J. Chem. Soc. Nigeria, Vol. 49, No. 4, pp 586 - 593 [2024]

EFFECT OF DYE SULPHONATION ON THE DYEING OF NYLON, 6, 6 WITH 1-hydroxy-2-phenylazo-6-[2-chloro-4-[phenylamino] triazin-6- ylamino] naphthalene-3-sulphonic acid REACTIVE DYE

B, Ameh[1], K. A. Bello[2], I. Y. Chindo[2] and A. I, Izang[4]

1. Department of Chemistry, Abubakar Tafawa Balewa University, Bauchi. benamehxx@gmail.com 08039470926
2. Department of Polymer and Textile Engineering, Ahmadu Bello University, Zaria. belloka2000@yahoo.com 08035929230
3. Department of Chemistry, Abubakar Tafawa Balewa University, Bauchi. iychindo@atbu.edu.ng 08036294391
4. Department of Chemistry, University of Jos. tonyizang@unijos.edu.ng 08036139047

ABSTRACT

The study investigated the synthesis of monofunctional reactive triazinyl dye, base in a particular chromophore and possess a single chlorotriazinyl reactive group and the dyeing behavior evaluated on nylon 6, 6 fabrics. It was found that percentage exhaustion of the dye on nylon fibre increased with decreased pH application due to sulphonation.

INTRODUCTION

Reactive dyes been the most recent of dyes and the most popular in the world among fibre and fabric artist used first only by surface designers and recently by weavers as well [2].

Reactive dyes are class of highly colored organic substances, primarily used for dyeing nylon that attach themselves to their substrate by chemical reaction that forms a covalent bond between the molecule of the dye and that of the fibre and is much more difficult to be removed by washing then by physical [9].

Many reagents can be used as a reactive system, but only a few have met the requirements to become commercially established in a significant segment of the market [4]. Until now, the sulphonation group has been firmly established as the main auxochrome in the reactive system. The present study aim to determine the role sulphonation played in determining dye exhaustion using pH application.

Sulphonation is a reversible reaction that produces benzene sulfuric acid by adding trioxide and fuming sulphuric acid [11]. Sulphonation is a major industrial chemical process used to make a diverse range of products including dyes, colour intensifiers and organic intermediates [10].

MATERIALS AND METHODS

Materials

Reagents and Solvents

Laboratory grade reagents from reputable company such as Zayo-Sigma Germany and

ISSN 0795 - 22066

other sources was used for the synthesis of this reactive dye. These include J-acid [1-Naphthol-6-amino-3-Sulphponic acid], other are cynurric chloride [2,4,6 Trichloro-s-triazine], sodium nitrite, aniline, concentrated hydrochloric acid, ethanol, sodium hydroxide, potassium chloride, soda ash, soap solution, ice cube and industrial methylated spirit.

Equipment

Some of the equipment used for this study include a mechanical stirrer, rotational evaporator, electric oven, melting point apparatus [Barnstead electric thermal 911] and uv visible 6400/6405 Jenway Spectrophotometer.

Method

Synthesis of 1-hydroxy-2-phenylazo-6-[2-chloro-4[phenylamino] triazin-6-ylamino] naphthalene-3-sulphonic acid reactive dye

To a mixture of aniline [4.66g, 0.005mol] dispersed in 20ml of water and 14.19ml, 0.125mol of cold concentrated hydrochloric acid [30%] added to it in a solution of sodium nitrite [3.26g 0.058 mol], in 20ml of water, the solution was then cooled to temperature of about 0 – 5^o C. After 30mins the process was controlled and pH adjusted to less than 2 with dilute hydrochloric acid [8]. Urea CO[NH$_2$] was then added to destroy any excess nitrous acid. The diazo solution resulting from this preparation was then added gradually to an aqueous solution of j-acid [1-Naphthol-6-amino-3-Sulphponic acid], 11.9g, 0.05mol and pH adjusted to 6 - 6.5. The mixture was stirred for 30mins at room temperature at pH of 6.5. After which the resulting solid red product [1-hydroxy-2-phenylazo-6-amino] naphthalene-3-sulphonic acid was collected and dissolved in [100ml] distilled water and reprecipitated by slow addition of potassium chloride [KCl] [30% $^w/_w$] to de stirred solution. Without separation, the obtained precipitated solid was collected and used directly.

Cynurric chloride [2,4,6 Trichloro-s-triazine], [9.4g, 0.051mol] and crushed ice [10-20g], was added to a solution of freshly prepared product above in distilled water [100ml] at a temperature below 5^o C and pH of 5 - 6. The mixture was stirred for a period of 30mins, and pH adjusted to 6.5 and the obtained red product 1-hydroxy-2-phenylazo-6-[2,4-dichlorotriazine-6-ylamino] naphthalene-3-sulphpnic acid was filtered and collected [15]. The product obtained above was dissolved in water [100ml] and re-isolated by gradual addition [20% $^w/_v$] of potassium chloride. As a result of unknown instability of dichlorotriazine no further characterization was required and the product obtained was immediately used [17].

Aniline [4.66g, 0.005 mol] was gradually added to the prepared products above 1-hydroxy-2-phenylazo-6-[2,4, dichlorotriazine-6-ylamino] naphthalene-3- sulphonic acid in distilled water [100ml], this was then followed by raising the temperature to between 30-40^{O}C with stirring at pH 5-6 for 2hrs [15]. When the reaction termination was confirmed, the solution was allowed to stand for 30 mins and the resulting precipitated products 1-hydroxy-2-phenylazo-6-[2-chloro-4-[phenylamino]triazin-6-ylamino]naphthalene-3-sulphonic acid was dissolved in distilled water [100ml] and reprecipitated by gradual addition of ethanol [1].

Determination of Mass and Percentage Yield of the Reactive Dye

The dye produced was weighed using a weighing balance, the mass obtained, and percentage yield calculated as shown below:

% yield = $\frac{Actual\ yield}{theoreticat\ yield}\ x\ 100$ .... (1)

Determination of Melting Point

The melting point of the synthesized dye was determined using Barnsted apparatus. A small quantity of the synthesized was placed in the capillary tube and inserted into the melting point apparatus and the temperature at which the dye melted was recorded.

Determination of Molar Extinction Coefficient

The molar coefficient of the dye was calculated using maximum absorbance value of a known concentration of the synthesized dye. The equation used for the calculation is given below:

Where ε = Extinction Coefficient

c = Concentration

L_o = Intensity of the Incident light

L = Intensity of the Transmitted light.

Therefore; $\log\frac{L_o}{L}$ [absorbance]

Hence, absorbance A = εcl

Thus, extinction coefficient, $\varepsilon = \frac{A}{cl}$ ………..(2)

Dyeing

The dyeing was performed on the nylon 6,6 materials using the synthesized dye. A 1% stock solution of the dye was prepared and 20ml taken and placed in the beaker and was made to 50ml using distilled water. Water was used in raising the temperature of the dye bath [12]. Nylon 6,6 [1.0g] was made and squeezed to removed excess water for a few seconds. The fabric was placed into a dye bath maintained at temperature between 40-50°C in the electro thermal hot plate and allowed to reach boil. The time for dyeing and the temperature varied accordingly. After this, the fabric was removed and rinsed thoroughly. The dye will first absorb the fibre and reacts with, either by substitution reaction for dye containing monocholorotriazines [mct] group [3].

Determination of Percentage Exhaustion [%E]

The effect of percentage exhaustion on the dye was determined spectrophotometrically. The absorbance of the dyebath solution before and after the dyeing process was measured using a 1 cm quartz cell housed in a uv-visible spectrophotometer [16].

The percentage exhaustion of the dyebath was calculated using eqn (3)

% E = $\frac{\mathrm{OD1}-\mathrm{OD2}}{\mathrm{OD1}}\ x\ 100$ ……..(3)

Where; OD1 = optical density of the dyebath before dyeing
OD2 = optical density of the dyebath after dyeing

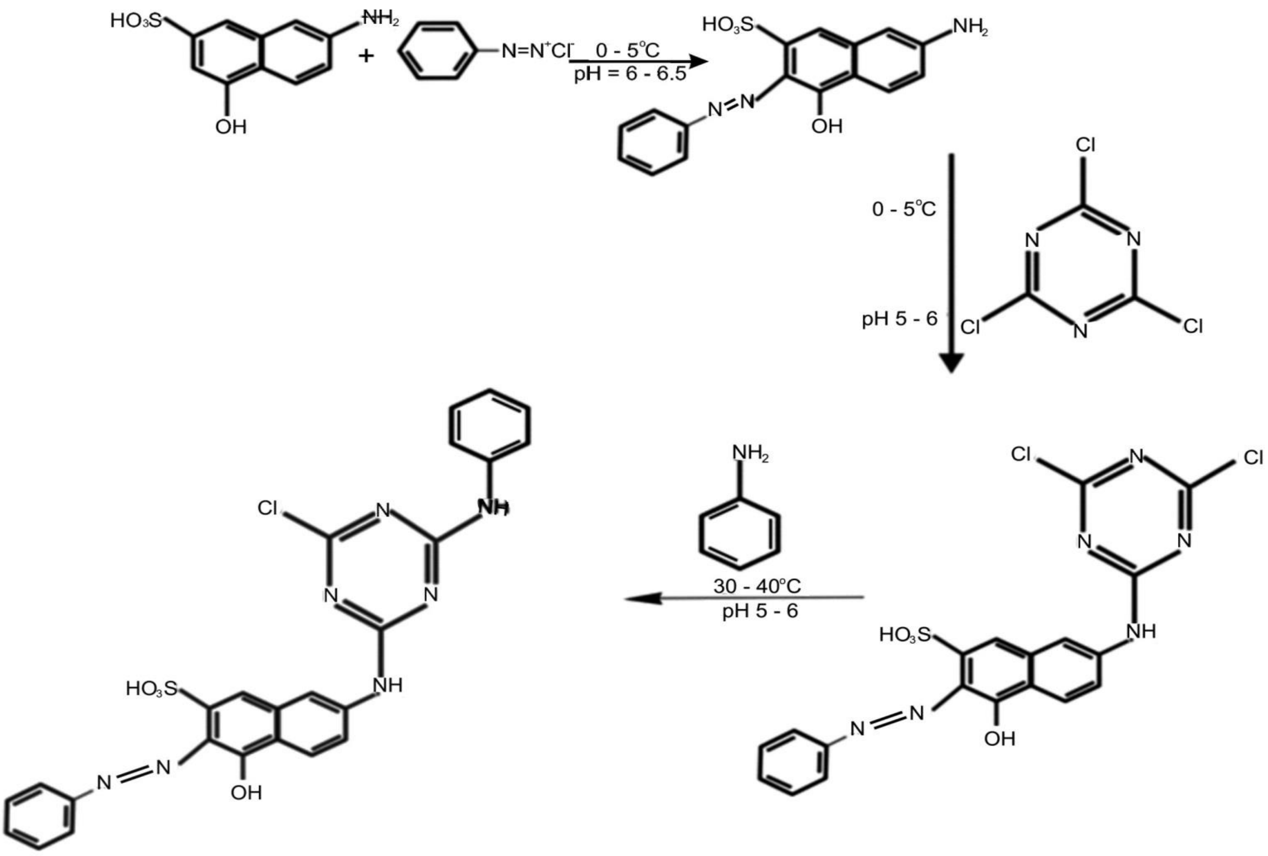
Measurement of the Dye pH

Effects of pH on dye adsorption are of great importance. Besides, controlling pH is very important in dyebath because of its effect on the dye cycle. Generally, a pH greatly influences the uptake of the dye [6].

In the case of most popular reactive dyes, a high pH activates the cellulose anions which can attack the dye molecule, leading to a reaction that produces a strong permanent covalent bond; contrary to nylon at higher pH the reverse may be expected. Also, in acid dyeing, a low pH helps to upturn the hydrogen bonds that attached acid to protein fibres, such as silk, wool and nylon as well [7].

Assessment of Change in Color and Staining

Grey scale for evaluating change in color and assessing the degree of staining adjacent undyed fabric was determined after the washing test. The procedure involves comparing the degree of contrast between the pair of color in the standard grey scale for assessing change in color. The fastness rating of the specimen under test is the number of this grey scale contrast [13].



3.1 Synthesis of 1-Hydroxy-2-phenylazo-6-[2-chloro-4-[phenylamino]triazin-6-ylamino]naphthalene-3-sulphonic acid reactive dye [15].

ISSN 0795 - 22066

Table 1: Physical Characteristics of the Synthesized Dye

Parameter	Result
Melting point	298-300^{O}C
Yield	20.6kg
Percentage yield	58%
Theoretical molecular weight	547.5g/mol
Colour	Reddish brown

Table 2: Extinction Coefficient of Dye in Acetone]

Parameter	Result
λmax [cm^{-1}]	484
Absorbance	0.756
Extinction coefficient [mol^{-1} cm^{-1}]	4200
Concentration [mol/dm^{3}]	1.8 x 10^{-4}

Table 3: Wash Fastness Rating of the Synthesized Dye

Parameter	Result
Colour	4
Staining on adjustment nylon	3

Table 4: Measurement of the Dye pH

pH	OD1	OD2	% Exhaustion
2.5	0.545	0.198	64
3.5	0.790	0.312	61
4.5	0.957	0.394	59
5.5	1.056	0.445	58
6.5	1.348	0.741	45
7.5	0.968	0.661	32
8.5	0.870	0.604	31
9.5	1.789	1.207	28
10.5	1.818	1.324	26
11.5	1.345	1.081	24
12.5	0.708	0.563	20

Discussion

Visible absorption spectra

From the results obtained on Table 1: The synthesized dye was reddish brown, percentage yield was satisfactory and molecular weight range was 547/5 g/mol. This explains the relationship between dye exhaustion and dye molecular structure, as large molecules promotes more intercellular interaction due to vanderwaals force between the dye and nylon fabric resulting in increase dye exhaustion [5].

Spectrophotometric measurements

The result on table 2: Shows the exhaustion coefficient of the dye. The wave length of maximum absorption was 484nm. The dye is bathochromic with its diazo component derive from anilines [14].

Wash fastness rating of the dye

The synthesized dye was subjected to international standard organizations ISO3 wash fastness test and the result observed and recorded in Table 3, the level of fastness displayed by reactive dyeing on nylon substrate to washing with sulphonate groups show a very good to excellent wash fastness with corresponding assessment of the extent of staining. The adjacent nylon shows little staining.

Effect of pH on dye exhaustion

The table 4: Shows the effect of pH on dye exhaustion. The result shows that percentage exhaustion of the dye on nylon fibres increases with decreased pH application. The reason being that at lower pH values, higher extent of protonation of the amino group on the nylon fibres leads to a higher dye exhaustion.

In addition, at lower pH the monochlorotriazinyl type of reactive dye was prevalent only at low concentration in the dyebath because at low concentration nucleophilic amino group in the substrate are unable to react with the dye [15]. Also, at low pH the monochlorotriazinyl reactive dye was prevalent only at concentration in the dyebath. Hence, most of the dye fibre interaction was assumed to have occurred between protonated amino groups.

CONCLUSION

Indeed, this study turned its attention to the alteration of characteristics properties of dyes, leading to the production of better-quality dye containing triazolyl group. This fact eventually provides cheaper and more efficient substitutes over the already existing dyes with availability of materials. The synthesized dye will be economically viable, safe, and environmentally friendly.

ACKNOWLEDGEMENTS

My deepest thanks goes to my supervisors Prof. K.A. Bello, Prof, I.Y. Chindo and all staff of Chemistry Department Abubakar Tafawa Balewa University, Bauchi.

REFERENCES

1. M.R.F, Ashwarth [1964]. Titrimetric Organic analysis Part 1: Direct method. 1st edition New York John Wiley and Sons Inc; P. 441

2. M. Balter, [2009]. Clothes make the [Hu] Man, Science 325 [5966]; 1329.

3. S, M, Burkinshaw, S.N. Chadi, and D.J., Martel, [2000]. Printing of Nylon 6, 6 with reactive dyes. *Dyes and pigment*. 45: 235.

4. M. Edyta and R. Edward, [2003]. The Characteristics structural feature if typical reactive dye molecule. *Autex Research Journal,* 3[2]; 116, 90-530 Lodz Poland,

5. A. I., Ezeribe, K.A., Bello H.M. Adamu C.J., Chukwa, D.A Borgo, and F. Omazogba, [2013]. Synthesis and dyeing properties of Bi-functional reactive Dyes and Cotton Fabric. *Academic journal of Interdisciplinary primary studies*. 3[5]; 125-130.

6. Fashion Apparel [2017]. pH level for Different Stages of Cotton and Polyester dyeing http://www,fashion apparel. Blogspot.com.

7. Hangzhom Emperor [2015]. Chemical Co. Ltd Inc. China. http://m.direct dyes.

8. E. Knetch, and E. Hibbert, [1925]. New Reduction Methods in Volumetric Analysis London-Longman, Green and Co.

9. Mazharul, K.R. [2011]. Dyeing Processes http://textile learner. blogspot.com.

10. Norman, C.E. [2017]. Sulphonation and Sulphonation Processes. http://www.Chemton.com.

11. T.W., Sanda, H., Walter, Renggeberg and Samuel, L.N. [1955]. On the Mechanism of Sulphonation of Aromatic Nuclues and Sulphonic Formation. J. Organic Chemistry 66: 455-456.

12. Society of Dyes and Colourist [2017]. Colouration Technology. http://Online Library Wiley.com

13. Society of Dye and Colourist [1990]. Standard Methods for the Determination of the color fastness of textiles and leather 5th edition. Branford, UK; Society of Dyers and Colourist.

14. K.R, Srikat, and S. Pamsariyya, [1988]. Method of Chemical Modification of Cellulosic Fibres to improve their dyebility with reactive dyes. *J. Science* 23, 143-153.

15. G.H. Suleiman, and J.A. Taylor, [2005]. Dyeing of Nylon with Reactive Dyes; *Dye and Pigments*. 19-127.

16. M. Sumithra, and D. Arasi [2014]. Method of Dyeing of Nylon 6, 6 with Cold Brand Reactive Dyes. Assessment of its Fastness Property. *J. Tex Sci.* Eng. 52: 002.doi:1041 92/2165-8064; 52-007.

17. P. Vollhardt, [2007]. Organic Chemistry Structure and Function; 5th edition Boston. W.A. Freeman and Company.