Research Article

Synthesis of azo dye derived from mango seed kernel and an investigation of its use on polyamide fiber

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Abstract

Organol brown dye was synthesized by coupling of active ingredient from mango seed kernel with diazonium salt. The resultant dye was characterized by UV, IR and Mass spectroscopy. The dyeing assessment of the synthesized dyes was evaluated on wool, silk, and nylon fabrics. The fastness property of dye was tested such as washing, rubbing and light fastness. The results showed better hue with good color fastness to washing, rubbing.

Keywords: Azo-dyes, wool, silk, nylon, dyeing

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Azo-dye synthesized from Mango seed kernel

Introduction

Organic color chemistry has been undergoing very exciting development as a result of the opportunities presented by dye applications in high technology fields: electronic devices, linear and non linear optics, reprography, sensors and biomedical uses.[1-4] Azo dyes constitute the largest group of colorants used in industry.[5] Azo dyes does not occurs in nature and synthesized by chemical synthesis [6] that is an azo coupling between a diazonium compound and a dialkylaniline ($C_6H_5NR_2$), phenol or other aromatic compound which produces an azo compound.[7] Synthesis of dyes from aromatic amines is an account for revolutionized the dye industry. In making the azo linkage, many combinations are possible. In this reaction the diazonium salt is an electrophile and the activated arene is a nucleophile in an electrophilic aromatic substitution.

An azo dye has the general structure (Ar–N=N–Ar') and is produced by the reaction of an aryl diazonium salt with an aromatic amine or a phenol. The formation of a diazotizing reagent starts with protonation of nitrous acid under acidic conditions, and azo coupling carried out at low temperature in the presence of nucleophilic substrate increases with increasing basicity of phenolate. Chromophore and auxochromes plays an important in the production of dyes. They are used in dyes for clothing as food dyes and as pigments in paints and pH indicators.[8] The emergence of diverse classes of synthetic dyes including azo-dye occurred due to constant effort to find specific dye or a particular class of dye for application on diverse materials of industrial importance mainly textile fibres, aluminium sheet, leather, electro optical devices, ink–jet printers etc.[9] Many azo compounds have been applied as chromogenic reagents for the determination of several metal ions.[10]

The major components of mango seed are starch, fat and protein. The oil of mango seed kernel consist of about 44–48% saturated fatty acids (majority stearic) and 52–56% unsaturated. Mango seed kernels contain protein and do have most of the essential amino acids, with highest values of leucine, valine and lysine. Mango seed kernels were shown to be a good source of polyphenols, phytosterols as campesterol, sitosterol and tocopherols.[11] Though mango seed kernel contains various amino acids as shown in below table, which contains active nitrogen group that are diazotize to form diazonium complex. Yet, researcher has not paid attention towards the synthesis of azo dyes from mango seed kernel. Therefore, the present study focused on synthesis of azo dye derived from mango seed kernel.

Table 1 The amino acids contained in mango seed kernel based on dry weight compared to the FAO/WHO reference

	Qyantity (mg/100g)			
Amino acid	Fowomola, 2010	Om El- Saad El-Gammal, 2011	Arogba, 1999	World Health Organization, 1985
Essential amino acid				
Isoleucine	3.23	2.68	4.4	4.20
Lysine	3.13	3.94	6.9	4.20
Methionine	1.04	0.38	1.2	2.20
Phenylalanine	4.46	2.75	3.4	2.80
Threonine	2.04	3.46	3.4	4.00
Tyrosine	3.17	2.04	2.7	2.80
Valine	3.80	6.07	5.8	4.20
Non essential amino acids				
Arginine	5.17	14.27	7.3	
Alanine	6.40	4.86	4.2	
Aspartate	6.33	8.66	6.5	
Cysteine	2.30	-	-	
Glutamate	13.00	15.66	18.2	
Glycine	3.50	2.81	4.0	
Histidine	2.31	2.19	5.5	
Leucine	8.40	-	-	
Proline	3.00	4.50	3.5	
Serine	2.93	3.94	3.3	

The dyeing assessment of the synthesized dye was evaluated on natural fiber such as wool, silk and synthetic polyamide (Nylon) fiber. It can be widely used in the chemical industries for the synthesis of direct, acid, reactive and azoic dye, as well as in the pharmaceutical industry. [12,13]

Materials and Methods:

Source: Mango seed

Mango seeds from fruit were separated manually and sun dried for five weeks. After that the outer hard cover and inner kernel was detached and sun dried for two weeks. Mango seed kernel (MSK) was dried at 50^{o}C and grounded into fine powder using a stainless-steel grinder and stored in glass bottle until utilization. [14]

Preparation of MSK azo dye:

Preparation of azo dye from MSK powder (5g) with con H_2SO_4 and distilled water heated for 10 min at 5^{o}C by adding drop wise $NaNO_2$ in 4cm^3 of distilled water in cold water bath. The resultant solution is step-I solution.

In step-II 2-napthol (2.6g) and 15cm^3 of 2N NaOH was added in to 500 cm^3 beaker in cold water bath so as the reaction mixture attend temperature of cold water. setp-I solution was added drop wise into the step-II reaction mixtures by constant stirring and maintaining the temperature below 10^{o}C. After complete addition HCL was added with vigorous stirring and shaking till the Dark red brown dye segregated from the mixture. After washing with distilled water and air dried it further characterized.

Characteristics analysis to confirm formation of Azo Dye from MSK

Prepared dye was screened by TLC, MP, UV, IR and MS to confirm formation of resultant azo compound. The same dye was applied on natural and synthetic fibre to prove its utility and stability.

Application of AZO DYE synthesized from MSK[7]

***Preparation of 1% MSK dye solution*:**

The *MSK* dye (1g) was pasted with warm water and then 80cm^3 of boiling water was added in it and stirred to give a clear solution. The resulting dye solution was made up to 100 cm^3 with boiling water.

Application MSK dye on natural fiber: wool and silk fabrics
Material was added to a solution that included 2-4% H_2SO_4 and 10-20% Glanber's salt at 40ºC. After 20 min, dissolved dye (1%) solution was added to this mixture. After 40 min, temperature was raised to boiling point. The operation was continued for 60 min, followed by washing, and drying with air.

Dyeing on synthetic fiber: nylon fabric
Material was added to a solution that included 3-4% formic acid and boiled. After 1 hr ammonium acetate was added to the solution due to the dark color of the dye, followed by washing, and drying with air.

Fastness Properties
All the dyeing for the fastness test was carried out at pH 5 which has been demonstrated to be the optimum.

Light Fastness
The light fastness of the dyed fabrics was tested by exposing them to the Xenon Lamp of an Atlas 3 SUN Weather –O meter, according to the conditions of AATC Test method 16E – 1993 (AATCC, 1993).

Washing Fastness
Fastness to washing was assessed by washing the reduction – cleared dyed fabrics according to the ISO C06/C2S, wash - test using soap solution (5 g/l, liquor ratio 50:1) for 45 minutes at 60ºC). The change in shade and staining of adjacent fabrics were assessed according to Society of Dyers and Colourists grey scale (ISO, 1994)

Rubbing Fastness
Rubbing fastness was determined according to ISO, 2001 Test Method (ISO, 2001).
Absorption maxima (λmax), exhaustion (E), and fixation (F) of synthesized dyes on wool, silk, and nylon fabrics was tested as reference 15.

Result and Discussion:

The dye was synthesized from natural resources mango seed kernel by diazotization reaction characterization of it is shown table 2.

Table 2 The characteristics of azo compound from MSK

Characteristics	Inferences
Colour	Dark brown
Yield	4.24 g
M.P	200 ºC
TLC (Rf value)	0.86
M.W.	365

The finely grounded and moisture free MSK powder was subjected to diazotization reaction mechanism is shown figure 1.

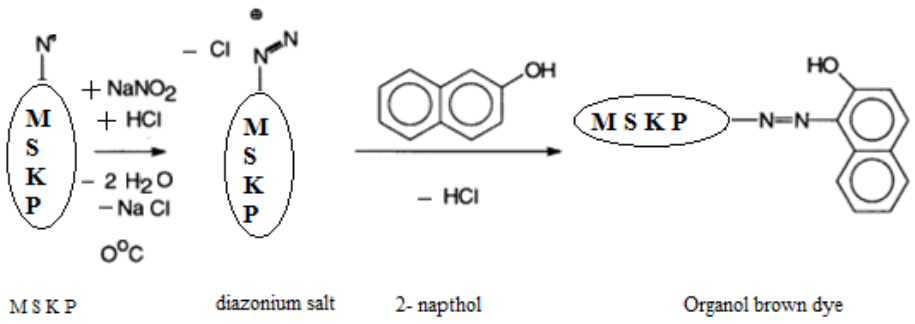

Figure 1 Probable synthesis reaction of organol Brown dye formation from MSK powder as starting material

Characteristics analysis to confirm formation of Azo Dye from MSK:

Due to atmospheric oxygen the light brown colored azo-compound get converted in to dark brown. The increase in color in a hydrochloric acid filtrate of the digestion mixture is a function of enzyme activity. The dyes released from the bound dye formed *in vivo* are largely polar and have λ maxima 274.5 nm and 246 nm indicate the presence of azo group in this compound.

From above analysis U.V, TLC, FTIR and MS it is objerved that the dye prepared from azocoupling of MSK it is a Organol brown dye which may show following possible structure and reaction.TLC shows the spot, it is a dark brown in color which is having Rf value 0.86 which is equivalents to the Rf value of Organol-brown dye. This separated spot is used for further analysis as M.S. and FTIR.

FTIR of azo compound:

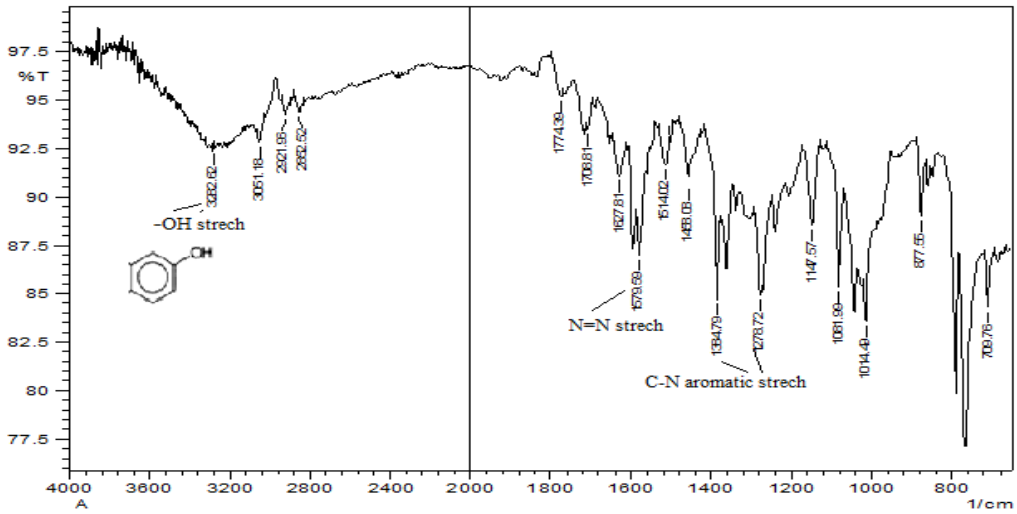

Figure 2 FTIR of AZO Dye from MSK powder

The bands obtained in azo compound from MSK powder are 3232.62 cm^{-1},3051.18 cm^{-1}, 2921.96 cm^{-1} (aromatic O-H stretch), 2852.52 cm^{-1} (aromatic C-H stretch), 1579.59 cm^{-1} (N=N stretch), 1334.79 cm^{-1},1278.72 cm^{-1} (C-N stretch). The FTIR azo compounds (Figure 2) shows band with aromatic O-H stretch and N=N bonding which belong to organol brown compound. The N=N and C-N bonding confirms the presence of azo compound.

M.S of azo dye from MSK powder

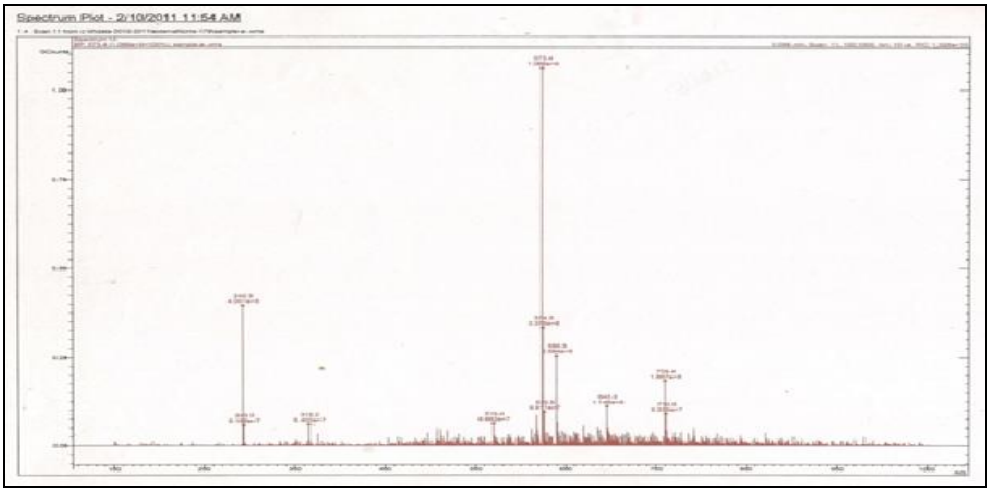

Figure 3 Mass spectroscopy of azo dye from MSK powder

From the above mass spectrum (Figure 3) of MSK azo-dye shows peak at 243.3 m/e, which indicate that it contains a molecule with the molecular formula $C_{15}H_{19}N_2O$. This compound shows the similarity with standard organol brown dye. The remaining peaks seen in a mass spectrum it may be impurities obtained in the same as the crude MSK powder was used.

In the standard azo coupling reaction p- nitroaniline is get reacted with diazonium salt to give azo dye. Enzyme derived from MSK is enriched with amino acids. It has been observed that the amino acids present in MSK plays a important role in formation of diazotized compound as other minerals get disintegrate in concentrated hydrochloric acid. It contains Nitrogen as a reactive group in its structure.

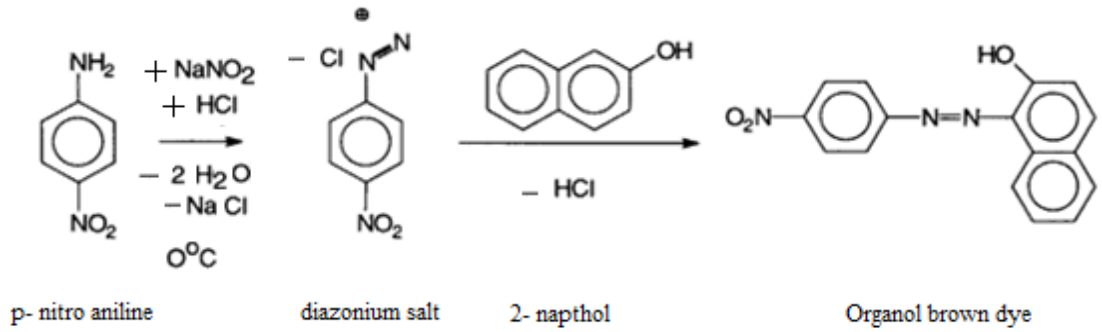

Figure 4 Standard azo coupling reaction by using p - nitroaniline as starting material

The same reaction is carried out using MSK powder (Figure 1). instead of p- nitroaniline and the final product is obtained which shows the characteristics similar to that of standard reaction product. Hence it concludes that the nitogen present in the MSK powder is reacted with diazonium salt to give azo compound **(**Figure 5) and according to spectral data the credible structure of the dye compound prepared from MSK is,

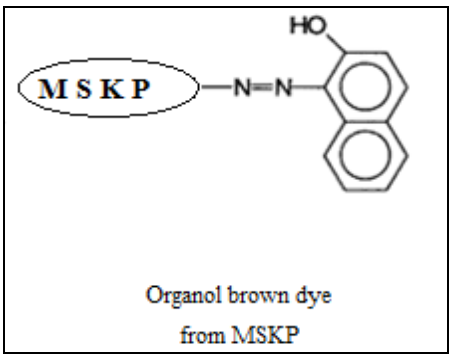

Figure 5 Probable structure of synthesied organol Brown dye from MSK powder

Applications of MSK dye on Polyamide fibre:

a) On natural fibre i. Silk, **ii.** Wool
b) On synthetic fibre –Nylon

The Structure of Polyamide fibre having both presence of amino group and carboxylic group at the terminal ends. The Naphtol molecule serves the bonding linkage between polyamide fibre and Dye prepared from MSK. The below structure shows the dyeing mechanism of Polyamide fibres.

Step-I:

$$NH_2—X—COOH \longrightarrow {}^{+}NH_3—X—COO^{-}\ \text{(Fibre in water)}$$

Step-II:

Table 3 Absorption maxima (λmax), exhaustion (E), and fixation (F) of synthesized dyes on wool, silk, and nylon fabrics

Dye	Absorption maxima (λmax)(nm) in acetone	Dyeing of wool		Dyeing of silk		Dyeing of nylon	
		% E	% F	% E	% F	% E	% F
MSKP dye	274.5	74.2	82.1	68.4	76.2	65.0	72.5

The exhaustion of the dye bath and the fixation of dye on nylon fabric were comparatively lower than that of wool and silk fabrics. This is due to comparatively higher cohesive energy density of nylon polymer chain molecules and the lower para electro-negativity of the terminal polar groups which ultimately hinders the affinity and penetration of the dye molecules to some extent. Moreover, the presence of electron donating or electron attracting groups did not bring about mark increase or decrease in λmax (274.5) in the visible region. However electron donating or attracting substituents, such as –OCH3 or –NO2 in the coupler increase the polarity.

The dyes were applied at 1% depth on wool, silk, and nylon fabrics. This dye gave reddish brown shades with a good levelness, brightness, and depth on the fabrics. The variation in the shades of the dyed fabrics results from both the nature and position of the substituent present on the diazotized compounds.

Fastness properties of dye on wool, silk, nylon fabric

Table 4 Fastness properties of the dyes on wool, silk, nylon fabrics

Dye	Colour	Type of fabric	Washing fastness	Rubbing fastness Dry	Rubbing fastness Wet	Light fastness
MSK Dye	**Brown**	Wool	6	4	4	5
		Silk	5	4	5	6
		Nylon	6	4	5	6

The dyeing showed an average fastness to light and washing with fair fastness to rubbing. A remarkable degree of level in surface area after washing was observed. This may be attributed to the good penetration and affinity of the dye to the fibre structure.

Conclusion

Azo dye was successfully synthesized by standard methods of diazotization and coupling using mango seed kernel powder. The result on the elemental analysis and spectral studies of dye was consistent and hence confirm the predicted structure. The synthesized dye showed excellent fastness to light, washing with good fastness to rubbing. It also showed remarkable levelness after washing. The nature of the substituent in the coupling components also showed little influence on the visible absorption and the shade of the dyeing

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