Available online at www.ijtnbm.yazd.iau.ir

The Iranian Journal of Textile Nano-bio Modificatio

IJTNBM 3 (2022) 9–29

Investigation of the Ability of Natural and Synthetic Fibers Dyeing Using Azo Dyestuffs Prepared in Mild Conditions on the Nano-Silica Gel Substrate and Nitrosyl Chloride Reagent

N.Alizadeh [1*], H. Akbarpour [2]

**1Faculty of Petroleum and Chemical Engineering, Research and Science Branch, Islamic Azad University, Tehran, Iran*
2Department of Sewing and Garment Design Technology, Technical and Vocational University (Tohid), Amol, Iran

Received 8 May 2022; Revised 14 September 2022; Accepted 24 September 2022

Abstract

Using nitrosyl chloride reagent, supported by nano silica gel, some of the azo dyestuffs, based on α-naphthol and β-naphthol, was synthesized in a very short time at room temperature, with high efficiency, which reduced the corrosion of the pot, environmental pollution and the other problems. The molecular structure of the synthesized dyestuffs was characterized by FTIR, 1HNMR, 13C-NMR and UV-Vis spectroscopic techniques. The results showed that the structure of the synthesized dyestuffs corresponded with the general structure of the dye azo, and the applications are categorized into disperse or acidic dyes. The synthesized dyestuffs were applied to dyeing nylon and polyester, as we explored the ability of dyeing. Also, according to the results obtained in washing stability, nylon and polyester fibers are equal in α_b and β_c , respectively, and are higher than other washing fastness measurement modes. In general, the Light fastness of polyester fibers is slightly better compared to nylon fibers and its washing stability is lower. Finally, results indicated that the new method had a good ability for producing the azo dyestuffs.

Keywords: Nano-Silica Gel, FTIR, Nylon, Polyester, Nitrosyl Chloride.

---

1. Introduction

Azo dyes are by far the most important chemicals, accounting for over 60% of the known commercial dyes. They are widely used in the textiles, leather, cosmetics, and food industries [1-6]. Azo dyes can be produced by banding aryldiazonium salt with phenol, naphthalene or (I), (II) and (III) aryl amines. Aryldiazonium salt is

---

[*]* Corresponding author. *E-mail address: najmeh.alizadeh@srbiau.ac.ir*

produced by the composition of liquid Nitro Acid (obtained from sodium nitrite with hydrochloric Acid or sulfuric Acid), with aromatic amines of kind (I), obtained at temperatures less than10°C and for a duration of several hours [7]. Aryldiazonium salt is electrophilic and in alkaline solution can be coupled with an amine or phenolic compound [8]. At this point, the presence of high concentrate liquid acids, causes the amortization of the pot, environmental pollution and other problems [9]. In this study, we presented a new method for synthesizing azo dyestuffs that, using nano-silica gel substrate as a catalyst, provides a suitable field for deployment acids and their derivatives, as nitrosyl chloride on the nano-silica gel substrate, by deployment of nitrosyl chloride reagent on nano-silica gel substrate, using nitrosyl chloride as the reactive agent and a catalyst, until diazotization. To the ensuing reaction, copulation was made possible between aryl diazonium salt and an amine or phenolic compound, in a very short time and at room temperature, without the presence of liquid acids, with minimal degradation on the pot and environmental pollution [10,11].

In this context, a certain number of aromatic amine, as a diazo component, and alkaline solution α–naphthol and β -naphthol as a coupling component, were used for preparing azo dyestuffs. Then, to evaluate the dyeing properties of the dyestuffs of the synthesized, the most appropriate was selected in terms of their solubility. The dyestuffs of the what was selected based on α–naphthol is shown in Table (1) and what was selected based on β-naphthol is shown in Table (2). Selected dyes were analysed and identified by spectroscopy methods.

Table.1. Synthesized dyestuffs based on α–naphthol

Dye	Raw Material	More Product	Less Product	Yield
α_a	3-chloro- phenylamine	4-(3-choloro-phenylazo)-naphthalene-1ol	2-(3-choloro-phenylazo)-naphthalene-1ol	75
α_b	o-tolyamine	4-o-tolylazo-naphthalene-1ol	2-o-Tolylazo-naphthalene-1ol	70

Table.2. Synthesized dyestuffs based on β–naphthol

Dye	Raw Material	Product	Yield
β_c	3methoxy-phenyl amine	1-(3methoxy-phenyl azo)-naphthalene-2ol	70
β_d	2-amino-benzoic acid	2-(2-Hydroxy-naphthalene-1ylazo)- benzoic acid	90

2. Materials and Methods

2.1. Materials

Aniline, α–naphthol, β-naphthol, nitrosyl chloride, 3-chloro-aniline, 2- amino- benzoic acid, o-toluidine, o-anisdine, acetone, chloroform, acetic acid, sodium nitrite, sodium hydroxide(Merck), silica gel (60mesh), nanosilica gel (20mesh)(Aldrich), non-ionic detergent, sodium chloride, distilled water, cotton, wool, polyester, nylon, acrylic, vacuum desiccators, steer heater, and oven.

2.2. Methods

The dyeing process was performed under identical conditions in high temperature laboratory dyeing machine**.** Light fastness was measured by light fastness test Tehran model 142BZ, which was equipped with a lamp specification: ALITE AK MH-BT 400W-E40 SUPER WHITE SERIE. Spectra FTIR, ^{1}H-NMR and ^{13}C-NMR of the synthesized dyes was characterized, respectively, by Nicolet MAGNA-550, Brukeravance 100 MHz and 400MHz. Absorption spectra UV-Vis [12] of synthetic dyestuffs was measured by absorption spectrophotometer Cary 100scan UV-Vis.

2.2.1. Preparing nano silica gel substrate supported by nitrosyl chloride

In order to activate the surface of nano silicagel, 5g nanosilica gel (20 mesh) was put in an oven at 110℃ for 1hour,then10 ml nitrosyl chlorideis added to nano silica gel, while stirred under the hood on the stirrer heater, carefully and gradually. Stir mixture continued for 1hour, until it separated the additional nitrosyl chloride. The mixture of nitrosyl chloride and nanosilica gel was heated under the hood at 70℃, and then it was put in vacuum desiccator for 24 hours. Finally, it obtained white powder nano-silica gel, supported by nitrosyl chloride.

2.2.2.Optimization of the dosage of nano silica-gel substrate supported by nitrosyl chloride and the wet silica gel

To obtain the optimized amounts of nano silica-gel substrate, supported by nitrosyl chloride, the dosage started from 0.2 gr, and the dyestuffs were synthesized in accordance with the agenda preparation. The results showed that consumption of 0.2 gr is high, because colour of the solution was dark. The dosages were reduced to half, and the decrease was continued, respectively (0.2, 0.1, 0.05, 0.04, 0.02), until we approached the optimized amounts (0.02). To obtain the optimized amounts of wet silica-gel, the dosage started from 1 gr, containing 0 .5 g dry silica gel, and 0.5 g of distilled water. Also, the dyestuffs were synthesized in accordance with the agenda preparation. The results show that consumption of 1 gr of wet silica gel is high, because the viscosity of the solution is high and the most silica-gel is absorbed while filtering. The dosages were reduced to half, and this decrease was continued, respectively (1, 0.5, 0.2, 0.1, 0.05), until we approach the optimized amounts (0.5).

2.2.3. Synthesis of the azo dyestuffs base on α-naphthol and β-naphthol

Aryl diazonium solution was mixed at 5ml the solution alkaline of the α-naphthol or β-naphthol, containing 2.5ml solution α–naphthol or β-naphthol 2%, and 2.5ml solution sodium hydroxide 5%, and was stirred well. At this point, coupling reaction was performed, and azo dyestuffs attained red tint yellow. At the room temperature dye solution evaporated slowly, and the dyestuff was available as powder.

2.2.4. Preparation of aryl diazonium solution

0.01 mol Amine aromatic was dissolved in acetone minimum (less than 10 ml) and was stirred until the emergence of a yellow colour of limpid. 0.01 mol sodium nitrite was dissolved in the less than 10 ml, and then both solutions were added to the others that were being stirred. The optimal quantity nano-silica gel, supported by nitrosyl chloride, was added to the solution and was stirred well. Finally, to prepare the solution of aryl diazonium, 0.05 g wet silica gel, containing 0.025 gr dry silica gel and 0.025 gr of distilled water, was added to the solution, for freeing nitrosyl chloride, supported on nano-silica gel substrate. The reason for the preparation of the solution of aryldiazonium was the halo appearance of pale yellow to orange. The solution, then, was filtered until silica gel particles were separated from the solution.

2.2.5. The dyeing with synthesized dyestuffs

Preparation of polyester and nylon fibres was done through washing with a non-ionic detergent (3%) at 60℃ for 20 minutes. In order to better compare and evaluate, the washed materials were dyed in a bath with L: R dyeing 40:1, containing 1.5% dye and 10% acetic acid (pH =5.5), in accordance with the diagram of the dyeing in Figure 1, (nylon fibres at T =100℃ and polyester fibre at T =120℃).

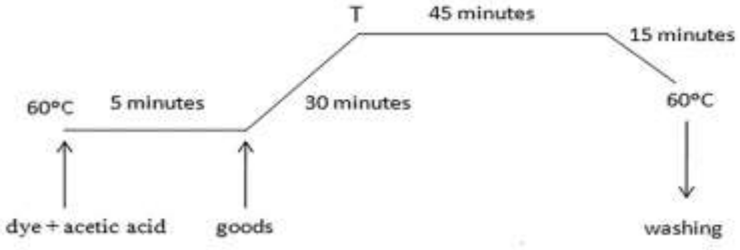


Fig.1. Schematic of Dyeing diagram

2.2.6. Measurement the amounts of exhaustion

Absorption amounts, waste water of dyeing bath and washing bath in the vicinity of control solution, in the maximum wavelength for each dye, was measured by the spectrophotometer UV-Vis absorption. Then, using the absorption equation, the concentration of each dye was obtained in the bath. The exhaustion percentage (%E) of each dye in the bath was measured by equation1:

$$E= [A-(B+C)/A] \times 100\ (\%) \qquad Eq(1)$$

where A, B and C represent the concentration of dye in the bath dyeing, in the bath dyeing effluent and in the bath washing effluent, respectively (g/l).

2.2.7. Measurement of the properties of fastness

The fastness of the dyeing materials with synthesized dyes were evaluated against exposure, washing and staining. To measure light fastness, half the goods were covered and the other half were exposed to direct light radiation lamp 400W-E40, for 40 hours by Light Fastness Test, and the obtained results were compared with standard blue. To measure washing and staining fastness, samples of dyeing were washed along with raw fabric in a bath containing 1% sodium chloride, at 50°C for 30 min. At the end, washed samples and pre-dyed samples were compared and investigated by grey standard, and the amount of colour change was determined.

3. Results and discussion

3.1. Synthesis and identification of dye

The effect of adding wet silica gel to the solution was that nitrosyl chloride was released from the substrate of then nanosilicagel. The nitrosyl ion makes the solution acidify [13,14]. In the acid solution, sodium nitrite produces nitrous acid, nitrous acid wade reaction with amine aromatic produces aril diazonium salt. Aril diazonium salt has two state of mesomer, the formation mechanism of which is shown in Figure (2) [15,16].

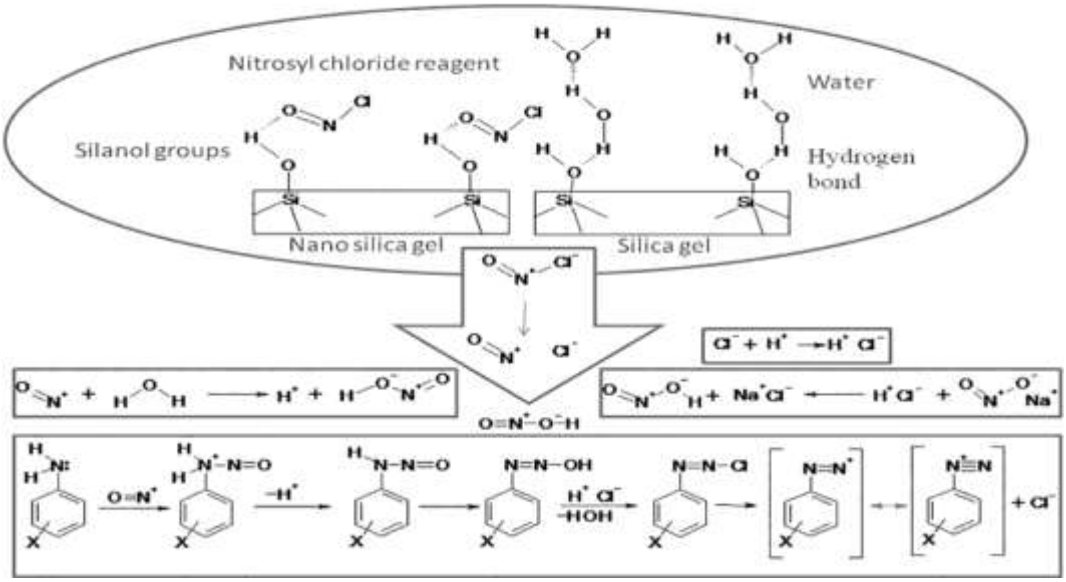


Fig .2. The stages of formation of the aryl diazonium salt

The second stage of the production process of azo dyestuffs was the reaction of coupling between the aryldiazonium salt and the solution of the α-naphthol or β-naphthol alkaline, which with α-naphthol leads to production of two products with different percentages (A has higher percentage, B less), and with β-naphthol, one product that the general process of the dyestuffs synthesis is shown in Figure (3) [17].

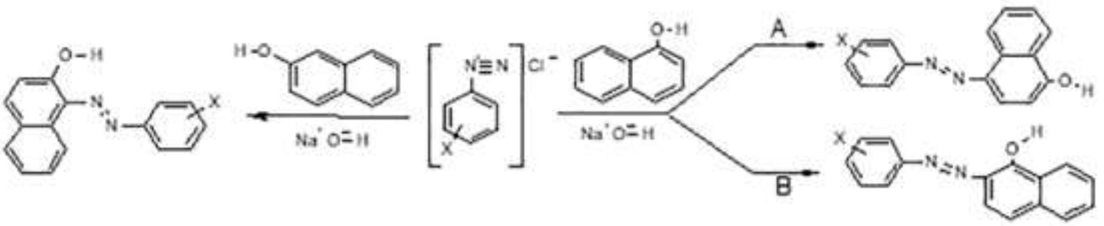


Fig 3. Coupling reaction, the aryldiazonium salt with the solution of the α-naphthol and β-naphthol alkaline.

Analysis and identification of synthesized dyestuffs spectroscopy methods showed that the chemical structure of synthesized dye stuffs conforms to the general structure of mono azo dyes. In this context, the FT-IR spectrum of synthesized dyestuffs, the presence of azo group is shown in the area 1586−1588 cm^{-1}[19,18], (Fig.4). Azo bond in the presence of synthesized dyestuffs showed well that, diazotization and to the ensuing reaction, copulation, has been done well. The absorption spectra observed for the **α_a** sample at wavelengths 3470,1437, 1588,1268, 1033 and 765 cm^{-1} correspond to the presence of the -OH group, aromatic rings, -N = N- group, CL, CO and CN groups, respectively. Also, the absorption band observed for **α_b** sample at wavelengths of 3405,3045,1619, 1586,1333,1271 and 1033 cm^{-1}, respectively, related to the presence of -OH group, tensile vibration of $-CH_3$ group, aromatic rings, group -N = N- is the bending vibration of $-CH_3$, CO and CN groups. On the other hand, the absorption band observed for the **β_c** sample at wavelengths of 3370, 2910, 1620, 1586, 1333, 1271 and 1059 cm^{-1}, respectively, are related to the presence of the -OH group, tensile vibration of the -CH_3 group, aromatic rings, -N=N-, tensile vibration of -CH_3 group, flexural vibration of -CH3 group, CO and CN and finally for **β_d** sample at wavelengths of 3405,1754,1611, 1586,1272,1074 and 873 cm^{-1}, respectively, related to the presence The group -OH, COOH, aromatic rings, the group -N = N-,, CO, CN and COOH [20]. H-NMR spectrum of synthesized dyestuffs, the presence of 10 aromatic protons (4 protons phenyl ring and 6 protons naphthalene ring) and a hydroxyl proton in the chemical structure of all synthesized dyestuffs showed that the general structure of dye stuffs conforms with the mono azo, perfectly (Figs (5 and 6)). C-NMR spectrum, the presence carbons of benzene and naphthalene aromatic rings conform to the chemical structure of synthesized dyestuffs (Figures 7 & 8). More details about the data spectroscopy methods are shown in Table (3) [21,20].

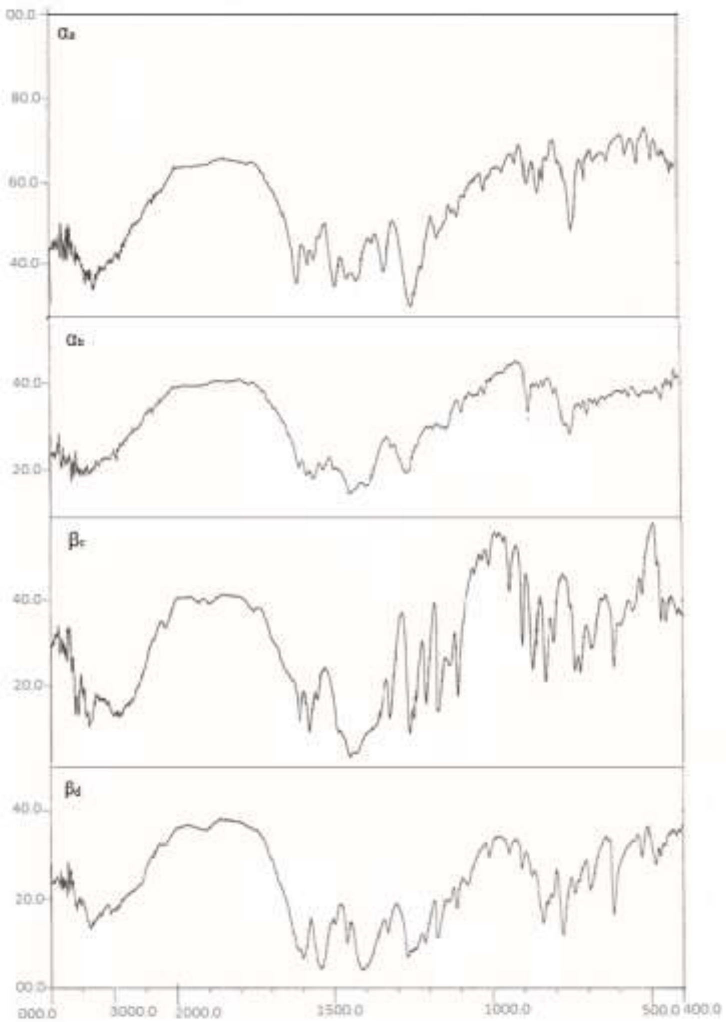
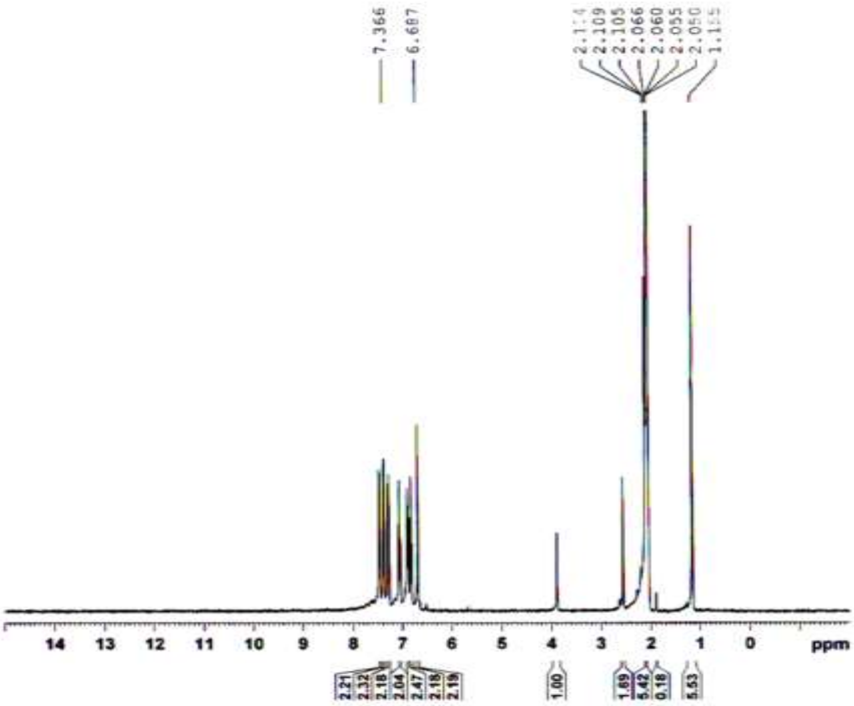
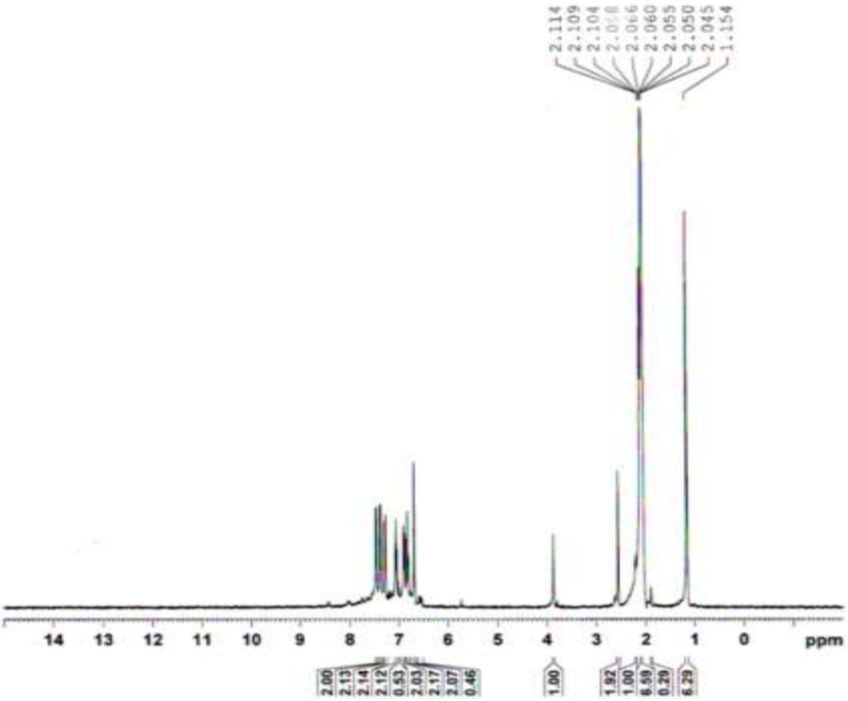
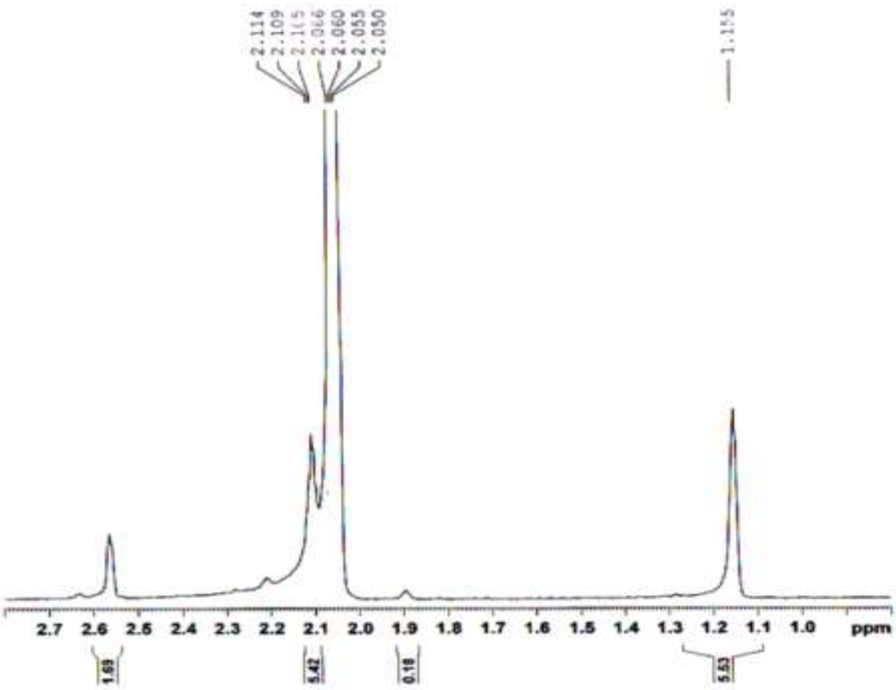
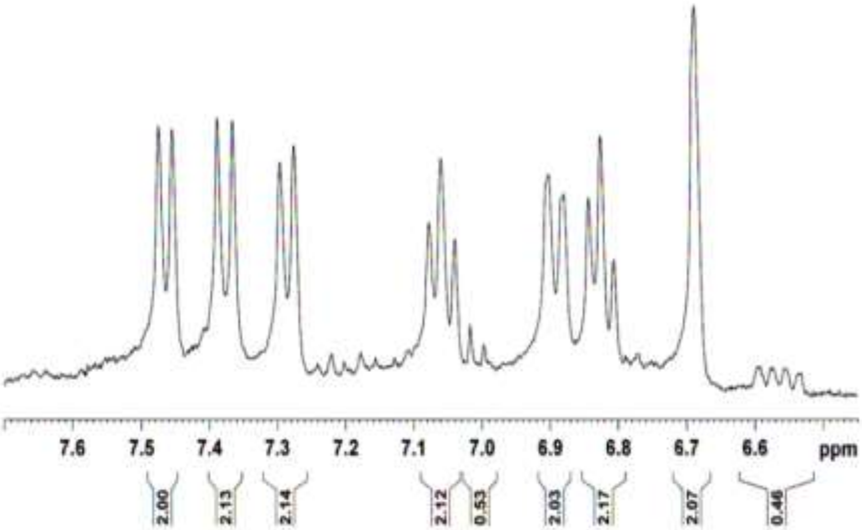


Fig (4). FT-IR spectrum of synthesized dyestuff


7.366
6.687
2.114
2.109
2.105
2.066
2.060
2.055
2.050
1.155
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.21
2.32
2.18
2.04
2.47
2.18
2.19
1.00
1.89
5.42
0.18
5.53


2.114
2.109
2.104
2.058
2.066
2.060
2.055
2.050
2.045
1.154
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.13
2.14
2.12
0.53
2.03
2.17
2.07
0.46
1.00
1.92
1.00
6.59
0.29
6.29


2.114
2.109
2.105
2.066
2.060
2.055
2.050
1.155
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
ppm
1.69
5.42
0.18
5.53


7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
ppm
2.00
2.13
2.14
2.12
0.53
2.03
2.17
2.07
0.46

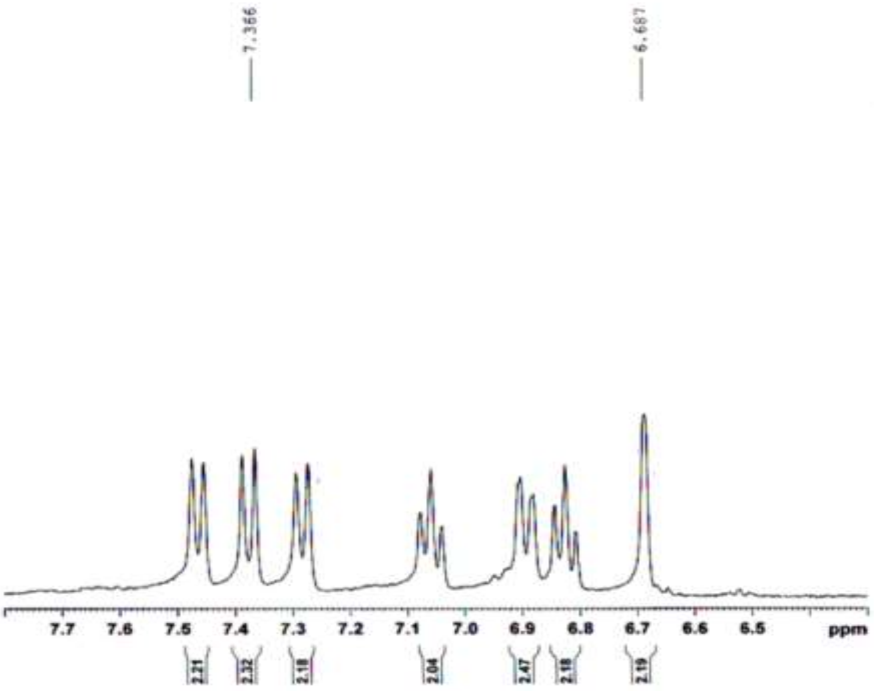
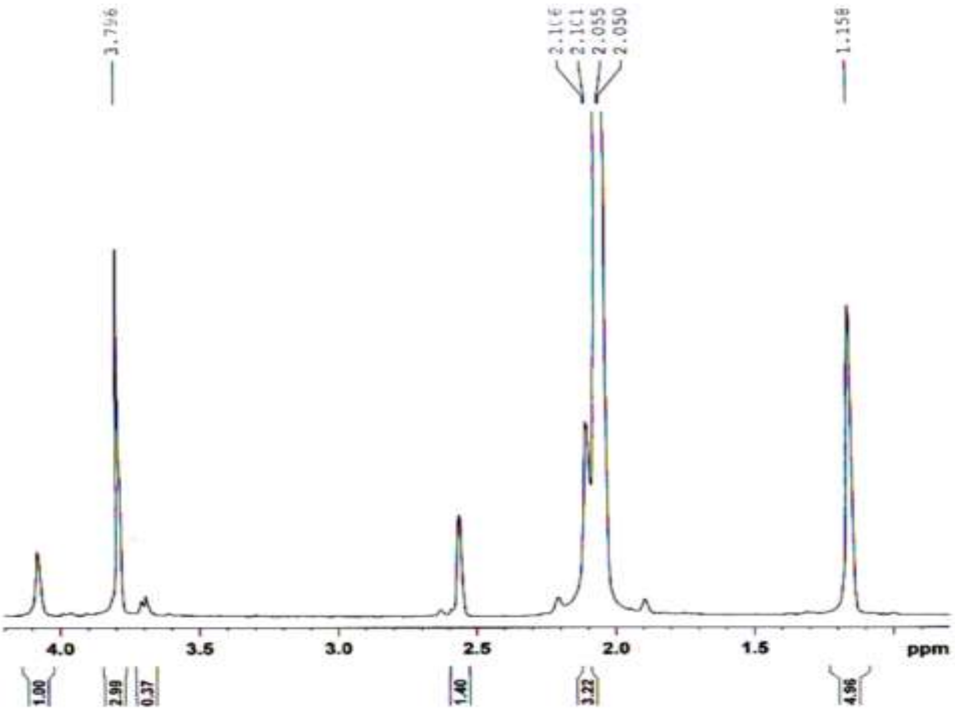
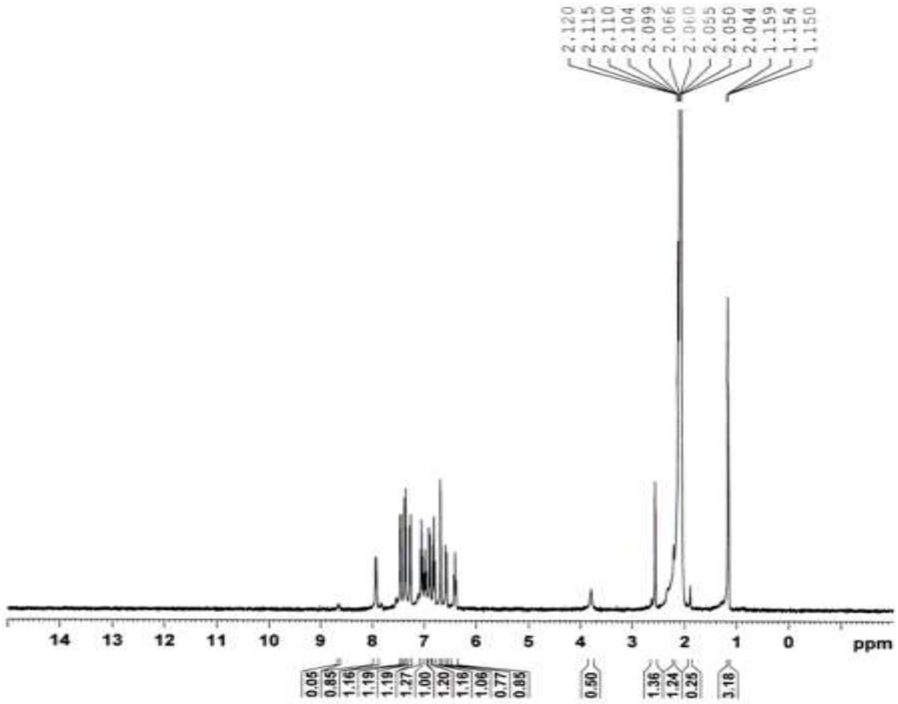
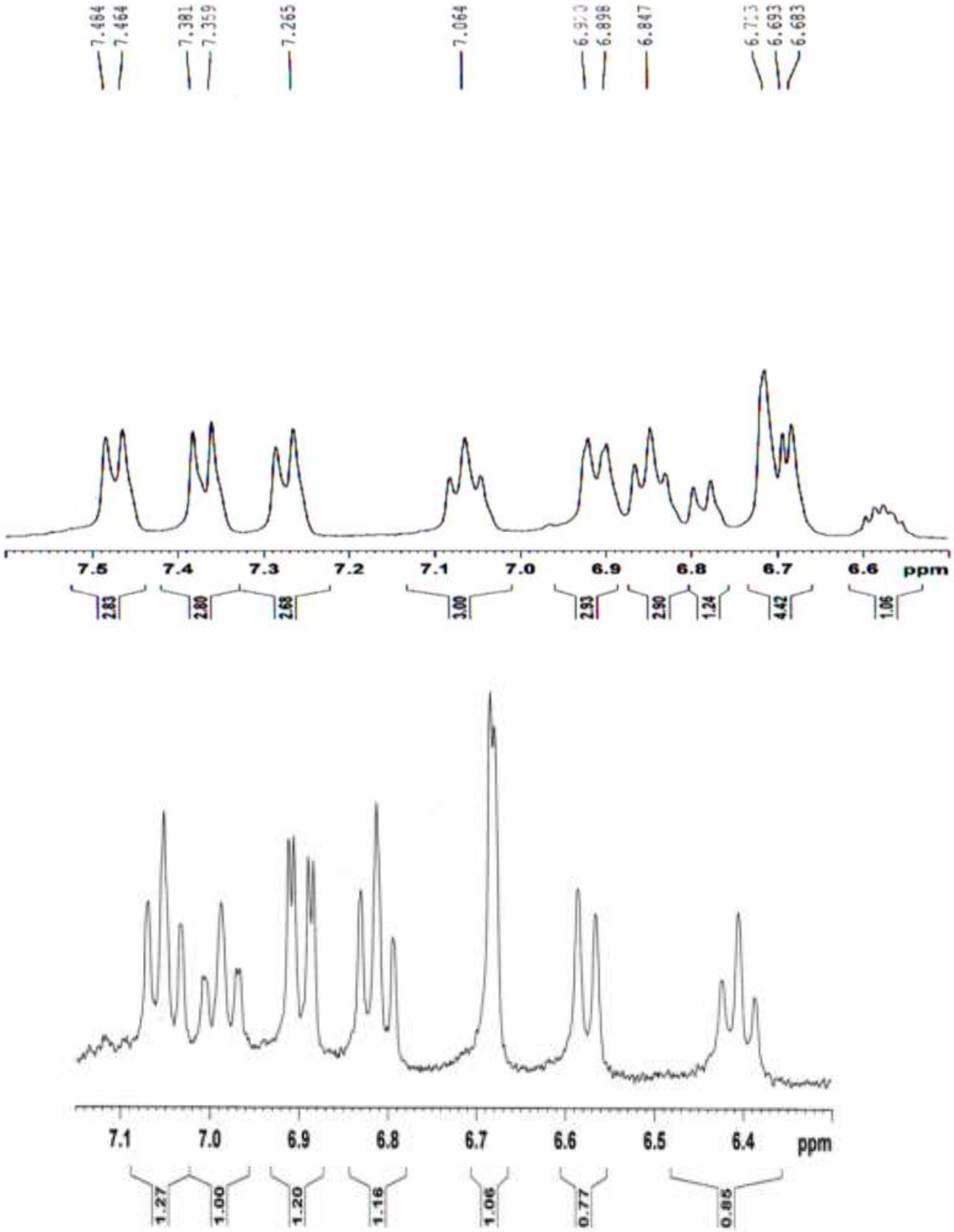


Figure 5: H-NMR spectrums of synthesized dyestuffs (α_a and α_b)

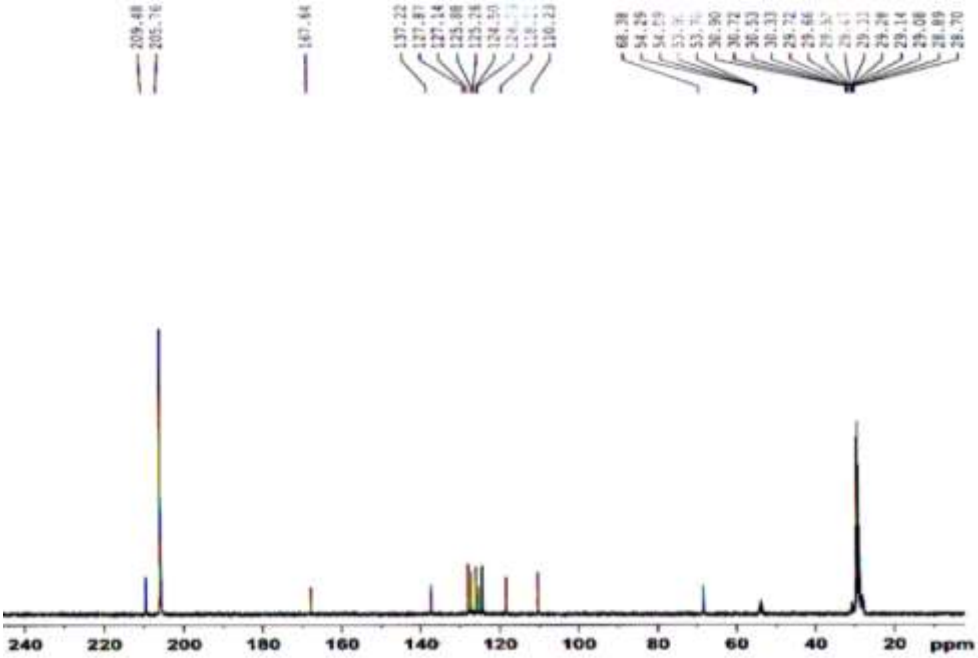

3.796
2.106
2.101
2.055
2.050
1.158
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
2.99
0.37
1.40
3.22
4.96

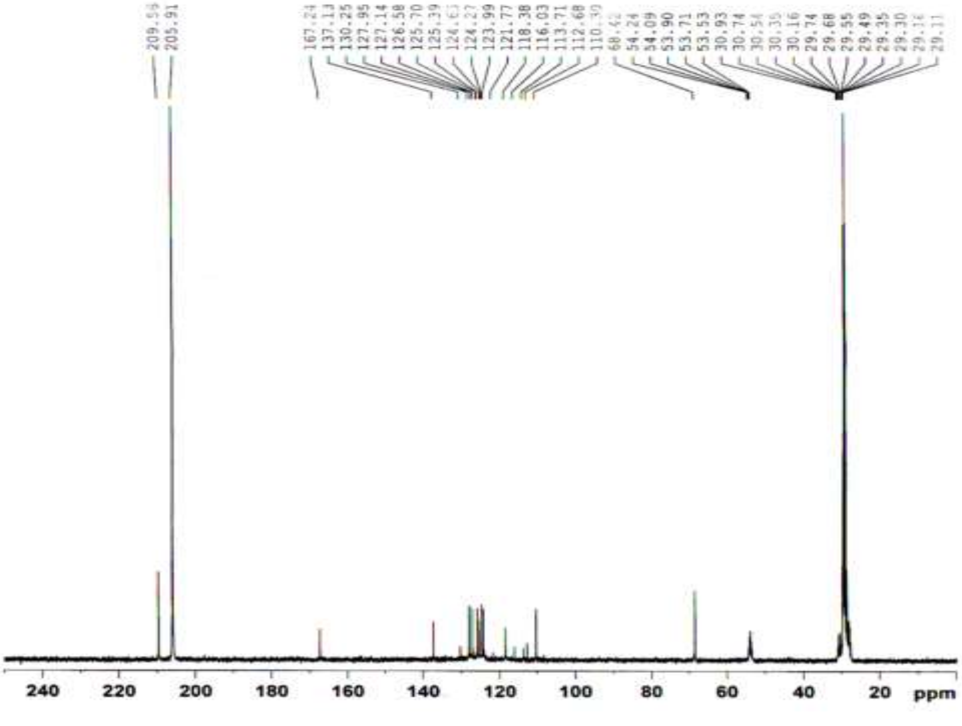

2.120
2.115
2.110
2.104
2.099
2.066
2.060
2.055
2.050
2.044
1.159
1.154
1.150
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.05
0.85
1.16
1.19
1.19
1.27
1.00
1.20
1.16
1.06
0.77
0.85
0.50
1.36
1.24
0.25
3.18

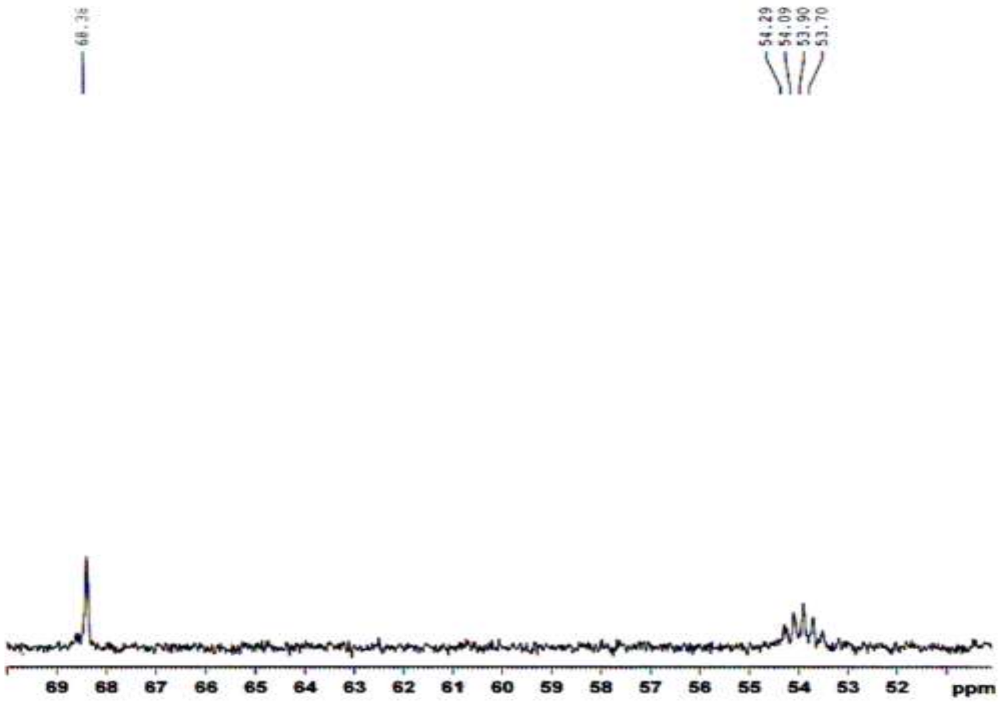


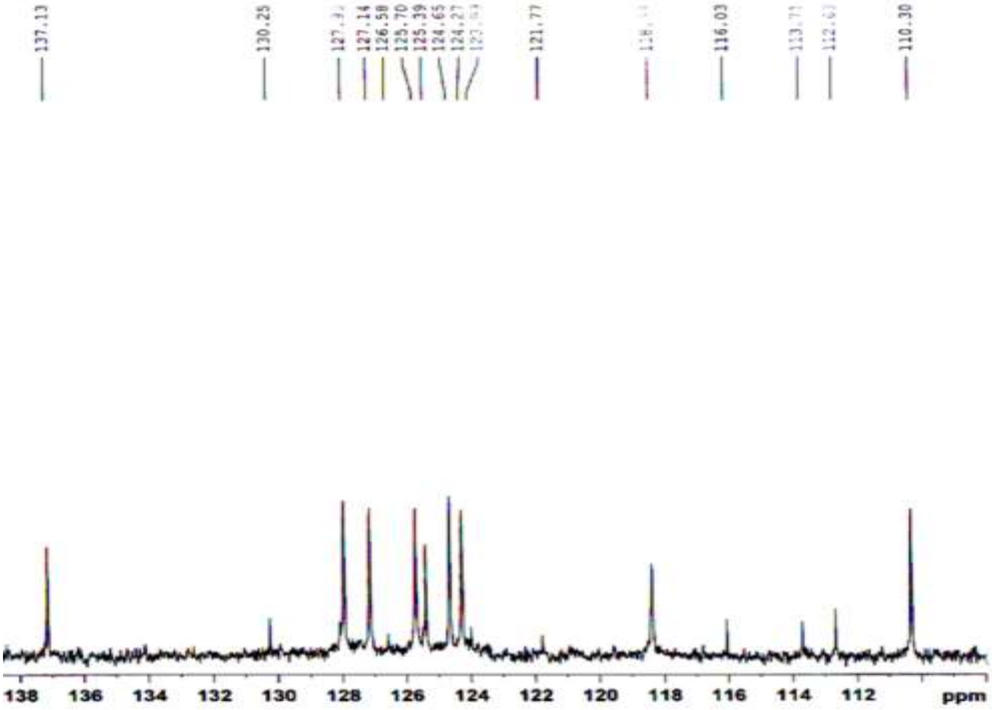
c βd β

Figure 6: H-NMR spectrums of synthesized dyestuffs (β_c and β_d)


209.48
205.76
167.64
137.22
127.87
127.14
125.88
125.28
124.50
110.23
68.38
54.29
30.90
30.72
30.53
30.33
29.72
29.33
29.28
29.14
29.08
28.89
28.70
240
220
200
180
160
140
120
100
80
60
40
20
ppm


209.56
205.91
167.24
137.13
130.25
127.95
127.14
126.58
125.70
125.39
124.63
124.27
123.99
121.77
118.38
116.03
113.71
112.68
110.39
68.42
54.24
54.09
53.90
53.71
53.53
30.93
30.74
30.54
30.35
30.16
29.74
29.68
29.55
29.49
29.35
29.30
29.16
29.11
240
220
200
180
160
140
120
100
80
60
40
20
ppm


68.36
54.29
54.09
53.90
53.70
69
68
67
66
65
64
63
62
61
60
59
58
57
56
55
54
53
52
ppm


137.13
130.25
127.14
126.58
125.70
125.39
124.65
124.27
121.77
116.03
110.30
138
136
134
132
130
128
126
124
122
120
118
116
114
112
ppm

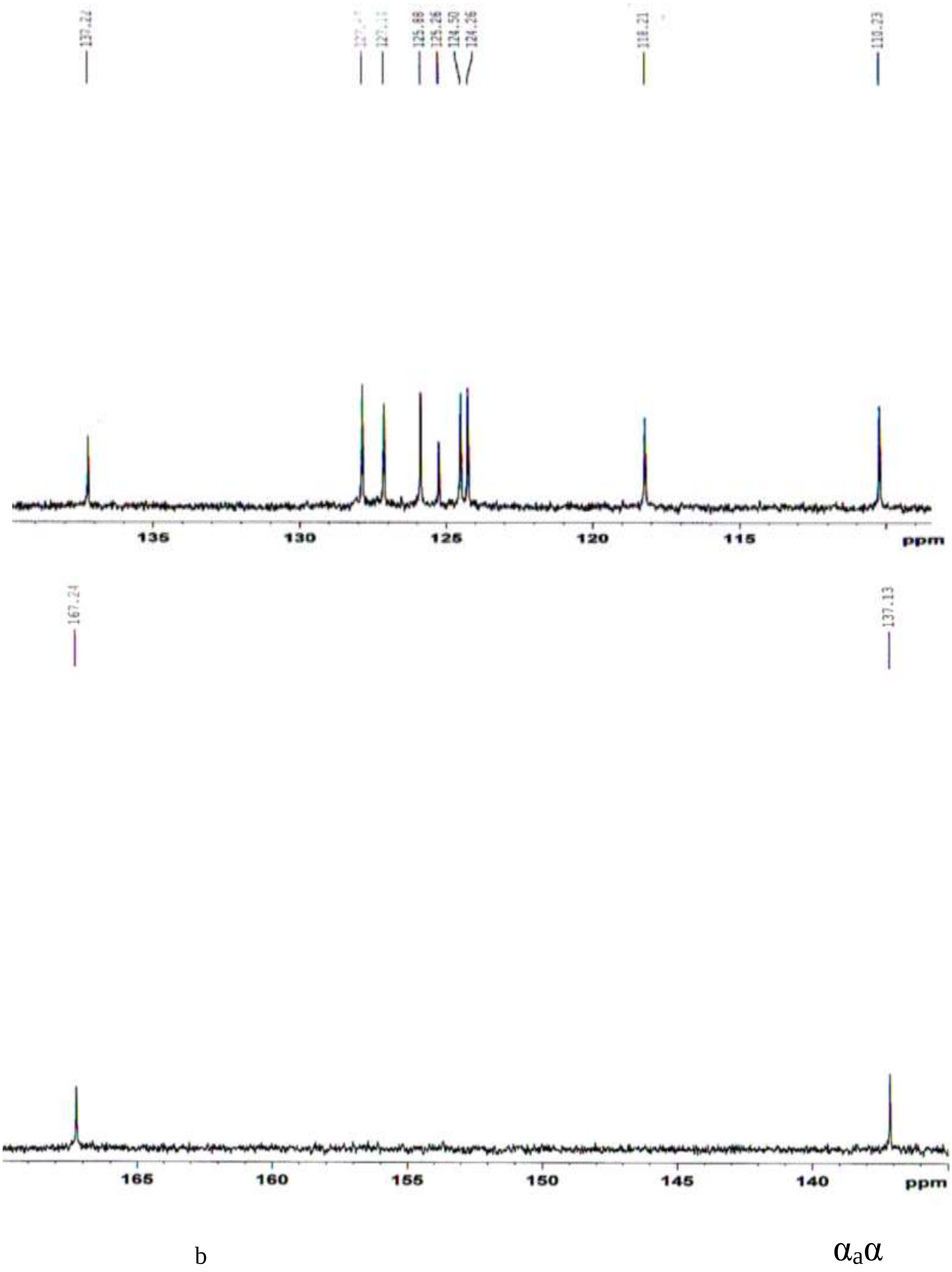
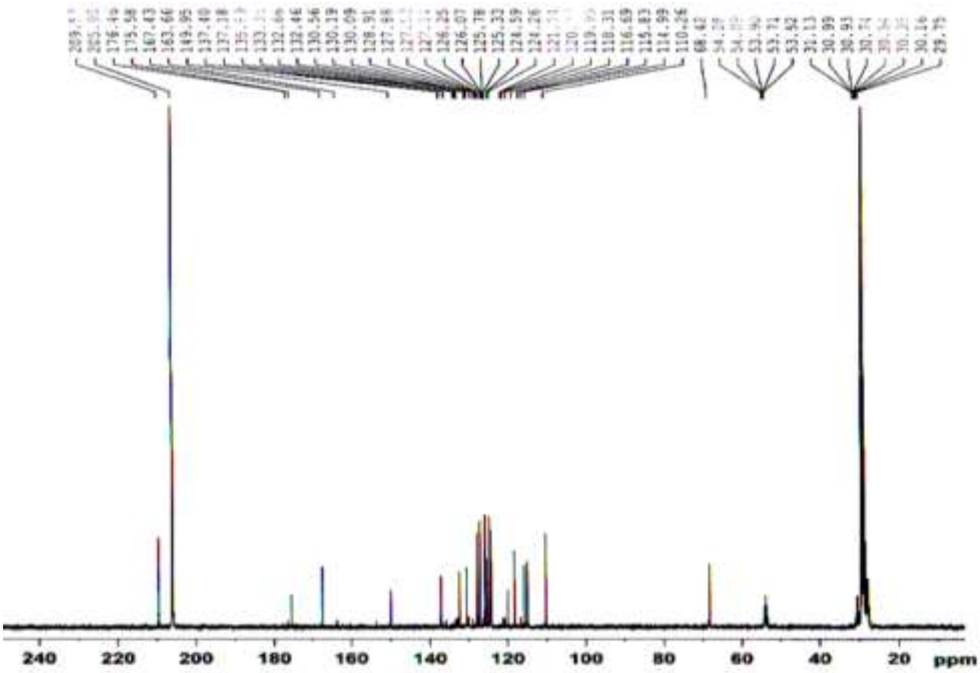
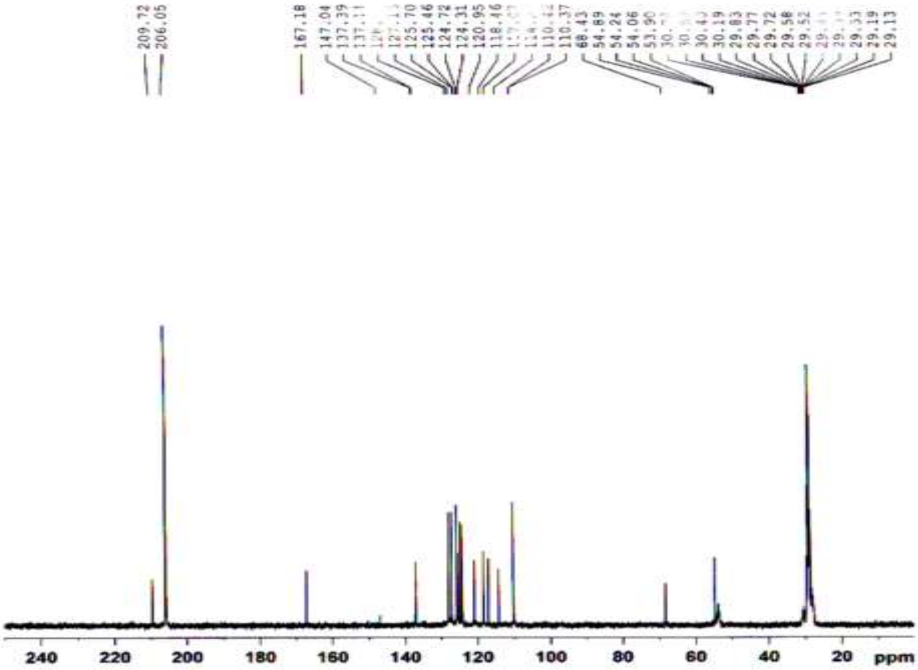
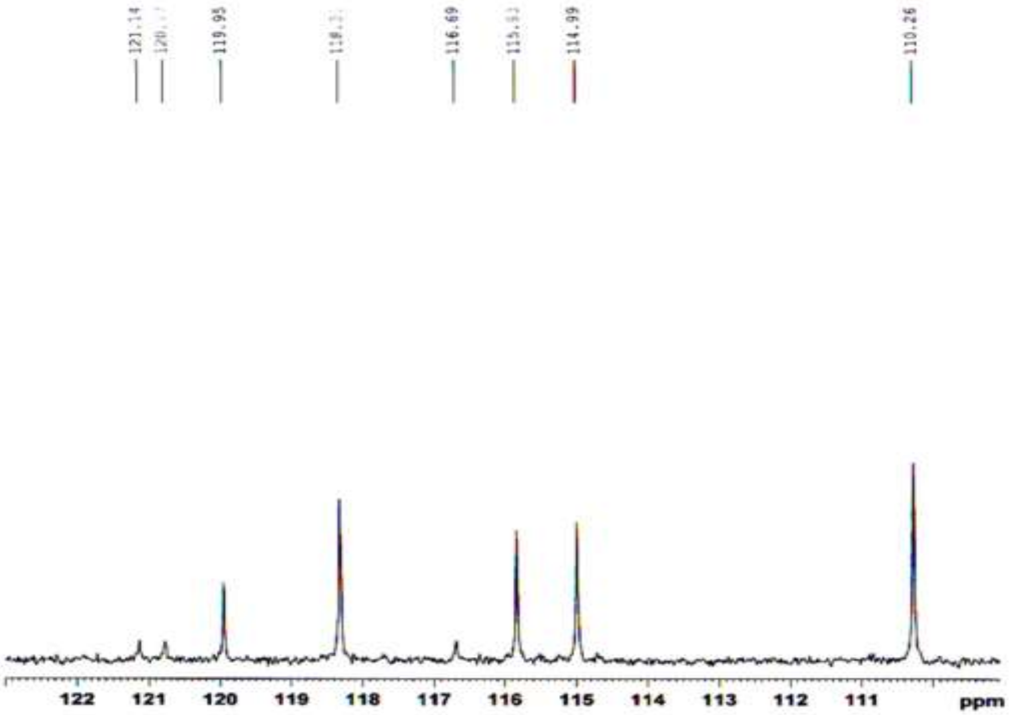
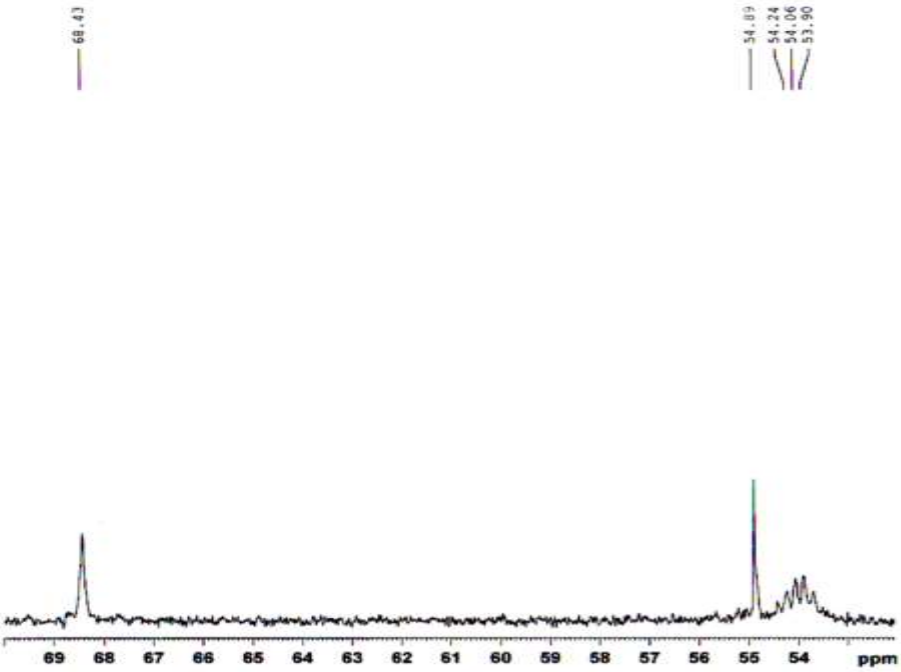


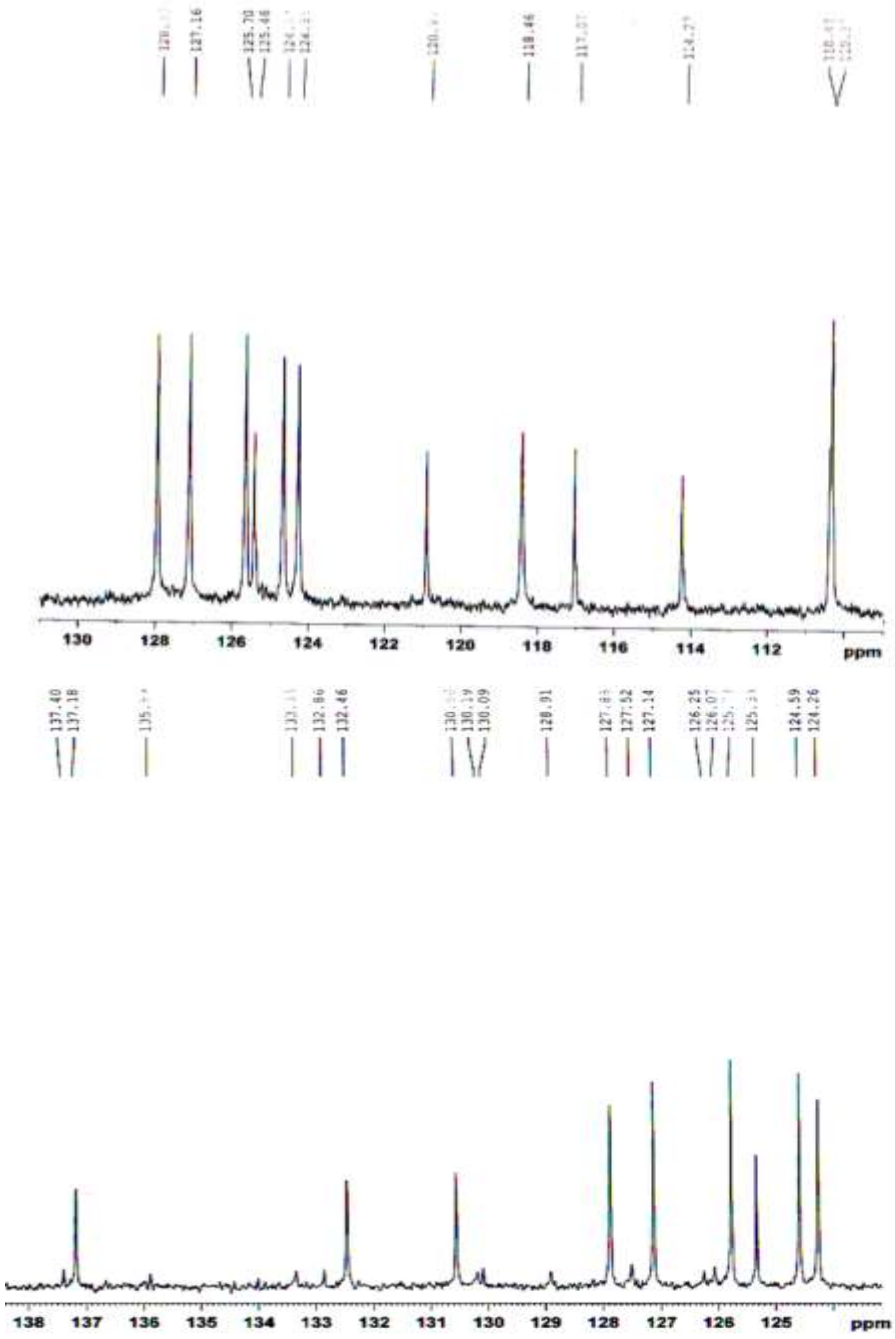
Figure 7: C-NMR spectrums of synthesized dyestuffs (α_a and α_b)


176.49
175.58
167.43
163.66
149.95
137.40
137.18
132.66
132.46
130.56
130.19
130.09
128.91
127.88
126.25
126.07
125.78
125.33
124.59
124.26
118.31
116.69
115.83
114.99
110.26
68.42
53.90
53.71
53.52
31.13
30.99
30.93
30.16
29.75
240
220
200
180
160
140
120
100
80
60
40
20
ppm


209.72
206.05
167.18
147.04
137.39
125.70
125.46
124.72
124.31
120.95
118.46
110.37
68.43
54.89
54.24
54.06
53.90
30.40
30.19
29.83
29.77
29.72
29.58
29.52
29.33
29.19
29.13
240
220
200
180
160
140
120
100
80
60
40
20
ppm


121.14
119.95
116.69
114.99
110.26
122
121
120
119
118
117
116
115
114
113
112
111
ppm


68.43
54.89
54.24
54.06
53.90
69
68
67
66
65
64
63
62
61
60
59
58
57
56
55
54
ppm



c βd β

Figure 8: C-NMR spectrums of synthesized dyestuffs (βc and βd)

Table 3: The data FT-IR, H-NMR and C-NMR spectrums of synthesized dyestuffs

Dye	FTIR (cm^{-1})	^{1}HNMR (ppm)	^{13}C-NMR (ppm)
α_a	3470 (-OH), 1588 (-N=N-) 1268 (C-O), 1033 (C-N)	δ=3.9 (1H, OH) 6.7-7.6 (4H, phenyl ring and 6Hnaphthalene ring)	δ =110-140 (6C, phenyl ring and 10C, naphthalene ring)
α_b	3405 (-OH), 1586 (-N=N-) 1271 (C-O) δ=110-128 (6C, phenyl ring and 10C, naphthalene ring) 1033 (C-N), 3045 (str CH_3) 1333 (br, CH_3)	δ =3.9 (1H, OH) 6.7-7.4(4H, phenyl ring and 6H, naphthalene ring) 2.1 (3H, CH_3)	δ =110-128 (6C, phenyl ring and 10C, naphthalene ring) δ =53-54 (1C, CH_3)
β_c	3370 (-OH), 1586 (-N=N-) 1271(C-O), 1059(C-N) 2910 (str CH_3), 1333 (br,CH_3)	δ =4.1 (1H, OH) 6-7.5 (4H, phenyl ring and 6Hnaphthalene ring) 3.8 (3H, OCH_3)	δ =110-128 (6C, phenyl ring and 10C, naphthalene ring) δ =55 (1C, OCH_3)
β_d	3405 (-OH), 1586 (-N=N-) 1272 (C-O), 1074 (C-N) 1747-873 (COOH)	δ =3.8 (1H, OH) 6.4-7.5 (4H, phenyl ring and 6H, naphthalene ring) 8 (1H, COOH)	δ =110-128 (6C, phenyl ring and 10C, naphthalene ring) δ =167.5 (1C, COOH)

3.2. Dyeing different fibres with synthesized dyestuffs

In order to study the dyeing properties of synthesized dyestuffs, the dyeing operation was done with four synthesized dyes on two fibres, namely polyester and nylon, and the parameters of dyeing ability and fastness properties were investigated [22]. To evaluate the dyeing ability of synthesized dyestuffs, the percentage exhaustion of each of the synthesized dyestuffs was measured. To measure the percentage exhaustion, the maximum wavelength (λ_{max}) of each synthesized dyestuff was first determined. Using the amount of dye solution absorption in different concentrations in the maximum wave length, the calibration curve of each dye was prepared, and using the data of each of the curves, the absorption equation of each the synthesized dyes was obtained. The related results are shown in Table 4.

Table 4: The absorption equation and the amount of solution absorption of the synthesized dye with different concentrations in the maximum wavelength

Dye	λ_{max}(nm)	Amount of absorption of the synthesized dye with different solution concentrations							The equation absorption
-	-	0.07	0.06	0.05	0.04	0.03	0.02	0.01	-
α_a	439	0.0703	0.0759	0.0603	0.05	0.0236	0.0151	0.0114	Abs=0.55766×C-0.0144
α_b	403	0.2310	0.2328	0.2203	0.1419	0.1216	0.0831	0.0304	Abs=1.87302×C+0.0753
β_c	491	0.3361	0.2810	0.2194	0.1733	0.0990	0.0642	0.0476	Abs=1.50032×C-0.0467
β_d	493	0.5292	0.4722	0.3846	0.3441	0.2420	0.1490	0.0765	Abs=7.81393×C-0.0113

Using amount absorption and the absorption equation, the concentration of each dye was calculated in the bath dyeing and washing effluents and using equation 1 and the concentration of dye, the exhaustion percentage of the samples before the dyeing operations was obtained. The results are shown in Table 5. The results of exhaustion measurement percentage on dyed goods showed that synthesized dyestuffs have an excellent dyeing ability on non-hydrophilic fibres. The best exhaustion percentage was observed on nylon fibre with dyestuffs β_d, which is due to the chemical structure of the dyestuffs β_d and general nature of the fibre of nylon [23]. Dyestuffs β_d have a carboxylic acid group and can form ionic bonding with nylon fibres. Therefore, the exhaustion percentage of synthesized dyestuffs on non-hydrophilic fibres showed that the synthesized dyestuffs type of application can be classified as disperse or acidic dyes [22,23]. Fastness Properties of synthesized dyestuffs is a very good standard for its usefulness in the textile industry. Thus, fastness properties were measured by dyeing goods. The results showed that synthesized dyestuffs had light fastness, which is about average to good, washing and staining fastness was good to excellent (seen Table6).

Table 5. Percentage exhaustion samples dyed with synthesized dyestuffs Legend: Abs. B. - Absorption of dyeing bath waste water, C. B. - concentration of dyeing bath waste water, Abs. W. - Absorption of washing bath waste water, C. W. - concentration of washing bath waste water, E – exhaustion.

Goods	Dye	α_α	α_β	β_χ	β_δ
Polyester	Abs. B.	0.0209	0.3031	0.0784	0.1564
	C. B.	0.0633	0.1216	0.0833	0.0215
	Abs. W.	0.0137	0.0927	0.0157	0.1098
	C. W.	0.0503	0.0092	0.0415	0.0154
	E [%]	24.2	12.74	16.68	50/07
Nylon	Abs. B.	0.0209	0.3031	0.0784	0.1564
	C. B.	0.0633	0.1216	0.0833	0.0215
	Abs. W.	0.0137	0.0927	0.0157	0.1098
	C. W.	0.0503	0.0092	0.0415	0.0154
	E [%]	24.2	12.74	16.68	50/07

3.3. Fastness properties of synthesized dyestuffs on different fibres

According to table 6, the Light fastness of polyester and nylon fibers was compared, in which polyester fibers were higher in α_a and β_c than nylon fibers, and in other cases, not many changes were seen. On the other hand, according to the results obtained in washing stability, nylon and polyester fibers are equal in α_b and β_c , respectively, and are higher than other washing fastness measurement modes. In general, according to the results shown in Table 6, the Light fastness of polyester fibers is slightly better compared to nylon fibers and its washing stability is lower.

Table 6. The results of light and washing fastness test

Dye	Goods	Light fastness	Washing fastness
α_a	Nylon	5	4.5
α_a	Polyester	7	4
α_b	Nylon	5	5

α_b	Polyester	5	4
β_c	Nylon	5	4.5
β_c	Polyester	7	5
β_d	Nylon	5	4
β_d	Polyester	5	4

4.Conclusion

Our exploration in this study showed that through the establishment of solid acids or their derivatives, such as nitrosyl chloride on nano-silica substrate, some of the organic chemistry reactions such as diazotization, can be found. It means that using solid acids can cause to reduce the process time. To the ensuing reaction, copulation was done to synthesis azo dyestuffs, for a very short time at room temperature with high efficiency, without the presence of concentrated acids in the liquid. The molecular structure analysis of synthesized dyestuffs by spectroscopy techniques showed that the molecular structure of synthesized dyestuffs conforms to the general structure azo dyestuffs and new methods; the synthesis of some organic compounds is possible to minimize the degradation on the pot as well as environmental pollution. Investigating the dyeing ability of synthesized dyestuffs and measurement fastness properties of the dyeing goods on non-hydrophilic fibres showed that synthesized dyestuffs type of application can be classified as disperse or acidic dyes.

5.References

[1] R. Khadeeja, S. Tanvir, S. Amna, H. Sabir, M. Faisal, S.H. Muhammad, S.A. Muhammad, R.I. Muhammad. Effect of Reactive Black 5 azo dye on soil processes related to C and N cycling. PeerJ, 6,2018.

[2] Zollinger, H. Azo Dyesand Pigments in Color Chemistry: Synthesis, Properties and Application of Organic Dyes and Pigments 161–163, 2003.

[3] Benkhaya, S., El Harf, S. & El Harf, A. Classifcations, properties and applications of textile dyes: a review. Appl. J. Environ. Eng. Sci. 3, 311–320, 2017.

[4] Pandian, B., Arunachalam, R., Easwaramoorthi, S. & Rao, J. R. Tuning of renewable biomass lignin into high value-added product: development of light resistant azo-lignin colorant for coating application. J. Clean. Prod. 256, 120455, 2020.

[5] Vazquez-Ortega, F., Lagunes, I. & Trigos, A. Cosmetic dyes as potential photosensitizers of singlet oxygen generation. Dyes. Pigm. 176, 108248, 2020.

[6] Yamjala, K., Naiar, M. S. & Ramisetti, N. R. Methods for the analysis of azo dyes employed in food industry–A review. Food Chem. 192, 813–824, 2016.

[7] B.Samavia, K. Azeem, J. Khan Chowdhury Ahmed, S.Maliha, B. Khaled, A. Muhammad Aqeel. Effect of azo dye on ammonium oxidation process and ammonia-oxidizing bacteria (AOB) in soil.RSC Advances, **5**(44), 34812–34820,2015.

[8] A. NaghamMahmood,. Review in azo compounds and its biological activity. Biochemistry & Analytical Biochemistry, **4**(2), 169−172, 2015

[9] S.Behera, B.Mallick, N.Tiwari and C.P. Mishra,. Risk of Acid Attack on Plants: A Review. Energy, Environment and Material Science, 15(43), 66−71, 2015.

[10] A. Bamoniri, A. PourAli and M.R. Nazifi,. Facile synthesis of 1-naphthol AZO dyes with nano SiO2/HIO4 under solvent-free conditions. Chemical Society of Ethiopia, 27(3), 439−445, 2013.

[11] M. Mirjalili, F. Zahed and A. Hassanabadi,. A New Nano Silica Gel Supported by Thionyl Chloride as a Solid Acid for the Efficient Diazotization of Aniline Derivatives: Application and Synthesis of Azo Dyes. Journal of Chemistry, 9(2), 1042−1046, 2012.

[12] S. Popa , M. E. Radulescu-Grad, Alina. Perdivara & G. Mosoarca1; Aspects regarding colour fastness and adsorption studies of a new azo-stilbene dye for acrylic resins, Journal of Scientifc Reports, 1-9, 2021

[13]H. Kolhduzan, S.S. NuriKhorasan, S.M. Bidoki, S. Vaezifar,. Synthesis and Characterizton of Nanosilica Prepared by Precipitation Method.Journal of Color Science and Technologi, 2(1), 57−6, 2008.

[14] S. Rudiger, U. Gro,. Nan-aqueaus sol-gel synthesis of nano-structured mental fluandes, Journal of Fluorie chemistry, 2007, 128(1), 353−362, 2007.

[15] S. Manisha and M.P. KAUSHIK,. An efficient method for the esterification of amino acids using silica chloride, Journal of Catalysis Communications, 7(9), 644–646, 2006.

[16] P. DelphiaShalini Rosalyn, S. Senthil, P. Kannan, G. Vinitha, A. Ramalingam,. Investigation on substituent effect in novel azo-naphthol dyes containing polymethacrylates for nonlinear optical studies, Journal of Physics and Chemistry of Solids, 68(9), 1812–1820, 2007.

[17] T.Bingto, Z. Shufen, Y. Jinsong and L.Feng,. Synthesis of a novel water-soluble cross linking polymeric dye with good dyeing properties, Journal of Dyes and Pigments, 68(1), 69−73, 2006.

[18] G. Ramazan, G. BulentEmrah and K. Irkan,. Synthesis and spectroscopic properties of new azo-dyes, Journal of Dyes and pigments, 73(1), 40−53,2007.

[19] K. Gharanjig, F. Ameri, F.S. Dadras, A. Khosravi,. Synthesis and Application of 3-(6-((4-ethyl -2-hydroxyethyl) amino) phenyl) diazinyl)-1, 3-dioxo-1H-benzo- [de]2 isoquinolin (3H)yl) propanoic acid as a Disperse Dye J. Color Sci. Tech, 3(1), 257−266, 2010.

[20] M. Sadeghi Kiakhani, K. Gharanji, M. Arami, N.M. Mahmoodi, and J. Mokhtari,. The Dyeing of Wool with Monoazo Disperse Dyes Based on Naphthalimide Containing Butyric Acid. Journal of Color Science and Technology, 3(1), 9−15, 2009.

[21]F. Karcl, A. Demric, I. Sener and T. Tilki,. Tahir.symttesis of 4-amono-1-H- benzo[4,5]imidazo[1,2-α]pyrimidin-2-one and its disperse azo dyes. Journal of Dyes and Pigmants, 71(2), 97−105, 2006.

[22] Q. Fengxian, C. Yonglin, X. Hongliang, Y. Jiang, Z. Yuming and L. Juzheng,. synthesis and properties of polymer containing azo-dye chromophores for nonlinear optical applications.Journal of Dyes and Pigments, 75(2), 454−466, 2007.

[23] N. Shazia, S. Khurram, A. Muhammad, Z. Muhammad and H. Mazahar,. Study of Exhaustion of Direct Dyes under Optimized Conditions Spectrophotometrically. Asian Journal Chemistry, 24(1), 33−36, 2012.