



Study on the Dyeing Properties of a Novel Reactive Dye with One Vinylsulfone Reactive Group, on Cotton Substrates, Before and After Its Ultrafiltration Treatment

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Abstract

Reactive dyes are widely used in the textile industry due to their versatility of shades, high wash fastness properties, and the ease of application. Dyeing properties such as exhaustion, substantivity, fixation, time to half dyeing, migration index and effect of metal salts were studied for a novel reactive dye (named RR_{Na}) synthesized with one vinylsulfone as reactive group. The aim of this study is to figure out the influence of the ultrafiltration process this dye went through on its aforementioned properties. It was found that the ultrafiltrated reactive dye shows higher exhaustion, substantivity, dye uptake than the original dye, which is attributed to the purification performed by the ultrafiltration process. The migration index is slightly lower for the ultrafiltrated dye which indicates that its mobility is lower, due to the possible formation of more covalent bonds between the dye and the substrate. The effect of metals (Fe, Co, Cu) was also studied and the color strength of the dyeings in the presence of sulfate salts was compared with the control sample. It was found that Co²⁺ and Cu²⁺ have a detrimental effect on the shade obtained, whereas Fe³⁺ reduces color strength to a lower extent.

Keywords Migration index · Substantivity · Exhaustion · Dye fixation · Cellulosic fibers

1 Introduction

Reactive dyes are the most important class of synthetic dyes applied for cellulosic substrates because of their high wet fastness, brilliance, exceptional application versatility, and wide range of hues [1–5]. Fabricated to bond covalently with the substrate, reactive dyes comprise a chromophore and a reactive group, while they own their excellent wet fastness to the formation of covalent bonds with the macromolecules of the fibers [6]. They are applied either from a solution with high pH or from neutral solutions that are later alkalinized through a separate step. Reactive dyes are categorized by their functional group. Industrially, the organic synthetic dyes prevail for textile dyeing; azo dyes among them are the major synthetic organic dyes covering up to 70% of all synthetic dyes used. Azo dyes are compounds containing

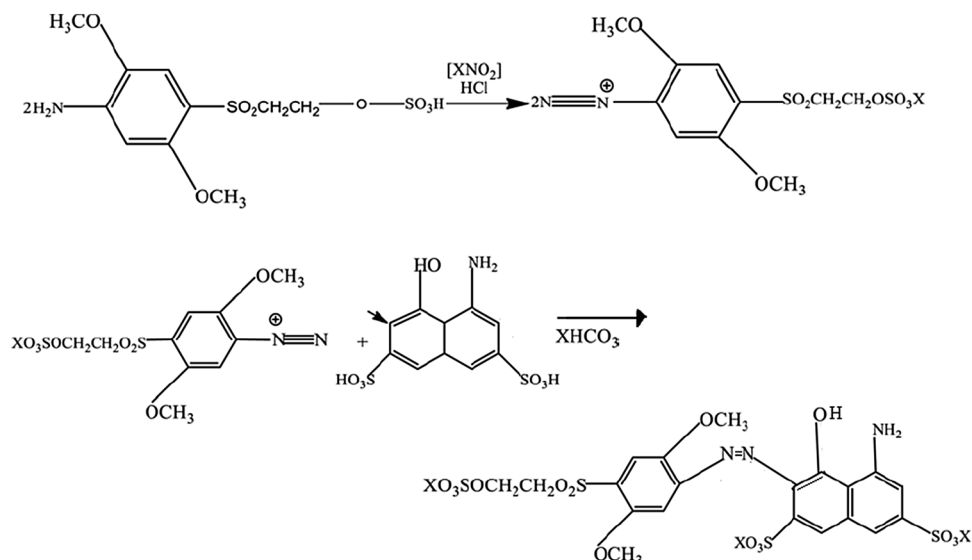
one or more chromophore azo groups –N=N–. N-atoms are bonded to neighboring C-atoms by *sp*² hybridization which may belong to benzene, naphthalene or heterocyclic aromatic rings. The most important method of preparing aromatic azo compounds is “azo coupling” and involves the reaction of aromatic diazo compounds with amines or phenols [7, 8]. The water-soluble part of the dye is necessary when dyeing cellulose fibers as well as protein fibers and usually consists of 1–4 sulfo-groups –SO₃. The chromophore is the part of the molecule that provides color and must have the necessary affinity to the substrate to be dyed satisfactorily.

In a previous published work, three new azo reactive dyes of different metallic salts (Na, K, Li) were synthesized. The dyes were purified/concentrated by ultrafiltration technology. Subsequently, they were characterized as compounds and tested on cotton, wool and polyamide fabrics investigating their dyeing exhaustion and ink-jet printing [8, 9]. Reactive Red DMAVS is synthesized according to the reaction sequence shown in Fig. 1 and is destined to dye cotton fabrics. The mono-azo reactive dyestuff was synthesized by diazotizing the amine 4-amino-2,5-dimethoxyphenylene-β-hydroxyl-ethyl-sulfone sulphate ester and coupling it with

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Fig. 1 Synthesis of dyestuff RR_{Na} where X stands for Na [7]



equimolar amount of 1-amino-8-hydroxy-naphthalene-3,6-disulfonic acid [10]. The synthesis of the mono functional vinylsulfone reactive dye is novel in the sense that there are no commercially available CAS registered dyes of the above structure in any salt form [9]. The yield of RR_{Na} dyestuff has been calculated at 720.5 g/moles amine [8].

Hydroxyl groups found on the surface of the cotton fibers ($Cell-OH$) act as nucleophilic groups and upon their deprotonation, in the presence of alkali solution, they are converted into cellulose anions which are even more nucleophilic ($Cell-O^-$). The reactive dye, with the effect of alkali solution and removal of the sulfonic group, is converted into the highly reactive vinylsulfone. The sulfonic group causes electron delocalization by activating the double bond toward nucleophilic attack. The cellulose anion reacts with the vinylsulfone to give the anionic intermediate which is stabilized by coordination. The addition reaction is completed by protonation and finally the permanent formation of a covalent C–O bond between dye and fiber occurs [2]. Along with the dye-fiber bonding, the competing reaction of dye hydrolysis occurs in the bath. The hydrolyzed dye is slightly adsorbed to the fiber, but it is easily lost after reduction clearing.

It is calculated that approximately 55–60% of global dyestuff consumption concerns cotton fibers, since the essential simplicity of the dyeing process makes them attractive. However, the use of these dyes causes certain problems, including the use of high electrolyte concentrations, in order to enhance, if possible, their exhaustion in the dyebath [1–5]. Despite electrolytes, the exhaustion of the dyebaths are still limited and the discharge of colored effluents leads

to pollution problems [6]. For a compound to be used as a reaction dye, the rate of hydrolysis of the fiber-dye bonds must be negligible compared to the rate of retention of the dye on the fiber [6].

Apart from exhaustion, fixation parameter is crucial for their dyeing. Fixation rate is 50–70% for monofunctional and 70–85% for bifunctional reactive dyes even under optimized dyeing conditions [11]. Development of bifunctional dyes provided prominent improvements in the fixation efficiency. The introduction of commercial low-salt reactive dyes and dyes fixable at neutral pH led to reductions of the use of inorganic chemicals [12]. The most common dye auxiliaries applied are inorganic salts, organic compounds, various acids, water and surfactants [13]. NaCl and $NaCO_3$ promote the cationic charge on the cellulose and facilitate the movement of the dye molecules toward the fibers as well as their fixation. Additionally, the substantivity of a dye refers to the process during which dye molecules are attracted by physical forces at the molecular level to the textile. High fixation and substantivity lead to better dye utilization and results in less hydrolyzed dye and less effluent waste [6].

The effect of metals like Al, Fe, Cu, Ni, Na, K, Co, complexed on dye molecules or present as auxiliaries in dyebaths, is also important for industrial water treatments [13]. On the other hand, the migration index defines the migration properties of an individual dye applied by a certain process, with the ideal migration index rising to 100. The process of dyeing is based on both routes of adsorption and diffusion of the molecules in the fiber. The movement of the dye from one part of the fiber to another (migration) or the formation of chemical bonds that hold

the dye in the fiber (fixation) are relevant to migration index [14].

The application of filtration, and ultrafiltration specifically, to dyestuffs aims to yield ultra-pure dyes with higher color performance, brighter hues and higher solubility [8, 9]. Ultrafiltration (UF) is performed by membranes with a pore diameter of 2–50 nm and is motivated by the pressure difference on both sides of the membrane. The ideal membrane is required to have high porosity and a narrow pore size distribution. Therefore, UF is a physical process employing interactions, not a chemical one. Compounds with a MW < 1000 permeate the membrane leaving the large molecules concentrated on the side of feedstock of the membrane. Ultrafiltration, apart from pretreatment, is also used in the post-treatment of dyebath wastes [6]. In this way, water and auxiliaries (mainly NaCl) are saved, but the environment is also protected with the least deposition of harmful wastes in water resources. Regarding ultrafiltration membranes, materials such as polysulfone or polyamide are used.

The present piece of work describes the kinetic properties of dyeing on cotton substrate with the previously synthesized reactive dye RR_{Na}, before and after passing an ultrafiltration purification process. The properties of exhaustion, substantivity, fixation, migration index, colorimetric measurements as well as the effect of metals such as Fe, Cu and Co on dyeing, were studied.

2 Experimental

2.1 Materials

The previously synthesized novel reactive dye (RR_{Na}) with elemental formula C₂₀H₁₉N₂O₁₅S₄Na₃ and MW = 724 (Fig. 1) was used before and after ultrafiltration [9]. Commercially, available lightweight (140 g/m²) knitted cotton fabric was kindly supplied by KYKE SA Hellas (Thessaloniki, Greece) and used throughout this work. Simple

chemicals like CH₃COOH, NaCl, Na₂CO₃, used as auxiliaries in dyeing, were obtained from Fluka Chemie AG, Switzerland.

Bleaching of the commercial fabric was estimated to be obligatory for the removal of impurities and the uniformity of white hue on the cotton surfaces to receive the dyestuff. A 30-min water reflux boiling took place for cotton fabrics in the presence of 5 g/L H₂O₂, 3 g/L Kahatex TE and 1 g/L Na₂CO₃. Bleached fabrics were removed, rinsed with cold water and left to dry before dyeing.

2.2 Dyeing Procedure

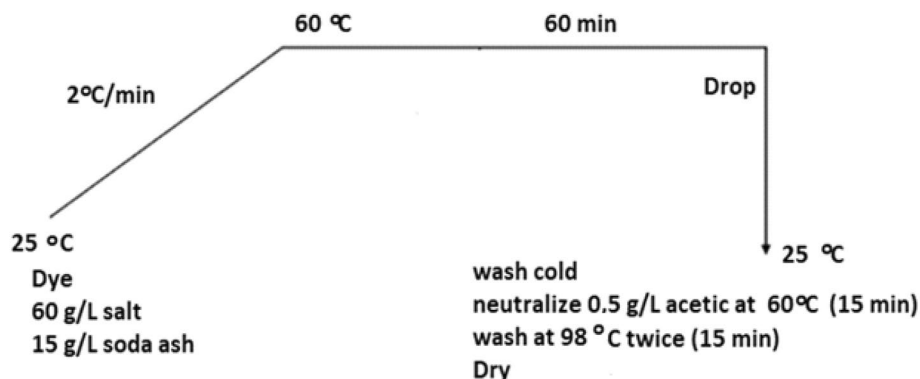
An exhaust dyeing process was applied for the dyeing of cotton with RR_{Na} reactive dye. The dyeing was performed in a Zeltex Vistacolor dyeing machine (Zeltex Inc., USA) with 2 g cotton fabric (of square shape 11.5 × 11.5 cm) and depth of dyeing 0.5, 1, 2, 4, 6, 8, 10% *o.w.f* (on the weight of fiber) in a liquor ratio 1:10. In Fig. 2, the dyeing process, steps, and conditions for the cotton fabrics is presented.

The half-time of dyeing, *i.e.*, time taken to reach 50% of exhaustion (*t*₅₀) after the addition of alkali was determined, for 2 g of cotton fabric at depth of 1 and 2% *o.w.f* in a liquor ratio 1:10 (Fig. 2). 8 dye-tubes were prepared, including the dye, using 60 g/L NaCl, 15 g/L Na₂CO₃ at 60 °C dyebaths. The tubes were removed after 3, 6, 9, 12, 15 min, then the dyed samples were removed and immersed in 1 L of cold water for 15 min to prevent further fixation. All the samples were then washed at 98 °C with 20 mL water for 15 min and left to dry. The shades provided to cotton fabrics by RR_{Na} were in red–purple palette.

2.3 UV–Vis Spectrometry

Absorption spectra were obtained with a Shimadzu UV-1800 spectrophotometer equipped with UVProbe ver. 2.61 software (Shimadzu, Japan). The scan range was 700–400 nm with slit width of 1 nm and peak threshold 0.001. The Starna glass cuvettes (type 1, material G, Hainault Industrial Estate,

Fig. 2 Cotton dyeing process in the present study



England) had a 10 mm path length. The baseline was taken with deionized water as solvent.

2.4 Color Measurement

Color measurements were performed using a Macbeth CE 3000 spectrophotometer under D65 illumination, with 10° standard observer plus UV-component included and specular component included. The samples were folded twice and four measurements were performed each time [15, 16]. All colorimetric indexes were recorded for all dyed fabrics. Dyed cotton fabrics were tested for their color strength. The color strength (K/S) of the dyed fabrics was evaluated by a light reflectance technique at the maximum absorption (usually $\lambda_{\max} = 560$ nm) using the Kubelka–Munk equation (Eq. (1)):

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

where R is the reflectance of the dyed fabrics at the maximum absorption wavelength, S is the scattering coefficient, and K is the absorption coefficient of the dyed fabrics. These K/S values represent the dyeability of the dyed samples. Reproducibility was checked by taking four measurements and calculating the variation in percentage reflectance values over the range 400–800 nm. It was found to be satisfactory in all cases.

2.5 Determination of Dye Exhaustion

Exhaustion values were calculated by measuring spectrophotometrically the absorbance of the samples at its $\lambda_{\max} = 570$ nm before and after dyeing. The percentage dye exhaustion ($E\%$) values were determined by using Eq. (2):

$$E\% = \frac{C_0 - C_f}{C_0} \times 100, \quad (2)$$

where the dye concentration before adding fabric into the dyebath (C_0) and after dyeing (C_f) according to calibration curve are implicated.

2.6 Measurement of Dye Fixation

Pieces of 2 g cotton fabrics were dyed at depth of shade at 1% o.w.f in a liquor 1:10 (as described in 2.2) at 60 °C for 60 min. The samples were then washed with cold water, neutralized at 60 °C with 0.5 g/L CH_3COOH , and finally washed at 98 °C twice for 15 min. The K/S values were measured before washing and after washing [17]. The dye fixation ($F\%$) was evaluated using Eq. (3):

$$F\% = \frac{\left(\frac{K}{S}\right)_{\text{afterwashing}}}{\left(\frac{K}{S}\right)_{\text{beforewashing}}} \times 100. \quad (3)$$

2.7 Measurement of Substantivity

Pieces of 2 g cotton fabrics were dyed with depth of dyeing at 1% o.w.f using 1:10 liquor ratio (as described in 2.2) at 60 °C for 60 min. The substantivity ($S\%$) was calculated as shown in Eq. (4):

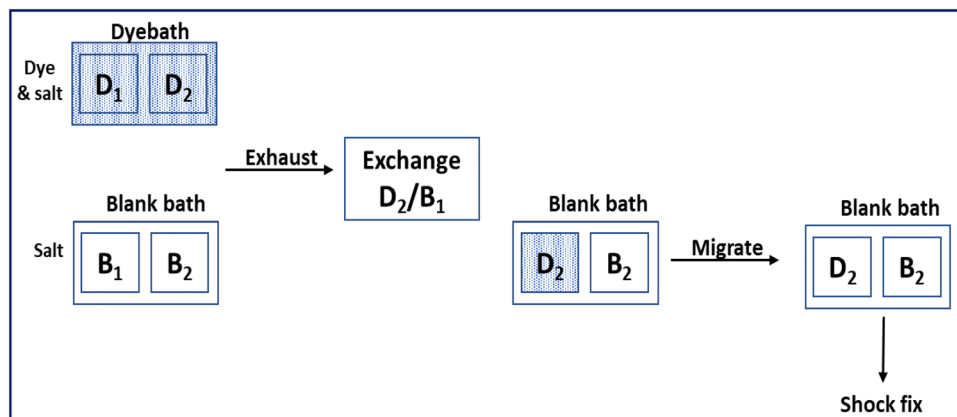
$$S\% = \frac{A_{in} - A_{fin}}{A_{in}} \times 100, \quad (4)$$

where A_{in} and A_{fin} the initial and final absorbance of the dyebath samples in UV absorption recordings, respectively.

2.8 Migration Test

2 pieces of cotton of 2 g each, named D_1 and D_2 , were dyed with depth of dyeing at 1% o.w.f in a liquor ratio of 1:10, with 60 g/L NaCl, at 60 °C, for 20 min (see Tube Dyebath 1, Fig. 3). 2 pieces of cotton 2 g each, named B_1

Fig. 3 Migration test process [18]



and B_2 , were dyed at depth of dyeing of 1% *o.w.f* in a liquor ratio 1:10, with 60 g/L salt, at 60 °C, for 20 min (see Tube Blankbath 2, Fig. 3). After 20 min at 60 °C, both tubes were removed from dyebath. D_2 was taken from tube 1, squeezed, and placed in tube Blank bath 2, while throwing away sample B_2 . Dyeing was continued at 60 °C for 40 min for samples $B_1 + D_2$ in blank bath 2. Later, samples were removed, squeezed, and put separately in shock fixing baths: B_1 sample in shock fix bath consisting of 100 g/L NaCl, 20 g/L Na_2CO_3 , liquor ratio 10:1, $T = 60$ °C, $t = 60$ min. D_2 sample in shock fix bath consisting of 100 g/L NaCl, 20 g/L Na_2CO_3 , liquor ratio 10:1, $T = 60$ °C, $t = 60$ min. Both samples B_1 and D_2 were then rinsed in cold water and dried in open air. The K/S values were measured for B_1 and D_2 samples, as described in 2.4. The migration index ($MI\%$) was evaluated using Eq. (5) [18]:

$$MI\% = \frac{\left(\frac{K}{S}\right)_{B_1}}{\left(\frac{K}{S}\right)_{D_2}} \times 100. \quad (5)$$

2.9 Effect of Metal Cations

Four samples (2 g each) were dyed with depth of dyeing 2% *o.w.f* in a liquor ratio 1:10 (as described in 2.2). 4 dye pots were then prepared: one with the dye, the fabric and bath of 60 g/L NaCl, 15 g/L Na_2CO_3 used as the control pot. The other three pots in the presence of the metal salts, while all dyeings were carried out at 60 °C for 60 min. The metal salts used were 0.5% *o.w.f*. $\text{Fe}_2(\text{SO}_4)_3$, 0.2% *o.w.f*. CuSO_4 , and 0.2% *o.w.f*. CoSO_4 (Fluka Chemie AG, Switzerland). The samples were finally washed with cold water, neutralized at 60 °C with 0.5 g/L CH_3COOH for 15 min, washed at 98 °C twice (15 min), and left to dry. The K/S values of all dyed samples were measured as described in 2.4.

2.10 Ultrafiltration Process

A laboratory ultrafiltration unit equipped with tubular membrane supplied by PCI Membranes (UK) was used throughout this work. The membrane used for the ultrafiltration process was the polyamide type AFC 40. Aqueous dye solutions of 0.5% w/v RR_{Na} for that case were prepared. An initial volume of 3 L of the dye solution was passed through the ultrafiltration unit at constant temperature of 40–50 °C. 6 L of water at 40–50 °C was added into the unit to maintain the initial volume of 3 L constant keeping diafiltration rate at 1:2 volume. The flow rate was 40–70 L/h/m² and the unit was

operating at constant 18 bar pressure for the whole duration. After the completion of diafiltration a concentration step was performed reducing the dye volume from 3 L to 1.5 L [10]. The dyestuff gathered after drying the UF product is named UF- RR_{Na} . All dyeings and measurements described in previous paragraphs were performed with both RR_{Na} and UF- RR_{Na} dyestuffs.

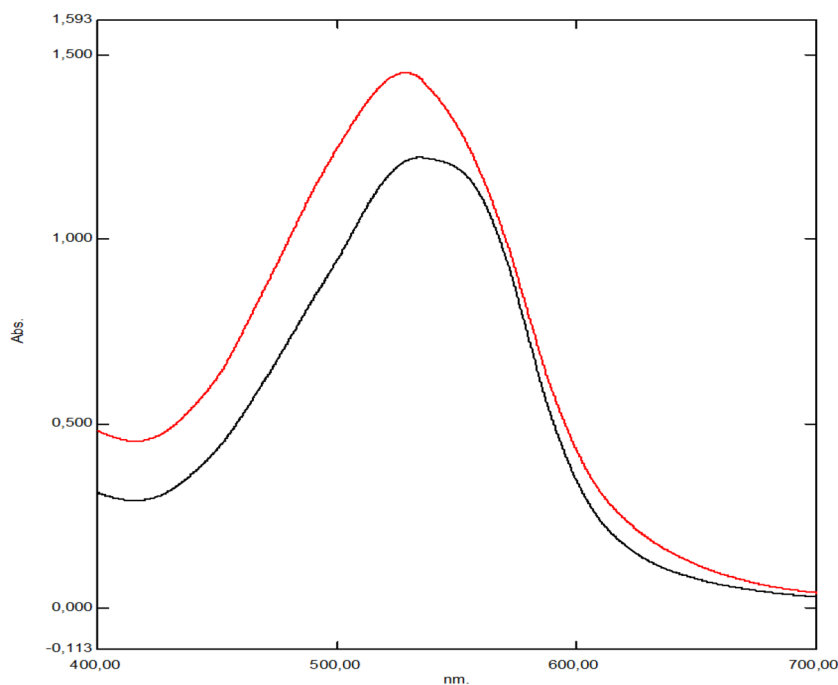
3 Results and Discussion

Figure 4 shows the UV–Vis spectra of the reactive dye before and after ultrafiltration; as can be seen RR_{Na} shows an absorbance of 1.22 at $\lambda_{\text{max}} = 531$ nm and the UF- RR_{Na} of 1.45 at $\lambda_{\text{max}} = 529$ nm. While the λ_{max} setback between the two is negligible, the higher absorbance (about 20%) obtained for the UF-dye is attributed to this very purification/concentration process which resulted in a more concentrated dye, by the elimination of inorganic salts and other by-products of low MW. Analogous results were obtained for all dyestuffs treated with UF process, verifying the upgrading of the dye performance [19, 20].

Figure 5a shows that $E\%$ values calculated are decreasing with increasing of depth of dyeing for both RR_{Na} and UF- RR_{Na} dyes. This decrease in $E\%$ at higher depths of shade can be explained in terms of the fact that at lower % *o.w.f*. more dye can be absorbed by the reactive cotton dye-sites, leading to more dye retained on cotton. Likewise, as the concentration of the dye in the dyebath is increasing, the percentage of dye molecules absorbed by the cotton reactive dye-sites is decreasing. That decrease is analogous for both RR_{Na} and UF- RR_{Na} dyes, while the UF- RR_{Na} dye shows in general lower $E\%$ values in all cases. Thus, the purification process resulted in a much stronger dye [12]. Figure 5b shows the effect of dyeing time on exhaustion of dyes (kinetic of exhaustion) on the fiber, regarding the experiment of 1% *o.w.f*. As shown, $E\%$ values increase with dyeing time for both dyes, as anticipated. Figure 5b also shows that exhaustion of both RR_{Na} and UF- RR_{Na} dyes occurs mostly within the first 30 min of dyeing. The time at which 50% color retention occurred is 8.6 min for the UF- RR_{Na} dye and 9.0 min for the RR_{Na} dye. The visual evaluation of the cotton fabrics dyed, may be seen in Fig. 5c, where the rise of the % *o.w.f*. led to deeper purple hues on cotton for the original RR_{Na} dye.

Figure 6a shows the dye uptake for both RR_{Na} and UF- RR_{Na} dyes in terms of K/S values for the dyed samples. In all depths of shade the UF- RR_{Na} dye shows higher K/S values compared to the untreated RR_{Na} dye, *i.e.* stronger results, a behavior explained by the UF process resulting in a purer dye with higher tinctorial strength [12]. Figure 6b shows the effect of dyeing time in terms of the K/S values obtained for both dyestuffs. The same pattern is observed, where the

Fig. 4 UV–Vis spectra of RR_{Na} (black line) and UF-RR_{Na} (red line) dyestuffs



K/S values of the UF-RR_{Na} dye are higher than those of the RR_{Na} and secondly, most of the dye has been adsorbed after 30 min of dyeing. Kinetic observation of the K/S changes was performed on a 1% *o.w.f.* dyeing experiment so that the changes are more evident. Similar trends would be anticipated in higher % *o.w.f.* of dyeings.

In Table 1, the colorimetric data of the samples dyed with the RR_{Na} dye before and after UF treatment are given. Defined by CIE, color may be expressed by three values/coordinates: L^* for lightness, axis black-white, a^* for red-green axis, and b^* for blue-yellow axis, as perceived by human eye. Moreover, C^* represents chroma and h^0 is the hue angle. Those values entirely retrieved by reflectance spectrophotometer are included in Table 1. Table 1 shows that K/S values for both dyes are increasing with increasing depth of shade. The K/S values of all dyed samples with UF-RR_{Na} dye are higher than the corresponding K/S values obtained with RR_{Na} dye, showing stronger dyestuff. UF process resulted in a purer dye with higher coloristic strength due to the displacement of inorganic salt and other impurities, which are present in dye because of its synthesis pathway (especially in industrial terms), into the permeate solution during UF process [10]. The purity of UF-RR_{Na} can be related to dyestuffs' solubility too, as shown in previous work. Higher solubilities (RR_{Na}: 150 g/L while UF-RR_{Na}: 260 g/L at 95/25 °C) allow the use of UF-dyes in the production of highly stable, high coloristic value formulations [8]. The reflectance values, $R\%$, are decreasing at higher application strengths indicating that more dye has been absorbed at high depths of shade. This decrease in $R\%$ is in line with the K/S increase at higher depths of shade. The other colorimetric parameters L^* , a^* , b^* , C^* , h^0 are similar for both RR_{Na}

and UF-RR_{Na} dyes indicating that there is little visible hue changes among these two dyes (Fig. 5c).

Figure 7 shows the effect of dyeing time on the fixation (kinetics of fixation) for a specific dyeing experiment. As can be seen $F\%$ values increased with dyeing time, which can be explained in terms of the reaction between cotton –OH groups and the vinylsulfone reactive group present in the dye, occurring at higher level and at prolonged dyeing times. As it can also be seen from Fig. 7, the RR_{Na} and UF-RR_{Na} reactive dyes show similar fixation pattern, with the UF-RR_{Na} dye showing slightly higher fixation rates. The final $F\%$ of reactive dyes synthesized, about 70–80% is considered very good, able to be compared with the fixation rates of bifunctional dyes [1, 21–23]. During UF, no particle size alteration exists for the dyestuff itself. The structure of the dye and its MW is certain (see 2.1). The membrane pore size secures the elimination of by-products that are produced during synthesis and would affect the dyeing performance. On the other hand, the extent of dye-fiber reaction is very important in the textile industry since higher fixation rates result in less hydrolyzed reactive dye in the effluents [24]. The extent of dye-fiber reaction and the ultimate discharge of unfixed dye vary widely, based on the type of reactive group and the dyeing technology used. The use of two reactive groups on a dye molecule results in higher fixation efficiencies [22]. A high percentage fixation leads to better dye utilization and results in less hydrolyzed dye and less effluent waste. Studies have shown that 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 [4, 5]. Removal of unfixed dye at the washing stages is often not easy due

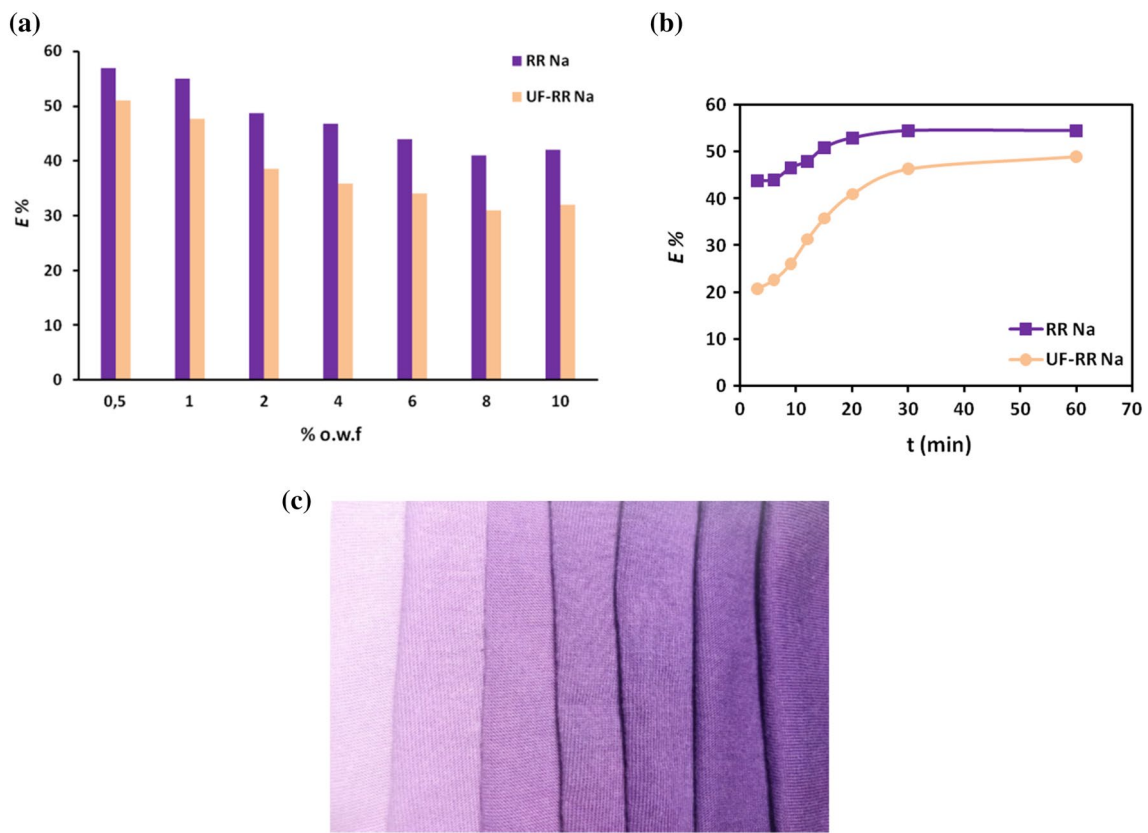


Fig. 5 **a** Effect of depth of shades on the exhaustion of the dyed cotton fabrics and **b** effect of dyeing time on the exhaustion of 1% *o.w.f.* dyed cotton fabrics, for both dyestuffs. **c** Visual result of cotton fabrics

dyed with the RR_{Na} dyeing in 0.5, 1, 2, 4, 6, 8, 10% *o.w.f.* correspondingly, under the same conditions

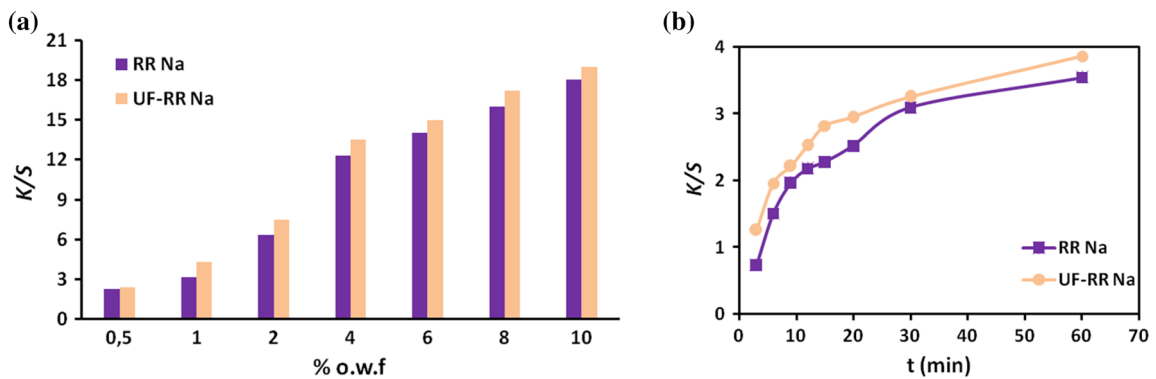


Fig. 6 **a** Effect of depth of shades on the color strength for all dyed fabrics and **b** effect of dyeing time on the color strength of dyed cotton fabrics at 1% *o.w.f.*, with both dyestuffs

to the higher substantivity built into such dyes [2]. The low fixation of dyes causes environmental issue since dyes lost in dyeing process contaminate the water sheds and are toxic to living organisms.

Next, the influence of alkali environment is studied. Figure 8a shows the substantivity of both RR_{Na} and UF-RR_{Na} dyes on the dyeing of cotton samples. As can be seen, the 5%

value of the UF-RR_{Na} dye is relatively higher (43%) compared to the substantivity of the RR_{Na} dye (34%). It demonstrates that the UF process resulted in a purer reactive dye. It has to be noted that the substantivity is measured in the absence of alkali which explains the relatively low exhaustion values obtained. Reactive dyes with high substantivity have been considered not to be desirable because the

Table 1 Colorimetric data L^* , a^* , b^* , C^* , h° and K/S values of the cotton samples with the reactive dyes at $\lambda_{\max} = 560$ nm

	<i>o.w.f</i>	<i>R%</i>	<i>K/S</i>	L^*	a^*	b^*	C^*	h°
RR_{Na}	0.5%	14.8	2.3	50.4	14.5	−18.4	23.4	308.1
	1%	9.5	3.1	42.4	16.8	−20.0	26.1	310.0
	2%	7.1	6.0	37.6	13.8	−22.4	26.3	301.0
	4%	3.7	12.3	28.0	16.5	−20.5	26.3	308.9
	6%	3.2	14.4	24.5	15.4	−19.9	25.2	307.7
	8%	2.8	16.3	24.5	16.0	−20.9	26.3	307.3
	10%	2.6	18.1	22.9	15.7	−19.4	25.0	309.0
UF-RR_{Na}	0.5%	15.0	2.4	50.7	12.9	−19.5	23.4	303.5
	1%	12.1	4.3	46.3	15.1	−19.2	24.4	308.2
	2%	6.8	6.3	36.4	16.2	−20.5	26.2	308.3
	4%	6.4	13.5	36.1	15.2	−21.5	26.3	305.2
	6%	5.8	15.0	34.8	15.8	−21.6	26.0	306.5
	8%	3.4	17.2	32.6	15.4	−22.0	25.4	306.8
	10%	3.1	19.1	32.0	14.8	−21.7	25.8	308.9

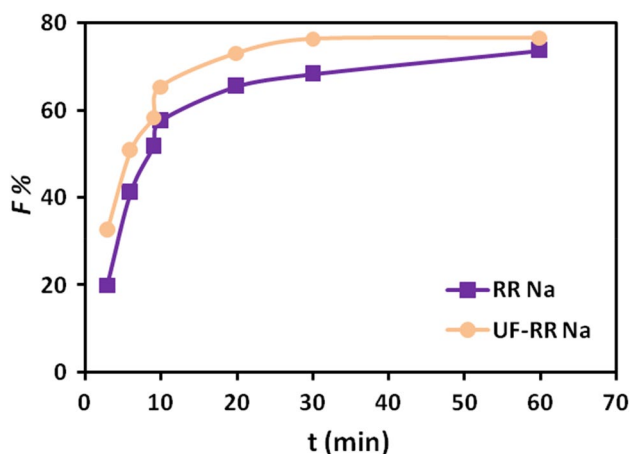


Fig. 7 Effect of dyeing time on the $F\%$ values regarding RR_{Na} and UF-RR_{Na} dyeings at 1% *o.w.f*

unreacted dye is difficult to remove by washing off, after the dyeing process and such dyes have too low diffusion coefficients [25]. Figure 8a shows the effect of alkali, Na₂CO₃, on the $E\%$ of cotton samples dyed with RR_{Na} and UF-RR_{Na} too. As illustrated, the $E\%$ is higher for the UF reactive dye than the originally synthesized dye, because UF process eliminated dye impurities, resulting in a more “active” dye. Color fastness or wash fastness results will be helpful to support the $E\%$ conclusions too, when available. The $E\%$ calculations took in consideration the dyeing experiments including caustic soda. It is known that alkali is necessary for covalent bond fixation of a reactive dye on the cotton fiber [26]. Under alkaline conditions reactive dyes react with hydroxyl groups of cellulose, mostly by nucleophilic substitution or addition, to form the covalent bonds. Thus, there is no wonder that the alkali results are reported much higher than the $F\%$ values in lower pHs.

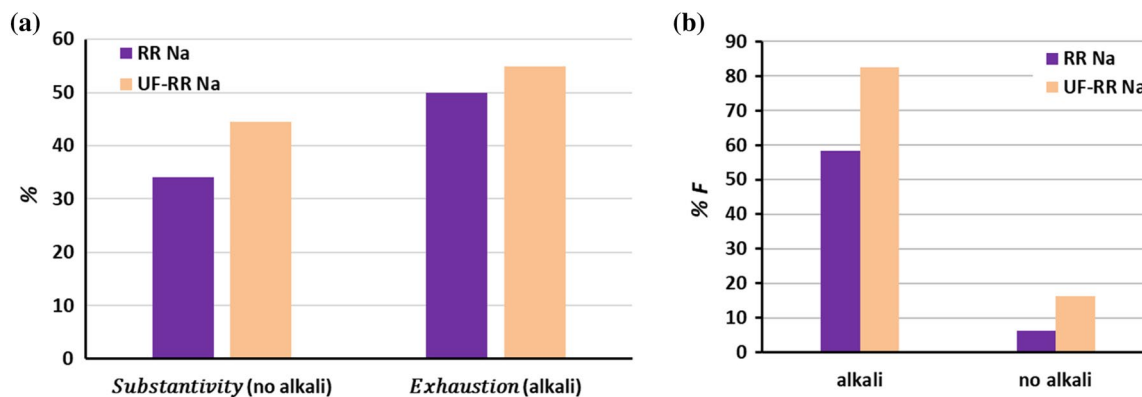


Fig. 8 **a** Substantivity and exhaustion percentages and **b** Fixation percentages of RR_{Na} and UF-RR_{Na} dyeings in the absence or presence of Na₂CO₃

Figure 9 shows the migration index for both RR_{Na} and UF-RR_{Na} dyes. Migration of the dye is defined as the ability of the absorbed dye to move from a heavily absorbed area of the substrate to a less absorbed area resulting in more level dyeings. The migration process comprises of adsorption of the dye on to the fiber surface, migration through the dye liquor, and re-adsorption onto the fiber with consequent diffusion of the dye to the interior of the fiber. Migration itself is heavily influenced by the dyeing temperature. The migration index defines the migration properties of an individual dye reflecting its potency in producing dyeings. Figure 9 shows that both reactive dyes show a high migration index with RR_{Na} dye showing higher MI%. The difference in the MI between the two states of the dye can be attributed to the higher mobility of the RR_{Na} dye compared to the UF-RR_{Na} one. The UF process has resulted in a purer reactive dye with higher fixation rates and greater covalent bond formation and thus less migration. The migration of a dye depends on the chemistry of the dye, molecular structure, physical chemistry, and stereochemistry are all important. External factors such as concentration of the dye added to the dyebath, time, temperature, liquor ratio, rate of liquor circulation, and fabric construction also play a key-role [18].

Finally, Table 2 shows the colorimetric data of the dyeings obtained for both RR_{Na} and UF-RR_{Na} dyes in the

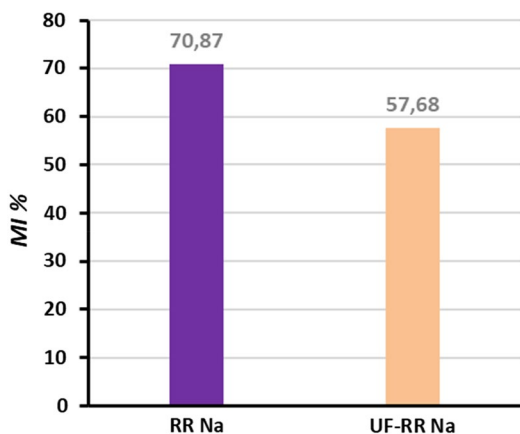


Fig. 9 Migration index on cotton samples dyed with RR_{Na} and UF-RR_{Na} under the same conditions

presence of metal salts. All sulfate reagents applied were hydrolyzed so that the ions Fe³⁺, Cu²⁺, Co²⁺ were available in dyebaths. The presence of Fe³⁺ in the dyebath resulted in slightly lighter dyeings, with higher R% and lower K/S values for both RR_{Na} and UF-RR_{Na} dyes. However, the hues in the presence of Fe³⁺ are much “redder” as can be understood from the higher a* values. The presence of Cu²⁺ and Co²⁺ metal ions had a detrimental effect in dyeing showing color shift in λ_{max} and big reduction in the dye uptake as can be seen from the lower K/S values of both dyes. Additionally, the color coordinates a* and b* have been greatly reduced, resulting in “greener” and “bluer” dyeings.

Additionally, Fig. 10 demonstrates the effect of metal salts present in the dyeing compared to blank dyeing for UF-RR_{Na} dye, which is anyway stronger. The effect of metal cations on the color strength is illustrated. The big drop in dye uptake in terms of K/S and the very big impact on the shade obtained can be seen (especially for the case of CuSO₄); the conclusion is in line with the colorimetric data obtained in Table 2. It is found in literature that i) the addition of either NaCl or Na₂SO₄ to a reactive dye dyebath utilizes the inherent propensity of the dyes to aggregate in solution *via* coplanar association, and that ii) such electrolyte-induced dye aggregation reduces the solubility of the dye in the dyebath [27]. The case seems similar herein too. Considering that knitted cotton fabric is commonly used as sheets or undergarments, it would be important to detect whether there is any metal ion residue on dyed fabric. Yet, the image demonstrates unsuccessful dyeings in these cases to go any further.

4 Conclusions

Crucial dyeing properties of a novel reactive dye with one vinylsulfone group, such as exhaustion, substantivity, fixation, migration index as well as the effect of metals in the dyeing dyebath were studied, before and after ultrafiltration process took place for the dyestuff. Regarding the kinetics of the dyeings, it is concluded that the change in E% values is small after 30 min, with the values close for two dyestuffs (always greater for UF-dye). The coloring strength (K/S) increases with time and the highest is observed for UF-dye. Substantivity and Fixation percentages show greater affinity of UF-dyes with cotton substrates under corresponding

Fig. 10 Dyed cotton fabrics with UF-RR_{Na} and metal sulfates: a Blank b Fe³⁺ c Cu²⁺ d Co²⁺

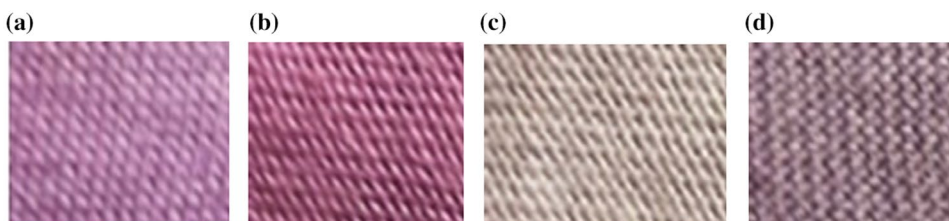


Table 2 Colorimetric data L^* , a^* , b^* , C^* , h° and K/S values of the cotton samples dyed with both reactive dyes at 2% o.w.f

	Sample	λ_{\max}	$R\%$	K/S	L^*	a^*	b^*	C^*	h°
RR_{Na}	Blank	560	7.1	6.0	37.6	13.8	-22.4	26.3	301.0
	Fe ³⁺	560	7.8	5.4	39.8	17.5	-18.7	25.6	313.0
	Cu ²⁺	490	17.4	1.9	52.7	5.3	-12.5	13.6	293.2
	Co ²⁺	510	14.8	2.4	48.9	8.1	-14.4	16.6	299.5
UF-RR_{Na}	Blank	560	6.8	6.3	36.4	16.2	-20.5	26.2	308.3
	Fe ³⁺	560	8.2	5.0	41.1	19.4	-18.9	27.1	315.6
	Cu ²⁺	490	17.5	1.9	52.9	5.1	-12.3	13.4	292.7
	Co ²⁺	510	11.6	3.3	44.8	8.8	-16.2	18.5	298.5

dyeing conditions. All the observations are attributed to UF process having resulted in a much purer dye by the elimination of inorganic salts and also dye by-products. Finally, the migration index appeared higher in the original dye compared to the UF-one. Concerning the effect of metals ions (Fe³⁺, Cu²⁺, Co²⁺) on the dyeing process, it was observed that Fe³⁺ slightly affects the K/S values, while Cu²⁺ and Co²⁺ drastically deteriorate the coloring ability and even cause differences in shade (a^* , b^*) for both dyes. UF process employs physical interactions for purification; this publication proves that the very same colorant performs better in dyeing, in all values calculated, without any chemical alterations, just after being ultrafiltrated.

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Declarations

Conflict of interest The authors declare no conflict of interests from this study and that no funding support was received for realizing it.

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