

Synthesis of Reactive Dyes Containing Acrylamido Group and Their Application to Cotton Fabric

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Authors' contributions

This work was carried out in collaboration between all authors. Author MIHM designed the study and wrote the first draft of the manuscript. All authors contributed in practical work and managed the analysis of the study. All authors read and approved the final manuscript.

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ABSTRACT

Three reactive dyes, viz yellow dye, red dye and orange dye containing acrylamido group were synthesized and they were analyzed and characterized by HPLC, mass spectrometry and elemental analysis. These dyes were applied to cotton by exhaust dyeing process. Maximum performance of these dyes was observed using 20 g/l soda ash at 70 – 95°C for 60-120 min. These synthesized reactive dyes showed good colour fastness properties indicating stable bond formation between acrylamido group and cotton fabric.

Keywords: Reactive dye; cotton fabric; colour fastness; acrylamido group.

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1. INTRODUCTION

Reactive dyes, which form covalent bond between the dye and the cellulosic substrate as a result of an alkaline 'fixation' step during dyeing, are the fastest growing class of cellulosic dyestuffs [1,2]. Since the introduction of reactive dyes for cellulose in the mid-1950s, a large number of different reactive groups have been commercially exploited [3,4]. In 1980s, Sumifix and Ciba introduced a new range of bifunctional reactive dyes for dyeing of cellulose. The introduction of sulphatoethyl sulphone group (SES) to monochlorotriazine (MCT) dye (by Sumitomoto) and alkylvinyl sulphone (AVS) residue to monofluorotriazine (MFT) dye incorporated the technical benefits of both parts of the reactive dyes [5-7].

Indeed reactive dyes nowadays regularly appear with a number of different reactive groups within the molecule. The 'molecular engineering' approach of the 1980's [8,9] in which correct selection of reactive groups was considered vital as a means of ensuring that the dyes exhibited high degrees of compatibility, is less widely used by dyestuff manufacturers today. Machinery developments offering much improved dye liquor-fabric interchange, together with automated dosing system [9] and microprocessor control of the dyeing parameters for level dyeing and shade reproducibility are not as necessary as 10 years ago. Hence these days, the reactive dye chemist is able to concentrate on producing more cost effective production, viz the use of tinctorially strong products with high fixation efficiency, which can be applied in short, highly productive processes so as to minimise adverse environmental impact. Nowadays a dyestuff may contain an MFT/ MCT group and an SES/ AVS group within the same molecule.

The α -bromoacrylamido reactive group, widely exploited by Ciba for wool in 1990's, this reactive grouping was synthesized by Phillips et al. [10,11] and they also observed the potential dyeing performance on cotton in warm exhaust dyeing. But the present authors have no information on acrylamido reactive grouping for cellulose. For this purpose, a study was undertaken to synthesize reactive dyes containing acrylamido group and to evaluate the dyeing (exhaust) performance of these dyes on cotton fabric.

2. EXPERIMENTAL

2.1 High Pressure Liquid Chromatography (HPLC)

HPLC was performed with a Hewlett Packard 1100 series machine (Metalab supplies Ltd.) fitted with a quaternary pump. The column was a 10 cm Purospher RP-18 (5 μ m) packing and a LiChrocart 125-4 HPLC column cartridge: solvent A, acrylonitrile; solvent B, water with 0.25% dicyclohexyl ammonium phosphate; flow rate 2 ml/min; temperature 40°C; injection volume 5 μ l; samples were analysed using a diode array detector at a wavelength of 450 nm. The gradient programme used is shown in Table 1. Retention time (t_R) was in min and stop time was 7 min.

Table 1. Gradient programme for HPLC analysis

Time (min)	Solvent A (%)	Solvent B (%)
0	30	70
5	50	50
6	40	60
7	30	70

2.2 Mass Spectrometry

Mass spectra were recorded with a Micromass Instruments LCT orthogonal time-of-flight mass spectrometer fitted with a Z-Spray electrospray ion source operating in negative mode at 3 kV needle potential. Nitrogen was used as a drying and sheath gas. Data were stored in the continuum mode on a Micromass Instruments MassLynx data station utilizing Version 3.5 software pack. Infusion was at a rate of 20 μ l/min with Harvard Instruments syringe pump utilised for sample introduction.

2.3 Micro-Analysis

Elemental analysis for carbon, hydrogen, nitrogen and sulphur were carried out on a Carlo Erba 1108 (German) elemental analyser.

2.3.1 Synthesis of 1-acrylamido-4-(1',3',6'-tri-sulphonaphth-2'-yl)-azo-3-ureidoaniline

2-Aminonaphthalene-3, 6, 8-trisulphonic acid (19.2 g, 0.05 mol) was dissolved in 200 ml water and then cooled to 5°C in an ice-bath. Its pH was adjusted to below 1 by adding HCl (36%). Sodium nitrite (3.5 g, 0.05 mol) was dissolved in

25 ml water and this solution was added dropwise to the above solution maintaining this condition. Completion of reaction was checked by Ehrlich's indicator and sulphone indicator. At the end of the reaction, about 0.5 g sulphamic acid was added to destroy excess nitrous acid. An immediate yellow precipitate of diazonium salt resulted. The reaction mixture was stirred for further 15 min at this condition. 3-ureidoaniline (7.6 g, 0.05 mol), dissolved in dilute hydrochloric acid, was added slowly to the above diazonium salt suspension, with continuous stirring at below 5°C. The pH was raised to 6 - 7 with aqueous sodium hydroxide solution (10% w/v) and maintained at this condition with stirring until completion of the coupling. The reaction mixture was filtered to remove any insoluble impurities. Then sodium chloride was added to the filtrate to give 12% w/v solution and filtered. The filtered cake was dried at 40°C. The yield was 24.2 g. HPLC showed 97.58% pure at t_R 1.20.

The above product (11 g, 0.02 mol) was dissolved in 50 ml water and then cooled to below 5°C in an ice-bath. Acryloyl chloride (1.7 ml, 0.02 mol) was added dropwise to the above solution with continuous stirring. The pH of the reaction mixture was kept at 4.5 - 5.5 using sodium carbonate solution (10% w/v) and temperature was maintained below 5°C. After 15 min, the solution was filtered to remove any insoluble impurities. The solution was left overnight and then filtered. The filter cake, a yellow product termed as yellow dye, was dried at 40°C and the yield was 6.7 g. HPLC showed the product was 91.18% pure at t_R 1.74, and mass spectral analysis gave a molecular ions at m/z 598 ($M - H$)⁻ (100). Elemental analysis found: C, 40.2; H, 2.8; N, 11.9; S, 16.3. $C_{20}H_{17}O_{11}N_5S_3$ requires C, 40.0; H, 2.9; N, 11.6; S, 16.0%.

2.3.2 Synthesis of 8-acrylamido-2-phenylhydrazino-1-oxo-1,2-dihydro-naphthalene-3,6-disulphonic acid

8-amino-1-naphthol-3, 6-disulfonic acid (H-acid) (18.5 g, 0.05 mol) was dissolved in 100 ml water in a beaker at 20 - 25°C and its pH was adjusted to 6 - 7 with sodium hydroxide solution (10% w/v). Acetic anhydride (6 ml, 0.0625 mol) was added dropwise to the solution with stirring. The addition was continued the disappearance of HPLC peak of H-acid. Then pH of the above solution was raised to 8.5 - 9.5 with sodium hydroxide solution (10% w/v) and heated at 40°C

for 1 h maintaining this condition. The solution was cooled to 25°C and filtered. Sodium chloride was added to give 15% w/v solution and the filter cake was dried at 40°C. The yield was 31.9 g. HPLC showed the N-acetyl H-Acid solution was 86.41% pure at t_R 0.83.

Aniline (4.6 ml, 0.05 mol) was dissolved in a 100 ml beaker with HCl (36%) at 0 - 5°C and its pH was adjusted to below 1. Sodium nitrite (3.5 g, 0.05 mol in 25 ml water) was added dropwise maintaining above conditions. Completion of the reaction was checked with Ehrlich's indicator and sulphone indicator. At the end of reaction, about 0.5 g of sulphamic acid was added to destroy the excess nitrous acid. The synthesized N-acetyl H-acid (20.5 g, 0.05 mol) was dissolved in 100 ml water and cooled to below 5°C. Then, the above diazonium salt solution was added dropwise at 0 - 5°C and at pH 8 - 9. After completion of the coupling reaction for about 30 min, its pH was lowered to below 1 with HCl (36%). This solution was heated to 85 - 90°C for 1 h to hydrolyse the dye. After cooling to room temperature, this solution was filtered and sodium chloride was added to the filtrate to give 10% w/v solution. After 1 h, this was again filtered and the filter cake was dried at 40°C. The yield was 16.4 g. HPLC was checked and 100% pure product at t_R 1.87 was obtained.

The above dye (8.5 g, 0.02 mol) was dissolved in 100 ml water. Acryloyl chloride (1.7 ml, 0.02 mol) was added dropwise maintaining its temperature below 5°C and its pH was controlled to about 4.5 - 5.5. More acryloyl chloride was added to obtain maximum (83.61% conversion). Then, sodium chloride was added to give 15% w/v solution and the filter cake, a red product termed as red dye, was dried at 40°C. The yield was 12.3 g. HPLC of this product showed 83.03% pure at t_R 2.51 and mass spectrometry gave ions at m/z 498 ($MNa - H$)⁻(76) and 476 ($M - H$)⁻ (5). Elemental analysis found: C, 47.6; H, 3.1; N, 8.7; S, 12.8. $C_{19}H_{15}O_8N_3S_2$ requires C, 47.8; H, 3.1; N, 8.8; S, 13.4%.

2.3.3 Synthesis of 6-acrylamido-2-(1',5'-disulphonaphth-2'-yl)-hydrazino-1-oxo-1,2-dihydro-naphthalene-3-sulphonic acid

6-Amino-1-naphthol-3-sulfonic acid (J-acid) (12 g, 0.05 mol) was dissolved in 200 ml water at pH 7. This was cooled to 0 - 5°C in an ice-bath and then added acryloyl chloride (4.1 ml, 0.05 mol) to this solution under stirring condition. Its pH was

controlled to 2 - 3 by sodium carbonate solution (10% w/v). This solution was filtered to remove any insoluble impurities. To the filtrate, sodium chloride was added to give 25% w/v solution to separate the desired product. The yield was 19.1 g. HPLC of the dried salt out filter cake showed that it contained 97.96% desired product at t_R 0.91.

2-Naphthylamine-1,5-disulphonic acid (15.5 g, 0.05 mol) was dissolved in 100 ml water at stirring condition. It was cooled to 0 – 5°C in an ice-bath and its pH was controlled below 1 by adding HCl (36%). Then, NaNO₂ (3.5 g, 0.05 mol in 25 ml water) solution was added to the above solution. Completion of the reaction was checked with Ehrlich's indicator and sulphone indicator. At the end of reaction, about 0.5 g of sulphamic acid was added to destroy the excess nitrous acid. Colour of the diazonium salt was yellow.

J-acid product (15 g, 0.05 mol) was dissolved in 100 ml water in another beaker. This was then added dropwise to the above diazonium salt solution. At this low pH, these two reactants did not react each other and remained as a mixture. Then pH of this solution was raised to 5.5 - 6.5 by adding NaOH solution (10% w/v). At this condition, the colour of the solution was changed to red (or deep orange). After 30 min, the solution was filtered to remove any insoluble particles and then NaCl was added to the filtrate to give 12% w/v solution. This was again filtered and the filter cake, a reddish orange product termed as orange dye was dried at 40°C. The yield was 13.8 g. HPLC of this dried product showed 100% desired product at t_R 1.95 and mass spectrometry gave ions at m/z 628 (MNa – H)⁺ (16) and 606 (M – H)⁺ (92). Elemental analysis found: C, 45.1; H, 2.7; N, 6.5; S, 16.3. C₂₃H₁₇O₁₁N₃S₃ requires C, 45.4; H, 2.8; N, 6.9; S, 15.8%.

2.4 Exhaust Dyeing Procedure

All dyeings were carried out using 2% prepared dye (on the weight of fabric) in sealed stainless steel dye pot in a dyeing machine (Mathis Labomat, Switzerland). Each dye pot was prepared with 2% depth of shade and 50 g/l NaCl solutions in the fabric-liquor ratio of 1:10. Then 5 g of bleached unmercerized knitted cotton fabrics were immersed in the dye pot. Exhaustion was done at T°C (50, 60, 70, 80 and 95°C) for 60 min. After 1 h, the pot was taken out and then Na₂CO₃ solution (10 g/l and 20 g/l) was added (Fig. 1). The fixation of dye was continued for further t min (60 min and 120 min). Dye, salt and Na₂CO₃ were calculated on the basis of fabric.

2.5 Washing-off and Soaping-off Processes

After completion of dyeing, the dyed cotton fabric samples were removed from the dye pots, rinsed in cold water and then rinsed in warm water for 5 min. The dyed fabric sample was soaped-off using 1 g/l washing detergent in a beaker at 100°C on a hot plate for 30 min in a fabric-liquor ratio of 1:50. The fabric was then rinsed well with tap water and then dried at room temperature over night. Colour yield of this fabric was measured.

2.6 Measurement of Colour Yield

A Spectroflash 600 spectrometer (with Datacolor v2.1 analytical software) was used to measure visual colour yield. This is expressed in terms of K/S value measured at λ_{max} of the dye. The K/S value shows the strength of the dye at a given concentration, the higher the K/S value, the more the quantity of the dye absorbed.

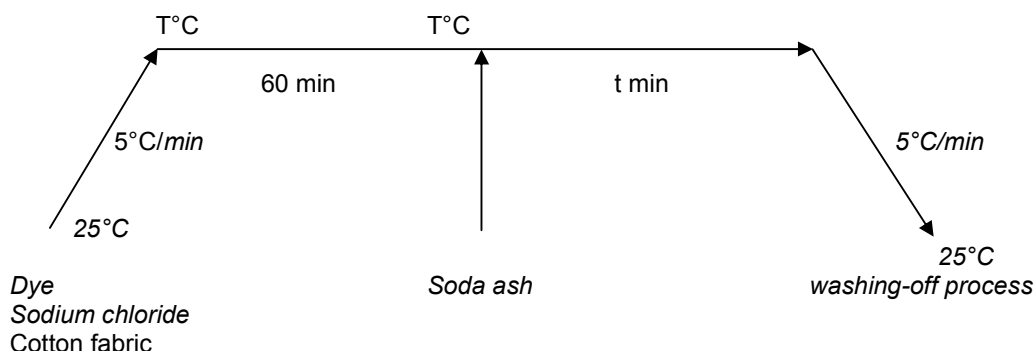


Fig. 1. Dyeing profile of synthesized reactive dyes to cotton

2.7 Colour Fastness Measurement

The synthesized dyes were dyed with 2% depth of shade and 50 g/l NaCl solution in the fabric-liquor ratio of 1:10. The dyeing was continued at 95°C for 2h. After 1 h of dyeing, 20 g/l Na₂CO₃ was added for fixation of dye. The visual colour yield of yellow, red and orange dyes is 18.3, 10.8 and 25.3 respectively. These sample were used to assess light and wash fastness of dyes. Colour fastness of dyed fabric samples were measured by Gray scale. Fastness grade 5 is the control or no fading and 1 severe fading.

The light fastness of the reactive dyed cotton fabric was determined by a Xenotester using Xenon arc lamp (Xenotest 150 S of W. C. Heracus GmbH, Germany) under the following conditions: Relative humidity, 78%; black panel temperature, 45°C, radiation generated, Xenon burner surrounded by an optical filter system; and exposure period, 60 h.

Wash fastness of reactive dyed cotton fabric was determined using 5 g/liter anionic detergent solution [12,13] at 50°C, 75°C and 100°C for 30 min in the fabric-liquor ratio of 1:50.

3. RESULTS AND DISCUSSION

3.1 Synthesis of Reactive Dyes

The synthesis of 1-acrylamido-4-(1',3',6'-trisulphonaphth-2'-yl)-azo-3-ureidoaniline is shown in Scheme 1. The reaction procedure involves two stages. In stage 1, 7-amino-1, 3, 6-trisulphonaphthalene reacts with 3-ureidoaniline to form structure I and then this reacts in the second stage with acryloyl chloride to form the structure II.

The synthesis of 8-acrylamido-2-phenylhydrazino-1-oxo-1,2-dihydro-3,6-disulphonic acid is shown in Scheme 2. The reaction procedure involves three stages. Stage 1: H-acid reacts with acetic anhydride to form N-acetyl H-acid (structure III). Stage 2: N-acetyl H-acid reacts with aniline to form structure IV. Stage 3: In this stage IV reacts with acryloyl chloride to form structure V.

The synthesis of 6-acrylamido-2-(1',5'-disulphoaphth-2'-yl)-hydrazino-1-oxo-1,2-dihydro-naphthalene-3-sulphonic acid is shown in Scheme 3. In the first stage of reaction, J-acid reacts with acryloyl chloride to form 6-

acrylamido-1-hydroxy-3-naphthalene sulphonic acid (structure VI). This was then react with 2-aminonaphthalene-1,5-disulphonic acid to give structure VII.

All the three synthesised dyes, yellow dye, red dye and orange dye, were essentially pure organically, as judged by HPLC, mass spectrometry and elementary analysis, but contained varying quantities of water and inorganic salts, largely sodium chloride.

3.2 Exhaust dyeing Application of Synthesized Reactive Dyes

3.2.1 Effect of temperature on colour yield of synthesized reactive dyes

The three synthesized dyes were applied at 2% depth of shade on weight of fabric at 50, 60, 70, 80 and 95°C using 50 g/l sodium chloride as salt and 20 g/l soda ash as alkali. Each dyeing was conducted at 10:1 liquor ratio on bleached unmercerized knitted cotton fabric allowing 60 min exhaustion in salt and 120 min fixation in soda ash. The yellow dye and orange dye showed the highest vital colour yield at 95 °C, whereas red dye showed at 80°C and is shown in Fig. 2. Although the colour yield of red and orange dyes at temperatures between 70°C and 95°C, and 80°C and 95°C, respectively were very similar.

3.2.2 Effect of soda ash on colour yield of synthesized reactive dyes

The synthesized dyes were applied at 2% depth of shade using two different soda ash concentrations, viz 10 g/l and 20 g/l. Each dyeing was conducted at 50, 60, 70, 80 and 95°C using 50 g/l sodium chloride in a liquor ratio of 1:10. The fixation time was 120 min. The color yield of yellow dye and orange dye was higher when 20 g/l soda ash was used at 95°C for 120 min and is shown in Fig. 3. But in the case of red dye, the difference of soda ash sensitivity was not significant.

3.2.3 Effect of time on colour yield of synthesized reactive dyes

The synthesized dyes were applied at 2% depth of shade using two different fixation times, 60 min and 120 min. Each dyeing was conducted using 50 g/l sodium chloride and 20 g/l soda ash at 50, 60, 70, 80 and 95°C in a liquor ratio of 1:10. The colour yield of yellow dye and orange

dye was higher than that of red dye in Fig. 4. In the case of red dye, the colour yield was highest when soda ash was 20 g/l at 70°C for 60 min. The slightly lower colour yield produced at higher temperature and longer dyeing time might be due to the hydrolysis of dye.

3.3 Colour Fastness

It can be seen from Table 2 that the light fastness of the three reactive dyed cotton fabric on exposure to Xenotester for 60 h is very good.

However, photo-fading might occur due to the attack of singlet oxygen to the most electron-rich portion of the dye molecule [14,15]. Wash fastness of the reactive dyed fabric treated with an anionic detergent solution upto 75°C is 3-5 according to grey scale which is good. At the boiling, washing performance is poor. Hence, the colour fastness indicates the formation of stable bond between the acrylamido group and cotton fabric and these dyes will be commercially viable dyestuff.

Table 2. Fastness properties of cotton fabric samples dyed with prepared reactive dyes

Dyes	Light fastness		Wash fastness grade			
	0	60 h	0	50°C	75°C	100°C
Yellow dye	5	5	5	4-5	4	2-3
Red dye	5	4-5	5	4-5	3-4	2
Orange dye	5	4-5	5	4-5	3-4	2

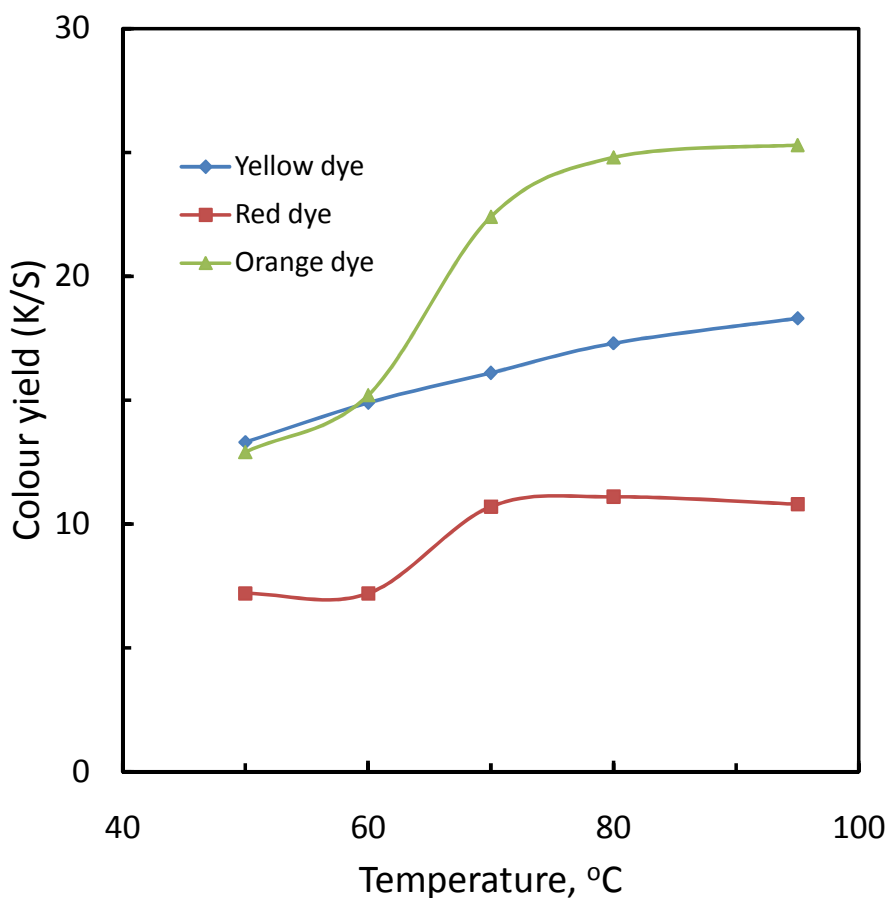
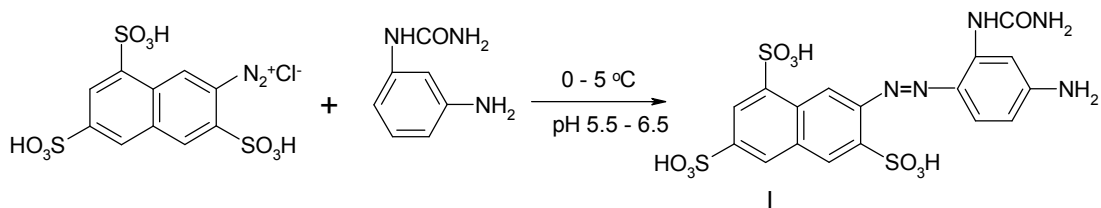
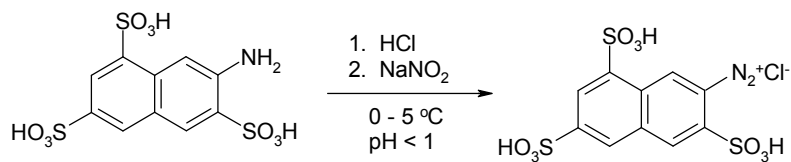
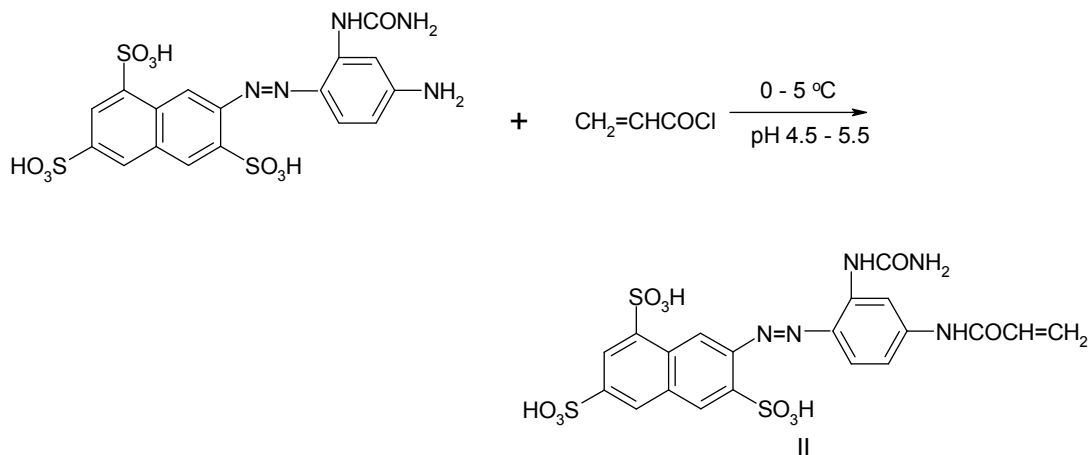


Fig. 2. Effect of dyeing temperature on colour yield of synthesized reactive dyes (2% depth) using 20 g/l soda ash for 120 min

Stage 1

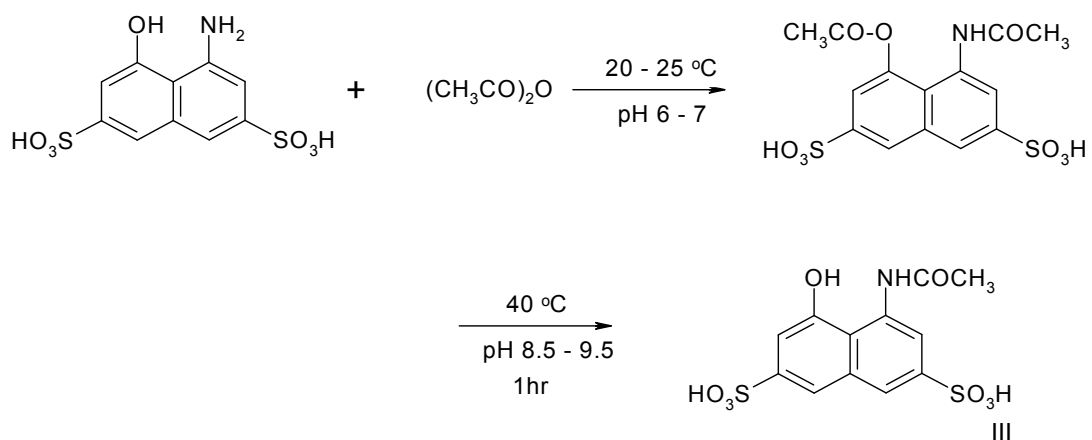


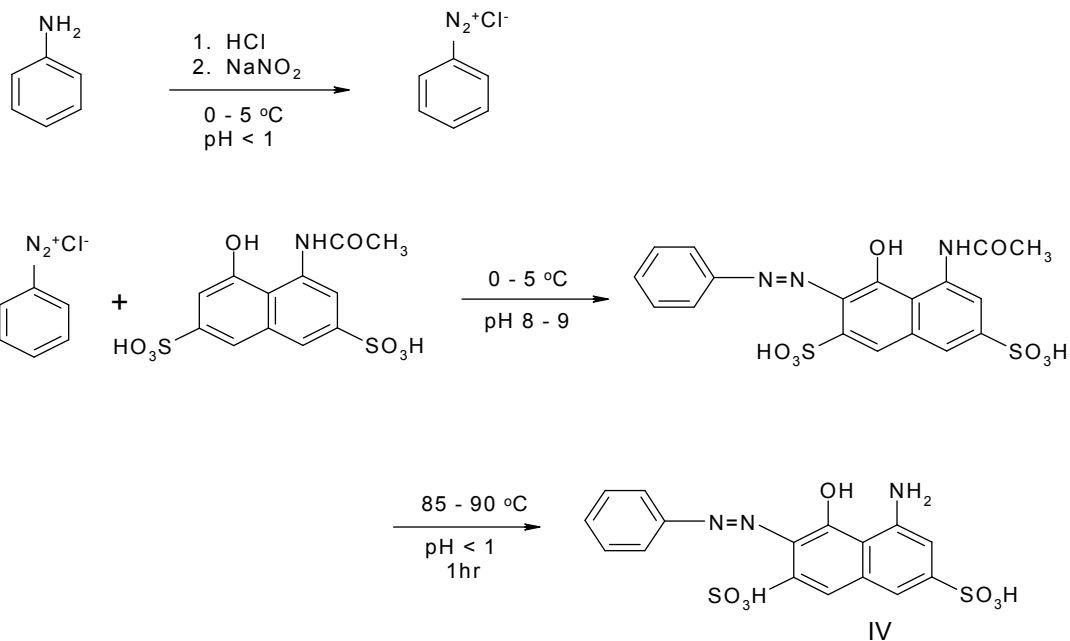
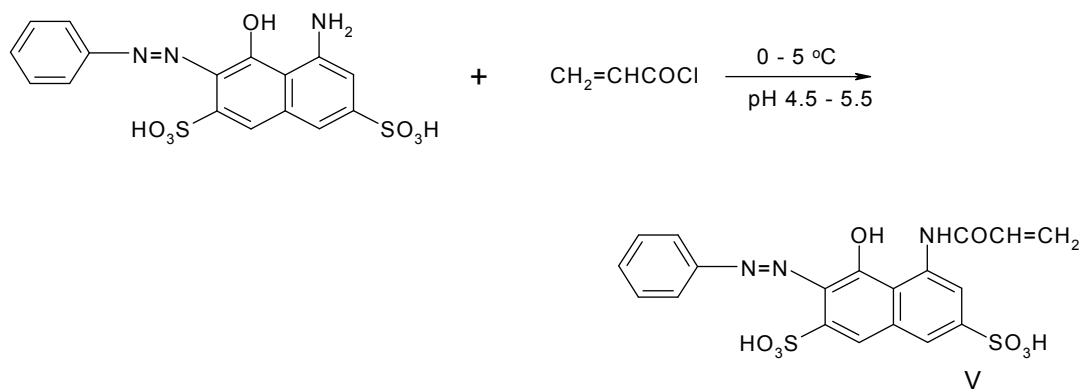
Stage 2



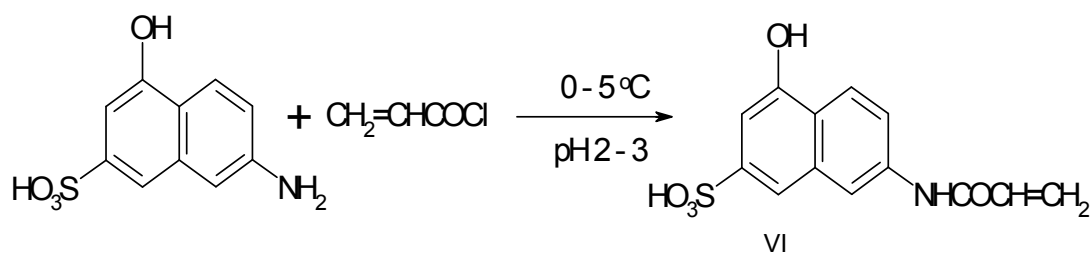
Scheme 1. Synthesis of 1-acrylamido-4-(1',3',6'-trisulphonaphth-2'-yl)-azo-3-ureidoaniline (yellow dye)

Stage 1

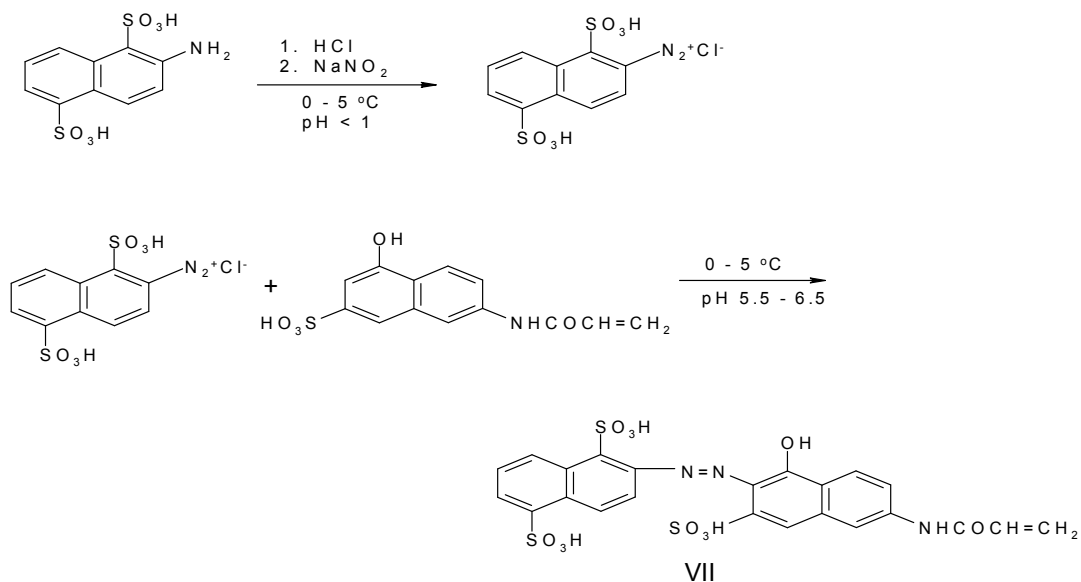


Stage 2**Stage 3**

Scheme 2. Synthesis of 8-acrylamido-2-phenylhydrazino-1-oxo-1,2-dihydro-na-phthalene-3,6-disulphonic acid (red dye)

Stage 1

Stage 2



Scheme 3. Synthesis of 6-acrylamido-2-(1',5'-disulphophthal-2'-yl)-hydrazino-1-oxo-1,2-dihydronaphthalene-3-sulphonic acid (Orange dye)

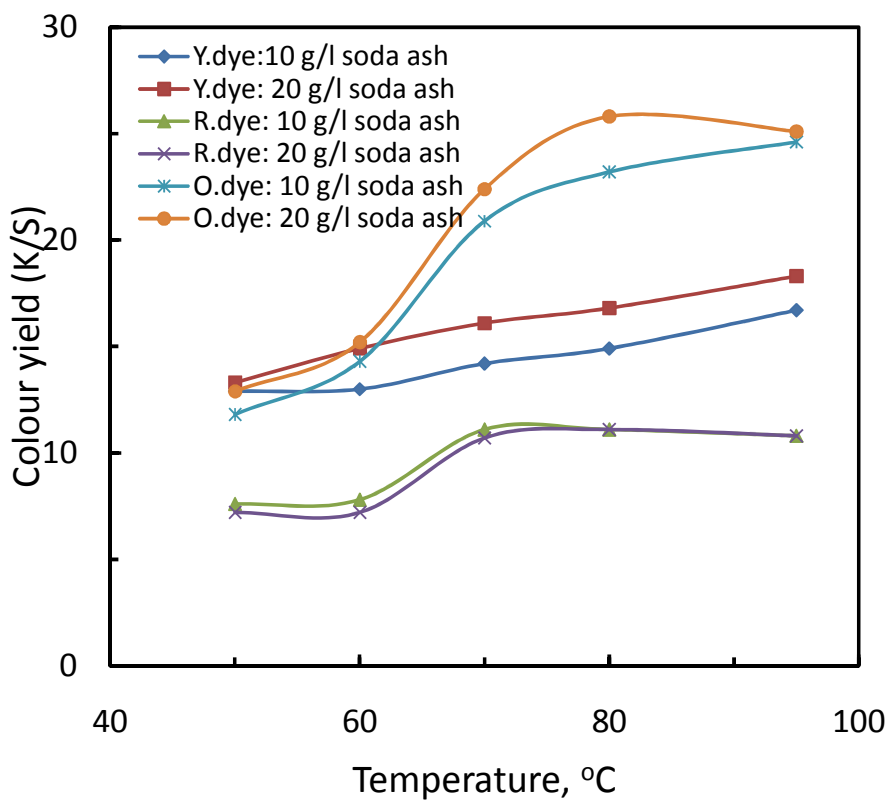


Fig. 3. Effect of soda ash concentration on colour yield (K/S) of synthesized reactive dyes (2% depth) for dyeing of 120 min

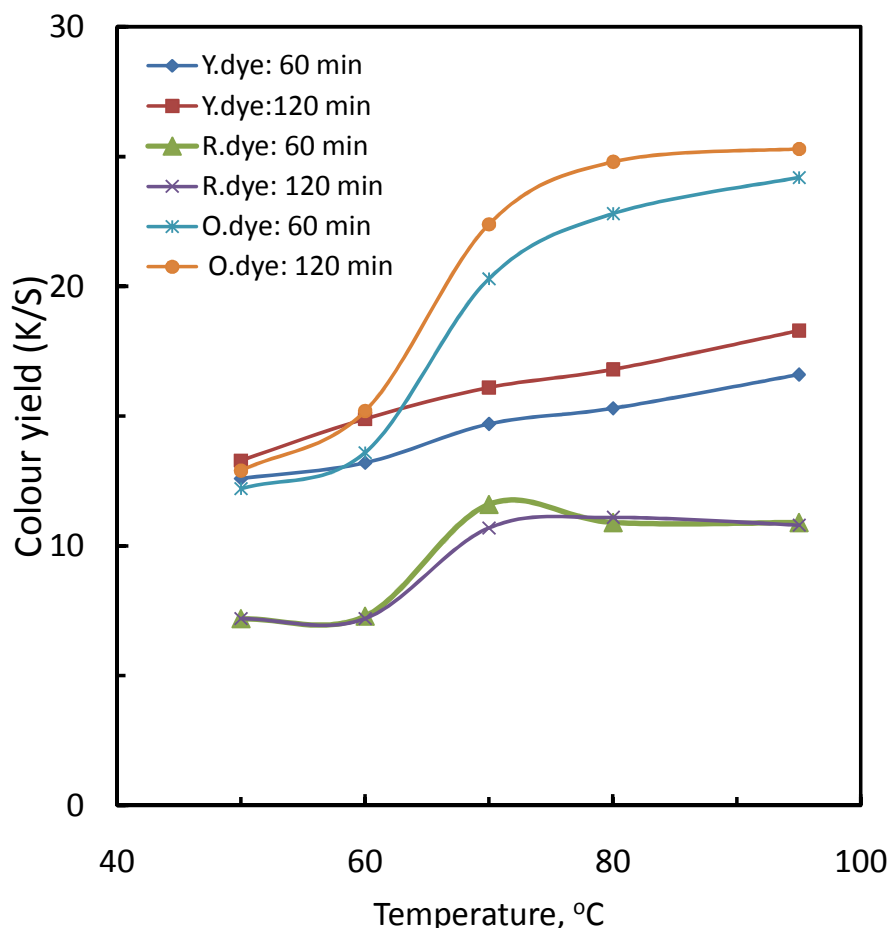


Fig. 4. Effect of dye time on colour yield (K/S) of synthesized reactive dyes (2% depth) using 20 g/l soda ash at 95°C

4. CONCLUSION

Three reactive dyes containing acrylamido group were synthesized and applied to cotton by exhaust dyeing. Yellow dye and orange dye produced maximum color yield using 20 g/l soda ash at 95°C for 120 min fixation time. But in the case of red dye, the fixation temperature and time were 70°C and 60 min, respectively. At higher temperature and longer fixation time, this dye hydrolyzed. The light and wash fastnesses of the dyed cotton fabric have shown good performance.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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