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Syntheses, Characterization And Spectroscopic Properties of Azo Dyes Using Diethylamine Functionalized Polyethylene Glycol As A Mild, Efficient And Reusable Catalyst

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ABSTRACT

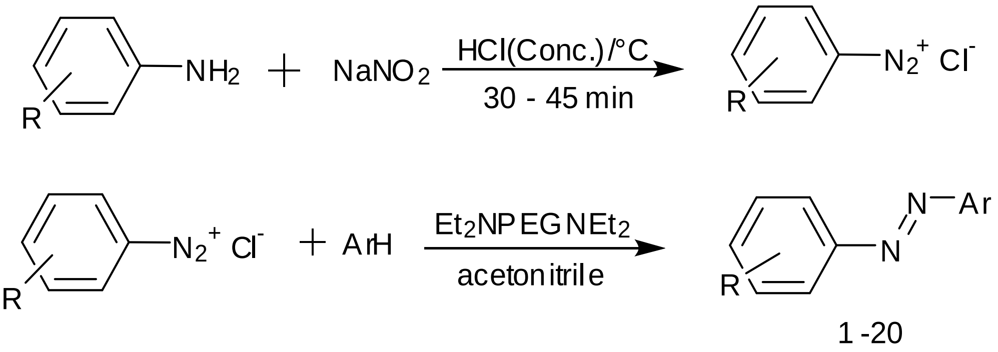
A variety of azo dyes were synthesized in the presence of diethylamine functionalized polyethylene glycol. There are many reports for the synthesis of these dyes in the presence of sodium hydroxide. But few researches concerned with the application of another catalyst in the synthesis of these significant organic colorants. We report their immediate synthesis in the presence of modified polyethylene glycol with tertiary amine moiety in good to high yields. Investigations of solvent and pH effects on the products were performed using UV-visible spectra. The applied catalyst is non-toxic, mild and reusable without significant decrease in productivity.

Keywords: Azo dyes, Diethylamine functionalized polyethylene glycol 600, UV-visible spectra, medium effects.

INTRODUCTION

One of the most important intermediates in the synthesis of aromatic compounds is diazonium salts [1] that are used for the synthesis of azo compounds. As an organic colorant, azo dye compounds have versatile applications as dyes and pigments. They are widely used in dying textiles. While they are the most applicable class of commercial colorants in textile industry but also, azo dyes, have several other applications [2] such as, color additives for drugs, cosmetics, foods and colorants for digital printing and photography [3]. Some dyes are used as chiral receptors [4], novel glassy materials [5] and liquid crystals [6]. They are used as chiral switches in photochemistry because they can perform cis-trans isomerization under photochemical reactions and might undergo energy transfer [7-9].

At the best of our knowledge, there are few reports concerning the use of catalyst, except for sodium hydroxide, in the synthesis of azo dyes [10]. In this paper, we report the synthesis and characterization of the colorants that are shown in scheme 1. We used modified polyethylene glycol with tertiary amine moiety as an efficient catalyst. Our complete investigation includes determination of the effects of solvent and pH on the UV-visible spectra of azo dyes. These derivatives were synthesized immediately with good to high yields. The applied catalyst can be recovered and reused without significant decreasing in productivity.



Scheme 1. Synthesis of azo dye derivatives **1-20** by the reaction of diazonium salts and phenoles in acetonitrile

MATERIALS AND METHODS

All reagents were purchased from Aldrich and Merck companies. All materials were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. UV–visible (UV-vis) spectra were recorded on a 160 Shimadzu spectrophotometer. IR spectra were measured on a Perkin–Elmer 783 infrared spectrophotometer. ^{1}H NMR spectra were measured using a BRUKER DRX-250 Avance spectrometer at 400.13. All spectra were recorded in $CDCl_3$ using TMS as an internal standard. Chemical shifts are reported as δ values (ppm). All the reactions were monitored by thin-layer chromatography (TLC).

Synthesis of the catalyst: The catalyst was prepared according to the reported procedure [11].

General procedure of dye synthesis:
Traditional method of diazotization: Aniline derivative (0.5 mmol) was dissolved in HCl (1.5 ml, 6N). This solution was cooled to 0–5 °C, and a solution of $NaNO_2$ (0.4 ml, 10 % wt) added drop wise to the reaction mixture, maintaining the temperature below 5 ° C. The mixture was stirred at 0-5 °C for 30 min. At the end of the reaction, the excess of HNO_2 was eliminated by adding solid urea [12].

General procedure for azo coupling procedure: To a cold (0–5 °C) solution of diazonium salt (prepared as above) was added slowly a solution of phenol (0.5 mmol) and diethylamine functionalized PEG (0.04 g) dissolved in 2 mL acetonitrile with constant stirring and maintaining temperature at 5 °C. The product synthesized immediately. At the end of the procedure, the reaction mixture neutralized by adding Na_2CO_3 (10 % wt). The resulting solid was filtered, washed with water and cold ethanol. Recrystallisation from water-ethanol gave pure dye.

RESULTS AND DISCUSSION

In this project we report the synthesis of azo dye derivatives in the presence of diethylamine functionalized PEG as a non-toxic and reusable catalyst. Diazotization procedure was performed by traditional method, the reaction of aniline derivative, HCl and $NaNO_2$ at low temperature. The reaction of phenol derivatives and diazonium salt in coupling reaction, which was accelerated in the presence of diethylamine functionalized PEG as an efficient catalyst, gave the products in good to high yields (50-98%). In order to optimize the reaction conditions the reaction of diazonium salt of aniline and 2-naphthol, was selected as model reaction in order to synthesis azo dye 7. Optimization conditions were solvent and catalyst amount optimizations respectively. These experiments showed that the best condition for mentioned reaction was acetonitrile (CH_3CN) as solvent in the presence of 0.04 gr catalyst for 0.5 mmol of each reagent.

Recycling of the catalyst was also investigated. After filtering the crude precipitate, the remaining was biphasic. Extraction of the organic phase by using ethyl acetate as solvent and evaporation of solvent gave the recovered catalyst. The catalyst was used for performing the next cycle. Recycling of the catalyst was repeated for four runs and considerable decrease in the yield of the product was not observed. The results are given in table 1.

Table 1. Recyclability of catalyst for model reaction, the synthesis of azo dye **7**, in 4 cycles

Cycle [a]	I	II	III	IV
Yield (%) [b]	81	79	79	76

[a] 0.04 gr catalyst, 0.5 mmol 2-naphthol and 0.5 mmol diazonium salt of aniline in CH_3CN, 0-5 °C;
[b] Isolated yield

The optimized reaction condition was used for the fast and simple synthesis of a variety of azo dye derivatives in good to high yields (50-98%) using 2-naphthol and resorcinol as phenols. The synthesis of azo dyes 1-20 are summarized in table 2. All azo dyes, which crystallized from ethanol : water (1:1), were crystalline as powders ranging in color from orange to dark brown. Purity of the all dyes was checked by Thin Layer Chromatography (TLC) using ethylacetate : n-hexane (1:1) solvent system and one spot was observed for each dye [10,12-15]

Table 2. Different azo dye derivatives synthesis in the presence of diethylamine functionalized polyethylene glycol as catalyst

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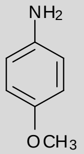
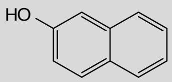
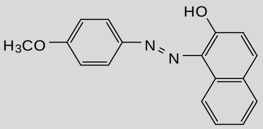
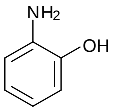
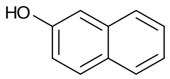
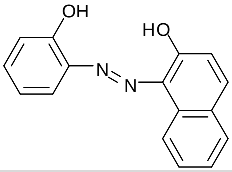
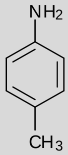
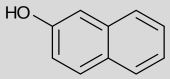
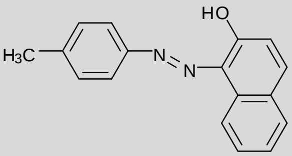
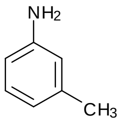
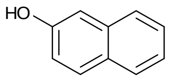
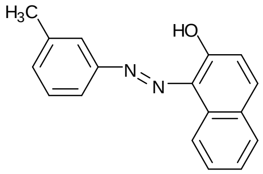
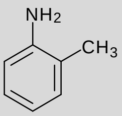
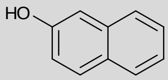
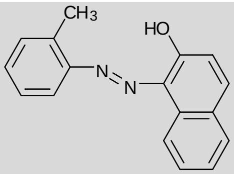
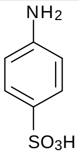
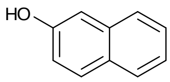
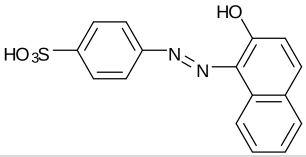
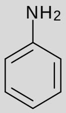
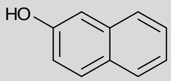
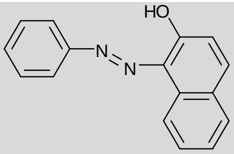
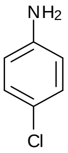
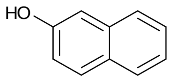
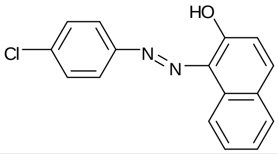
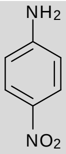
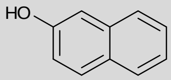
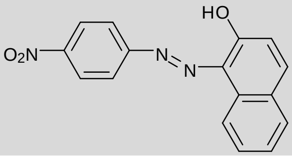
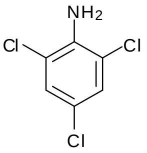
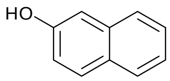
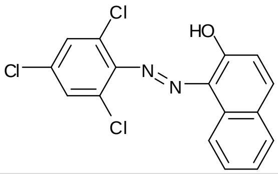
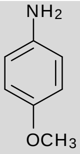
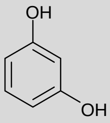
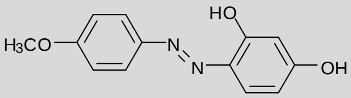
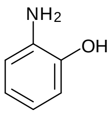
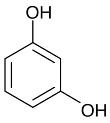
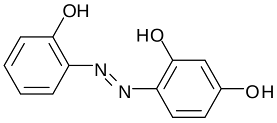
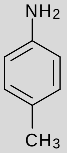
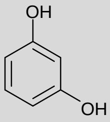
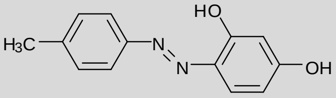
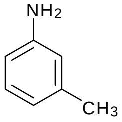
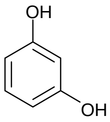
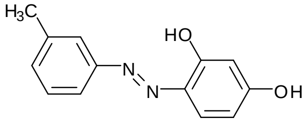
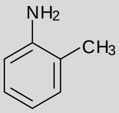
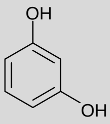
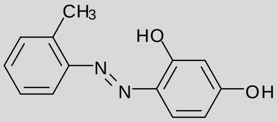
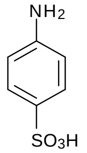
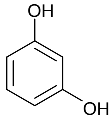
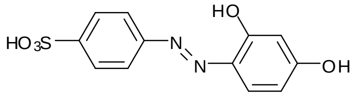
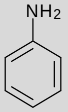
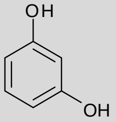
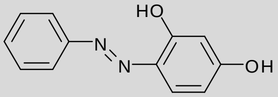
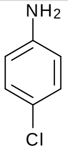
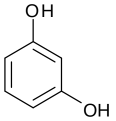
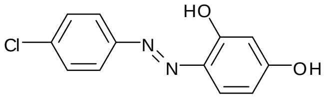
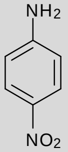
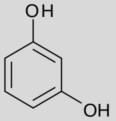
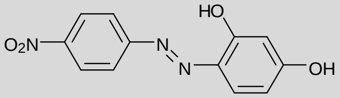
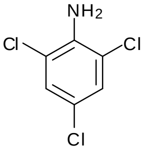
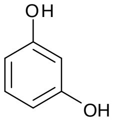
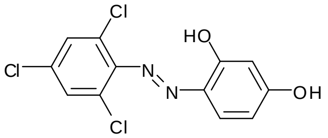
1				98
2				50
3				98
4				90

5				98
6				70
7				81
8				70
9				98
10				98
11				50
12				80
13				80
14				80
15				80

16				90
17				80
18				86
19				95
20				90

[a] 0.04 gr catalyst, 0.5 mmol phenol and 0.5 mmol diazonium salt in CH_3CN, 0-5 °C; [b] Isolated yield

IR and ^{1}H NMR spectra of the synthesized dyes showed important signals at their respective positions, which confirmed the structures of products, as shown in table 3.

Table 3. Spectral data of some the synthesized azo dyes

Azo dye	^{1}H NMR [δ (ppm), $CDCl_3$]	IR[υ_{max} (cm^{-1}), KBr]	mp (°C)
3	16.22 (1H, s, -NH/OH); 7.69 (2H, d, *J*= 8.0 Hz, Ar-H); 7.27 (2H, d, *J*= 8.0 Hz, Ar-H); 6.93-8.63 (6H, m, naphthyl); 2.43 (3H, s, $-CH_3$);	3448 (-OH), 1612 (-C=N), 1504 (-N=N)	134
7	16.28 (1H, s, -NH/OH); 6.86-8.56 (11H, m, Ar-)	3448 (-OH), 1620 (-C=N), 1496 (-N=N)	129-131
10	15.55 (1H, s, -NH/OH); 7.47 (2H, s, Ar-H); 6.90-8.50 (6H, m, naphthyl)	3560 (-OH), 1616 (-C=N), 1495 (-N=N), 736 (-CCl)	143
11	13.65 (1H, s, -NH/OH); 7.79 (2H, d, *J*= 8.9 Hz, Ar-H); 7.73 (1H, d, *J*=8.6, Ar-H); 7.0 (2H, d, *J*= 8.9 Hz, Ar-H); 6.54 (1H, dd, *J*=1.8Hz, *J*=8.6Hz, Ar-H); 6.43 (1H, d, *J*=2.0 Hz, Ar-H); 5.30 (1H, s, -OH); 3.86 (3H, s,$-OCH_3$)	3448 (-OH), 1616 (-C=N), 1498 (-N=N), 1240 (-C-O)	250
17	13.78 (1H, s, -NH/OH); 7.80 (3H, m, Ar-H); 7.50 (2H, t, *J*=8.0 Hz, Ar-H); 7.43 (1H, t, *J*=8.0, Ar-H); 6.56 (1H, dd, *J*=8.7Hz, *J*=2.12Hz, Ar-H); 6.43 (1H, d, *J*=2.0, Ar-H); 5.30 (1H, s, OH)	3445 (-OH), 1620 (-C=N), 1497 (-N=N), 1235 (-C-O)	140-142
18	13.49 (1H, s, -NH/OH,); 7.76 (3H, m, Ar-H); 7.47 (2H, d, *J*=8.0 Hz, Ar-H); 6.56 (1H, d, *J*=8.0 Hz, Ar-H); 6.43 (1H, s, Ar-H); 5.30 (1H,s.-OH)	3445 (-OH), 1605 (-C=N), 1463 (-N=N), 1232 (-C-O), 805 (-CCl)	250

IR spectrum of azo dye 7 (orange color) showed a broad peak at 3448 cm^{-1} for –OH group and a peak at 1496 cm^{-1} for –N=N of azo group. ^{1}H NMR spectrum of this mentioned product showed one singlet at

16.28 ppm for Ar-OH due to intramolecular proton transfer between nitrogen and oxygen atoms and a multiplet at 6.86-8.56 ppm for aromatic protons.

For Spectral UV-vis investigations, a variety of azo dyes were synthesized using 2-naphthol and resorcinol, as phenol moieties, and different diazonium salts. The effect of solvent polarities on photophysical properties of dye derivatives, were analyzed in six different solvents of different polarity. The effects of solvent polarity on absorption of these mentioned dyes are summarized in Tables 4. The absorption spectra of all dyes were recorded at the concentration of about 5 × 10^{-6} mol/L.

Table 4. Influence of solvent polarity on absorption maxima (λ_{max} in nm) of azo dyes

Azo dye[a]	$CHCl_3$ λ_{max}	acetone λ_{max}	ethanol λ_{max}	CH_3CN λ_{max}	DMF λ_{max}	DMSO λ_{max}
1	417	417	412.5	414	417.5	420
3	480.5	421	483	464	462.5	460.5
4	487.5	481	488, 691.5	481.5	484	519
5	487.5	483	485.5, 741.5	482.5	485	488.5
6	483.5, 358.5	477	480.5	477.5	479	485
7	479	472	474.5	475.5	475.5	474.5
8	483	471	473.5	472.5	476	478
9	488	482.5	483.5	480.5, 730.5	486.5	488.5
10	461	441	436.5	446.5	461.5	445.5
11	384	406, 347	384	383.5	389	389.5
13	384	383	384	379.5	388	388.5
14	388	393	387.5	389	393	392.5
15	388	385	389	385.5	392	393
16	389	389	389	388.5, 733	390.5	391.5
17	379.5	388	382, 743, 710	376.5, 728	385	386
18	384.5	384.5	388.5	382.5	390.5	392.5
19	405.5	409	413	405	550.5	407.5
20	378.5	382.5	376.5	372, 731	464.5	378

at the concentration of 5 × 10^{-6} mol L^{-1}

As it has been shown in table 4, the presence of electron attracting substituents or electron donating substituents led to the changes in the absorption maxima (λ_{max}) of the visible spectra.
Moreover, electron attracting groups, such as $-SO_3H$, in the structure of the diazonium salt increased the polarizability and resulted in bathochromic shifts of the visible absorption band. While electron donating groups, such as $-OCH_3$, in the structure of the reagent led to the hypsochromic shifts of visible absorption band. Moreover, the effects of pH in absorption maxima of the synthesized azo dye 20 have been investigated in fig.1.

Herein we report an easy, fast and efficient route to the synthesis of azo dye derivatives from diazonium salts and phenols as starting materials in the presence of diethylamine functionalized PEG as a mild and recyclable catalyst, which gave the products in good to high yields (50-98%). The method is simple and the products are easily separated from reaction mixture without further purifications using time consuming procedures like column chromatography. The point that makes highlight our method is few reports on using catalysts in azo dye synthesis.

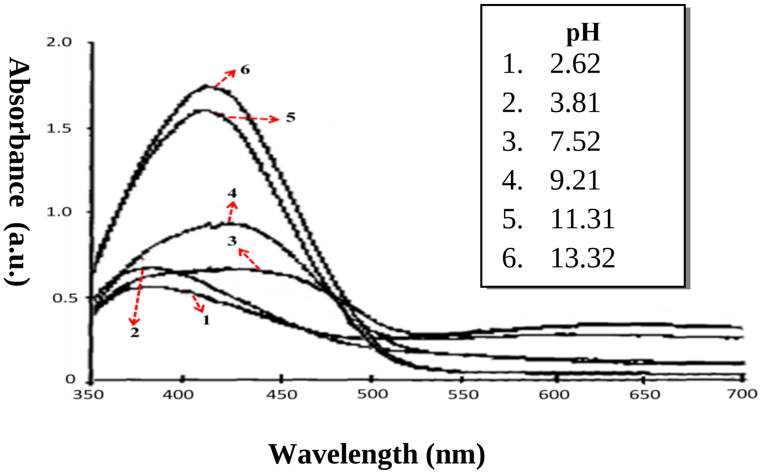


Figure 1. Absorption spectra of dye **20** in different pH values

Supporting Information-

The effects of solvent polarity on absorption of dye derivatives are given in supporting information.

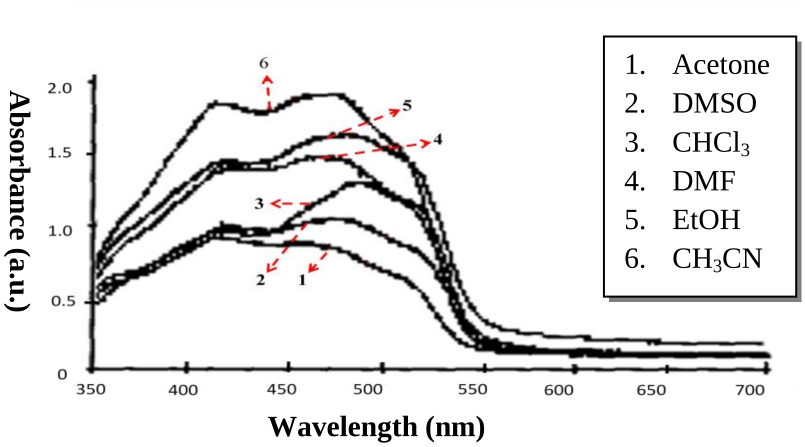


Figure 2. Absorption spectra of dye **3** in different solvents

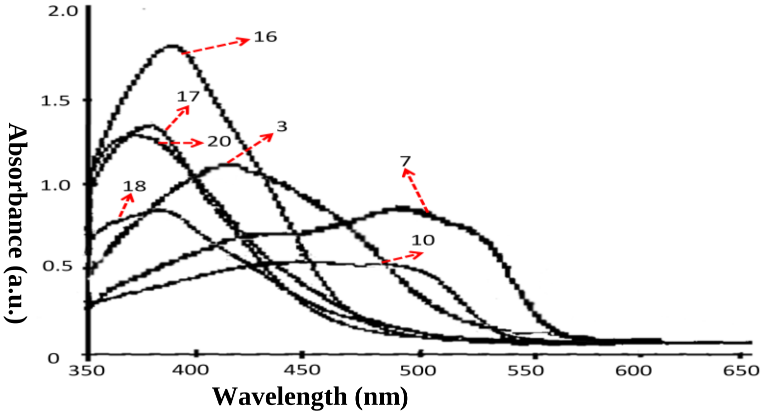


Figure 3. Absorption spectra of different azo dyes in acetonitrile

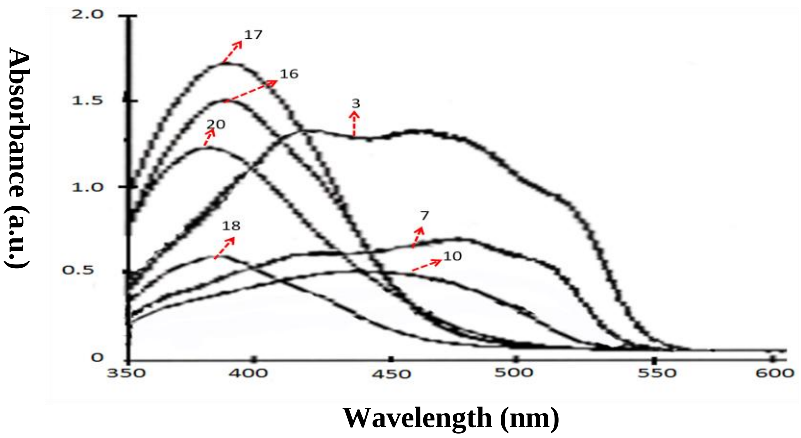


Figure 4. Absorption spectra of different azo dyes in acetone

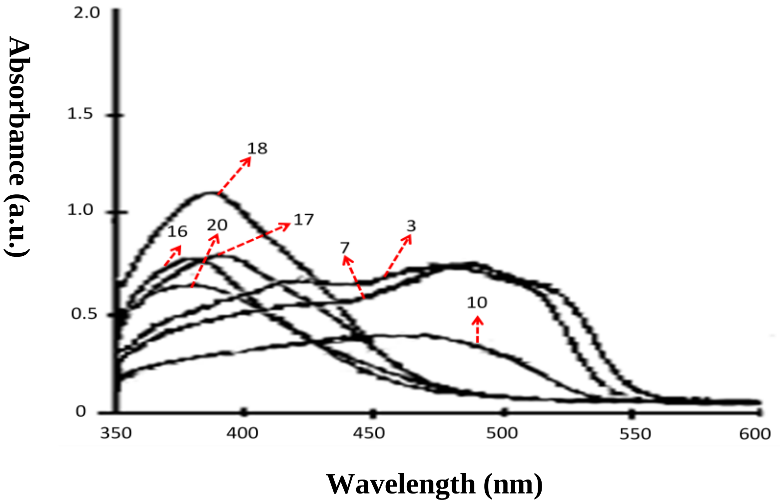


Figure 5. Absorption spectra of different azo dyes in chloroform

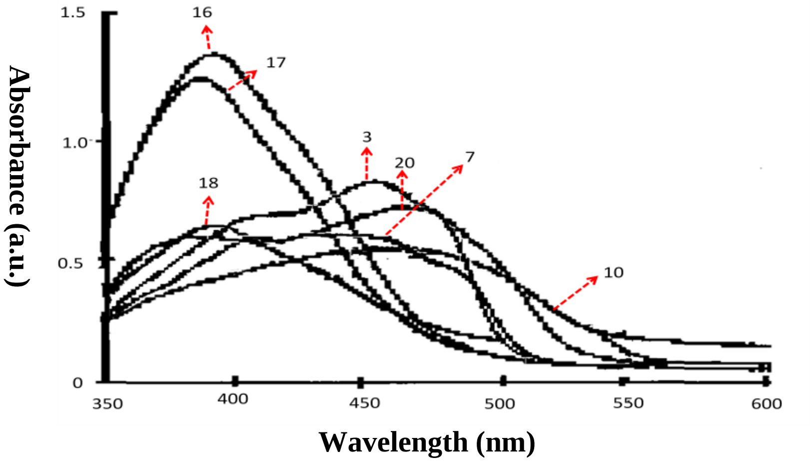


Figure 6. Absorption spectra of different azo dyes in N,N-dimethylformamide

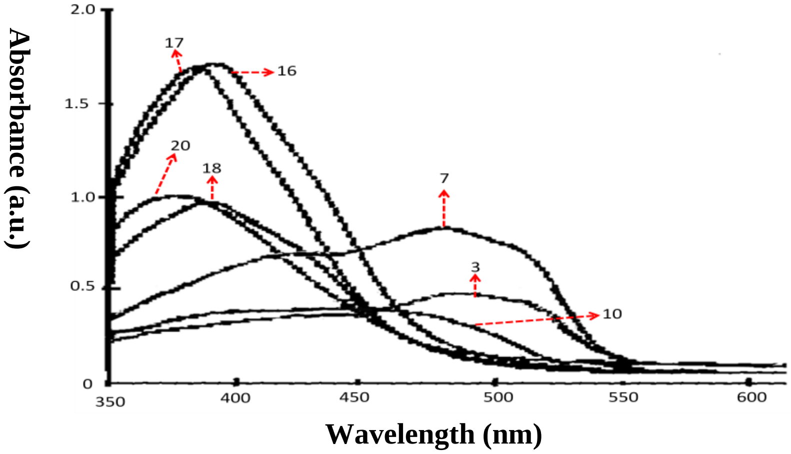


Figure 7. Absorption spectra of different azo dyes in ethanol

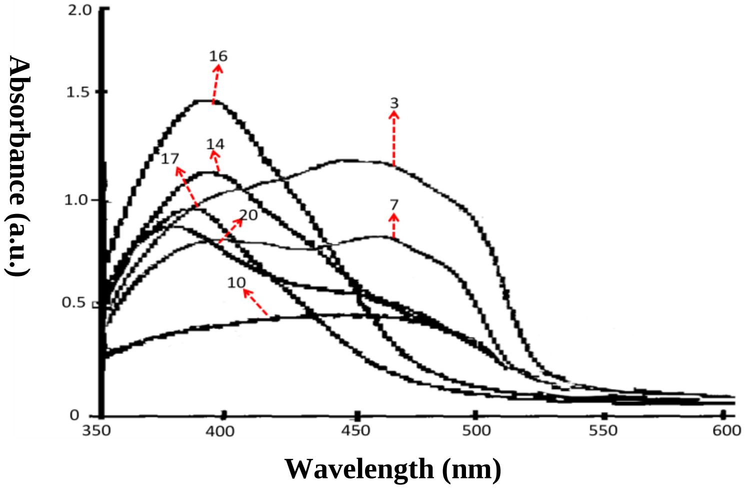


Figure 8. Absorption spectra of different azo dyes in dimethylsulphoxide

APPLICATIONS

The applied diethylamine functionalized polyethylene glycol catalyst is non-toxic, mild and reusable without significant decrease in productivity.

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