Sodium Edate and Sodium Citrate as an Exhausting and Fixing Agents for Dyeing Cotton Fabric with Reactive Dyes and Reuse of Dyeing Effluent

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Abstract: The present paper is aimed at studying the possibility of using organic salts (tetrasodium edate (SE) and trisodium citrate (SC)) in dyeing of cotton fabrics with two reactive dyes, namely C.I. Reactive Red 120 (RR120) and C.I. Reactive Black 5 (RB5) in place of inorganic salt (sodium sulphate (SS) and in the absence of alkali. For this purpose, dyeing of cotton fabrics with reactive dyes using sodium edate, sodium citrate and sodium sulphate is investigated and the results obtained are compared. Factors affecting dyeability such as the concentration of sodium edate, sodium citrate and sodium sulphate, time, pH, temperature, liquor ratio and dye concentration are investigated. The dyed fabrics are evaluated with respect to the dye exhaustion and fixation, and the fastness properties. Fastness to washing and light of samples that have been dyed with reactive dyes are generally higher using SE and SC compared with SS conventional method. The fastness improvement may be as a result of better dye penetration and thus good covalent fixation with cotton fabrics. The overall results suggest that sodium edate and sodium citrate offer the potential as an exhausting and fixing agent for reactive dyeing of cotton.

Moreover, the reuse of the dyebath and the chemicals those remain after the original dyeing process and after pre-treatment using advanced oxidation process are also studied. Such recycling of exhausted dyebaths further offers the potential of lowering costs through the reduction of the amounts of water, chemicals and energy consumed. [Journal of American Science. 2010; 6(10):109-127]. (ISSN: 1545-1003).

Keywords: Cotton fabric dyeing; Bi-functional reactive dyes; Sodium edate; Sodium citrate; Water reuse; Fastness.

1. Introduction

Dyeing is usually a textile wet process to impart color to textile materials. Textile wet finishing processes, especially exhaustion methods, have higher rates of energy consumption due to both higher fluid temperatures and volume [1].

Moreover, the increased awareness of environmental issues has been driven much interest in eco-friendly textile wet processing techniques. The main challenge that textile industries faces is to modify production at a competitive price by using safe dyes and chemicals as well as by reducing treatment costs [2,3].

Exhaustive dyeing of cotton fabric with direct, vat, sulphur, and, especially, reactive dyes requires the presence of electrolytes (NaCl or Na_2SO_4), which suppresses negative charge build-up at the fibre surface and promotes increased dye-uptake [2]. The quantities of electrolyte present can vary up to 100 g/l depending on the depth of colour required, the structure of the dyes or the dyeing recipe [4].

Reactive dyeing of cotton fabrics in addition to its consumption of high concentrations of potentially toxic non-biodegradable salt relies on an elevated pH (commonly over 10.5) for covalent fixation of the dyes on cotton. Under alkaline conditions reactive dyes react with hydroxyl groups of cellulose, mostly by neucleophilic substitution or addition, to form the covalent bonds. These strong bonds would be expected to lead to excellent wash fastness properties. However, the dyes can also react with hydroxyl groups of water present so that they are no longer able to react with cellulose. Thus, low reactive dye fixation and the use of high salt concentration would lead to environmental problems [2].

Progress has been made in reducing salt requirements for some newer reactive dyes, but salt concentrations are still too high [5]. Recently, reduced salt by the replacement of nonbiodegradable inorganic salt (sodium chloride or sodium sulphate) with biodegradable organic one (tetrasodium edate or trisodium citrate) in the exhaustive dyeing of cotton

fabric using reactive, direct and solubilised vat dyes has been reported [6]. Also, in another study [2], the use of polycarboxylic acid salts have proved the most effective class evaluated, promoting higher exhaustion and fixation of reactive dyes on cotton fabric than sodium chloride.

Moreover, textiles can be dyed with almost any color to achieve a variety of aesthetic and functional purposes. But by using currently available techniques, the dyeing process often has detrimental environmental impacts. The major use of energy in the dye process involves heating of water for the dyebath in order to facilitate a quick dyeing process and better dye penetration into textile materials. The less water used, the lower the heat energy required [7]. Even though it appears to be in plentiful supply on the earth's surface, water is a rare and precious commodity, and only an infinitesimal part of the earth's water reserves (approximately 0.03%) constitutes the water resource which is available for human activities. The growth of the world's population and industry has given rise to a constantly growing demand for water in proportion to the supply available, which remains constant [8].

The main objective of this research is to explore the possibilities to reduce the colorants and chemical auxiliaries in the fabric dyeing effluents of cotton fabric dyeing by two reactive dyes (C.I. Reactive Red 120 (RR120) and C.I. Reactive Black 5 (RB5)) by: (1) The improvement of the dye exhaustion onto the target fabrics with optimized dyeing conditions; (2) Replacement of non biodegradable inorganic salt (sodium sulphate (SS)) with biodegradable organic salts (tretrasodiumedate (SE) and trisodiumcitrate (SC)). (3) Reuse of the dye bath and the chemicals that remain after the original dyeing process and after pre-treatment using advanced oxidation process. Such recycling of exhausted dyebaths further offers the potential of lowering costs through the reduction of the amounts of water, chemicals and energy consumed.

2. Experimental
2.1. Materials
2.1.1. Cotton fabric

Mill desized, scoured and bleached cotton fabric (Poplin) is supplied by Misr Company for spinning and weaving, Mehala El-kubra, Egypt. Cotton fabric of the following specification is used for dyeing:

Table 1: Cotton fabric (Poplin) construction.

| Threads (cm)		Count		Width (cm)	Weight (g/m²)
Warp	fill	warp	fill		
109	72	40	40	160	120
(100% Cotton fabric Poplin)					

The cotton fabric is further treated with a solution containing 4 g/l of sodium carbonate and 3 g/l of non-ionic detergent (nastapon, from Clariant-Egypt) under the boiling condition for 4 hours, after which time it is thoroughly rinsed and air dried at room temperature [9].

Moisture content % = 0.050 / 1g cotton fabric.

2.1.2. Dyestuffs and chemicals

Two reactive dyes namely C.I. Reactive Red 120 (Procion HE3B, RR120) and C. I. Reactive Black 5 (Procion B, RB5)) are obtained from ICI (Imperical Chemical Industries Limited Dyestuffs Division Manchesester, England). The dyes are of commercial grade and are used as received (Scheme 1).

C.I. Reactive Red 120 (RR120):
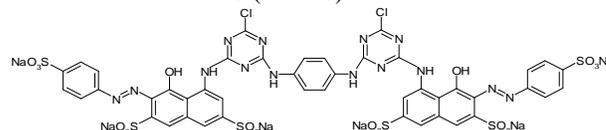
C.I. Reactive Black 5 (RB5):
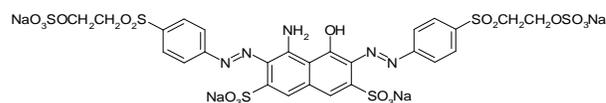
Scheme 1: Dyes profile: C.I. Reactive Red 120 (RR120) and C.I. Reactive Black 5 (RB5).

All other reagents, sodium carbonate, sodium sulphate (SS), tetrasodiumedate (SE), trisodiumcitrate (SC), detergent nastapon and dimethyl formamide are commonly used laboratory reagent grade.

2.2. Dyeing conditions

In a dyebath containing different concen - trations of SE or SC (0-60 g/)l and 1.03×10^{-4} M of C.I. Reactive Red 120 or C.I. Reactive Black 5 with liquor ratio 1:30, cotton fabric is added at 35 °C and the temperature is raised to 80 °C or 60 °C for RR120 and RB5 respectively, over 20 min. L.R 1:30 is used due to maximum depth of shade on fabric. After which time the dyeing is continued for 30 min. Then

20 g/l of sodium carbonate is added portion wise and the dyeing is maintained for further 45 min. For comparison, the same method of dyeing is applied using SS (50 g/l). The optimum amount of exhausting agent SE or SC that produces comparable results with that of SS is selected. To find out whether SE or SC can also act as fixing agent for reactive dyeing, cotton fabric is dyed as described above with the selected amount of SE or SC using variable amounts of sodium carbonate (0-25 g/l). For comparison, the same method of dyeing is applied using SS (50 g/l) in absence of sodium carbonate. To reveal the effect of adding SS (0-25 g/l) in a dyebath containing SE or SC (40 g/l and 25 g/l for SE and SC, respectively) on the dyeability of cotton fabric with reactive dyes (C.I. Reactive Red 120 and C.I. Reactive Black 5), dyeing of the fabric is followed as described above with the selected amount of SE or SC and without sodium carbonate.

2.3. Measurements and analyses

2.3.1. Dye exhaustion

The uptake of the reactive dye by cotton fabric is measured by sampling the dyebath before and after the dyeing. The concentration (M/l) of the dyebath is measured on JENWAY - 6300 UV - Visible spectrophotometer at λ_{max} of the dyes (λ_{max} = 512 nm and 597 nm for RR120 and RB5, respectively).

The dye exhaustion percentage on cotton fabric (E %) is calculated according to the following equation [10]:

$$E \% = ((C_1 - C_2) / C_1) \times 100 \qquad (1)$$

where C_1 and C_2 are the concentrations of dye in the dyebath before and after dyeing, respectively.

2.3.2. Dye fixation

The dye fixation ratio (F %), the percentage of the exhausted dye chemically bound on the cotton fabric, is measured by refluxing the dyed samples in 50% w/w aqueous DMF for 10min at L.R. 1:20 to extract the unfixed dye [11]. This procedure is repeated until the extract is clear. The concentration of the extract is measured spectrophotometerically at λ_{max} for each dye. The percentage dye fixation ratio (F%) and the fixation efficiency (FE%) are calculated using Eqs. (2) and (3), respectively [10, 12]:

$$F \% = ((C_1 - C_2 - C_3) / (C_1 - C_2)) \times 100 \quad (2)$$

$$FE\% = (E \times F) / 100 \qquad (3)$$

where C_3 is the amount of extracted dye after dyeing cotton.

2.4. Reuse of dye bath

2.4.1. Reuse of dye bath after dyeing

This experiment is carried out to determine the effect of reuse of dye bath on the dyeing results. After the fresh bath dyeing is finished, a certain amount (fixed percentage 10%, 25%, 45% and 65%) of the spent dye bath was reused. Addition of dye and chemicals is conducted to compensate for any consumption and loss in the previous dyeing cycle. pH adjustment was also necessary. The dye bath is reused in this way for a total of four times.

2.4.2. Reuse of dye bath after degradation

Wastewater from the initial dyeing contain RR120 and RB5 are diluted to one litter with bi-distilled water and then degradable with UV/Visible/H_2O_2 at optimum conditions of degradation ([RR120] = [RB5] = 1×10^{-4}M, [H_2O_2] = 25mM and pH 3.09 and 2.03 for RR120 and RB5 respectively, [13]). After degradation, H_2O_2 is removed; degradable wastewater is boiled for 2 hours and then cooled, adjusted to the initial volume with bi-distilled water then reused for dyeing treatments. To determine whether all H_2O_2 removed from the decolorized wastewater or no; titration of degradable wastewater against 0.01N $KMnO_4$ is carried out [14]. The dyeing process is carried out as the standard dyeing procedure. The dyed samples are thoroughly washed with hot water and then with cold water, followed by soaping in a nonionic detergent solution (2g/l) nastapon, washing and air-drying.

2.5. Fastness testing

The dyed samples are tested according to the American Association of Textile Chemists and Colorists (AATCC) standard methods [15].

2.5.1. Color fastness to washing

i) The composite specimens are sewed between two pieces of bleached cotton fabric and wool fabrics.

ii) The composite specimen is immersed into an aqueous solution containing 5g/l soap non-ionic detergent, at 60°C with L.R. 1:50, the samples are then removed, rinsed in hot and cold bi-distilled water.

iii) Evaluation of the wash fastness is established using the Grey- Scale for the change in

color for dyed samples and staining for bleached cotton fabric and wool fabrics [16].

2.5.2. Color fastness to light

   i) A specimen from the dyed fabric to be tested and standards are exposed simultaneously under specified amounts of color change.

   ii) The specimens are exposed to the light for about 20 hours.

   iii) Evaluation of results is carried out by using the Grey- Scale [16], if the final assessment is greater the preliminary assessment becomes significant with very high light fastness, standard (7) fades to a contrast equal to Grade (4) on the Grey-Scale. If the final assessment is slower the rating (6) to a contrast equal to Grade (3) indicates that the sample has changed very slightly.

3. Results and Discussion

   The primary objective of this work is to investigate the possibility of using sodium edate (SE) and sodium citrate (SC) as exhausting and fixing agent in the dyeing of cotton fabric with two reactive dyes (C.I. Reactive Red 120 (RR120) and C.I. Reactive Black 5 (RB5)) and the comparative results of the cotton fabric using sodium sulphate dyeing methods and in this regard the different factors that may affect this process are investigated.

3.1. Effect of sodium sulphate concentration

   The effect of SS concentration on the dyeability of cotton fabrics with RR120 and RB5 is conducted at different concentrations (0-60 g/l, dye concentration 1.03×10^{-4}M and L.R 1:30 for 2 hours dyeing time at pH 7.03 and temperatures 80 and 60 for RR120 and RB5, respectively). As shown in Figure 1, the exhaustion and fixation efficiency of dyed fabrics increase as the concentration of sodium sulphate (SS) increases up to 50 g/l after which a negligible increase in the exhaustion and fixation efficiency is observed. The use of 50 g/l of SS is considered as the standard exhausting amount necessary for RR120 and RB5 dyeing of cotton fabrics

   Cellulose carries a negative charge in pure water. As the dye is also anion hence negatively charged, there is electrostatic anion-anion repulsion between dye and cellulose. Therefore, by adding inert electrolyte such as Glauber′s salt (sodium sulphate (SS)) to the dyebath, this electrostatic barrier, known as the Donnan potential, can be largely suppressed, facilitating dye/fabric contact and allowing better interaction of the Yoshida and van der Waal, forces

and hence improving substantivity. The diffusion coefficient of the dye is therefore a function of both dye and electrolyte concentration [17].

   Moreover, the generally accepted model for dyeing of reactive dyes into cellulosic fabrics consists of two phases i.e. adsorption and diffusion phase and fixation phase. The extent to which reactive dyes are affected by the addition of electrolytes to the dyebath is known as salt sensitivity. The addition of SS increases the rate of strike of the dye; when cellulose is immersed in a solution of a reactive dye it absorbs dye from the solution until equilibrium is attained, and at this stage most of the dye, is taken up by the fabric [18].

   The results in Figure 1, support this statement, in that (*E%*) and (*FE%*) of the dyeing increase with increasing concentration of the salt applied. The exhaustion value of reactive dyes is a linear function of salt concentrations particularly at lower salt concentrations within the cellulose in the presence of a fixed amount of added dyes, although the slope decreases with increasing salt concentration. It is considered that the initial rapid rise is due to the response of dye to the lowering of electrical potential barrier to diffusion as the concentration of electrolyte increases.

3.2. Effect of adding tetrasodiumedate and trisodiumcitrate

   Reduced salt and reduce environmental pollution by the replacement of non biodegradable inorganic salt (SS), with biodegradable organic salts (tetrasodiumedate (SE) or trisodiumcitrate (SC)) in exhaustive dyeing of cotton fabric using the two reactive dyes is reported in the present work, the exhaustion behavior of this organic salts are compared with inorganic salt (SS)[2, 19].

   Moreover, it is anticipated from the structure of SE and SC that this compounds in addition to their confirmed viability as exhausting and fixing agent in reactive dyeing of cotton fabric, it may have the feature of being a mild organic base with a capacity of buffering action in the dyebath [2, 10].

3.2.1. Effect of adding different concentrations of SE

   Figure 2 shows the effect of SE concentrations on the dyeability of cotton fabrics with RR120 and RB5 reactive dyes. Dyeing conducted at different concentrations of SE ranges from 0 to 60g/l with initial dye concentration 1.03×10^{-4}M and L.R. 1:30 for 2 hours dyeing time at pH 9.52 and temperatures 80 and 60°C for RR120 and RB5 respectively.
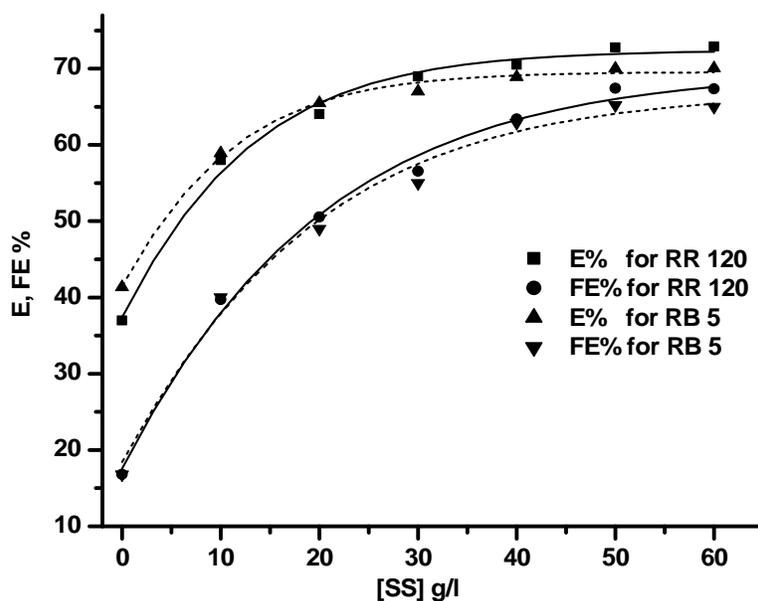
Figure 1: Effect of different SS concentrations on the percentage exhaustion (E %) and fixation efficiency (FE %) of RR120 (—) and RB5 (…..) on cotton fabric with initial dye concentration 1.03×10^{-4}M, L.R.1:30 and pH 7.03 for 2 hours dyeing time at temperatures 80 and 60 °C for RR120 and RB5 respectively.

The exhaustion and fixation efficiency reaches maximum values at 40g/l SE (Figure 2) for RR120 and RB5 respectively, after which a negligible increase in the exhaustion and fixation efficiency values is observed. It is clear that SE is rather an effective exhausting agent [2, 10] for bifunctional monochlorotriazine reactive dye RR120 and bifunctional vinylsulphone reactive dye RB5.

The high exhaustion and fixation efficiency values in presence of 40g/l SE reflects the fact that SE can be used as an alternative biodegradable exhausting agent and the enhanced effect in bifunctional dyes that would further enhance dye sorption [2].

3.2.2. Effect of adding different concentrations of SC

SC is used as an exhausting agent in the dyeing of bleached cotton fabrics with RR120 and RB5 dyes. The concentration of exhausting agent (SC) is investigated by increasing its from 0 to 60g/l with initial dye concentration 1.03×10^{-4}M and L.R. 1:30 for 2 hours dyeing time at pH 8.31 and temperatures 80 and 60°C for RR120 and RB5, respectively (Figure 2).

Figure 2 shows that 25 g/l SC for the two reactive dyes produce higher percentage of dye

exhaustion and fixation efficiency than that of SS; this is interesting in light of the present goal of lowering salt concentrations for co-friendly dyeing methods. When a cellulosic fabric is immersed in dye liquor, it acquires a negative electrical charge. The negatively charged fabric surface repels the negatively charged dye ions present in the dyebath, when cations from the salts can counter the negative charge of fabric, thereby faciliting absorption of dye anions onto the fabric. If a dye contains more sulphonic acid or chloride groups, its ions will accordingly acquire more negative charge and will be repelled by the fabric with greater force. Therefore, the effectiveness of a salt in promoting exhaustion varies directly with the number of sulphonic acid groups in the dye molecules [19]. Organic salts (SE and SC) are contains more cations per mole than inorganic salt (SS), the dye in the presence of SC is more attracted by the cotton fabric than SE and SS.

3.3. Effect of alkali concentrations
3.3.1. Effect of sodium carbonate in presence of inorganic salt (SS)

Alkali is necessary for the reaction between reactive dyes based on monochlorotriazine (RR120) and vinylsulphone (RB5) and cellulose molecule. Alkali is responsible for producing an alkaline

environment at which the reactive dyes can combine with the cellulose molecule chemically [2]. Generally either sodium hydrogen carbonate or disodium carbonate (or a blend) is the alkaline ingredient when dyeing cotton fabric with reactive dyes. In the present study variable amount of sodium carbonate ranges from 0 to 25g/l (Figure 3) applied after 30min from dyeing time are used as the alkali for fixation in presence of 50g/l SS with dye concentration 1.03×10^{-4}M and L.R. 1:30 for 2 hours dyeing time at pH 10.02 and 11.01 and temperatures 80 and 60°C for RR120 and RB5, respectively.

It is evident from the results in Figure 3 that the E % and FE% increase gradually as the concentration of sodium carbonate in the padding solution is increased reach maximum values at 15g/l and 20g/l for RR120 and RB5 respectively. When sufficient alkalinity is provided the fixation reaction between the reactive dye and the cotton fabric takes place easily. The exhaustion values of the two dyes applied reached the saturation levels at low alkaline concentration values because the excellent dyeing properties of cellulosic fabrics with reactive dyes.

3.3.2. Effect of sodium carbonate alkali in presence of organic salts (SE) and (SC)

Variable amount of sodium carbonate ranges from 0 to 25g/l applied after 30min from dyeing time as the alkali for fixation to the selected concentrations from different organic salts in the dyebath are studied. The dyeing conducted with dye concentration 1.03×10^{-4}M and L.R. 1:30 for 2 hours dyeing time at temperatures 80 and 60°C for RR120 and RB5 respectively. The effects of adding sodium carbonate to a dyebath contained 40g/l add at pH 9.52 and 25g/l add at pH 8.31 from SE and SC, respectively are given in Figure 4. Figure 4 shows the effect of sodium carbonate concentration (0-25 g/l) on E% and FE %values of the dyed cotton fabrics using both dyes (RR120 and RB5). Figure 4 shows that the E% and FE% values obtained using SE and SC are independent on sodium carbonate concentration. On the other hand, the E %and FE

%values of dyed samples using SE and SC are significantly higher than those obtained using SS in the absence of sodium carbonate. This result emphasizes the fact that alkali is necessary for covalent bond fixation using SS as this salt is neutral electrolyte. Whereas SE and SC are alkaline polycarboxylic sodium salt and in addition to be as exhausting agent would also act as fixing agent [2].

3.4. Effect of using SS together with SE and SC

Having the information that SE and SC can act as exhausting and fixing agents; it is desirable to study the effect of adding different concentrations from SS ranges from 0 to 25g/l to the selected concentrations from SE (40g/l) and SC (25g/l) in the dyebath. The dyeing conditions are selected with dye concentration 1.03×10^{-4}M and L.R. 1:30 for 2 hours dyeing time at temperatures 80 and 60°C for RR120 and RB5, respectively. The effects of adding SS to a dyebath contained 40g/l add at pH 9.52 and 25g/l add at pH 8.31 from SE and SC, respectively, for RR120 and RB5 are shown in Figure 5.   Figure 5 shows that the (E%) and (FE%) values for dyed samples of both dyes are independent on the concentration of SS added. It is known that SS as a neutral electrolyte is an effective exhausting agent (using optimum amount of salt (50g/l)) in the dyeing of cellulosics with anionic dyes. The major effect of the electrolyte on such dyes, in addition to its extinguishing effect on the negative charge on cotton fabrics, is to increase the degree of aggregation of the dye molecules in solution by the common-ion effect. The electrolyte suppresses the ionization of the dye molecule in solution, thereby effectively reducing its solubility in the dyebath and modifying the equilibrium in favor of movement of dye molecules from the solution to the fabric [20, 21]. On the other hand the alkalinity effect of (SE) and (SC) in the dyebath seems to have suppressed the effect of the amount used of SS in such alkaline medium, which favors more dye ionization [2].
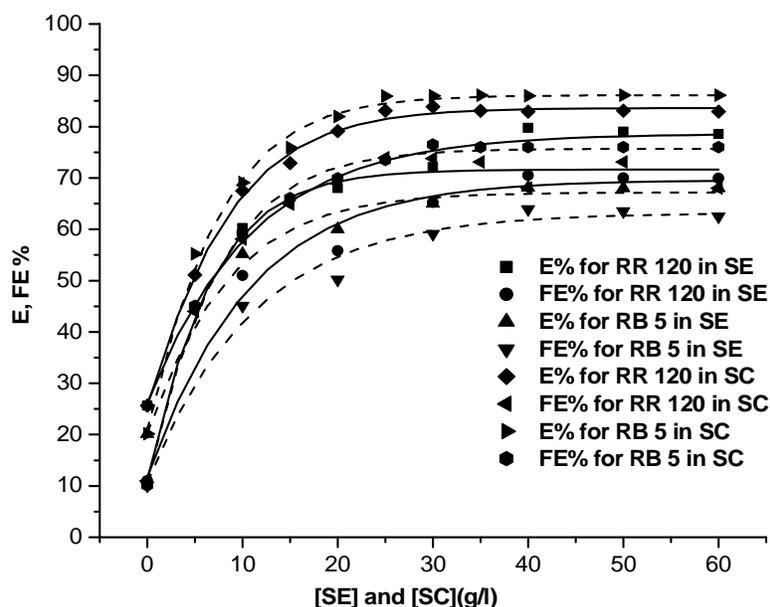
Figure 2: Effect of different salts concentrations (SE and SC) on the percentage exhaustion (*E*%) and fixation efficiency (*FE*%) of RR120 (—) and RB5 (…..) on cotton fabric with initial dye concentration 1.03×10^{-4}M and L.R.1:30 for 2 hours dyeing time at pH 9.52 and 8.31 and temperatures 80 and 60°C for RR120 and RB5 respectively.

Figure 3: Effect of sodium carbonate concentrations on the percentage exhaustion (*E*%) and fixation efficiency (*FE*%) of RR120 (—) and RB5 (…..) on cotton fabric with initial dye concentration 1.03×10^{-4}M and L.R.1:30 for 2 hours dyeing time in presence of 50g/l SS at pH 10.02 and 11.01 and temperatures 80 and 60°C for RR120 and RB5, respectively.
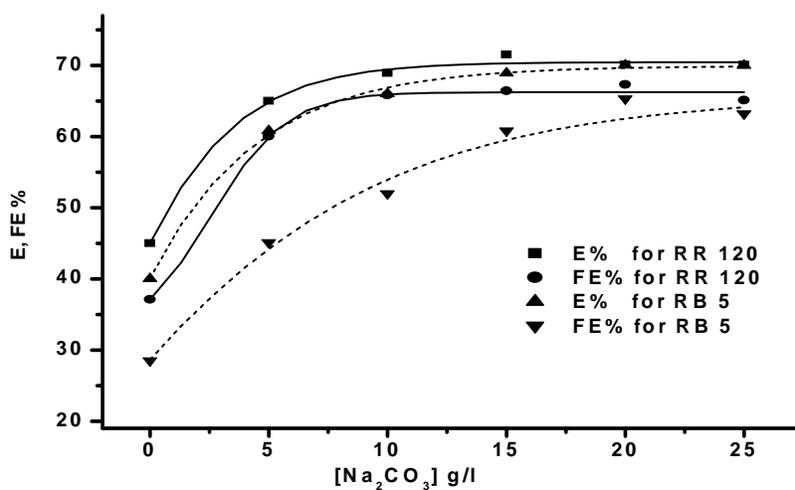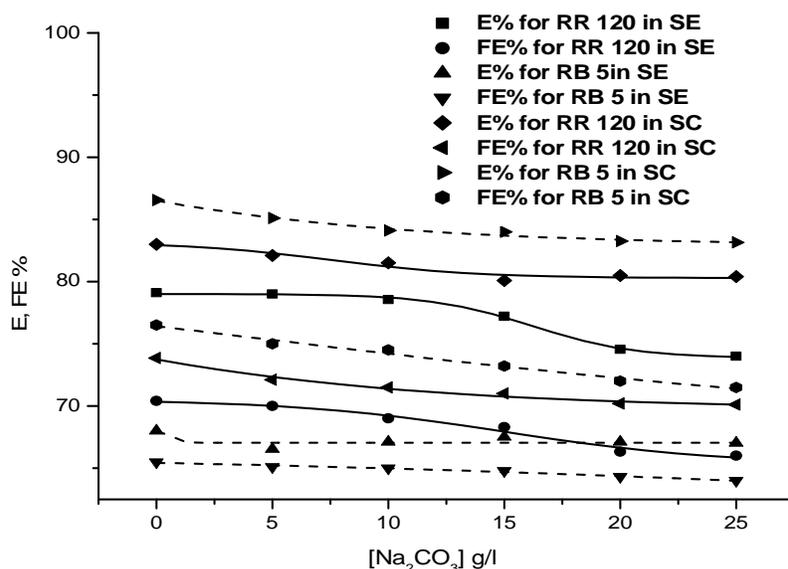
Figure 4: Effect of sodium carbonate concentrations on the percentage exhaustion (*E*%) and fixation efficiency (*FE*%) of RR120 (—) and RB5 (.....) on cotton fabric with initial dye concentration 1.03×10^{-4}M and L.R.1:30 for 2 hours dyeing time in presence of 40g/l SE and 25 g/l SC at pH 9.52and 8.31 and temperatures 80 and 60°C for RR120 and RB5, respectively.

Figure 5: Effect of different inorganic salt concentrations (SS) on the percentage exhaustion (*E*%) and fixation efficiency (*FE*%) of RR120 (—) and RB5 (.....) on cotton fabric with initial dye concentration 1.03×10^{-4}M and L.R.1:30 for 2 hours dyeing time in presence of 40g/l SE and 25 g/l SC at pH 9.52 and 8.31 and temperatures 80 and 60°C for RR120 and RB5 respectively.
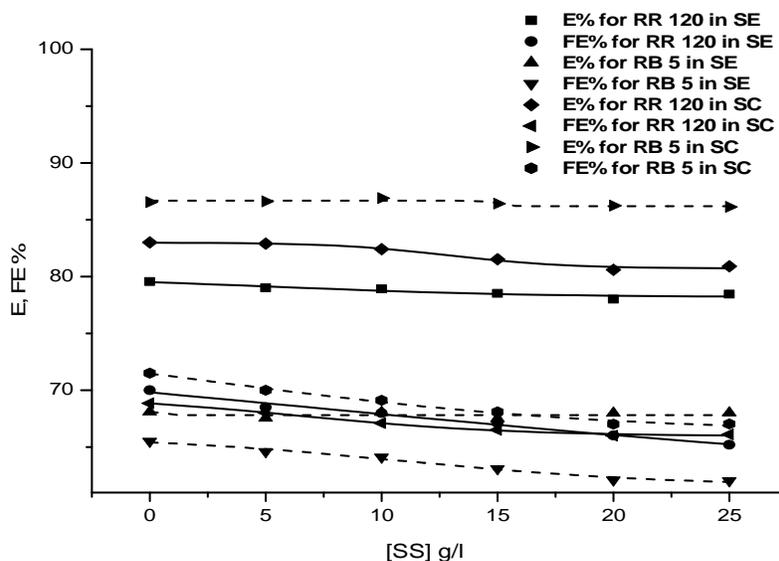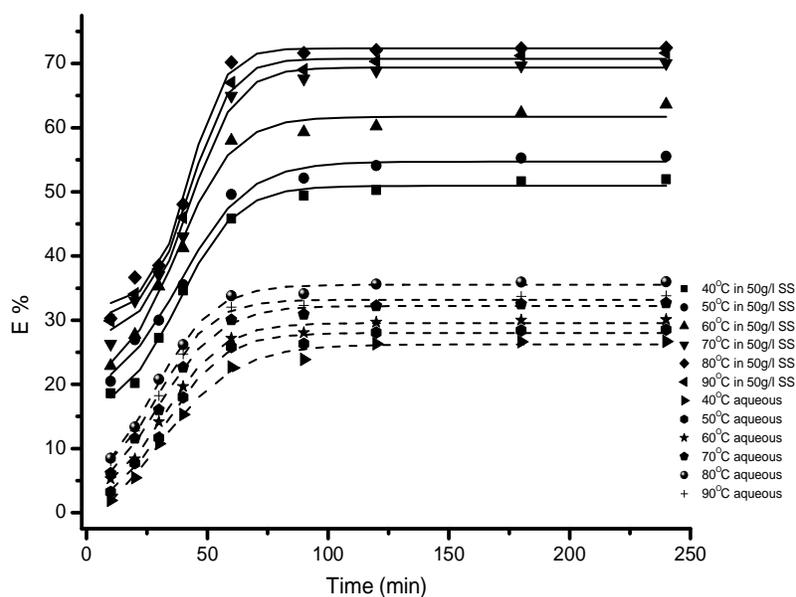
Figure 6: Effect of Time on the percentage exhaustion (E %) of RR120 on cotton fabric at initial dye concentration 1.03x10^{-4}M and L.R.1:30 in aqueous (…..) and in presence of 50g/l SS (―).

3.5. Effects of some dyeing parameters on dye exhaustion and fixation efficiency

3.5.1. Effect of treatment time

In the case of treatment time, a proper exhaustion-fixation percentage was sufficiently achieved in 1 hour. Figure 6 represents the effect of time on RR120 in aqueous and in presence of 50g/l SS (RR120 concentration of 1.03x10^{-4}M and L.R. 1:30). It appears from Figure 6 that, in aqueous and presence of SS there is rapid uptake of RR120 during the initial stage of the dyeing process within the first 60min, indicating a high affinity between RR120 molecules and the cotton fabric surface due to the diffusion of dye molecules [22]. Following, the dyeing process slows suggesting a gradual equilibrium, possibly finally, the saturation is reached, showing the final equilibrium at approximately 80 - 240mins, beyond which no further dyeing takes place [23]. Similar effects are also obtained in presence of 40g/l at pH 9.52 and 25g/l at pH 8.31 from SE and SC, respectively, and in case of RB5.

3.5.2. Effect of pH

pH control is important in order to achieve a constant pH during dyeing, which can lead to an optimum dye exhaustion.

Figure 7 shows the effect of pH on the percentage exhaustion (E%) and fixation efficiency (*FE*%) of RR120 and RB5 on cotton fabric. The dyeing is conducted at different pH values ranges from 6.04 to 11.01 with initial dye concentration 1.03x10^{-4}M and L.R.1:30 for 2 hours dyeing time at temperatures 80 and 60 ^{o}C for RR120 and RB5, respectively. As can be observed from Figure 7, the best (*E*%)**,** and (*FE*%) are obtained at high pH values (10.02 and 11.01, for RR120 and RB5, respectively) in presence of 50g/l SS and 20g/l sodium carbonate used as alkali for fixation add after 30min from dyeing time.

Moreover, the percentage exhaustion (*E*%) and fixation efficiency (*FE*%) on cotton fabric using SE and SC, reaches maximum values at pH 9.52 and 8.31for RR120 and   RB5, respectively.   The percentage exhaustion (*E*%) and fixation efficiency (*FE*%) values of dyed samples using SE and SC were significantly higher than those obtained using SS in the absence of sodium carbonate. This result emphasizes the fact that alkali is necessary for covalent bond fixation using SS as this salt is neutral electrolyte. Whereas SE and SC are alkaline polycarboxylic sodium salt and in addition to be as exhausting agents would also act as fixing agents.

Reactive dyes containing chlorotriazinyl groups react with nucleophiles by an activated heteroaromatic nucleophilic substitution mechanism [24]. Chlorotriazine reactive dye fixation involves the

formation of a covalent bond between a hydroxyl group, under alkaline conditions in the fabric, and the dye molecule, by the nucleophilic displacement of chloride ion [25].

Nucleophilic substitution characterizes reactive dye-fabric fixation that occurs when a leaving group in the reactive system is displaced by a nucleophilic group on the polymer chain. The

reaction of a reactive dye with a hydroxyl group of cellulose is typical of this process (Scheme 2), [26-28]. The same process accounts for the competitive hydrolysis reactions between the dye and water during dye application (Scheme 3).
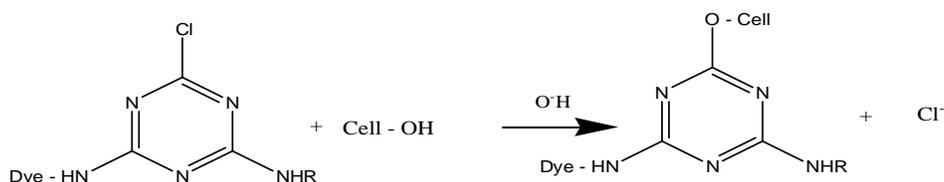
Scheme 2: Reaction of a monochlorotriazine dye with cellulose
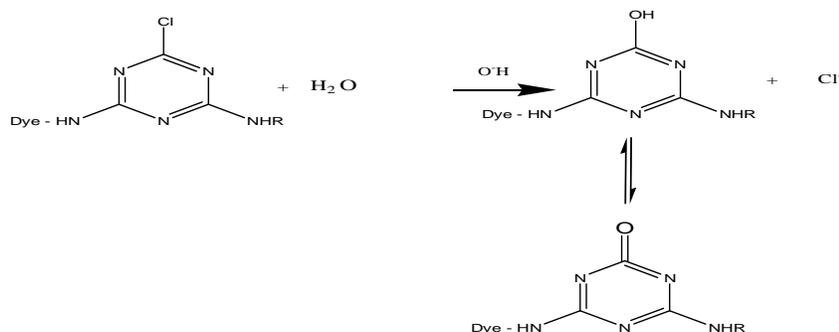
Scheme 3: Hydrolysis of a monochlorotriazine dye with water

(1) $Dye - SO_2 - CH_2 - CH_2 - OSO_3Na + NaOH \xrightarrow{O^-H} Dye - SO_2 - CH = CH_2 + Na_2SO_4 + H_2O$

(2) $Dye - SO_2 - CH = CH_2 + Cell - OH \xrightarrow{O^-H} Dye - SO_2 - CH_2 - CH_2 - O - Cell$

(3) $Dye - SO_2 - CH = CH_2 + H_2O \xrightarrow{O^-H} Dye - SO_2 - CH_2 - CH_2 - OH$
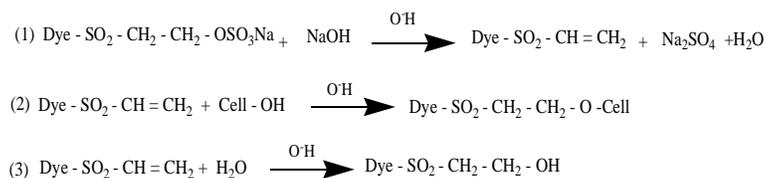
Scheme 4: Reaction, hydrolysis of a vinylsulphone dye

Figure 7: Effect of pH on the percentage exhaustion (E%) and fixation efficiency (FE%) of RR120 (—) and RB5 (…..)on cotton fabric at initial dye concentration 1.03×10^{-4}M and L.R.1:30 for 2 hours dyeing time in presence of 50g/l SS and 20g/l sodium carbonate concentration used in fixation at temperatures 80 and 60°C for RR120 and RB5 respectively.

Moreover, nucleophilic addition characterizes the dye-fabric reaction in which a nucleophilic group in the fabric adds across an activated carbon-carbon double bond in the reactive group contain a vinylsulphone moiety. Systems based on activated double bonds also undergo hydrolysis as shown in Scheme (4), [29].

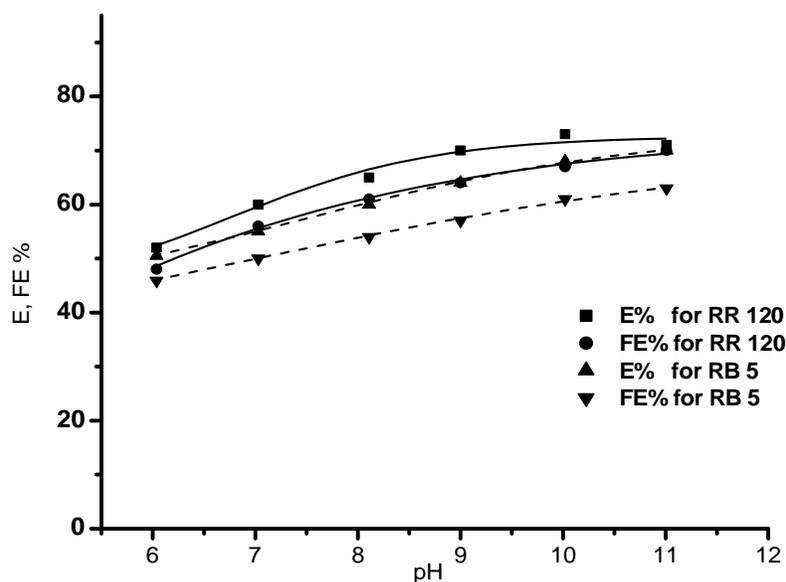Hydrolysis of reactive dye also occurs whenever dye fixation is conducted in the presence of hydroxyl ions [30, 31]. Since the hydrolyzed dye is usually very similar to the parent reactive dye in diffusion, it exhausts along with the reactive form onto the fabric surface. In practice, fabric fixation predominates over hydrolysis due to important factors. Firstly, cellulose has lower dissociation content than water, resulting in approximately a 25 - fold excess of cellulosate ions over hydroxyl ions. Secondly, the affinity of the dye for the fabric reduces the amount of dye available for hydrolysis in the dyebath [32]. Thirdly, the pH within the fabric is primarily maintained by cellulosate ions and the charge on the fabric surface expels hydroxide ions from the fabric interior [33].

3.5.3. Effect of dyeing temperature

The effect of dyeing temperature (40-90 ℃) on the percentage exhaustion (E%) and fixation efficiency (FE%) of RR120 and RB5 on cotton fabric at initial dye concentration 1.03×10^{-4}M and L.R.1:30 for 2 hours dyeing time in presence of 50g/l SS and 20g/l sodium carbonate used in fixation is demonstrated in Figure 8. As can be observed, the percentage exhaustion (E%) and fixation efficiency (FE%) increase with increasing of dyeing temperature and reaches a maximum values in presence of different salts (SS, SE and SC) at 80°C and 60°C for RR120 and RB5, respectively, then it decreases. This increase in dye uptake can be attributed to better dye exhaustion at 80°C and 60°C temperatures for RR120 and RB5. However, temperature higher than 80°C and 60°C results in decrease in percentage exhaustion (E%) and fixation efficiency (FE%) for RR120 and RB5, which may be attributed to decrease in dye molecule stability at higher temperatures [34].

Moreover, it is known that increasing the temperature allows for the swelling of the cotton

fabrics, which leads to a higher dye-uptake [35]. The reason for the higher fixation efficiency is explained by Ibrahim, *et al.*, [36], that the raising temperature may result in opening up the structure of the cellulose, increasing the accessibility of cellulose hydroxyl, enhancing the mobility as well as reactivity of the dye molecules and overcome the activation energy barrier of the dyeing process.

3.5.4. Effect of liquor ratio

The effect of liquor ratio (L:R) on the exhaustion (*E%*) and fixation efficiency (*FE%*) of RR120 and RB5 is shown in Figure 9. The dyeing process conducted at different L.R. increases from 1:10 to 1:50 with initial dye concentration 1.03×10^{-4}M for 2 hours dyeing time in presence of 50g/l SS and 20g/l sodium carbonate used as alkali for fixation add after 30min at pH 10.02 and 11.01 and temperatures 80 and 60°C for RR120 and RB5, respectively.

As expected, the dyeability of reactive dyes decreases in substantivity to a greater or lesser extent when the L.R. is increased. It follows logically that as the L.R. is increases the probability of contact time between the dye molecules and fabric surface decreases, i.e. fewer dye molecules (per unit of time) are adsorbed onto the fabric surface. Equilibrium between adsorption and desorption is thus displaced, desorption becoming stronger, i.e. substantivity is lower [37]. The low liquor ratios serving to lower costs by reducing the amounts of water and chemicals used as well as reducing the energy consumed in liquor circulation and heating.

Whenever, L.R 1:10 is used the (*E%*) are 90.001 and 84.123 and the (*FE%*) are 85.231 and 81.421 compared with that at L.R 1:50 the (*E%*) are 65.211 and 61.324 and the (*FE%*) are 50.23 and 58.403 % for RR120, and RB5 respectively. This may be attributed to that the diffusion of dye molecules at low liquor ratios happens in a restricted volume of water, so dye molecules could be more controlled to be directed towards the fabric than in higher L.R., because the diffusion of dye molecules in the dyebath increase as the volume of water increase [18, 38].

3.5.5. Effect of different dye concentrations

The exhaustion (*E%*) and fixation efficiency (*FE%*) of RR120 and RB5 are sensitive to their concentrations (Figure 10). Therefore, the dyeing is conducted at different initial dyes concentrations

$(2.03 \times 10^{-5}$M to 1.10×10^{-3}M) and L.R. 1:30 at temperatures 80 and 60°C at pH 10.02 and 11.01 for RR120 and RB5 respectively, in presence of 40g/l SE at pH 9.52 and in presence of 25g/l SC at pH 8.31.

Figure10 shows that the (*E%*) and (*FE%*) obtained at different dye concentrations. (*E%*) and (*FE%*) are decreased quickly with increasing depth of shade on fabric or dye concentrations in all conditions for RR120 and RB5 [39].

These results explained as follows: more dye becomes fixed to the fabric, the net negative charge on the fabric increases with the increasing concentration of sulphonate groups present on the dye. At higher concentration of dyes the electrostatic repulsion between the negatively charged dye and the dyed fabric increases, resulting in a lower proportion of dye fixation. Additionally, the number of available sites present on the fabrics reduces and competitive hydrolysis increases [10].

RR120 has greater molecular weight than RB5, it gives better dyeing properties with cotton fabric. Moreover, it is obvious that the dye exhaustion is related to dye molecule structure. Larger molecule usually means more intermolecular interaction due to van der Waals force between reactive dyes and cotton fabric contributed a great part in the dye exhaustion [40]. For bis-monocholorotriazine reactive dyes such RR120, the two triazinyl groups not only increase the fixation efficiency of a dye but also facilitate the enhancement of substantivity. Accordingly, such products are particularly suited to and now occupy an important position in exhaust applications [41]. This dye is designed to have substantially increased substantivity, exhaustion and fixation values.

For Bis-Sulphatoethylsulpone reactive dyes (i.e. RB5), having two vinylsulphone types fabrics–reactive groups posse's outstanding dyeing properties. This particular reactive system is somewhat different from the halotriazine system of being the product of hydrolysis (unfixed dye molecules), a hydroxyethylsulphone, is generally much less substantive to cotton fabric than the reactive dye itself and is easily washed-off after completion of dyeing cycle. The substantivity for the cellulose is enhanced and the bis-vinylsulphone structure formed shows excellent fixation efficiency under alkaline conditions [42,43].
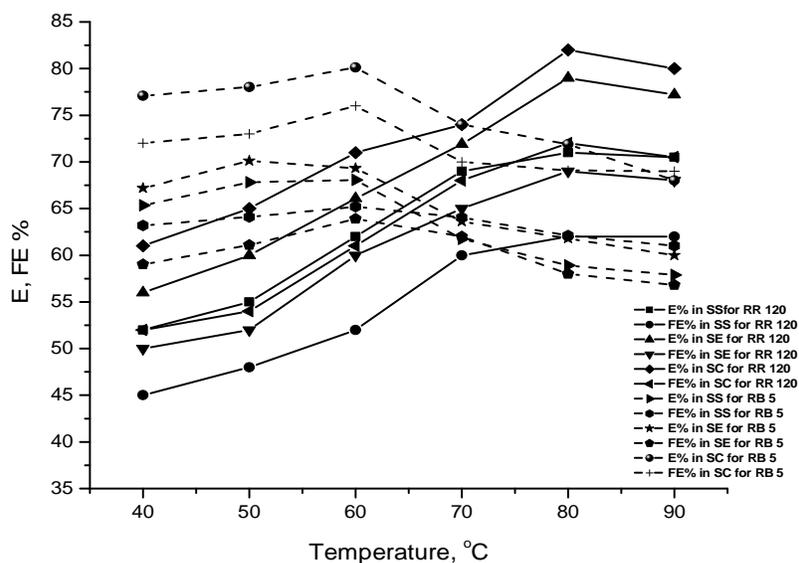
Figure 8: Effect of temperature on the percentage exhaustion (E%) and fixation efficiency (FE%) of RR120 (—) and RB5 (…..) on cotton fabric with initial dye concentration 1.03×10^{-4}M and L.R.1:30 for 2 hours dyeing time in presence of 50g/l SS and 20g/l sodium carbonate concentration used in fixation at pH 10.02 and 11.01, in presence of 40g/l SE at pH 9.52 and in presence of 25g/l SC at pH 8.31.
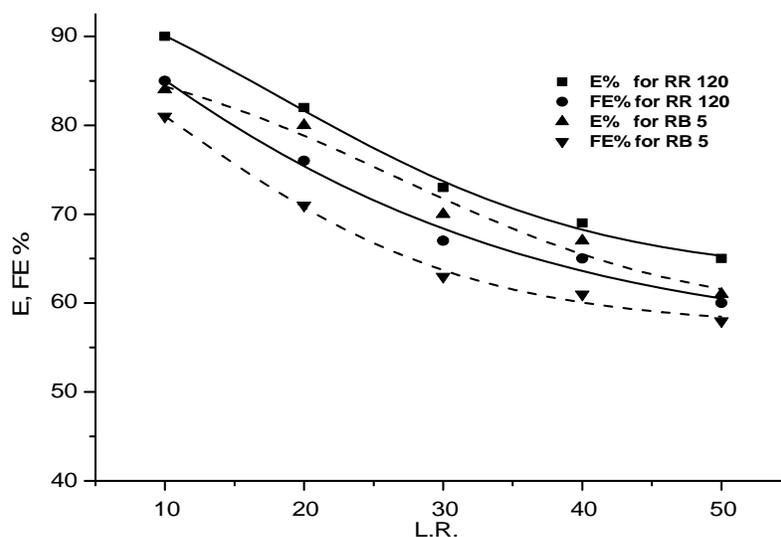
Figure 9: Effect of liquor to fabric ratio (L: R) on the percentage of exhaustion (*E*%) and fixation efficiency (*FE*%) of RR120 (—) and RB5 (…..) on cotton fabric with initial dye concentration 1.03×10^{-4}M for 2 hours dyeing time in presence of 50g/l salt concentration (SS) and 20g/l sodium carbonate concentration used in fixation at temperatures 80 and 60°C with pH 10.02 and 11.01 for RR120 and RB5 respectively.

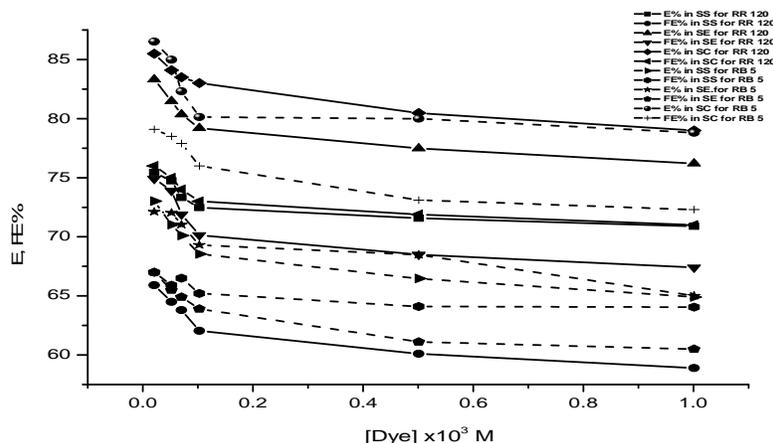Figure 10: Effect of different dye concentrations on the percentage of exhaustion (E%) and fixation efficiency (FE%) of RR120 (___) and RB5 (…..) on cotton fabric at L.R.1:30 for 2 hours dyeing time in presence of 50g/l SS and 20g/l sodium carbonate concentration used in fixation at pH 10.02 and 11.01 for RR120 and RB5 respectively, in presence of 40g/l SE at pH 9.52 and in presence of 25g/l SC at pH 8.31.

3.6. Reuse of dyebath

3.6.1. Reuse of dyebath after dyeing

The considerable rationalization of dyeing processes that have occurred in recent years has been directed towards increasing productivity and reducing costs. In the latter context, since energy costs are intimately linked to water usage, attention has focused on reducing the amount of water used in dyeing [44, 45].

The feasibility of reusing dyebath effluent has been the subject of many previous investigations. The high exhaustion levels achieved when dyeing nylon fabric with acid dyes favored this approach [41].

In the present study, after the fresh bath dyeing of both RR120 and RB5 is finished a certain amount (fixed percentage 10%, 25%, 45% and 65%) of the spent dyebath is reused. The dyebath is reused in this way for a total of four times cycles. The residual dye can be reused in subsequent dyeing; for this, the concentration of dye in the exhausted dyebath must be determined spectrophotometrically; no attempt is made to determine the ionic strength of the exhausted standard dyebath. The dye concentration increased to the desired level of 1.03×10^{-4}M for each dye using stock dye solution. Addition of dye and chemicals are conducted to compensate for any consumption and loss in the previous dyeing cycle as the standard dyeing [46].

This experiment is carried out to determine the effect of reuse of dyebath on dyeing results. The dyeing process is carried out as the standard dyeing procedure with dye concentration 1.03×10^{-4}M and

L.R. 1:30 at temperatures 80 and 60 ^{o}C for RR120 and RB5, respectively, for 2 hours dyeing time. Dyeing in presence of 50g/l SS and 20g/l sodium carbonate used as alkali for fixation add after 30min from dyeing time at pH 10.02 and 11.01 for RR120 and RB5, respectively. Dyeing in presence of 40g/l added at pH 9.52 and 25g/l added at pH 8.31 for organic salts (SE and SC), respectively, for RR120 and RB5 are also carried out.

Such recycling of exhausted dyebaths further offers the potential of lowering costs through the reduction of the amounts of water, chemicals and energy consumed; the reductions in water and chemical usage will also serve to reduce effluent treatment costs. The results of the percentage of dye exhaustion (E%) and fixation efficiency (FE%) for the reuse of reactive dyebaths are show in Tables 1 and 2 for RR120 and RB5. Tables 1 and 2 show the percentage of dye exhaustion (E%) and fixation efficiency (FE%) of RR120 and RB5 on cotton fabric in presence of different salts at optimum dyeing conditions decreases slightly (not more than 2% compared to the standard dyeing) with increasing the reuse percentage (10 and 25%) as well as with increasing reuse cycles (first and second reuse) and decreases greatly (more than 9% compared to the standard dyeing) with increasing the reuse percentage (45 and 65%) as well as with increasing reuse cycles (third and fourth reuse). This show that high reuse percentage (45 and 65%) and high reuse cycles (third and fourth reuse) of dyebath contain reactive dyes is unfeasible under the experimental conditions.

Table 1: Percentage exhaustion (E%) and fixation efficiency (FE%) of RR120 for reuse of the dyebath with initial dye concentration 1.03x10^{-4}M and L.R. 1:30 at temperature 80°C in presence of different salts at optimum dyeing conditions for 2 hours dyeing time.

Salt add	Dyebath status	Reuse %							
		10%		25%		45%		65%	
		FE%	E%	FE%	E%	FE%	E%	FE%	E%
[SS]=50g/l, [Na$_2$CO$_3$] = 20g/l and pH 10.02	Fresh	71.201	66.022	70.323	65.820	69.320	65.123	68.322	64.323
	1st Reuse	70.112	65.313	69.325	63.720	67.720	61.324	60.223	60.324
	2nd Reuse	68.325	63.327	67.326	62.020	65.130	61.325	58.821	58.025
	3rd Reuse	67.026	62.339	65.524	60.030	64.720	60.328	57.323	56.326
	4th Reuse	66.514	61.128	64.326	59.320	62.020	59.399	57.224	55.428
[SE]= 40g/l and pH 9.52	Fresh	79.925	70.554	79.123	70.214	78.569	70.025	78.021	70.213
	1st Reuse	78.121	70.021	77.154	69.124	75.321	67.014	74.231	65.241
	2nd Reuse	76.021	68.410	75.345	66.021	72.231	64.212	72.012	62.321
	3rd Reuse	75.541	67.023	74.541	65.231	72.114	63.437	70.512	62.012
	4th Reuse	74.234	65.541	72.232	63.012	71.214	61.032	69.124	61.031
[SC] =25g/l and pH 8.31	Fresh	84.121	73.812	83.215	73.412	82.417	73.121	81.324	72.541
	1st Reuse	84.521	73.012	82.564	72.214	80.735	72.014	79.022	70.231
	2nd Reuse	82.012	72.012	81.001	71.012	80.412	70.211	78.214	68.231
	3rd Reuse	81.241	70.412	80.023	69.241	78.521	67.325	76.145	65.012
	4th Reuse	80.541	70.014	78.541	69.021	76.213	66.012	75.001	64.243

Table 2: Percentage exhaustion (E%) and fixation efficiency (FE%) of RB5 for reuse of the dyebath with initial dye concentration 1.03x10^{-4}M and L.R. 1:30 at temperature 60°C in presence of different salts at optimum dyeing conditions for 2 hours dyeing time.

Salt add	Dyebath Status	Reuse %							
		10%		25%		45%		65%	
		FE%	E%	FE%	E%	FE%	E%	FE%	E%
[SS]=50g/l, [Na$_2$CO$_3$] = 20g/l and pH 11.01	Fresh	70.214	63.321	70.014	63.014	69.521	62.541	69.121	62.014
	1st Reuse	69.014	60.121	69.004	58.010	66.021	56.014	54.231	52.213
	2nd Reuse	67.211	59.211	65.354	57.234	64.031	55.321	52.231	50.021
	3rd Reuse	65.014	58.415	63.324	56.214	62.523	54.012	51.457	50.321
	4th Reuse	64.254	56.002	62.012	54.021	61.121	52.234	51.121	49.881
[SE]= 40g/l and pH 9.52	Fresh	68.112	63.901	67.521	63.521	67.123	63.014	66.854	62.714
	1st Reuse	67.541	60.114	66.045	57.141	61.214	55.241	60.321	52.012
	2nd Reuse	66.020	58.542	64.325	56.023	60.113	53.213	55.021	50.471
	3rd Reuse	65.321	57.321	62.012	54.234	59.021	52.214	53.452	50.041
	4th Reuse	65.071	56.471	61.021	53.214	58.023	52.031	51.021	49.021
[SC] =25g/l and pH 8.31	Fresh	86.111	73.815	85.012	73.145	84.512	72.541	84.013	72.014
	1st Reuse	85.032	73.412	84.047	72.014	80.124	70.236	79.014	69.561
	2nd Reuse	83.014	71.421	80.147	70.145	78.021	69.024	78.231	68.020
	3rd Reuse	81.254	69.023	78.012	67.231	76.031	66.213	74.024	64.354
	4th Reuse	81.047	68.541	76.562	65.519	75.024	64.014	72.041	63.025

3.6.2. Reuse of effluent after degradation

This experiment is carried out to determine the effect of reuse of degradable effluent using advanced oxidation process [14] on dyeing results. The dyeing process is carried out as the standard dyeing procedure with dye concentration1.03x10^{-4}M and L.R.1:30 at temperatures 80 and 60°C for RR120 and RB5 respectively, for 2 hours dyeing time. Dyeing in presence of 50g/l inorganic salt concentration (SS) and 20g/l sodium carbonate used as alkali for fixation add after 30min from dyeing time at pH 10.02 and 11.01 for RR120 and RB5, respectively. Dyeing in presence of 40g/l added at pH 9.52 and 25g/l added at pH 8.31 for organic salts concentration (SE) and (SC), for RR120 and RB5, respectively are also carried out.   .

The reuse of degradable wastewater gives promising dyeing results (Table 3). Table 3 gives the results of the percentage of dye exhaustion (E%) and fixation efficiency (FE%) difference from the

standard values not more than 0.50% for RR120 and RB5 in presence of different salts at optimum dyeing conditions, these dyeing are all within acceptable limits (0.90%), [15], it may be concluded that these wastewater samples are of reusable quality. These results show that wastewater, which has been decolorized by advanced oxidation, can be successfully reused in the first instance for a subsequent dyeing procedure.   .

3.7. Color fastness

The color fastness of ionic dyes ranges from very poor to very good to excellent according to their structure and the type of bonding between them and cotton fabrics. It is reported that the type of ionic sites in the fabric with which ionic dyes are bonded has great influence on their color fastness. Therefore the color fastness will greatly be increased by increasing the attraction between the ionic sites and the ionic dyes [47].

The color fastness property of the dyed fabric is assessed according to the international Grey Scale (1-5).

3.7.1. Color fastness of standard dyed samples

The shade of the dyed fabric is related to the amount of dye uptake. The color fastness of reactive dyes on cotton fabric with different dye concentrations at best dyeing conditions in aqueous medium and in presence of inorganic salt (SS) and organic salts (S.E) and (SC) are compared. Table 4 shows that the fastness to washing and light of cotton fabric independent on dye concentrations for all dyeing conditions.

As shown in Table 4 the fastness tests to washing and light of samples that has been dyed with RR120 and RB5 are nearly comparable in three different salts range from very good to excellent in case of staining and very good in case of alteration for RR120 and RB5. Generally, dyeing in presence of different salts (SS, SE and SC) gives improved results for staining and alteration compared with that dyeing in aqueous medium (without salt added) which gives poor ranges for staining and alteration.

It is clear from Table 4 that reactive dyes gives better washing fastness on cotton fabric samples. The fastness improvement may be as a result of better dye penetration and thus good covalent fixation with cotton fabrics. [48].

3.7.2. Color fastness of dyed samples when reuse of dyebath after dyeing

The results in Table 5 shows that the color fastness of samples dyed with RR120 and RB5 in different salts with optimum dyeing conditions at fixed reuse percentage (25%) for a total of four times

cycles decreases slightly with increasing reuse cycles and gives improvement results compared to the standard dyeing above. This means that reuse of dyebath is feasible under the experimental conditions.

3.7.3. Color fastness of dyed samples after reuse of degradable effluent

The results in Table 6 shows that the color fastness of dyed samples when degradable wastewater is of reusable quality for dyeing with RR120 and RB5 in presence of different salts with optimum dyeing conditions gives improved results compared with that for standard dyeing above. This means that the reuse of effluent after decolorization is feasible for dyeing under the experimental conditions used in this study.

4. Conclusion

This study explores the viability of replacing the inorganic exhausting (sodium sulphate) and fixing (sodium carbonate) agents, which are widely used in the dyeing of cotton fabric with reactive dyes causing some environmental concerns, with organic sodium edate and sodium citrate that functions as exhausting and fixing agents. Factors affecting dyeability such as the concentration of sodium edate, sodium citrate and sodium sulphate, time, pH, temperature, liquor ratio and dye concentration are investigated. The dyed fabrics are evaluated with respect to the dye exhaustion and fixation, and the fastness properties. The fastness properties of dyed samples using sodium edate and sodium citrate are better than those obtained using sodium sulphate conventional method. Moreover, the reuse of dyebath shows that the dye exhaustion decreases slightly with increasing reuse percentage as well as with increasing reuse cycles. This decreased dye exhaustion can be contributed to the accumulation of impurities in the dye bath. However, this kind of change is so small that it will not cause any significant color deviation in bulk dyeing operations. That means reuse of dye bath is feasible under experimental conditions.

Table 3: Percentage of exhaustion (E%) and fixation efficiency (FE%) of RR120 and RB5 after re-use of degradable wastewater with initial dye concentration $1.03x10^{-4}M$ and L.R. 1:30 at temperature 80 and 60°C in presence of different salts at optimum dyeing conditions for 2 hours dyeing time.

Salt add	[SS] = 50g/l, [Na$_2$CO$_3$] = 20g/l and pH 10.02 (RR120) and 11.01 (RB%)		[SE] = 40g/l and pH 9.52		[SC] = 25g/l and pH 8.31	
	RR120	RB5	RR120	RB5	RR120	RB5
E%	71.854	69.132	78.124	67.512	82.514	84.321
FE%	64.981	63.012	69.321	62.003	72.013	72.001

Table 4: Color fastness properties according to AATCC standard for RR120 and RB5 with different dye concentration for standard dyeing at best conditions in aqueous medium and presence of different salts.

Salt add	Initial dye concentration x10^{4}M	RR120				RB5			
		Washing fastness			Light fastness	Washing fastness			Light fastness
		Alt	SC	SW	Alt	Alt	SC	SW	Alt
Aqueous and pH 7.03	0.210	2-3	2-3	1-2	5	2-3	2	2	4
	0.521	2-3	2	2-3	5	2	2	2	5
	0.701	2-3	2	2	5	2-3	2	2-3	5
	1.030	2-3	2-3	2	5	2-3	2	2-3	4
	5.010	2-3	3	2-3	5	2-3	2	2-3	5
	10.110	2-3	2-3	2-3	5	2-3	2	2-3	5
[SS] = 50g/l, [Na$_2$CO$_3$] = 20g/l and pH 10.02 (RR120) and 11.01 (RB5)	0.210	4	4-5	4	6	4	4-5	4	6
	0.521	4-5	4	4-5	6	4-5	4	4-5	6
	0.701	4	4-5	4	7	4	4-5	4	7
	1.030	4-5	4-5	4-5	7	4-5	4-5	4-5	7
	5.010	4-5	4-5	4-5	7	4-5	4-5	4-5	7
	10.110	4-5	4-5	4-5	7	4-5	4-5	4	7
[SE] = 40g/l and pH 9.52	0.210	4-5	4-5	4-5	6	4-5	4-5	4	7
	0.521	4-5	4-5	4-5	7	4-5	4-5	4	7
	0.701	4-5	4-5	4	7	4-5	4-5	4-5	7
	1.030	4-5	4-5	4-5	7	4-5	4-5	4-5	7
	5.010	4-5	4-5	4-5	7	4-5	4-5	4-5	7
	10.110	5	5	4-5	7	5	4-5	4-5	7
[SC] = 25g/l and pH 8.31	0.210	5	4-5	4-5	7	5	4-5	4-5	4
	0.521	5	4-5	4-5	7	4-5	4-5	4-5	7
	0.701	4-5	4-5	4-5	7	4-5	4-5	4-5	7
	1.030	5	4-5	4-5	7	5	5	4-5	7
	5.010	5	4-5	4-5	7	4-5	4-5	4-5	7
	10.110	5	4-5	4-5	7	5	5	4-5	7

Alt = Alteration, change in color; SC = staining on cotton; SW = staining on wool

Table 5: Color fastness properties according to AATCC standard for RR120 and RB5 with reuse of the dyebath at reuse percentage 25% and initial dye concentration 1.03×10^{-4}M at best dyeing conditions in presence of different salts.

Salt add	Dyebath Status	RR120				RB5			
		Washing fastness			Light fastness	Washing fastness			Light fastness
		Alt	SC	SW	Alt	Alt	SC	SW	Alt
[SS] = 50g/l, [Na$_2$CO$_3$] = 20g/l and pH 10.02	Fresh	4-5	4	4	7	4-5	4	4	7
	1st Reuse	4-5	4	4	7	4-5	4	4	7
	2nd Reuse	4	4	4	7	4	4	4	6
	3rd Reuse	4	4	4	7	4	4	4	6
	4th Reuse	4	4	4	6	4	4	4	6
[SE] = 40g/l and pH 9.52	Fresh	4-5	4-5	4-5	7	4-5	4-5	4-5	7
	1st Reuse	4-5	4	4	7	4-5	4	4	7
	2nd Reuse	4-5	4	4	7	4-5	4	4	7
	3rd Reuse	4-5	4	4	7	4-5	4	4	7
	4th Reuse	4-5	4	4	6	4-5	4	4	6
[SC] = 25g/l and pH 8.31	Fresh	5	4-5	4-5	7	5	4-5	4-5	7
	1st Reuse	5	4-5	4-5	7	5	4-5	4-5	7
	2nd Reuse	4-5	4-5	4	7	4-5	4-5	4	7
	3rd Reuse	4-5	4	4	7	4-5	4	4	7
	4th Reuse	4-5	4	4	7	4-5	4	4	6

Alt = Alteration, change in color; SC = staining on cotton; SW = staining on wool

Table 6: Color Fastness properties according to AATCC standard for RR120 and RB5 for reuse of the dyebath effluent after degradation with initial dye concentration 1.03×10^{-4}M at best dyeing conditions in presence of different salts.

Salt add	RR120				RB5			
	Washing Fastness			Light Fastness	Washing Fastness			Light Fastness
	Alt	SC	SW	Alt	Alt	SC	SW	Alt
[SS] = 50g/l, [Na$_2$CO$_3$] = 20g/l and pH 10.02 (RR120) and 11.01(RB5)	4	4	5	7	4-5	4-5	4-5	7
[SE] = 40g/l and pH 9.52	4-5	4	5	7	4-5	4	4-5	7
[SC] = 25g/l and pH 8.31	4-5	4	4-5	7	4-5	4	4-5	7

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5.References
1. Cay A., Tarakçıoglu I. and Hepbasli A., Applied Thermal Engineering, 29, 2554 (2009).
2. Ahmed N. S.E., Dyes and Pigments, 65, 221 (2005).
3. Arsheen M., Aleem M. A., Naheed K., Kamran A., Mnnaza S., Journal of Saudi Chemical Socity 14,69 (2010).
4. Madaras G. W., Parish G. J., Shore J., Batchwise dyeing of woven cellulosic fabrics. Bradford: SDC; 1993.
5. Taylor J. A., Rev Prog. Coloration, 30, 93 (2000).
6. Prabu H. G., Sundrarajan M., Coloration Technology, 118,131 (2002).
7. Fan Q., Hoskote S., Hou Y., Journal of Hazardous Materials, B112, 123 (2004).
8. Allegre C., Moulin P., Maisseu M., Charbit F., Journal of Membrane Science, 269, 15 (2006).
9. Hebeish A., El-Hilw Z.H., Coloration Technology, 117, 238 (2001).
10. El-Shishtawy R. M., Youssef Y.A., Ahmed N. S. E., Mousa A. A., Dyes and Pigments, 72, 57 (2007).
11. Bredereck K., Schumacher C., Dyes and Pigment, 21, 23 (1993).
12. Youssef Y. A., Mousa A. A., Coloration Technology, 118, 325 (2002).

13. Sallam H. B., Abo Farha S. A., Gamal A. M., Mahmoud G. E. A., Ismail L. F. M., in press (2010).
14. Uygur A., Coloration Technology, 117, 111 (2001).
15. AATCC Technical Manual, American Association of Textile Chemists and Colorists, 75, 311, North Carolina, USA (1999).
16. BS 1006: 1978, Color A02, A03 color fastness tests. Standard Methods for the Determination of the Color Fastness of Textiles and Leather (A02, A03), Bradfotd: SDC, 4th ed., (1978).
17. Johnson A., The theory of Coloration of Textiles, 2nd ed., Bradford: SDC, 121, (1989).
18. Koh j., Kim I.S., Shim W.S., Kim J.P., Dyes and Pigments, 64, 9 (2005).
19. Prabu H.G. and Sundrarajan M., Coloration Technology, 118, 131 (2002).
20. Trotman E.R., Dyeing and Chemical Technology of Textile Fabrics, Nottingham; 6th ed., (1984).
21. Auxiliaries. In: Shore J, editor. Colorants and auxiliaries: organic chemistry and application properties, vol. 2. Bradford: SDC; 1990.
22. Qin Q., Ma J., Liu K., Journal of Hazardous Materials, (2008) in press.
23. Youssef Y.A., Journal of the Society of Dyers and Colorists, 116, 316, (2000).
24. Karapinar E., Phillips D.A.S., Taylor J.A., Dyes and Pigments, 75, 491- 497. (2007)
25. Tam K.Y., Smitch J.B., Comption R.G., Brennan C.M., Atherton J.H., Journal of Colloid and Interface Science, 186, 387 (1997).
26. Ramsay D.W., Journal of the Society of Dyers and Colorists, 97, 102 (1981).
27. Mahapatra C.R., Indian Textile Journal, 96, 100, (1986).
28. Nkeonye P.O., Textile Dyer and Printer, 21, 20, (1988).
29. Suwanruji P., Freeman H., Supplement to Colorage, 58, 85 (2006).
30. Renfrew A.H., Cowell P., Journal of the Society of Dyers and Colorists, 114, 174 (1998).
31. Chattopa D.P., Chaudhary R., Man–Made Textiles in India, 40, 495 (1997).
32. Stead C.V., Colorage Annual, 17, 69, (1969).
33. Rattanaphani S., Chairat M., Bremner J.B. and Rattanaphani V., Dyes and Pigments, 72, 88 (2007).
34. Ali S., Hussain T., Nawaz R., Journal of Cleaner Production, 17, 61 (2009).
35. Sheikha S.A., Journal of Saudi Chemical Socity 14, 47 (2010)
36. Ibrahim N. A., Dawoud M. A., American Dyestuff Reporter, 77, 56 (1987).
37. Koh j., Kim I.S., Kim S.S., Shim W.S., Kim J.P., Kwak S.Y., J. App. Polym. Sci., 91, 3481 (2004).
38. Lidyard A.M., Woodcock A., Noonet P., Journal of the Society of Dyers and Colorists, 108, 501 (1992).
39. Koh j., Kim I.S., Shim W.S., Kim J.P., Dyes and Pigments, 64, 9 (2005).

40. Etters J.N., American Dyestuff Reporter, 86, 16 (1997).
41. Fan Q., Sunil H., Yoejun H., Journal of Hazardous Materials, 112, 123 (2004).
42. Matyjas E., Rybicki E., Autex Research Journal, 3, 90 (2003).
43. Limin K., Zhenghua Z., Dyes and Pigments, 36, 347 (1998).
44. Taylor J. A., Rev. Prog. Coloration, 30, 93 (2000).
45. Holme I., Rev. Prog. Coloration, 22, 1 (1992).
46. Cook F. L., Textile Chemist and Colorist, 12, 15 (1980).
47. Mahbubul, M. H., Christopher J. H., Color Technol., 118, 104 (2002).
48. Samanta A.K., Das D., Colorage, 20, 17 (1992).

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