in aqeous medium (Fig. 4b). This shows that the negative charge of anionic dye molecules is less pronounced when we are using alcohols as the dyeing medium. As a result, (a) the electrostatic repulsion between cellulose and anionic dyes in the presence of alcohols is reduced which enhances the dye adsorption even without the addition of salts, and (b) the electrostatic repulsion between dye molecules is also reduced which promotes their aggregation in the solvent. These two outcomes have contrasting effects on the dyeing properties of cellulose in the presence of alcohol. The latter can reduce the dyeability of cellulose with reactive dyes in the presence of alcohol and cause some unevenness in dyeing.

The dispersion systems with ZP values higher than + 25 mV and lower than -25 mV are considered stable systems. The dye solutions in alcohols showed ZP values in the range of -10 mV to -20 mV which shows their partial stability at room temperature. The

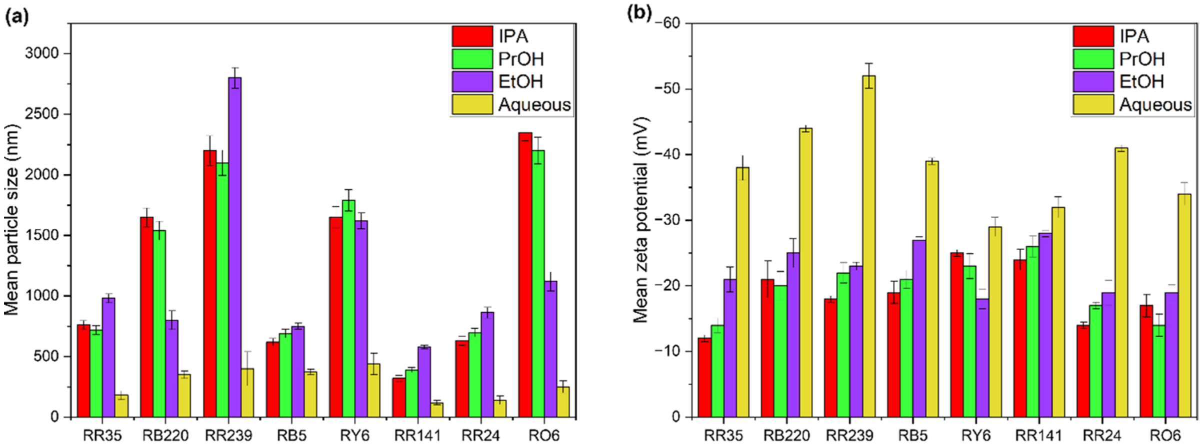


Fig. 4 The mean particle size (**a**) and zeta potential values (**b**) of the reactive dyes in aqueous EtOH, IPA, and PrOH

addition of electrolytes in aqueous dyeing is normally required to neutralize the surface charge of cellulose and reduce the electrostatic repulsion between anionic dyes and cellulose. The presence of salt in water can also increase the possibility of dye aggregation in an aqueous solution. These dye aggregates in water or alcohols are mixed and agitated during the dyeing process at a higher temperature (60 °C) and their partial dispersion stability should not be an issue.

The oversimplified schematic representation of the dyeing process for cotton fabric (i.e., alkali pretreated) in various solvent-assisted dyeing methods is depicted in Fig. 5. This process involves four distinct stages: dye dissolution, absorption, diffusion, and fixation. However, due to the presence of sulfonate groups, some dye particles do not fully dissolve in alcohols, leading to dispersion within the solution. Subsequently, the partially solubilized reactive dyes in dispersed form undergo adsorption onto the cotton fabric. It is worth noting that the majority of dyes exhibited adsorption onto the fabric, with slight variations depending on the specific dyes and solvents used. This phenomenon can be attributed to the strong affinity of reactive dyes towards cellulosic fabrics, facilitating the transfer of dye molecules from the solvent system to the surface of the fabrics. During the third step (Fig. 5), the reactive dyes permeated the cellulosic structure, specifically soda cellulose, resulting in the dissociation of hydroxyl groups on the cellulosic fabrics. This dissociation led to the generation of an anionic cellulosic nucleophile. During the final stage, the fixation of reactive dyes onto the cotton fiber occurred through the establishment of a covalent bond between the reactive groups of the dyes and the hydroxyl groups present in cellulosic fabrics (Lewis 2014).

The formation of covalent bonds with anionic cellulosic nucleophiles through nucleophilic substitution has been observed in monochlorotriazine-based reactive dyes (Lewis 2014). The vinyl-sulfone-based reactive dyes establish covalent bonds with an anionic cellulosic nucleophile through nucleophilic addition (Lewis 2014). In general, it can be observed that the alkali pretreatment process tends to enhance the swelling properties of cellulosic materials. As a result, the fiber pores exhibited a significant size, facilitating the efficient infiltration of dye molecules into the internal regions of the fiber.

As indicated in Table 2, the K/S values, exhaustion, fixation, and relative color strength of dyed cotton fabrics were evaluated using both solvent and aqueous mediums. In general, the color strength (K/S) values of the samples dyed using a solvent system were significantly higher compared to those dyed conventionally using an aqueous medium.

The dyeing performance of RR239 was evaluated using an aqueous medium. The resulting K/S values were found to be 6.7. The exhaustion and fixation percentages were determined to be 72.5% and 90.4%, respectively. In contrast, when PrOH was used as the medium, higher K/S values of 36%, a higher exhaustion percentage of 27%, and a higher fixation percentage of 9% were observed as compared to the aqueous medium. Additionally, the relative color strength values were found to be 138% higher when PrOH was utilized. The utilization of RB5 dyes in solvent-assisted salt-free dyeing results in K/S values that are 117% higher with PrOH, 253% higher with EtOH, and 58% higher with IPA compared to traditional aqueous dyeing methods.

Overall, the findings of this study suggest that the examined reactive dyes, with the exception of RR141, demonstrate suitability for dyeing cellulosic materials within a solvent-assisted system. To enhance the dyeing process, we introduced a small quantity of water (4.5:95.5; v/v) into the solvent-based system. This binary solvent mixture offers two key advantages: (1) reactive dyes are intentionally

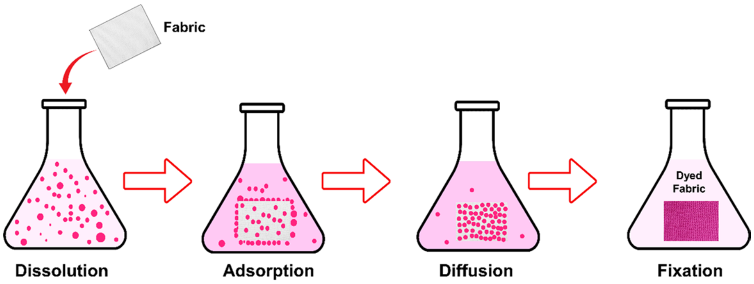


Fig. 5 Steps involved for the dyeing of cotton fabrics under solvent medium

engineered to exhibit strong water solubility while having limited solubility in alternative organic solvents, and (2) the presence of water vapor in the binary mixture, when combined with a combustible component, serves to reduce the flammability of the dyeing bath. This is a vital safety consideration, particularly for pilot-scale applications (Astbury, et al. 2004; Hristova 2010; Janes and Chaineaux 2013). Commercial reactive dyes are predominantly formulated for water-based dyeing processes, which are currently prevalent in the industry. Additionally, the inclusion of sulfonate groups during the dye manufacturing process serves to enhance solubility. The presence of a significant disparity in dye concentration between the solvent containing a small amount of water and the dye solution in the system leads to the formation of a substantial dye concentration gradient. This gradient facilitates the swift adsorption of dye molecules onto cellulosic fabrics. Additionally, the solvent containing a small amount of water exhibits favorable wetting characteristics, allowing the dye molecules to readily penetrate the cotton fibers. Consequently, these factors contribute to the exceptional dyeing properties observed in cotton fibers.

Moreover, several plausible rationales exist for the observed increase in K/S values during solvent dyeing.

- The hydrolysis of dye is significantly reduced in the presence of solvents, allowing for a greater number of dyes to be statistically immobilized on cellulose (Chen et al. 2015b).
- The Zeta Potential (ZP) values of dye solutions in alcohols exhibit lower magnitudes compared to those in water. Consequently, the electrostatic repulsion between cellulose and dye molecules is relatively diminished in the presence of alcohols. The phenomenon can be elucidated by the comparatively lower dielectric constant exhibited by alcohols in comparison to water (Akerlof 1932).
- Furthermore, alcohols with a surface tension ranging between 21–24 mN/m exhibit enhanced wetting properties on cellulose compared to water. Water, having a higher surface tension of around 72 mN/m, which is further increased in the presence of salts, is comparatively less effective in wetting cellulose (Behera et al. 2014).

In addition to this, bifunctional reactive dyes possess two reactive groups, which can be either identical or different in their chemical composition. Consequently, these dyes exhibit enhanced fixation rates and improved overall fastness properties when applied to cellulose materials. Fig. S1 displays the K/S curves of cellulosic materials that have been subjected to dyeing with different reactive dyes, both in solvent and aqueous systems and Table S1 presents the digital images of the dyed fabrics obtained through both aqueous and solvent-assisted dyeing methods. These images allow for an assessment of the uniformity of the dyeing process. For a more precise quantitative assessment, we calculated the average ΔE* (color uniformity) as described in Table 2. These comprehensive results have been documented in Table S2. The average ΔE* values for the dyed samples were consistently below 2 except for the samples dyed with RR141 in the presence of solvents. Thus, the dyed samples had generally very good color uniformity with ΔE* ≤ 2.

The less effective dyeing performance of RR141 in the solvent-assisted dyeing procedure can be attributed to its high water solubility and limited solubility in alcohols, which can be directly linked to the presence of eight sulfonate groups within its chemical structure (as illustrated in Fig. 1). The conventional dyeing of cotton using RR141 led to greater color strength values and better uniformity compared to when alcohols were present (Table 2, Table S2), additionally we have computed the dyeing levelness and it is described in Fig. 6. The dissolution and

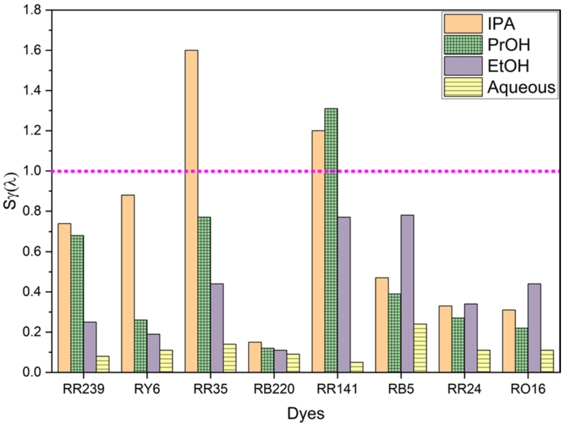


Fig. 6 Level dyeing property of reactive dye in different solvent-assisted dyeing systems and aqueous medium

dispersion of RR141 in alcohols posed challenges, as we observed the formation of significant aggregates during the preparation of the dye solution. The DLS measurement is unable to detect sediment aggregates of such a significant size.

The CIELab color values (*L**, *a**, and *b**), color strength (K/S values), exhaustion (E%), and fixation (F%) of the dyed samples are provided in Table 2. The color difference values can be assessed by three different coordinates (*L**, *a**, and *b** values) as suggested in the CIE 1976 system. In digital representation, color space is typically mapped onto a three-dimensional numerical space consisting of L*, a*, and b* values, each with a predetermined range. The lightness value L* is used to represent the darkest shade, which is denoted by L* = 0, and the lightest shade, which is denoted by L* = 100. The color channels a* and b* are used to denote the true neutral gray values, where a* = 0 and b* = 0. The x-axis represents the module ranging from green to red, with green being assigned negative values and red being assigned positive values. The b* axis is a representation of the blue-to-yellow component, where blue is assigned a negative value and yellow is assigned a positive value.

In RR 239, the fabric dyed with solvent assistance exhibits lower L* values, indicating a darker shade, in comparison to dyeing with an aqueous medium. This observation can be confirmed by cross-validating the color strength values (K/S) presented in the accompanying Table 2. In the context of solvent-assisted dyeing, it was observed that the slight increase of a* and b* color coordinates exhibited reddishness and bluishness respectively. On the other hand, RR141 exhibits lower L* values (45.43) in the aqueous medium compared to the solvent-assisted dyeing techniques. This indicates that lighter shades are achieved through the use of solvent-assisted dyeing techniques. Among these techniques, the highest L* values (60.47) were observed when using IPA as the solvent. The variation in L* values could additionally have an impact on the K/S values, as this may be attributed to the chemical characteristics of the dye and the quantity of sulfonate groups present, along with their interaction within the solvent medium. Typically, the augmentation of sulfonate groups is associated with a reduction in dye solubility and an elevation in particle dimensions.

In general, the L* values of the samples subjected to solvent-assisted dyeing techniques using RR35, RB220, RR239, RY6, RR24, RB5, and RO16 dyes were found to be lower compared to the L* values obtained from aqueous dyeing. The results indicate that solvent-assisted dyeing yields a deeper hue compared to aqueous dyeing, primarily attributed to the enhanced dye exhaustion and fixation achieved during the dyeing procedure.

In the case of RR239, RR35, RR24, and RO16 dyed fabrics, it has been observed that the a* value (representing the red and green elements in the samples) of the solvent-assisted dyed samples is higher compared to the samples dyed using an aqueous solution. This implies that the red component of the samples exhibits an increase, resulting in a shift towards a redder shade as indicated by the positive shift in the a* values. In comparison to the aqueous-dyed samples, the solvent-assisted dyed samples exhibit a decrease in the a* values of RR141 and RY6, which represent the red and green elements in the samples, respectively. This implies that the level of greenness in the samples is heightened, resulting in a visual shift towards a greener shade. This is indicated by the a* values shifting towards negative values. The samples dyed with solvent assistance using RY6 dyes exhibit a higher b* value, indicating a yellower color, compared to the samples dyed with water. This observation suggests that the solvent-assisted dyed samples display a more pronounced and vibrant shade of yellow.

In aqueous dyeing, the alkaline state causes cellulosic fibers to swell more, but the alkali is introduced in the second part of the aqueous dyeing system to neutralize the HCl formation and enhance the fixation. Only the exterior walls of the crystallites in the a & b areas are dyed in the aqueous system. Therefore, the non-accessible regions a & b are partially non-accessible during the exhaustion process. Moreover, we conducted XRD measurements on 8 dyed samples prepared in various solvents, including water, ethanol, IPA, and Propanol (refer to Fig. S2). All XRD peaks exhibited a similar pattern, indicative of a cellulose I structure. The crystallinity index, determined using Eq. 7, was consistent across all samples at 55 ± 2%. This indicates that solvent treatment does not alter the crystallinity of the dyed samples, suggesting that changes in crystallinity are not the reason for the observed improvement in dyeability of cotton samples.

Figure 7 shows digital images of the dyebath liquids at the end of the conventional and solvent dyeing processes. These images visually confirm that the concentration of remaining dyes in the dyebath after conventional dyeing is relatively higher than those after solvent-assisted salt-free dyeing which is in good agreement with the better exhaustion rates of the dyes on cellulose (Table 2). A large amount of salt (30 g/L) is added to the dye bath to neutralize the surface charge of cellulose and enhance the dye adsorption (i.e., exhaustion) rate. The exhaustion % of the solvent-assisted salt-free dyeing process is often better than that of conventional dyeing.

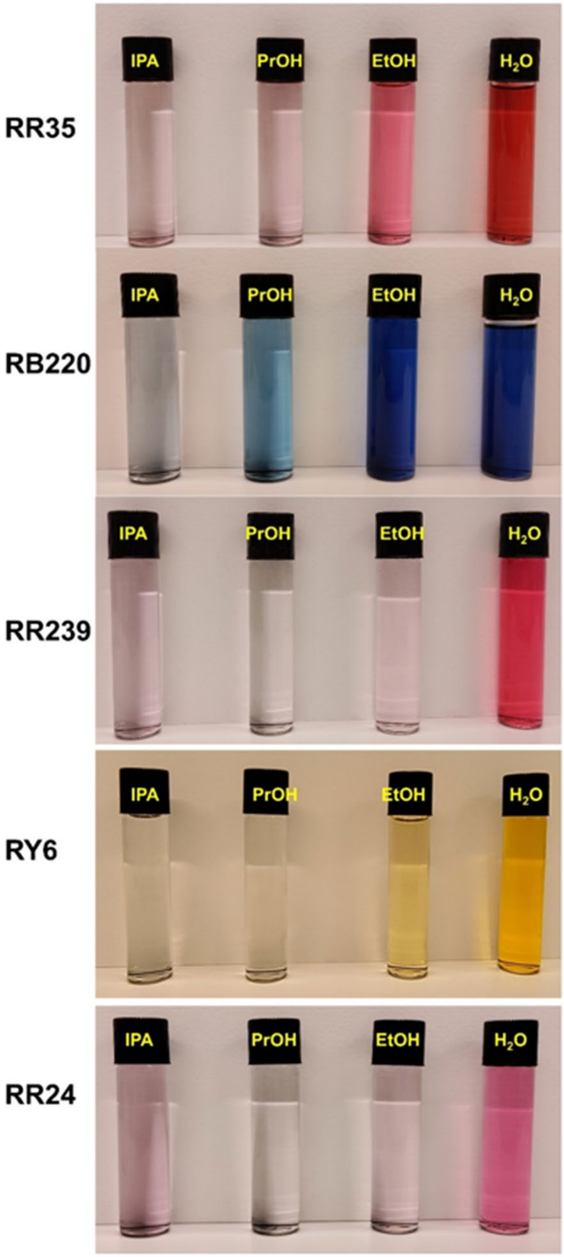


Fig. 7 Digital photographs of dyebath liquid at the end of the dyeing process for RR35; RB220; RR239; RY6; and RR24

Dyeing levelness

Reactive dyes exhibit a higher rate of adsorption in solvent-assisted dyeing systems compared to traditional aqueous dyeing mediums, often influencing their dyeing characteristics. As depicted in Fig. 6 and Table S1 (showing digital photographs of dyed fabric), the dyeing properties of eight commercially available reactive dyes, along with their corresponding Sγ(λ) values (indicating dyeing levelness), are presented. Dye levelness was assessed using Eq. (3), where a lower Sγ(λ) value indicates a higher level dyeing property. The experiment demonstrated that the values obtained in solvent-assisted dyeing mediums were greater than those obtained in aqueous mediums. According to previous research (Wang et al. 2018), values below 1 suggest that reactive dyes may achieve a high level of dyeing property with the application of mechanical force during the dyeing process.

Fastness properties

The colorfastness of cellulosic fabrics dyed with eight reactive dyes using both solvent-assisted and aqueous dyeing methods was assessed and compared, as presented in Table 3. The improved washing fastness characteristics observed in the fabrics dyed with the assitance of solvents can be attributed to the increased ability of the dyeing system to wet the fibers under solvent medium, particularly PrOH and IPA, are present. This is further supported by the significantly better color fastness towards to washing, that is exhibited by the samples dyed under PrOH and IPA conditions, indicating enhanced dye penetration and resulting the strong bond formation. Certain dyes, such as RR141 and RB5, have been seen to exhibit enhanced washing fastness, specifically achieving a rating of 4–5, when ethanol (EtOH) is utilized.

Table 3 The fastness of properties of reactive dyed fabric

Dyes (1%)	Samples		K/S values	Washing fastness		Crocking fastness		Light Fastness
				Color change	Color staining	Dry rubbing	Wet rubbing	Blue wool reference
RR35	Conventional dyeing		6.71	4–5	4–5	4–5	4–5	4
	Salt-free dyeing	IPA	7.41	4	4	4–5	4	5
		PrOH	8.01	4–5	4–5	4–5	4	4
		EtOH	9.16	4	4	4–5	4–5	4
RB220	Conventional dyeing		10.83	4–5	4–5	4–5	4	7
	Salt-free dyeing	IPA	12.98	4	4	4–5	4	6
		PrOH	10.18	4–5	4–5	4–5	4–5	6
		EtOH	16.21	4–5	4–5	4–5	4	6
RR239	Conventional dyeing		1.31	4–5	4–5	4–5	4–5	5
	Salt-free dyeing	IPA	4.57	4–5	4	4–5	4	5
		PrOH	2.81	4–5	4	4–5	4	4
		EtOH	6.14	4	4–5	4–5	4	3
RB5	Conventional dyeing		4.83	4	4	4–5	4	3
	Salt-free dyeing	IPA	3.58	4–5	4	4–5	4	3
		PrOH	6.01	4–5	4	4–5	4	3
		EtOH	6.51	4–5	4	4–5	4	3
RY6	Conventional dyeing		8.40	4–5	4–5	4–5	4	7
	Salt-free dyeing	IPA	6.59	4–5	4–5	4	4	6
		PrOH	2.23	4–5	4–5	4	4	6
		EtOH	3.02	4–5	4–5	4–5	4	6
RR141	Conventional dyeing		8.97	4–5	4	4–5	4	3
	Salt-free dyeing	IPA	7.41	4	4	4	3–4	3
		PrOH	13.83	4	4	4	3–4	3
		EtOH	19.13	4–5	4	4–5	4	3
RR24	Conventional dyeing		1.48	4–5	4–5	4–5	4–5	5
	Salt-free dyeing	IPA	2.74	4–5	4–5	4–5	4	4
		PrOH	2.59	4–5	4–5	4–5	4	4
		EtOH	3.37	4–5	4–5	4–5	4	4
RO16	Conventional dyeing		4.69	4–5	4–5	4	4–5	6
	Salt-free dyeing	IPA	2.64	4–5	4	4–5	4–5	5
		PrOH	4.86	4–5	4	4–5	4–5	5
		EtOH	6.19	4–5	4–5	4–5	4–5	5

Overall, the improved wettability facilitates the rapid penetration of dye molecules into the internal structure of the cellulosic material. During this particular occurrence, a significant portion of the reactive dyes are adsorbed onto the cellulosic materials and subsequently undergo a nucleophilic reaction with the hydroxy groups of cellulose. Ultimately, the fixation of these dyes onto cellulosic fibers occurs through the establishment of a covalent bond. The light fastness outcomes exhibit variability depending on factors such as the specific dyes used and the dyeing technique employed. In general, the utilization of solvent assisted dyeing techniques enhances the fastness properties of dyed materials, often yielding comparable results to those achieved using conventional dyeing methods. Nevertheless, the overall findings indicate that solvent-assisted dyeing yields comparable results to aqueous dyeing. Hence, solvent dyeing does not compromise the washing fastness properties.

In general, the rubbing fastness of dyes, whether solvent-based or aqueous-based, typically yields a value above 4. However, it is important to note that the fastness rating above 4 is generally deemed good. RR141 dye has been found to exhibit a wet rubbing fastness rating of 3–4, particularly when it is applied using IPA and PrOH as the dyeing medium. Generally, RR141 is not compatible with solvent-based dyeing processes as it tends to retain unfixed colours on its surface. These unfixed dyes have the propensity to dissolve in water and subsequently transfer onto the test fabric, hence leading to inadequate wet rubbing fastness.

It is imperative to understand that the light fastness of reactive dyes is dependent on various factors, including the chromophore composition, molecular weight, bond formation, and molecular structure. Generally, it can be observed that reactive dyes based on anthraquinone provide excellent light fastness, but azo chromophores tend to exhibit diminished light fastness. Furthermore, our research has demonstrated that dyes containing metal complexes exhibit exceptional light fastness. This is exemplified by the RB220 dye, which incorporates a metal complex within its azo chromophore, resulting in a highly favorable light fastness rating of 7.

Conclusion

In summary, our research showcases the feasibility and significant advantages of solvent-assisted salt-free dyeing for cotton fabrics, employing commercial reactive dyes. By substituting water with environmentally friendly solvents such as ethanol (EtOH), isopropyl alcohol (IPA), and propanol (PrOH), this dyeing approach generally enhances color strength (K/S) values and demonstrates improvements in exhaustion and fixation rates when compared to traditional aqueous dyeing methods.

Our study contributes valuable insights into the impact of various solvents on the spectral properties of reactive dyes, shedding light on how solvent polarity influences the dyeing process. The analysis of particle size distribution and zeta potential values shows the significant role of solvents in dye solubility and adsorption onto cotton fibers, further underlining the critical influence of solvent selection on dyeing performance and color uniformity. In conclusion, the results indicate that propanol (PrOH) is the optimal choice for the current commercial dyes being utilised. However, more experimentation is required with other commercially available reactive dyes.

Evaluation of washing, rubbing, and light-color fastness properties reveals that solvent-assisted dyeing yields results on par with aqueous dyeing, ensuring the durability of color retention in textiles. These findings position solvent-assisted salt-free dyeing as a compelling solution for mitigating the environmental impact associated with conventional water-based dyeing processes. The substantial reduction in water consumption and salt usage, as well as the reduction of environmental pollution, make this method an attractive and sustainable option for textile coloration.

While some challenges, such as the limited compatibility of certain dyes with solvent-based processes, were identified, the overall outcomes underscore the need for further exploration and adoption of solvent-assisted salt-free dyeing techniques in the textile industry. This method not only conserves resources but also enhances the overall sustainability of textile coloration practices.

To advance our research and assess its scalability and holistic viability, we recommend a comprehensive investigation into solvent recovery and sustainable reuse. This direction aims to promote environmental sustainability and cost-effectiveness in large-scale applications. Additionally, we propose conducting a detailed Life Cycle Assessment and a Technoeconomic Analysis to delve into the environmental impact and economic feasibility of implementing our method on a broader scale, further contributing to the field of textile dyeing and environmental conservation.

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Author's contribution A.P.P. and S.D. conducted research and wrote the main manuscript text and prepared figures and tables. A.T. supervised the project. All authors revised and reviewed the manuscript.

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Data availability The data and materials can be obtained from authors upon request.

Declarations

Ethics approval and consent to participate This work is not human subjects research.

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