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## Synthesis and Characterisation of Azo-Based Dichlorotriazine Reactive Dye with Halochromic Behaviour

*Sinteza in karakterizacija diklorotriazinskega reakcijskega  
barvila na azosnovi s halokromnim odzivom*

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### Abstract

Halochromism or pH sensitivity has tremendous potential for applications in various textile fields, such as protective clothing, wound dressings, etc. Reactive dye is mostly used to colour cotton or other regenerated cellulose fibres due to its better fastness and wide range of hue, from vivid to dull shades. In this research work, an azo-based dichlorotriazine reactive dye was synthesised from H-acid (4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid) and 4-nitroaniline, which incorporates a halochromic behaviour. The change of colour of this dye was evaluated both in the the solution stage and coloured fabric stage in various pH solutions. A visible change of colour with the alteration of pH was observed after dyeing textile fabric with the synthesised dye. However, a significant difference was observed in a few cases with regard to the change of colour with the alteration of pH in the solution stage and coloured fabric stage. The dyed fabric also displayed very good to excellent wash fastness properties. Generally, the reactive dye synthesised in this research demonstrated an obvious change of colour with the alteration of the pH level.

Keywords: chromism, H-acid, 4-nitroaniline, synthesis, halochromic, dichlorotriazine, reactive dye

### Izvleček

Halokromizem ali občutljivost na pH ima široke možnosti za uporabo na različnih tekstilnih področjih, kot so zaščitna oblačila, povoji za rane itd. Reaktivna barvila zaradi boljše obstojnosti in širokega razpona barvnih odtenkov, od živih do pastelnih tonov, večinoma uporabljajo za barvanje bombaža ali regeneriranih celuloznih vlaken. V tej raziskavi je bilo iz 4-amino-5-hidroksi-2,7-naftalendisulfonske kisline (H-kislina) in 4-nitroanilina sintetizirano diklorotriazinsko reaktivno barvilo na azosnovi. Barvilo omogoča halokromni odziv, to je spremembo barve, ki je bila ocenjena v raztopini in na obarvani tekstiliji pri različnih vrednostih pH raztopin. Po barvanju tkanine s sintetiziranim barvilom je bila opažena vidna sprememba barve s spreminjanjem vrednosti pH. V nekaj primerih je bila ugotovljena tudi pomembna razlika

v spremembi barve s spremembo vrednosti pH raztopine in na obarvani tkanini. Obarvana tkanina je imela tudi zelo dobro do odlično obstojnost pri pranju. Na splošno je reaktivno barvilo, sintetizirano v tej raziskavi, pokazalo zaznavno spremembo barve s spreminjanjem vrednosti pH.

Ključne besede: kromizem, H-kislina, 4-nitroanilin, sinteza, halokromen, diklorotriazin, reaktivno barvilo

## 1 Introduction

Chromic materials reversibly change colour as a reaction to a change in external stimulus. Based on the nature of the stimulus, the resulting chromism is classified as thermochromism (induced by temperature), photochromism (induced by light), halochromism (induced by pH), etc. [1]. Chromic materials are widely used to cover products to exhibit chromic phenomena in the field of smart or intelligent materials [2]. For various textile uses, such as wound dressings, protective garments, etc., the concept of halochromism may be of tremendous significance. Because of their flexibility, comfort, and ability to cover huge surfaces, these halochromic textile pH-indicators are more beneficial than traditionally applied sensor elements. For this reason, research usually focuses on the connection between the chemical construction of dyes and their halochromic nature in liquid instead of their performance in a textile substance. The performance evaluation of the dyes absorbed in a textile material is also essential [3].

Azo dyes have been well-accepted on the global market because of their simple synthesis process, the capability to produce a wide range of shades, and their vast applications in various fields, such as papers, textiles, additives, cosmetics and organic synthesis [4-5]. Around 60-70% of azo dye is consumed in the traditional textile wet-processing industry [6]. In the case of azo dye, an associated  $\pi$ -configuration is observed, and is linked to two aromatic subdivisions (generally benzene and naphthalene derivatives) by a nitrogen–nitrogen double bond (N=N) [7-8]. As a result of the fairly easy synthesis process and the wide range of colours, azo dyes are the most available category of colourants. Some azo dyes change colour because of their chromic characteristics related to extrinsic consequence [2]. Reactive dye has the ability to remove the unfixed dye from the fabric surface more efficiently, ensuring excellent washing fastness to dyed or printed fabric based on the colour change in shade and staining of an adjacent textile substrate [9]. Reactive dyes have the advantage over natural dyes and other synthetic dyes. They form a covalent bond between the dye and fibre after application to

the fibre surface. This covalent bond is produced between a carbon atom of the dye molecule and an oxygen, sulphur, or nitrogen atom of an amino, hydroxy, or thiol compound on the polymer matrix. Due to the formation of a strong covalent bond after the application of dyes to the textile substrate, this dye is difficult to remove and, as a result, has superior wash fastness characteristics [6].

Today, several examples of chromic phenomena have been applied in our everyday life, such as photochromic lenses for spectacles and thermochromic temperature indicators, for example, in baby spoons [10]. Another significant aspect of chromism is halochromism, which depends on the degree of acidity or pH level. Halochromic or pH-sensitive materials, included under the subclass of ionochromic materials, vary in colour depending on pH, and are currently subject to more frequent researches [11]. Halochromic dyes that cause a change from one colour to another due to a bathochromic or hypsochromic shift of the absorption peak upon (de)protonation are categorised as positive and negative halochromic dyes, respectively [12]. The basic principle of the colour change of a halochromic substance is the protonation or deprotonation of the dye molecule, causing a different electron arrangement, resulting in a change in the colour of that material. The origin of apparent colour alteration of halochromic dye is the ring-opening of the dye molecule upon (de)protonation, or on tautomerism, as tautomers have various colours and tinctorial strengths [13]. In addition to the more well-known thermochromism and photochromism, the comparatively less-utilised halochromism or pH sensitivity has tremendous potential for use in various textile applications as pH sensors [3]. Halochromic textiles have huge potential as sensors that can signal a medium's pH through the simple visual observation of colour, and can be implemented in a wide variety of fields [14]. Hesus et al. (1892) first declared that the human skin surface is acidic, and this concept was confirmed again by Schade and Marchionini (1928) [15, 16]. This acidic medium differs in the pH range between 4–6, which is influenced by a person's anatomical state and age. Due to the presence of different acids, such as amino acids, fatty acids and others

formed and discharged by the keratinocyte coating and the skin protuberances, the natural lactate-bicarbonate buffer structure of the body shifts on to an acidic medium [16]. In chronic wounds, the medium of pH has been found in the range of 7.15–8.9. A wound's pH shifts alkaline to neutral and later becomes acidic as the wound advances towards the healing process [17]. A halochromic wound dressing can be implemented as an indicator to monitor the state of the wound surface's healing just by observing the alteration of colour in the bandage without removing the gauze. Thus, a pH-indicator wound dressing can be an effective observation system.

Consequently, potential damage to a patient's wound area might be reduced, as well [14]. For this reason, the successful application of halochromic dye as a textile pH indicator on wound dressing can play a crucial role in the field of medical textiles. Furthermore, in the human body, pH value plays a significant role in many other crucial processes. Thus, halochromic textile might play a vital role in determining the acidity of sweat, nasal discharge, urine, etc. [18, 19]. On the other hand, a textile pH indicator in protective clothing can identify the existence of acid vapours in an operating environment [1]. However, no significant previous research attempt or literature has been found to synthesise reactive azo-based halochromic dye as a potential pH sensor for textile materials.

The principal aim of this research article was to synthesise a new azo-based dichlorotriazine reactive dye from H-acid (4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid) and 4-nitroaniline, which have halochromic properties. The change in colour of this dye was observed in various pH solutions. After that, 100% cotton woven fabric was dyed with the newly synthesised dye following the conventional dichlorotriazine reactive dyeing procedure. In addition, the halochromic behaviour of the dyed fabric was investigated at various buffer pH solutions. To investigate and analyse the halochromic behaviour of syn-

thesised dye in the solution stage, analytical methods such as UV-vis spectroscopy, were used. CIELAB values of the dyed fabric in various pH solutions were examined using a chroma meter. Finally, the purity and molecular arrangement of the synthesised dye were investigated using thin-layer chromatography (TLC).

## 2 Experimental

### 2.1 Fabric

In this research, 100% cotton plain weave fabric, with a mass of 102.93 gm/m<sup>2</sup>, and a fabric density of 48 threads/cm in warp and 32 threads/cm in the weft direction was used. The fabric was provided by Whaley's of Bradford (UK).

### 2.2 Chemicals

For dye synthesis, H-acid (4-Amino-5-hydroxy-2,7-naphthalenedisulfonic acid, 88%), cyanuric chloride ( $\geq 99\%$ ), 4-nitroaniline ( $\geq 99\%$ ), nitrous acid (HNO<sub>2</sub>) (99%), sulfamic acid (H<sub>3</sub>NSO<sub>3</sub>) (99%), dihydrogen phosphate ([H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup>) ( $\geq 99\%$ ) and disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) ( $\geq 99\%$ ) were supplied by Sigma-Aldrich, UK and used as received. Disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) and citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) were used for the preparation of buffers.

### 2.3 Synthesis of azo-based dichlorotriazine reactive dye

The synthesis of the dye comprised three steps: modification of H-acid (4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid), diazotising of nitroaniline (4-nitroaniline) to obtain diazonium salt, and coupling by reacting the obtained diazonium salt in the modified H-acid (4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid) solution.

#### Modification of H-acid (Step 1)

H-acid (4-Amino-5-hydroxy-2,7-naphthalenedisulfonic acid, 5.0 g, 0.012 mol) was dissolved in

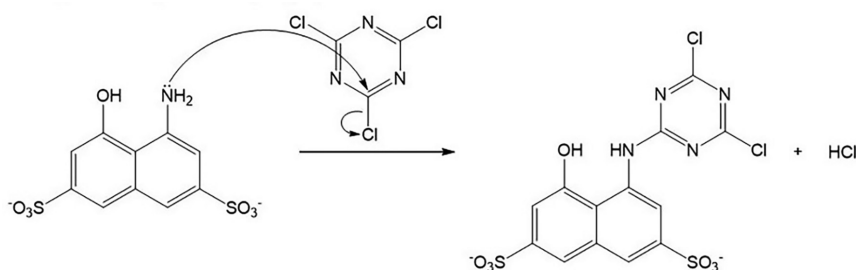


Figure 1: Route for the formation of dichlorotriazine reactive dye

50 cm<sup>3</sup> water and the pH adjusted to pH 7 with an NaOH dilute. The solution was then cooled to 0–5 °C in an ice bath. Cyanuric chloride (2.8 g, 0.015 mol) was dissolved in acetone (20 cm<sup>3</sup>), cooled in an ice bath to 0–5 °C, then added to the H-acid solution over 30 minutes at 0–5 °C with no pH control. The reaction, shown in Figure 1, was stirred for a further 15 minutes, monitored at intervals for the presence of free aromatic amine with Ehrlich reagent. Small amounts of cyanuric chloride dissolved in acetone were added at 15-minute intervals, if required, to lead the reaction to completion, after which the pH was raised to pH 6 using NaOH (1M).

### Diazotisation (Step 2)

4-nitroaniline (1.65 g of nitroaniline; 2.24 g of dinitroaniline, 0.012 mol) was dissolved in water (50 cm<sup>3</sup>) and cooled to 0–5 °C in an ice bath. Concentrated hydrochloric acid (3 cm<sup>3</sup>) was then added with mechanical stirring. A solution of sodium nitrite (1.0 g, 0.014 mol) in water (20 cm<sup>3</sup>) was added to the solution of nitroaniline in drop form over 15 minutes. When the addition of sodium nitrite was complete, the reaction solution was stirred for a further 30 minutes at 0–5 °C. A small quantity of sulfamic acid (99%, 97.09 g/mol) was added to destroy excess nitrous acid until starch–iodide paper no longer turned blue.

### Coupling (Step 3)

The modified H-acid solution of step 1 was cooled to 0–5 °C, and its pH raised to pH 9–10 with the addition of NaOH. The diazonium salt prepared in step 2 was poured into an ice-cold solution containing 7.4 g sodium acetate and 3.63 g acetic acid to raise its pH to a neutral level. The diazonium salt solution was immediately added to the modified H-acid from step 1 in drop form over 30 minutes at 0–5 °C. The pH of the solution was kept between 9.5 and 10, using NaOH dilute throughout the process. The solution was then left stirring for one hour, after which the temperature was no longer controlled.

### Precipitation and filtration procedure of the synthesised dye

After completing the dye synthesis, sodium chloride (20% w/v) was added to the synthesised dye solution to separate the dye. The solution was stirred continuously using a mechanical stirrer until all of sodium chloride was dissolved. The separation of the solid dye from the liquid mixture was achieved using vacuum filtration. In a Buchner funnel, the combination of precipitated dye and fluid was discharged over a filter paper. The liquor was drained over the funnel into a flask through a vacuum, and filter paper captured the solid dye. Finally, the filtrated dye was mixed with 0.6 g potassium dihydrogen phosphate and 1.4 g disodium hydrogen phosphate. The dye was then placed in a desiccator for 12 hours to dry thoroughly.

### 2.4 Dyeing procedure of synthesised dichlorotriazine reactive dye

The dyeing procedure, schematically presented in Figure 2, was carried out in Labomat BFA-8 (Mathis, Switzerland) infrared lab dyeing machine. Cotton fabric was dyed using the dichlorotriazine reactive dyeing technique. A higher dye concentration (5% on the mass of fabric) was applied to get a reasonably deep shade. With specific concentrations of dyestuff, 60 g/L of salt and 10 g/L of soda ash were applied for the dyeing of cotton fabric with synthesised dye. The liquor-to-goods ratio used in this dyeing process was 10:1. At first, the required amount of dyestuff was added to a dye bath at a temperature of 30 °C. The salt was then added in three steps at intervals of 10 minutes, 10 minutes and 15 minutes. The dye bath was run for 15 minutes in this condition. After that, soda ash was added in two steps, at 15-minute intervals. The fabric was dyed for 30–40 minutes at 30 °C [20].

After completing the dyeing process, the fabric was rinsed in cold water for 2 minutes, boiled at 80 °C for 5 minutes, warm-rinsed at 60 °C for 5 minutes, and finally rinsed in cold water for 2 minutes. The fabric was then dried thoroughly [20].

### 2.5 Preparation of McIlvaine buffer system

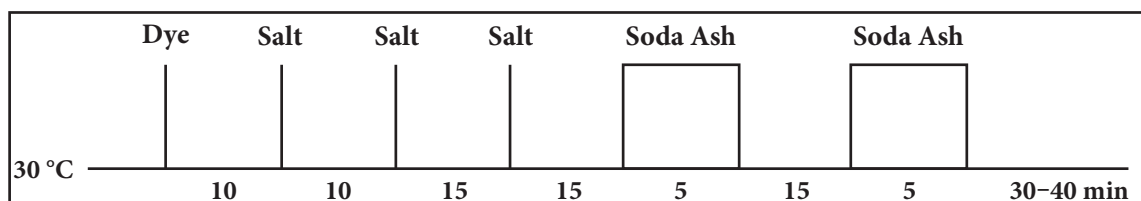


Figure 2: Standard exhaust method for dichlorotriazine-based reactive dye [20]

Table 1: McIlvaine buffer system in different pH [21]

pH required	0.2 M Na <sub>2</sub> HPO <sub>4</sub> (cm <sup>3</sup> )	0.1 M citric acid (cm <sup>3</sup> )
2.2	0.40	19.6
3.0	4.11	15.89
4.0	7.71	12.29
5.0	10.30	9.70
6.0	12.63	7.37
7.0	16.47	3.53
8.0	19.45	0.55

Buffers of different pH values were prepared to measure the change of colour of both dyes in solution and fabric. A total of 20 mL of buffer solution was prepared using 0.2 M disodium hydrogen phosphate and 0.1 M citric acid of the appropriate amount according to Table 1.

## 2.6 Analysis

### UV-vis spectrophotometry

In this study, the change of maximum wavelength and absorbance of dye in different pH solutions was identified using a M550 (CamSpec, UK) double-beam scanning UV/Visible spectrophotometer. All sample solutions were placed in quartz cuvettes with a 10 mm light path. The amount of dye concentration was calculated based on a calibration curve. The spectra were recorded from 400 nm to 700 nm.

### Colorimetric measurements

A CS-200 chroma meter (Konica Minolta, Japan) was used to measure the CIELAB values of the dyed fabric to analyse the change of colour in an aqueous solution at different pH values, maintained by hydrochloric acid (HCl) and sodium hydroxide (NaOH). Measurements of colour were performed under the following conditions: white tile: X = 271.04, Y = 281.28, Z = 285.31; viewing angle: 65°; capture angle: 1°.

### pH analysis

The pH analysis was performed using a Metrohm 654 digital pH meter (Metrohm, UK) combined with a reference electrode and glass electrode.

### Thin-layer chromatography (TLC) analysis

In this research, TLC was used to analyse the purity and individualise the chemical components present in the synthesised dye. Thin-layer chromatography

was performed using ethyl acetate-m-butanol-n-propanol-water in a ratio of 1:2:3:4 as the mobile phase, while an aluminium plate coated with silica gel 60 F254 (Merck, UK) was used as the stationary phase. The developed plate was studied under both visible and ultraviolet light (360 nm wavelength), and finally, the retention factor ( $R_f$ ) was determined [22, 23].

The value of  $R_f$  was calculated using the following equation (1):

$$R_f = \frac{\text{distance travelled by the component}}{\text{distance travelled by the solvent}} \quad (1)$$

### Colour fastness to washing

The colour fastness to washing test of dyed fabric was carried out according to the ISO 105-CO6:2010 (ISO, 2010) Standard in a GyroWash Tester (James Heal, UK). The washed specimen was evaluated visually using the Grey Scale according to the ISO 105-A02 (for assessing colour change) and ISO 105-A03 (for assessing staining) Standards.

### Determination of response time

The response time was recorded after immersing the synthesised dyes into various buffer solutions until a visible change in the colour of the solution occurred. The response time was also determined after absorption of the dyed fabric sample at different buffer solutions until the clear visible alteration of colour in the fabric surface appeared.

## 3 Results and discussions

The chemical structure of the synthesised dye is shown in Figure 3.



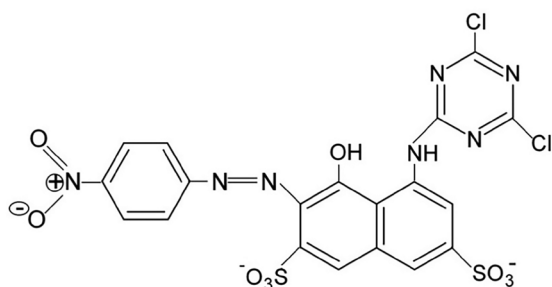


Figure 3: Structure of the synthesised dye

Figure 3 shows that the synthesised dye molecule contains an azo ( $-N=N-$ ) group as a chromophore or colour-bearing group, and two sulphonate groups ( $SO_3^-$ ) as a water solubilising group. Due to the presence of two sulphonate groups, the water solubility of this dye is high. The dye molecule possesses a bridging group, such as  $-NH-$ , which increases substantivity because of hydrogen bond formation. On the other hand, the dichlorotriazine group acts as the reactive functional system in this synthesised dye [24].

The UV-visible absorption spectrum of the synthesised dye was determined by dissolving it in distilled water (0.05 g/L solution) at a wavelength of between 400–700 nm. From Figure 4, the wavelength of maximum absorption ( $\lambda_{max}$ ) of the synthesised dye is identified at 506 nm, which appeared in the visible region of the spectrum due to the ascription on  $\pi-\pi^*$  transition of the azo ( $N=N$ ) chromophore group of synthesised reactive dye [25]. The spectral peak appears slightly wide, resulting in some impurities present in the dye [26].

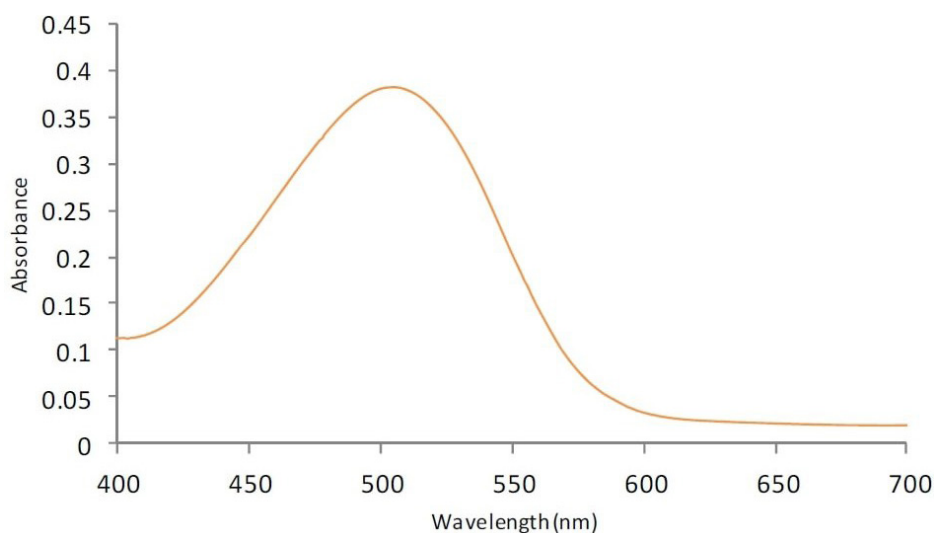


Figure 4: UV-vis spectrum of the synthesized dye

### 3.1 Visual observation of colour change in the solution stage of dye in different pH solutions

The synthesised dye solution (5 g/L concentration) is applied in different McIlvaine buffer solutions (pH range of 2.2–12) to detect the visual change of colour, as presented in Figure 5.

It is evident from the visual perception of the dye solution at different pH values shown in Figure 5 that at pH 2.2, the dye's solution appeared reddish-orange. After that, it turned red and continued until pH 7. However, the colour of the solution turned bluish-red at pH 8. The dye solution's colour became purple at pH 9.2 and finally turned dark blue in extremely alkaline conditions at pH 12.

### 3.2 UV-vis spectrophotometer results of the synthesised dye in different pH solutions

The shifts of maximum wavelength ( $\lambda_{max}$ ) and absorbance of the synthesised dye (0.05 g/L concentration) solution were analysed in a buffer solution of different pH values. The results are shown in Table 2.

Table 2 shows that in the visible area of the spectrum, a significant increase of absorbance is detected at 670 nm in pH 7.0. The  $\lambda_{max}$  differs with pH from 622 nm at extremely acidic pH to 430 nm at extremely alkaline pH, which corresponds to the visual colour transition from reddish-orange to dark-blue. The principal reason for the colour change is the protonation or deprotonation of the dye molecules, resulting in various electron configuration changes [27]. Protonation and deprotonation of studied dye are presented in Figure 6.

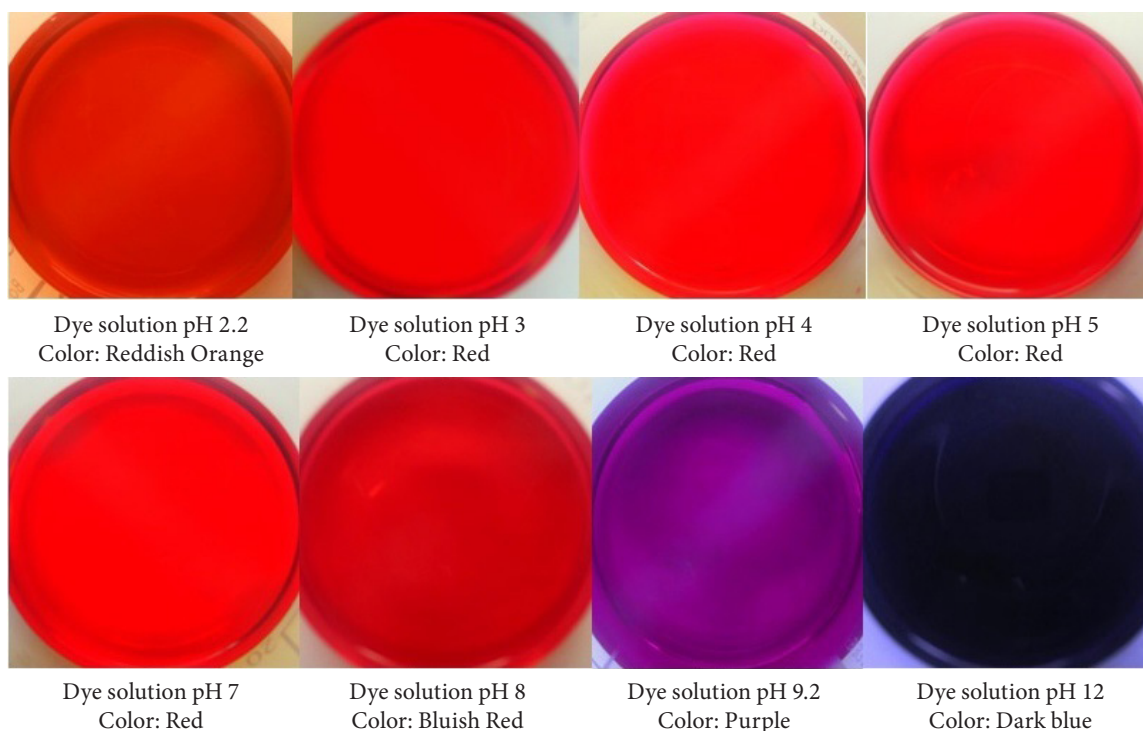


Figure 5: Colour change of synthesised dye in different pH solutions

Table 2: UV-vis analysis of dye synthesised from H-acid and 4-nitroaniline in different pH solutions

Mcllvaine's buffer pH	Dye solution pH	Maximum wavelength ( $\lambda_{max}$ ) (nm)	Absorbance
2.2	2.24	622.00	1.06
3.0	3.02	665.00	1.05
4.0	4.08	667.00	0.75
5.0	4.99	670.00	0.82
7.0	7.01	670.00	1.40
8.0	8.10	630.00	0.95
9.2	9.21	489.00	0.94
12.0	12.11	430.00	0.56

From pH 2.2 to 3.0, a significant bathochromic shift  $\lambda_{max}$  (43 nm) occurred due to the protonation of synthesised dye (Figure 6, structure I<sub>a</sub>) [28], while in acidic conditions, the proton and hydrogen bond of the dye's hydroxyl group might be powerful. Therefore, deprotonation becomes more difficult until it reaches acidic to alkaline conditions. The electron-donating substituents, such as hydroxyl (-OH) and amino (-NH-) groups, present in this structure are comparatively less active in acidic and neutral conditions. For this reason, from pH 3.0 to pH 7.0, a negligible bathochromic shift (5nm) was observed. However, these electron-donating

substituents gradually became active in alkaline conditions. As a consequence, the dye converted from protonated to deprotonated form (Figure 6, structure II<sub>a</sub>). Upon (de)protonation, the dye transformed into anionic form, while the dye's molecular chain became open (Figure 6, Structure II<sub>b</sub>), which results in a visible colour change of the synthesised dye. Finally, azo/hydrazone tautomerism was exhibited in the synthesised dye structure (Figure 6, Structure I<sub>b</sub>). For this reason, a significant hypsochromic shift  $\lambda_{max}$  (240 nm) was seen with a rise in pH from neutral (pH 7) to extremely alkaline (pH 12) condition [29].

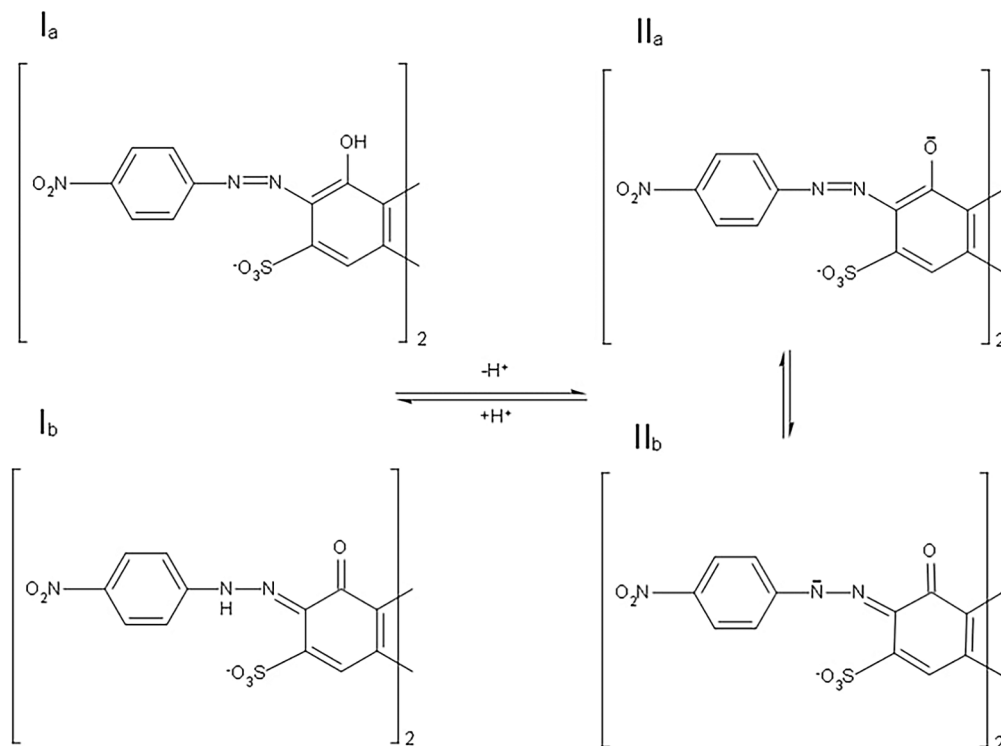


Figure 6: Acid -alkali equilibrium of the synthesised dye in aqueous buffer solutions

### 3.3 Colour change observation of dyed fabric in different pH solution

The appearance of the cotton fabric dyed with synthesised dye is shown in Figure 6.

The colour of the cotton fabric after dyeing with synthesised dye appeared reddish-pink, as seen in Figure 7. This research further investigated the halochromic behaviour of the dyed fabric sample in different pH solutions, as shown in Figure 8.

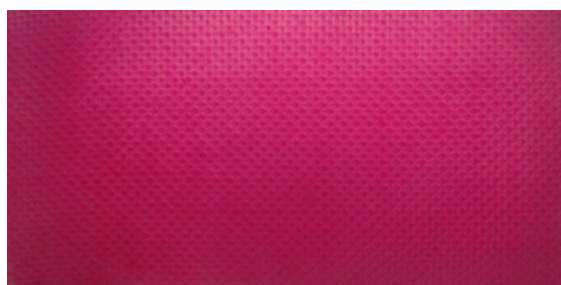


Figure 7: Cotton fabric's appearance dyed with synthesised dye concentration of 5% on the mass of fabric (o.m.f.)

It is evident from Figure 8 that an obvious change of colour was observed in the dyed fabric by changing the pH level. In an extremely acidic solution (pH 2.2), the colour of the dyed fabric appeared orange, while

at pH 3, the colour became light-orange. The colour of the fabric turned reddish-orange at pH 4. At pH 5, the colour became light-pink, turned in dark-pink at pH 6, and became reddish-pink at pH 7. However, at pH 8, the fabric's appearance became purplish-pink, turned bluish-pink at pH 9.2, and eventually turned darker-blue at pH 12.

### 3.4 Colorimetric measurements

Figure 9 shows that at various pH solutions, CIELAB values of the fabric coloured with the synthesised dye alter as well. According to CIELAB colour space,  $L^*$  constitutes lightness; coordinate  $a^*$  denotes red/green hue element, and coordinate  $b^*$  indicates yellow/blue hue attributes of the colour [30]. A significant change of CIELAB values has been observed in Figure 9 from pH 2.2 to pH 4.0 and from pH 8.0 to pH 12. On the other hand, a minor change of CIELAB values has been exhibited at pH values ranging from 4 to 8. In pH solution 2.2, the value of CIE  $L^*$  is considerably higher, the value of CIE  $a^*$  is positive, and the value of CIE  $b^*$  is also positive.

For this reason, the sample became lighter, reddish, and slightly yellowish, and the surface colour of the dyed fabric appeared orange in the solution. At pH 3.0, the value of CIE  $L^*$  is decreased, the value of CIE



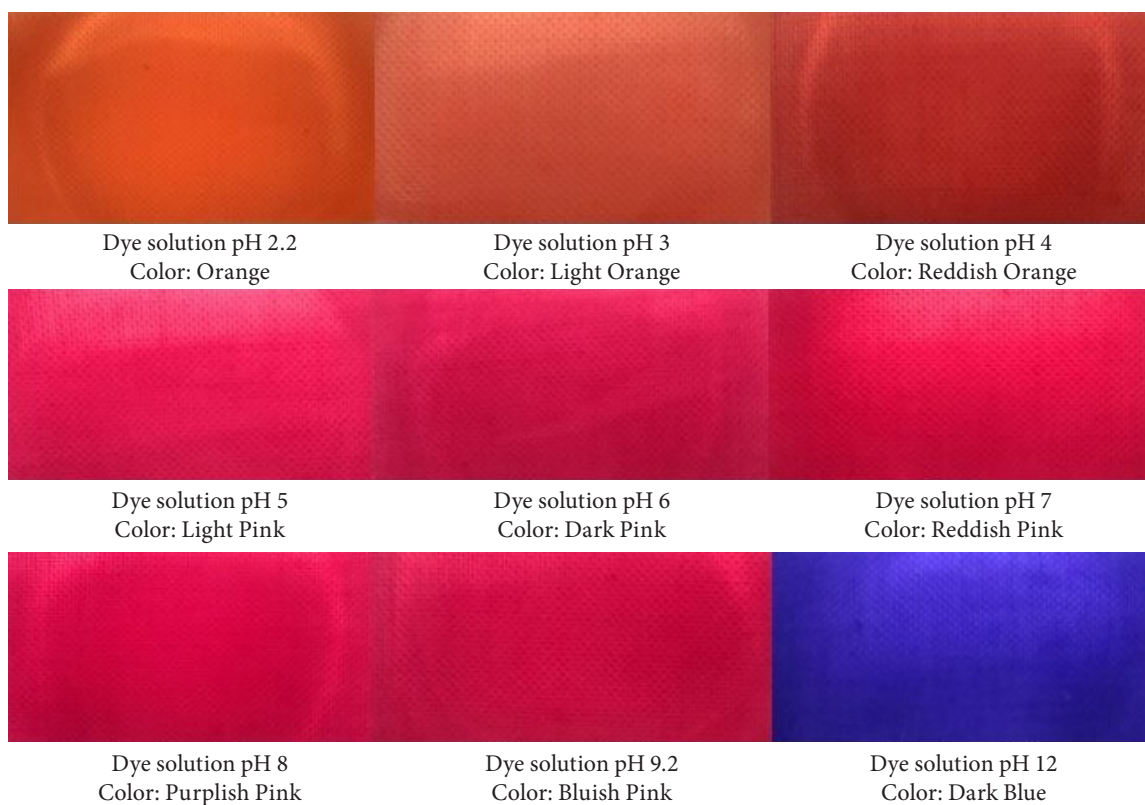


Figure 8: Colour change of cotton fabric dyed with synthesised dye in different pH solutions

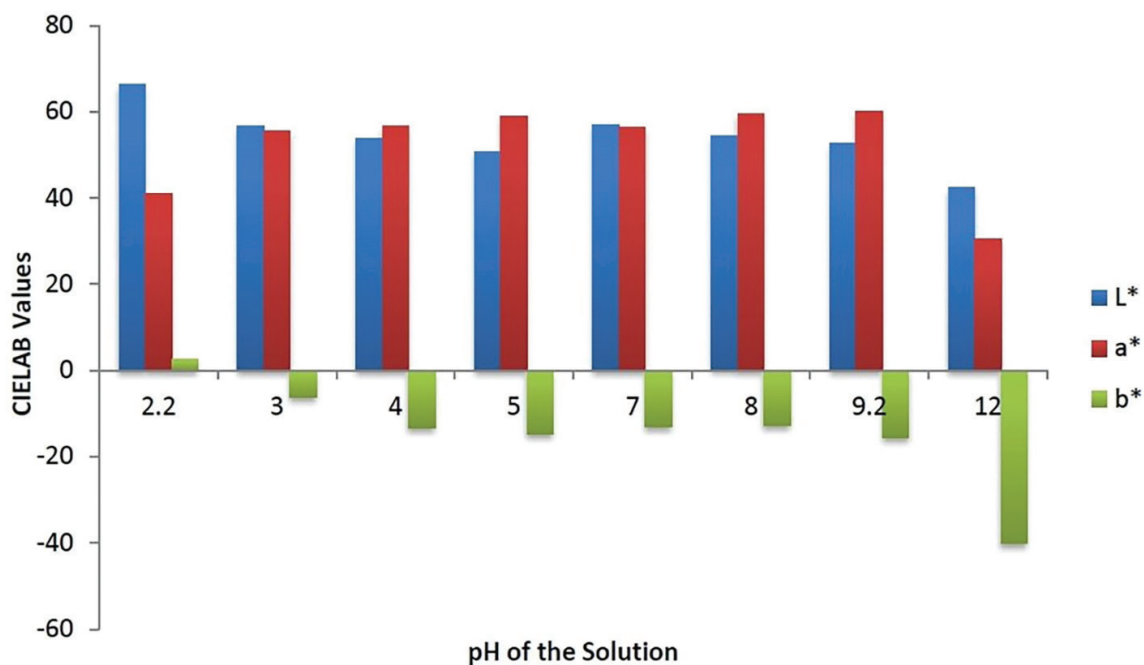


Figure 9: CIE LAB values of dyed fabric at different pH solutions

$a^*$  is increased and positive, whilst the value of CIE  $b^*$  is decreased and turned to negative. The sample became darker, more reddish, and marginally blue. The decrease of CIE  $b^*$  value usually brings a bluish tone to the fabric colour [31]. At pH 4, the sample became darker, slightly reddish, and bluer as the CIE  $L^*$  value decreased,  $a^*$  slightly raised, and  $b^*$  decreased significantly. The visual appearance of the fabric turned reddish-orange in the solution at pH 4. From pH 4 to pH 8, because of the slight variation of  $a^*$  and  $b^*$  values, the fabric's colour appeared in marginally different shades. The fabric's colour eventually became bluish-pink at pH 9.2 due to a lower CIE  $b^*$  value. Finally, in a powerful alkaline solution (pH 12), the value of CIE  $a^*$  and CIE  $b^*$  became the lowest, while the colour of the fabric shifted from bluish-pink to dark-blue.

The CIELAB values of dyed fabric immersed in different pH solutions are presented in Figure 9.

### 3.5 Wash fastness test analysis of fabric dyed with synthesised dye

The results of washing fastness of dyed cotton fabric are presented in Table 3.

The colour fastness to washing test of fabric dyed with synthesised reactive dye is assessed visually using a grey scale. The results, depicted in Table 3, showed that dyed fabric had very good (rating of 4–5) wash fastness properties. Furthermore, the dyed fabric showed slight to negotiable colour staining (rating of 4–5) on the adjacent cotton fabric. This result can be attributed to the elimination of unfixed dye molecules from the surface of the coloured cotton fabric during the wash fastness test, which then shifted to the adjacent white cotton fabric [32]. The synthesised reactive dyed fabric exhibited very good wash fastness because of the chemical fixation of dye molecules to the fibre surface through strong covalent bond formation, which ultimately resulted in the dyes' resistance to fading after washing [33]. Based on the obtained results, it can be concluded that the synthesised dye demonstrated a wash fastness rating analogous to the commercial reactive dye.

### 3.6 Thin-layer chromatography (TLC) analysis

The TLC analysed plate of the synthesised dye is shown in Figure 10.



Figure 10: TLC plate for the synthesised dye after the solvent almost reached the top of the plate

It is evident from Figure 10 that the TLC plate contains only one component, which appeared as a large red smear. This component is slightly spread on the TLC plate. Here, the distance travelled by the mixed solvent solution is 7.4 cm on the TLC plate. On the other hand, the distance travelled by the dye component was 4.6 cm. As a result, the  $R_f$  value of this component was 0.62. It is assumed that this component was the synthesised azo-based dichlorotirazine reactive dye. The value of  $R_f$  indicates synthesised dye is moderately polar. Based on the identification of only one component in the TLC analysis, the synthesised dye is deemed reasonably pure [23].

Table 3: Colour fastness to washing assessment of dyed cotton fabric

Change of colour	Visual assessment using grey scale					
	Colour staining of adjacent multifibre fabrics					
	Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
4/5	4/5	5	4/5	4/5	4/5	5

### 3.7 Response time analysis

The response time was recorded for colour changes of synthesised halochromic dye and colour changes of synthesised dyed cotton fabric in various buffer solutions. It was observed that the change in the colour of synthesised dyes occurred immediately after immersion in various pH solutions. On the other hand, it took a comparatively longer time to visualise a noticeable colour change when the dyed fabric was immersed in various buffer solutions. The response time of the cotton fabric sample dyed with synthesised halochromic reactive dye was approximately 25–30 minutes to visually notice a colour change in the fabric surface in various pH solutions. From this experiment, it is evident that, apart from the difference in halochromic behaviour, there is a substantial variation of retention time for synthesised dyes in solutions and fibrous textile matrices. The probable reason for this might be the gradual wetting properties of textile fabric, the strength of the interaction between the dyes and fibres, and the molecular structure [14, 34].

Generally, it can be assumed that this pH-sensitive reactive dye can be successfully applied to cotton fabric using a standard colouration process. However, it was observed that the diazo component used in this synthesis process produces some impurities. It is thus essential to recognise these impurities and address their effect on a dye's solubility. On the other hand, a significant difference in colour change in the solution stage and coloured fabric stage under various pH conditions was observed and may be because halochromism differs based on the constructional nature and molecular density of the fibrous substrates. Moreover, difficulties were encountered by dye molecules in accessing the fibre surface due to the slow wettability of fabric, and in the formation of a covalent bond between the dye and the hydroxyl group of cellulose, while after being applied to the fabric surface, dye molecules were immobilised as the surrounding micro-environment of the dye changed from solution to the fibrous textile matrix [14, 34]. This variation can be minimised in future work by synthesising halochromic reactive dye with a higher reactivity, more solubility, the higher affinity of dye molecules to the fabric surface, and the selection of a lower-density and more hydrophilic fabric matrix. As a result, the dye might show a comparatively similar level of colour transition both in the solution stage and the dyed fabric stage.

## 4 Conclusion

The fundamental aim of this research work was to synthesise an azo-based dichlorotriazine pH-sensitive reactive dye that will show a change in colour with the alteration of the pH solution. The colour change of this dye was observed in the solution and the dyed fabric stage. The synthesised reactive dye exhibited different halochromic properties in various pH environments. The dye synthesised from H-acid and 4-nitroaniline showed a colour transition from reddish-orange in pH 2.2 to red in pH 4.0, and eventually turned blue in alkaline conditions. In the dyed fabric, the colour turned orange to reddish-orange in the pH range 2.2–4.0, became light-pink at pH 5.0, turned bluish-pink in alkaline conditions (pH 9.2), and finally became deep-blue at pH 12. The halochromic dye synthesised in this research demonstrated colour transition from acidic to the alkaline environment both in the solution stage and dyed fabric state. As a result, the effectual application of halochromic reactive dye on cellulose fabric as textile pH sensors, such as those used to monitor wound healing through a change in colour on a wound dressing, might play a crucial role in the area of medical textile materials. However, some variation of colour change in the solution and dyed fabric stage was observed, and might be due to a change in the dye molecules' surrounding microenvironment after incorporation into the fibrous matrix. Overall, it can be concluded that the azo-based reactive dye synthesised in this research and applied to cotton fabric using a standard reactive dyeing process, as well as the dyed textile material itself, demonstrated decent halochromic attributes and could be used as textile pH indicators.

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