



ON THE SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF PARA-NITRO ANILINE-BASED REACTIVE DYE

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ABSTRACT: *The dye was synthesized by nitration of aniline to para-nitro aniline, diazotization and coupling reactions. The melting point of the para-nitro aniline was taken to yield 147°C. The result from the GC-MS shows that the compound with the highest relative abundance of 100% showed a molecular ion peak of 129.4 compounds which correspond to lower relative abundance. Also from the GC-MS result, the two peaks of masses 57.5 g and 83.4 g respectively correspond to fragments of the samples. Ultra-violet spectrophotometer was used to determine the absorption of the dye. The para-nitro aniline dye as synthesized showed the highest absorbance of 2.214 at 220 nanometers. The dye was applied to pure cotton and cellulose. The percentage shift of the dye toward the fabric i.e. percentage exhaustion of the dye was calculated to yield 73% which shows that the reactive dye has high exhaustion value. Fastness test was carried out on the dyed fabric to characterize the material's color resistance to fading and running. These tests are heat, light and wash fastness which is rated 1-5 according to Ukponwam and Odilora (2000) where 1 shows poor fastness and 5 very good fastness. The wash, heat and light fastness of 4, 5 and 5 respectively shows that the dyed fabric has an excellent fastness to washing, heating and sun drying.*

KEYWORDS: Diazotization, Chromatography, Dyestuff, Exhaustion, Fastness.



INTRODUCTION

Advances in structural theory led to investigation of correlations between chemical constitution and color but German chemists Carl Graebe and Carl Liebermann recognized that dyes contain sequences of conjugated double bonds:

$X = C - C = C - C = C \dots$, where X is carbon, oxygen or nitrogen. Also German Chemist Otta Witt proposed that dyes contain conjugated system of benzene rings bearing simple unsaturated groups (e.g., $-\text{NO}_2$, $-\text{N}=\text{N}-$, $-\text{C}=\text{O}$), which he called chromophores (unsaturated groups which are responsible for colors contained by all colored organic compounds) and polar groups (e.g., $-\text{NH}_2$, $-\text{OH}$), which he called auxochromes (compounds that generally deepen the color of a chromogen but cannot by themselves impart color to a compound). Examples of dyes each containing a different chromophore includes azobenzene, xanthen and triphenyl methane, Alizarin contain anthraquinone chromophore. The electromagnetic spectrum spans a wavelength range of 10^{12} meters, from long radio waves to short X-rays but human eyes detect radiation over only the small visible range of 400-700 nm. Organic compounds absorb electromagnetic energy, but only those with several conjugated double bonds appear colored by the absorption of visible light (Betraet, Bagwe & Daruwalla, 1977).

Without substituents, chromophores do not absorb visible light, but the auxochromes shift the absorption into the visible region, in effect, the auxochromes extend the conjugated system. Absorption spectra are used to characterize specific compounds in visible spectra, the absorption patterns tend to be broad bands with maxima at longer wavelength, corresponding to more extended conjugation. The position and shape of the absorption band affect the appearance of the observed color; many compounds absorb in the ultraviolet region, with some absorptions extending into the violet (400-430 nm) region. Thus, these compounds appear yellowish to the eye i.e. the perceived color is complementary to the absorbed color. Progressive absorption into the visible region gives orange (430-480 nm), red (480-550 nm), violet (550-600 nm), and blue (600-700 nm); absorption at 400-450 nm and 580-700 nm gives green. Black objects absorb all visible light. The brilliance of color increases with decreasing bandwidth. Dyes are ionizing, colored and aromatic organic compounds which show an affinity towards the substrate to which it is being applied. They are substances capable of coloring fabrics in such a manner that the color cannot be removed by rubbing or washing. Although the most common and important application of dyes are in coloring textiles, dyes have also been used for coloring a large number of other polymers, cosmetics, drugs, printing inks, oils, paints and soaps. Dyes have also been used as dyeing agents in photography for sensitizing and desensitizing photographic plates. Dyes are also used as indicators in titrations and as staining agents in biological studies (Rana, 2011). Non-textile uses of dyestuffs may include use as solvent dyes: these are insoluble in water but soluble in common organic solvents. These dyes are therefore used in varnishes, polishing, printing inks, blue pen inks, fats, oils, waxes and polymers, among others. Solvent dyes are generally derived from azo dyes, anthraquinone etc. Some important solvent dyes are brown dye, Sudan orange (Finar, 2013).

Reactive dye was introduced in 1956 and for the first time dyeing became possible by direct chemical linkage between dye and fiber (Shenai, 1993). But all classes of reactive dye do not react in the same manner. Fowler (1997) had written about a tri-chromatic system where the dyestuffs were Remazol Red RR, Remazol blue RR and Remazol Yellow RR. It was confirmed that all three dyes contain at least one vinyl sulphone group as their reactive



group. In his article he had not described any of his testing procedures though he gave his results. The fixation yields he had got were 83% for Red RR, 81% for blue RR and 79% for yellow RR. He declared that the RR combination can meet all requirements with high cost effectiveness, which is actually a meaning of compatibility between the dyes. Because one of the meanings of high cost effectiveness is utilizing each of the dye at the highest possible percentage in an equal period of time.

Sultana and Uddin (2007) tested the compatibility of the same three dyes by calculating their dye extinction coefficient, exhaustion and fixation percentages. They maintained that in a particular time if the exhaustion or fixation percentage of the dye does not superimpose each other they cannot be said to be compatible. In their experiment they got different dye extinction coefficients, particularly that value for Red RR was quite high from the other two. And the fixation of Red RR also had a significant difference from the others (Red RR 91.89%, Blue RR 77.48%, yellow RR 64.20%). So they decided against the compatibility of these three dyes.

Moreover, according to Cay, Atav and Duran (2007), these three dyes contain different reactive groups. Remazol Red RR is a heteroatom bi-functional dye which contains both the monochlorotriazine and vinyl sulfone group (MCT-VS). Blue RR is homo bi-functional containing two vinyl sulphone groups and yellow RR, a mono functional dye contains only a vinyl sulfone group. The behavior of bi-functional dyes was studied by several researchers. Dalal and Desai (1996) studied on some bi-functional reactive dyes to find out their dyeing capability. The dyes showed medium to good substantivity as detected by their exhaustion and fixation study (Son, Hong, Lim & Kim, 2005). They applied four hetero-bi-functional reactive dyes to nylon fibers using various pH and temperature conditions. They found that hetero bi-functional reactive dyes afford great chance for efficient reaction between dye and fiber due to the mixed double anchors. Besides, Ali, Khatri, Peerzada and Ahmed (2012) worked with MCT-VS, VS and MCT based reactive dye and found in comparison that MCT-VS dye had better color strength than MCT dye. And a VS dye had better color than MCT-VS dye. There was some modeling of adsorption isotherm systems, both for two parameters and three parameters isotherm in the article of Foo and Hameed (2010). According to Choudhury (2006), not all the models but dyeing on cellulose fiber with reactive dye generally follow the Langmuir and Freundlich model of adsorption isotherms. Recently, Ara, Hasan, Rahman, Salam, Salam and Alam (2013) studied with Remazol Red RR adsorption to activate carbon. They analyzed both Langmuir and Freundlich isotherm models and observed that the Freundlich isotherm was fitted with the adsorption behavior of Red RR. As Remazol RR combinations have different reactive groups, Cay et al. (2007), and Sultana and Uddin (2007) questioned their compatibility; as such, further analysis was necessary from a different angle. For that reason, this research had analyzed the compatibility not only by exhaustion and fixation, but also with their adsorption isotherm to understand their individual interaction with the fiber. Adsorption isotherm analysis of reactive dyes has been discussed by many researchers earlier, but this is the first time the adsorption isotherm was considered to explain the compatibility among three reactive dyes used for ternary shades. The Least Square Method of Cantrell (2008) was applied in this research to calculate the slope and y intercept of the isotherm models. And according to Taylor (1990), coefficient of determination, r^2 is much meaningful in graph explanation. So that was considered in this research to explain the fitting of the adsorption isotherm models.



Experimental

The synthesis of this dye involves a three step procedure of nitration of aniline, diazotization and condensation reactions. Nitration of Aniline: Concentrated Nitric acid was placed in a 200 ml flask while concentrated Sulphuric acid was added to it portion wise over 30 minutes. With efficient stirring at room temperature, 30 ml of aniline was added. The mixture was refluxed in a water bath while the temperature was held at 50 °C for 40 minutes. It was washed with 500 ml of cold water.

Diazotization of Aniline: 200 ml of 8 % aqueous HCl was added to 0.10 aniline in a reaction vessel (500 ml) while stirring. The mixture was cooled to 5-10 °C for a period of 1 hour. At this temperature, a solution of sodium nitrite (3.5 gram dissolved in 20 ml distilled H₂O) was added. The pH was maintained at 2.0, Odin, Ekpendum, and Nsi, (2004).

Condensation of Para-nitro-aniline with 1-naphthylamine: To the diazonium, salt solution was added 3.65 gram 1-naphthylamine in 10 ml 4 % sodium acetate solution while stirring. 30-gram sodium carbonate in 70 ml water was then added to get a pH of 7-7.5. The mono-azo dye formed was then salted for 3 hours at 60 °C with 20-gram sodium chloride, which was added gradually while stirring continued. The precipitate was then filtered out and weighed.

Acylation with cyanuric chloride: About 1.03 g of the mono-azo dye in 300 ml of distilled water was suspended in a flask of about 500 ml fixed with a stirrer and thermometer. During stirring and cooling to 0 °C - 2 °C, 4.6-gram cyanuric chloride solution in 50 ml acetone was gradually added. While this was on, the temperature was held between 0-2 °C and a pH of 6-6.5. Acylation was completed when the precipitate became constant. For a period of 30 minutes, the mixture was stirred and salted with 60 gram NaCl after which the dye was filtered. The yield was weighed with 1 gram carbamide solution.

Dyeing with Reactive Dye: To the solution was added 1g of the textile material (pure cotton) and was stirred continuously for 15 minutes until it was completely soaked. The temperature was gradually raised to 250°C and 2-gram NaCl was added and stirred. To the mixture was added in two parts at intervals of 15 minutes, 1 g Na₂CO₃ which was dissolved in 2 ml water. The mixture was stirred intermittently while the temperature was gradually raised to 40 °C. This temperature was maintained for a period of 10-15 minutes. The dyed fabric was washed for 10-15 minutes in 50 ml 0.5 % soap solution. It was rinsed with water and dried.

Melting Point Determination: The melting point of the dye was determined using paraffin oil and thermometer. The Para-nitro-aniline was inserted in a boiling tube merged with the thermometer. The two were heated in Paraffin oil on a hot plate, the point at which the solid changed into liquid.

Absorption Spectra (wavelength): 1.0 ml of the dye was dissolved in 10 ml distilled water and poured into the cuvettes. Distilled water was used as a blank. The wavelength on the spectrophotometer varied from 180, 200, 220, 240, 260, 280...600 nm. At each wavelength, the absorbance of each dye was taken. The values obtained are shown in table 2 and were plotted against that of wavelength to get the wavelength of the maximum.

Percentage Exhaustion: The amount of the dye put in the dye bath was weighed. After dyeing, the solution was evaporated to dryness. The amount of dye left was also weighed. The percentage exhaustion of the dyes on the fabric was calculated according to Kasali and Adeakin, (2004).

$$\% E = (A_d - A_b) \times 100$$

Where A_d and A_b are the quantity of the dye originally in the dye bath and of the residual dye in the dye bath respectively. The results are shown in table 1.

Fastness properties of the dyed fabrics: The finished article (dyed fabrics) was exposed to a number of conditions such as sunlight, washing with detergent and dry cleaning (heat). All the fastness evaluations were made with the aid of the Gray scale for color change. The wash fastness test was done by preparing a soap solution and placing the dyed fabrics into it. This was stirred continuously for 10 minutes at a temperature of 35°C. At the end, the fabric was removed, rinsed with water and dried in free air for 24 hours. The dried fabric was compared with a control sample. The light fastness assessment was carried out by exposing the dyed fabric to strong sunlight for a period of 3 hours. The exposed sample was compared with the control sample. The heat fastness evaluation was done by heat pressing iron at a temperature of 50 - 60°C for 3 minutes. The pressed fabric was compared with the control sample. The results are shown in Table 3.

Results and Discussions

The synthesis of the para-nitro aniline-based reactive dye and characterization using GC-MS and UV spectrometry has been accomplished and the following were the results obtained:

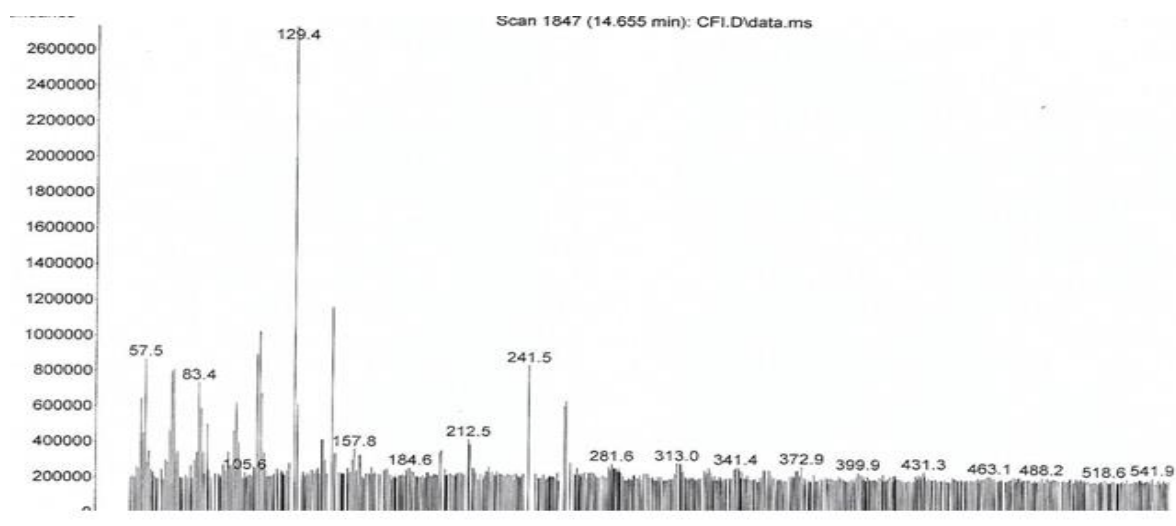


Fig. 1: UV spectra of the synthesized dye

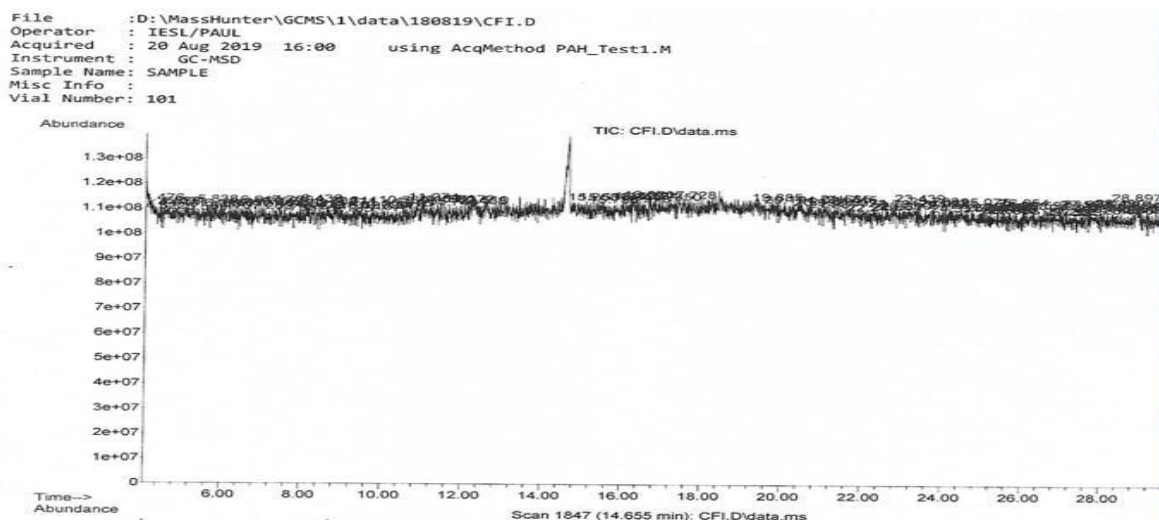


Fig. 2: GC-MS spectra of the synthesized dye

Table 1: Some physicochemical properties of the synthesized dye

Abs. Max (nm)	% Exhaustion	Melting point (° C)
220	73	147

Table 2: Values of Absorbance (a) and wavelength (nm) of dye

Wavelength	Absorbance
180	-
200	-
220	2.214
240	2.187
260	1.127
280	1.201
300	1.493
320	1.772
340	1.616
360	1.180
380	0.958
400	0.820
420	0.602
440	0.178
460	-149
480	-301

**Table 3: Fastness Test Assessment**

Wash fastness	Light fastness	Heat fastness
4	5	5

The fastness scale was rated 1-5. Scale 1 = poor result; scale 5 = very good result
Ukponmwam, Odilora, Ofor and Freeman, (1999).

DISCUSSION OF FINDINGS

The diazotization and condensation reactions led to the synthesis of the dye. Diazotization is the process of converting primary aromatic amines into its diazonium salts. These diazonium salts are important intermediates that can undergo coupling reactions to form azo dyes and electrophilic substitution reactions to introduce N=N functional groups. An azo coupling is an organic reaction between a diazonium compound that produces an azo compound. The diazotization of the dye was carried out by reaction of para- nitro aniline with HCl in the presence of Sodium nitrite at a reduced temperature. Temperatures are maintained at low degree Celsius because at high temperatures diazonium salts form by products and give phenol by reacting with H₂O at high temperatures which would lead to error.

Dye Exhaustion: Dye exhaustion simply refers to the shift of the dyes towards the fiber. When a fiber starts to absorb the dye thus the concentration of the dye in the dye bath decreases gradually. The percentage exhaustion of the dye on the fabric was calculated according to Kasali *et al.* (2004) using $\% E = (A_d - A_b) * 100$ where A_d and A_b are the quantity of the dye originally in the dye bath respectively and the result in table 1 i.e. 73% exhaustion shows that the dye gave a very good exhaustion and penetration properties.

Fastness Testing Color fastness is a term used in the dyeing of textile materials that characterizes a material's color's resistance to fading or running. The term is usually used in the context of clothes. Light fastness, wash fastness and heat fastness are the main forms of color fastness that are standardized. Fastness testing is rated 1-5 according to Ukponmwam *et al.* (1999) where 1 shows poor fastness and 5 shows very good fastness. The wash, heat and light fastness of 4, 5, 5 respectively as summarized in table 3 shows that the dyed fabric has an excellent fastness to washing, heating and sun drying. The light fastness result of the dyed fabric in table 3 shows that the fabric has a very good light fastness property that is it did not fade on exposure to sunlight. The heat fastness of 5 shows that the dyed fabric also has very good heat fastness property that is its color did not change when it was ironed at a temperature of 50 – 60°C while the wash fastness result of 4 shows good fastness property i.e. its color did not disappear completely when washed with water and soap.

Spectra Data: From the result summarized in table 1, it can be seen that the dye absorbed most at 220 nm. Also from table 1, it was observed that the dye did not observe at 180, 200 nm because it is below the wavelength of its absorption region. It is also seen that at 240 to 440 nm, it dropped positively but at 460 to 480 nm it dropped negatively and at 500 – 600 nm it did not absorb. The dye shows two absorption maxima, one in the UV range due to bonding-antibonding transition of C=C present in the aromatic moiety of the dye common in dye in the visible region, and is due to bonding-antibonding transition of azo linkage N=N of the dye



The data from the Gas Spectrophotometer-Mass Spectrophotometer analysis shows multiple fingerprints indicative of multiple products (Fig. 2). The compound with the highest relative abundance of 100% showed a molecular ion peak of 129.4 corresponding to lower relative abundance. Larger molecules with higher molecular masses are indicative of organo-metallic compounds. In figure 2, the clusters of peaks were not distinct. The distinct peak is of the solvent front. The two peaks of masses 57.5 and 83.4 correspond to fragments of the sample. The reactive dye was synthesized in low yield. Cyanuric chloride was used as a reactive component by utilizing its differential reactivity under differential reactivity under different temperature and pH conditions. Applications of dyes were made on cellulose fiber where they showed high fastness, light fastness and wash fastness and heat fastness of 5, 4, 5 respectively.

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