The Synthesis of a Novel Azo Dyes and Study of Photocatalytic Degradation

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Abstract. Six novel aromatic azo dyes were synthesized from 4-amino-2-nitrobenzoic acid with phenol, catechol, resorcinol, hydroquinone, salicylic acid and acetylsalicylic acid with very good yield. These azo dyes confirm by FTIR, CHNS and study the photo stability used TiO$_2$ and ZnO. The photocatalytic degradation of novel aromatic azo dyes was investigated using TiO$_2$ and ZnO as a catalyst under 125 watts UV lamp. A series of experiments was performed to reaching to the optimum condition of degradation. The photocatalytic degradation of azo dye follows the first order reaction. In all experiments photocatalytic degradation of the azo dye has been studied using different weight of TiO$_2$ and ZnO suspended in an aqueous solution of azo dye irradiated by irradiated by 125–UV lamp in 100 cm$^3$ a vessel reactor at room temperature with 10 cm$^3$/min air bubble has been passed through the solution. In addition, all result was measured using UV-Visible spectrophotometer.

Keywords: Azo dyes, Photocatalytic Degradation, TiO$_2$ and ZnO catalysts.

1- Introduction:

Azo dyes are important type of colorant compounds because of their wide application in technology and science$^{(1)}$. In fact, there are a roughly fifty percent of dyes which used today of industry are azo dye$^{(2)}$. Usually, these dyes are more stable from natural dye in the wild range of PH; thermally stable and the color don’t fade when exposed to oxygen and light$^{(3)}$. Azo dye compounds contain many application industry like photodynamic therapy, photosensitive and have biological activity due to their use in inflammatory$^{(4, 5)}$ anticancer$^{(6, 7)}$ antibacterial$^{(8-10)}$ and antifungal$^{(11-16)}$. A few years ago, there are many researchers intense on employing the semiconductors as catalyst. When the aqueous solution irradiated with light equal or greater than band gap of titanium dioxide the electrons rises from the valance band on the semiconductor surface to the conduction band to produce photoelectron in the conduction band of semiconductor leaving positive hole in the valance band. The aim of present work was study the photo activity of titanium dioxide. Photoelectrons in the conduction band react with adsorbed oxygen producing the highly reactive superoxide radical ion. The positive hole in the valance band reacts with adsorbed water to producing hydroxyl radical then reacts with pollutants.
2- Experimental Procedures:

Materials:

4-Amino-2-nitrobenzoic acid was supplied from Apollo Scientific. Hydrochloric acid, ethanol, sodium hydroxide, phenol and salicylic acid were supplied from Fisher scientific. Catechol, resorcinol, hydroquinone, sodium nitrate, acetylsalicylic acid were supplied from Sigma Aldrich.

Apparatus:

Fourier Transform Infrared Spectra (FTIR) by Shimadzu IR Affinity-1S. CHNS by Euro – EA-Elemental Analyzer. Melting point by Stuart SMP 10.

I/ Procedure of diazonium salt:

A mixture from hydrochloric acid (10ml), distilled water (10ml) and 4-amino-2-nitrobenzoic acid (0.5 g, $\gamma,\gamma$-d) mmol) was collected into conical flask (250 ml). The mixture was cooling into ice bath to 0°C. Then sodium nitrate (0.1894 g, 2.7451 mmol) in distilled water (3 ml) was add as dropwise to the mixture with kept the temperature at 0°C.

II/ Procedure of azo dyes:

1- Synthesis of 4-[(4-Hydroxyphenyl)azo]-2-nitrobenzoic acid (dye 1)

A solution from phenol (0.258 g, $\gamma,\gamma$-d mmol) and sodium hydroxide (10%, 10 ml) was added as dropwise to diazonium salt under vigorous stirring. After the addition, the mixture was allowed to warm to room temperature. Leave the mixture overnight and the mixture was neutralized with 1 M HCl. Filtered and washing by distill water and recrystallization by ethanol to afforded 4-[(4-Hydroxyphenyl)azo]-2-nitrobenzoic acid (dye 1) (0.5 g, 63.4%) as yellow-brown color; M.p. 259-260°C; FTIR ν (cm$^{-1}$) = 3500-2500 str. br. OH (COOH & OH), 1700 str. br. CO, 1600 str. m (C=C of Ar), 1520str. N=N, 1350 sy str of NO; CHNS: calc. (C=54.36, H=3.14, N=14.63) found (C=54.30, H=3.10, N=14.65).

2- Synthesis of 4-[(3,4-Dihydroxyphenyl)azo]-2-nitrobenzoic acid (dye 2)

A solution from catechol (0.3 g, $\gamma,\gamma$-d mmol) and sodium hydroxide (10%, 10 ml) was added as dropwise to diazonium salt under vigorous stirring. After the addition, the mixture was allowed to warm to room temperature. Leave the mixture overnight and the mixture was neutralized with 1 M HCl. Filtered and washing by distill water and recrystallization by ethanol to afforded 4-[(3,4-Dihydroxyphenyl)azo]-2-nitrobenzoic acid (dye 2) (0.55 g, 66.1%) as yellow-brown color; M.p. 270-273°C; FTIR ν (cm$^{-1}$) = 3500-2500 str. br. OH (COOH & OH), 1720 str. br. CO, 1600 str. m (C=C of Ar), 1500 str. N=N, 1350 sy str of NO; CHNS: calc. (C=51.44, H=2.97, N=13.85) found (C=51.40, H=3.00, N=13.86).

3- Synthesis of 4-[(2,4-Dihydroxyphenyl)azo]-2-nitrobenzoic acid (dye 3)

A solution from resorcinol (0.3 g, $\gamma,\gamma$-d mmol) and sodium hydroxide (10%, 10 ml) was added as dropwise to diazonium salt under vigorous stirring. After the addition, the mixture was allowed to warm to room temperature. Leave the mixture overnight and the mixture was neutralized with 1 M HCl. Filtered and washing by distill water and recrystallization by ethanol to afforded 4-[(2,4-Dihydroxyphenyl)azo]-2-nitrobenzoic acid (dye 3) (0.55 g, 66.1%) as red color; M.p. 220-223°C; FTIR ν (cm$^{-1}$) = 3500-2500 str. br. OH (COOH & OH), 1720 str. br. CO, 1600 str. m (C=C of Ar), 1490 str. N=N, 1320 sy str of NO; CHNS: calc. (C=51.44, H=2.97, N=13.85) found (C=51.42, H=2.98, N=13.84).
4- Synthesis of 4-[2,5-Dihydroxyphenyl]azo-2-nitrobenzoic acid (dye 4)

A solution from hydroquinone (0.3 g, 0.01 mmol) and sodium hydroxide (10%, 10 ml) was added as dropwise to diazonium salt under vigorous stirring. After the addition, the mixture was allowed to warm to room temperature. Leave the mixture overnight and the mixture was neutralized with 1 M HCl. Filtered and washing by distill water and recrystallization by ethanol to afforded 4-[2,5-Dihydroxyphenyl]azo-2-nitrobenzoic acid (dye 4) (0.55 g, 66.1%) as orange color; M.p. 170-173° C; FTIR ν (cm⁻¹) = 3500-2500 str. br. OH (COOH & OH), 1700 str. br. CO, 1590 str. m (C=C of Ar), 1520 str. N=N, 1300 sy str of NO₂; CHNS: calc. (C=51.44, H=2.97, N=13.85) found (C=51.43, H=2.99, N=13.85).

5- Synthesis of 4-[4-Carboxyl-3-hydroxyphenyl]azo-2-nitrobenzoic acid (dye 5)

A solution from salicylic acid (0.379 g, 0.01 mmol) and sodium hydroxide (10%, 10 ml) was added as dropwise to diazonium salt under vigorous stirring. After the addition, the mixture was allowed to warm to room temperature. Leave the mixture overnight and the mixture was neutralized with 1 M HCl. Filtered and washing by distill water and recrystallization by ethanol to afforded 4-[4-Carboxyl-3-hydroxyphenyl]azo-2-nitrobenzoic acid (dye 5) (0.65 g, 7.1%) as red-brown color; M.p. 183-186° C; FTIR ν (cm⁻¹) = 3500-2500 str. br. OH (COOH & OH), 1680 str. br. CO, 1600 str. m (C=C of Ar), 1520 str. N=N, 1330 sy str of NO₂; CHNS: calc. (C=50.72, H=2.72, N=12.69) found (C=50.68, H=2.70, N=12.63).

6- Synthesis of 4-[4-Carboxyl-3-nitrophenyl]azo-2-acetobenzoic acid(dye 6)

A solution from acetylsalicylic acid (0.494 g, 0.01 mmol) and sodium hydroxide (10%, 10 ml) was added as dropwise to diazonium salt under vigorous stirring. After the addition, the mixture was allowed to warm to room temperature. Leave the mixture overnight and the mixture was neutralized with 1 M HCl. Filtered and washing by distill water and recrystallization by ethanol to afforded 4-[4-Carboxyl-3-nitrophenyl]azo-2-acetobenzoic acid (dye 6) (0.92 g, 89.76%) as red-brown color; M.p. 210-213° C; FTIR ν (cm⁻¹) = 3500-2500 str. br. OH (COOH & OH), 1690 str. br. CO, 1600 str. m (C=C of Ar), 1510 str. N=N, 1340 sy str of NO₂; CHNS: calc. (C=51.44, H=2.95, N=11.25) found (C=51.41, H=2.91, N=11.20).

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\text{Scheme 1: synthesis of diazonium salt using 4-amino-2-nitrobenzoic acid and coupling with different aromatic compounds to afforded Azo dyes.}
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III/ Photo reactor and procedure:

The degradation process of a novel Azo Dyes has been tested in glass photo reactor. Photo degradation of a novel Azo Dyes reactor consisted of two parts. The first part of cooling the suspension solution in which the running water was passed through it. The second part called the reaction vessel solution with (100 ml) capacity. The removal of Azo Dyes was conducted under solar light. All experiments were performed by mixing 0.12 g of the catalyst with 50 mg/L of the dye solution. In order to ensure adsorption equilibrium between surface of catalyst and dye, the suspension solution was kept under stirring in the dark for 30 minutes. The solution of dye was bubbled with air (10 ml/min) during the irradiation. A 2 ml of suspension reaction mixture was withdrawn every 10 minutes, and then centrifuged at 4000 rpm to remove any residual sensitized zinc oxide particles. All samples taken were analyzed at a maximum absorption band by UV-Vis spectrophotometer.

![Fig. 1: main compartments of the photo catalytic degradation cell used in removal of a novel Azo Dyes.](image)

3- Results and Discussion

Six azo dyes were synthesized from 3-nitro-4-benzoicdiazonium chloride (diazonium salt) and phenolic components as a coupling compound. First for all, the diazonium salt was prepared under 0 °C and directly reaction it with coupling compound due to the diazonium salt decomposition above 5-10 °C. The diazonium salt beavers as electrophile with an electron rich coupling compounds. The hydroxyl group of phenolic coupling compounds direct the diazonium ion to the para position unless that position is occupied in this case the ion attaches ortho site of hydroxyl group. The azo dyes were characterized by various techniques. The Fourier-transform infrared spectroscopy (FTIR) is one of the efficient techniques used in the identification of functional groups of organic compounds. FTIR was used in the present study to confirm the presence of functional groups as following, the hydroxyl carboxyl and hydroxyl phenolic groups (COOH & OH) shown at 3500-2500 cm\(^{-1}\) as broad stretching vibration, the carbonyl group (C=O) of carboxylic and ester shown at 1680-1720 cm\(^{-1}\) as broad stretching vibration band, the (C=C) group of aromatic shown around 1600 cm\(^{-1}\) as meddle stretching vibration band, the azo group (N=N) shown at 1490-1520 cm\(^{-1}\) as meddle stretching vibration band, the symmetric stretching vibration of nitro group (NO\(_2\)) appear at 1350-1300 cm\(^{-1}\).

The photoactivity of titanium dioxide and zinc oxide as a catalyst has been studied using 0.12gm / 100 ml, the light intensity equal to 8.22 mW/cm\(^2\), and temperature equal to 298 K. The results are plotted in figure 3. The comparison study of the photocatalyst activity of titanium dioxide and ZnO on the degradation of a novel Azo dye was carried out using 0.12g/100ml catalyst with 50ppm of dye for up to 60min. It can be clearly observed that the TiO\(_2\) exhibited a higher photocatalytic activity as compared with zinc oxide that can be attributed to the increase in the effective surface area of the catalyst lead to enhancing its photocatalytic activity for degradation of dye.
Fig. 2: Comparison between zinc oxide and titanium dioxide using dye.

The optimum photo degradation efficiency which is equal to 87.12% for titanium dioxide whiles the zinc oxide was 54.33%. The results of the change in photocatalytic degradation efficiency (P.D.E) with concentration of dye plotted in Figure 4.

Fig. 3: The change of Photocatalytic Degradation Efficiency with irradiation time of different of concentration of dye

Conclusion

Several aromatic azo dyes were synthesized from 4-amino-2-nitrobenzoic acid with very good yield and confirm these azo dyes by FTIR and CHNS. Photocatalytic degradation process of novel Azo dyes was carried out using 0.12 g/cm³ and 50 ppm. It was found that TiO₂ is more effective than ZnO with 87.12 and 54.33 PDE% respectively.

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References:

[1] Pinka Patel & Pankaj S. Patel, Synthesis, characterization, and antimicrobial activity of heterocyclic azo dye derivatives, World Scientific News 95 (2018) 265-272.

[2] J. O. Otutu, SYNTHESIS AND APPLICATION OF AZO DYES DERIVED FROM 2-AMINO-1,3,4-THIADIAZOLE-2-THIOLONPOLYESTERFIBRE, IJRRAS, 15 (2), 2013.

[3] Awale A. G.1, Ghose S. B3. and Utale P.S.2, Synthesis, Spectral Properties and Applications of Some Mordant and Disperse Mono Azo Dyes Derived from 2-amino-1, 3-benzothiazole, Research Journal of Che.

[4] Kennedy DA, Vembu N, Fronczek FR, Devocelle M. Synthesis of mutual azo prodrugs of anti-inflammatory agents and peptides facilitated by α-aminoisobutyric acid. J Org Chem, 2011; 76(23): 9641-9647.

[5] Rohini RM, Kalpana Devi, Simi Devi. Synthesis of novel phenyl azo chalcone derivatives for antitubercular, anti-inflammatory and antioxidant activity. Der Pharma Chemica, 2015; 7(1): 77-83.

[6] Thoraya A Farghaly, Zeinab A Abdallah. Synthesis, azo-hydrazono tautomerism and antitumor screening of N-(3-ethoxycarbonyl-4,5,6,7-tetrahydro-benzo[b]thiien-2-yl)-2-arylhydrazono-3-oxobutanamide derivatives. ARKIVOC, 2008, 17: 295-305.

[7] Sharma R, Rawal RK, Gaba T, Singla N, Malhotra M, Matharoo S, Bhardwaj TR. Design, synthesis and ex vivo evaluation of colon-specific azo based prodrugs of anticaner agents. Bioorg Med Chem Lett, 2013; 23(19): 5332-5338.

[8] Himani N Chopde, Jyotsna S Meshram, Ramakanth Pagadala, Arvind J Munogole. Synthesis, characterization and antibacterial activity of some novel azo-azoimine dyes of 6-bromo-2-naphthol. Int J Chem Tech Res, 2010; 2(3): 1823-1830.

[9] Gopalakrishnan S, Nevaditha NT, Mythili CV. Antibacterial activity of azo compounds synthesized from the natural renewable source, Cardanol. J Chem Pharm Res, 2011; 3(4): 490-497.

[10] Pravin S Jogi, Jyotsana Meshram, Javed Sheikh, Taibi Ben Hadda, Synthesis, biopharmaceutical characterization, and antimicrobial study of novel azo dyes of 7-hydroxy-4-methylcoumarin. Med Chem Res, 2013; 22(9): 4202-4210.

[11] Jarrahpour AA, Motamedifar M, Pakshir K, Hadi N, Zarei M. Synthesis of novel azo Schiff bases and their antibacterial and antifungal activities. Molecules, 2004; 9(10): 815-24.

[12] Jyotirmaya Sahoo, Suman Kumar, Mekap, Paidesetty Sudhir Kumar. Synthesis, spectral characterization of some new 3-heteroaryl azo 4-hydroxy coumarin derivatives and their antimicrobial evaluation. J Taibah University Sci, 2015; 9: 187-195.

[13] Ke Y, Zhi X, Yu X, Ding G, Yang C, Xu H. Combinatorial synthesis of benzimidazole-phenol derivatives as antifungal agents. Comb Chem High Throughput Screen, 2014; 17(1): 89-95.

[14] Mahata D, Mandal SM, Bharti R, Gupta VK, Mandal M, Nag A, Nando GB. Sefassembled cardanol azo derivatives as antifungal agent with chitin-binding ability. Int Biol Macromol, 2014; 69: 5-11.

[15] Raghavendra KR, Ajay Kumar K. Synthesis and their antifungal, antihelmintic and dying properties of some novel azo dyes. IJPCBS, 2013; 3(2): 275-280.

[16] Jarrahpour AA, Motamedifar M, Pakshir K, Hadi N, Zarei M. Synthesis of Novel Azo Schiff Bases and Their Antibacterial and Antifungal Activities. Molecules, 2004; 9: 815-824.

[17] Jarrahpour AA, Motamedifar M, Pakshir K, Hadi N, Zarei M. Synthesis of Novel Azo Schiff Bases and Their Antibacterial and Antifungal Activities. Molecules, 2004; 9: 815-824.

[18] S. Kucharski and R. Janik, New J Chem., 1999, 23, 765.
[19] Hazim, Y. Algubury (2016). Study the ctivity of titanium dioxide nanoparticle using orange G.dye. Malaysian Journal of Science, 35(2): 319-330.

[20] Hazim, Y., Qasim Al-gubury and Y. Mohammed (2016). Prepared coupled ZnO–Co2O3 then study the photo catalytic activities using crystal violet dye. Journal of Chemical and Pharmaceutical Sciences, 9(3):1161-1165.

[21] Hazim Y. Al-Gubury1, Ali F. Hassan, Hajir S. Alteemi1, Mohammed B Alqaragully1, Abdeldjalil Bennecer3, Ayad F. Alkaim1, Photo Catalytic Removal of Paraquat Dichloride Herbicide in Aqueous Solutions by Using TiO2 Nanoparticle, Journal of Global Pharmacy Technology, 2017; 12(9):290-295.

[22] NOUR ABD ALRAZZAK, SAADON ABDULLA AOWDA, and ABBAS JASSIM ATIYAH, Removal Bismarck Brown G dye from Aqueous Solution Over a Composite of Triazole-Polyvinyl Chloride Polymer and Zinc Oxide, ORIENTAL JOURNAL OF CHEMISTRY, 2017, 33(5),1-8.

[23] SUAD T. SAAD, HAZIM Y. AL-GUBURY and NOUR ABD ALRAZZAK, Photocatalytic Degradation of Monoazo Dye in Ethanol using Zinc Oxide in Ultra-Violet Radiation, Asian Journal of Chemistry 2018; 30(10), 2334-2336.

[24] Hazim Y. Al-Gubury, Ali F. Hassan, Hajir S. Alteemi, Mohammed B

[25] Alqaragully, Abdeldjalil Bennecer, Ayad F. Alkaim, Photo Catalytic Removal of Paraquat Dichloride Herbicide in Aqueous Solutions by Using TiO2 Nanoparticle, Journal of Global Pharmacy Technology. 2017; 12(9):290-295.