original article

Decolorization of direct poly azo dye with nanophotocatalytic UV/NiO process

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ABSTRACT

Aims: The aim of the present study is to investigate the efficiency of ultraviolet/nickel oxide (UV/NiO) system as one form of advanced oxidation processes (AOP) for decolorization of red poly azo.

Materials and Methods: This study was conducted as a laboratory scale in a batch mode. Ultraviolet radiation was provided by a low pressure (11 W) UV lamp. Effects of various factors including pH, different irradiation durations, different concentration of nickel oxide, and initial dye concentration were evaluated.

Results: The results of the UV/NiO system's assessment showed that UV light alone cannot remove DR 80 dye. Nickel oxide is an effective catalyst in the decolorization of dye with the nanophotocatalytic process. The decolorization efficiency increases with decreasing pH value and the optimum pH value is 4. Fainally, the highest removal efficiency achieved by UV/NiO process for DR 80 dye with concentrations of 25 mg/l and 50 mg/l was 94.3% and 82.2%, respectively. UV/NiO-based decolorization process follows pseudo-second-order reaction kinetics.

Conclusions: From the findings of the present study, it can be concluded that UV/NiO process is an effective technique for decolorization of poly azo dye, DR 80, in aqueous solutions.

Key words: Decolorization, nanophotocatalytic process, nickel oxide, nanoparticle, poly azo dye.

INTRODUCTION

About one million tonne of different chromogens are synthesized annually worldwide of which approximately 10-15% remain in textile wastewaters after application. Azo dyes represent the largest class of dyes listed in general category of dyes (60-70% of all dyes).[1,2] Azo dyes contain at least one chromogenic factor of nitrojen-nitrojen double bond (−N = N-) called azo group with one or more aromatic groups.[3-5] The presence of very small amounts of color in water is visible, seriously affecting the aesthetic qualityand water clarity, and also the aquatic oxygen concentration and destroying aquatic environment. The researchers have found that during the decomposition process, some chromogens such as azo dyes produce aromatic amines which are potentially carcinogenic and mutagenic.[1,3,6,7] Azo dyes are generally resistant under aerobic conditions, and despite being reduced easily under anaerobic conditions, their products are aromatic amines that are potentially carcinogen and mutagenic.[3,6-9] In recent years, advanced oxidation technologies have been described as efficient methods to obtain high yields of oxidation of different types of organic compounds.[5,8,10] Moreover, during the two past decades, photocatalitic decomposition of toxic chemicals that have

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caused severe environmental pollution has been widely studied.

Catalysts of nano size have the required potential to minimize the toxic pollutants in water.[11] NiO is also used as an effective catalyst for the oxidation of a wide range of organic compounds.[12,13] Poly azo dye (Direct Red 80) is one of the important and widely used dyes in textile industry, which are carcinogenic and mutagenic due to the presence of aromatic foundations and are resistant to the biological decompositions.[3,5,6] In a study conducted by Smith *et al.* (1990) in South Carolina, they used an advanced photochemical oxidation process (UV/H_2O_2) and could remove 80 percent of organic color of paper-mill's sewage by H_2O_2 80 mg/L.[14] In a study done in 2008 on mono-azo RO 16 with the primary concentration of 50 mg/L and its removal by UV/TiO_2 process, with the inital pH of the dye as 6.5, and the concentration of TiO_2 at 0.4g/L, less than 90% removal was achieved after 120 minutes of exposure.[15] During researches done in 2005 on the removal of DR 80 with $UV/TiO_2/H_2O_2$ system and the initial concentration of 50 mg/L, full-color degradation was obtained in 60 minutes.[16] The purpose of this study was to evaluate the efficiency of UV/NiO system as a form of advanced oxidation process to remove the color of red poly-azo.

MATERIALS AND METHODS

The characteristic of nio and dr 80

The dye used in this study is Direct Red 80 with 25% purity which is prepared from Sigma Company's representative in Iran. This dye is a poly-azo dye and belongs to direct dyes' group having many usages and applications in the textile industry. In Table 1, the complete characteristics of the dye have been described, and in Figure 1 the structural formula of Direct Red 80 has been presented. The nanocatalyst used in this study was nickel oxide and its characteristics have been presented in Table 2.

Photocatalytic reactor set -up

The present study was designed as an experimental-interventional laboratory scale in a batch mode. For this purpose, a cylindrical plexiglass reactor with an effective volume of 4.5 liters was used. UV radiation used in this study was supplied by 11W low-pressure UV lamp with wave length of 253.7 nm and intensity of 22000 (μws/cm^2) and made by PHilips Company. The lamp was placed centrally within a transparent quartz tube of 3 cm diameters along the entire length of the reactor.

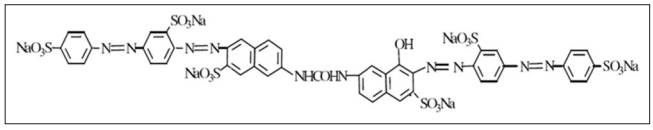

Figure 1: Structural formula of red sulophenil, 3BL

Chemicals and instrumentation

pH meter (WTW), centrifuge 3-30K (Sigma) and DR 5000 spectrophotometer devices were also used. Other chemicals were purchased from Germany's Merck company for carrying out this study for the dye concentrations.

Experiments

Initial dye concentration, the effect of pH, different concentrations of nickel oxide and different irradiation times were investigated. Solutions of sulfuric acid and sodium hydroxide 0.1N and 1N were used for pH adjustment. The amount of decolorizing Direct Red 80 was assessed by UV-Vis spectrophotometer (DR 5000), with decreasing absorbance at maximum wavelength of decolorization. Separation of the NiO particles presented in the sample was done with centrifuge of the Germany Sigma companyat 10000 revolutions per minute (rpm) for about 20 minutes.

RESULTS

1. According to Figure 2 decolorization efficiency for NiO with concentrations of 0.2, 0.4, 0.5 and 1 g/L was 40.7%,

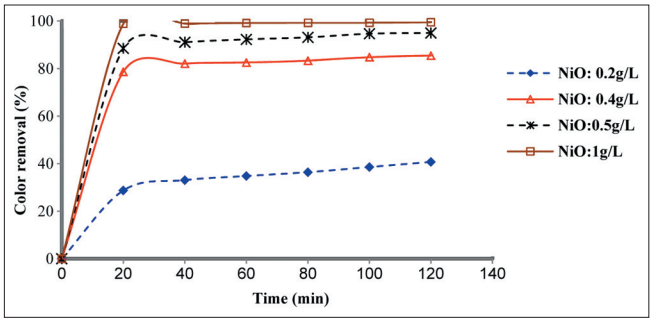

Figure 2: The effect of NiO alone on the percentage of DR 80 decolorization at dye's initial pH (C_0: 50 mg/L, pH: 5.5 ± 0.5)

Table 1: Features of Azo dye used in this study

Scientific name	Trade name	Chemical formula	λ_{max} (nm)	Molecular weight	Number of azo bonds
C.I. Direct Red 80	Red sulophenil	$C_{45}H_{26}N_{10}Na_6O_{21}S_6$	525	1373.07 g/mol	4

Table 2: Characteristics of the nanoparticle used in this study

Scientific name	Chemical formula	Molecular weight	Purity	Size	Color
Nickel oxide	NiO	74.69 g/mol	99.8%	6.3 nm	green

85.5%, 95%, 99.5% respectively.

2. According to Figure 3, the results of the experiment show that within 3 hours of UV light radiation alone, 5.3% of the dye concentration has decreased.
3. According to Figure 4, the results of experiments show that with the increase of nickel oxide loading from 0.05 to 0.2 g/L, in UV/NiO system, decolorization efficiency has been increased – to – respectively.
4. The photocatalytic degradation of DR 80, was studied at the pH rang of acidic, netural and basic. The results presented in Figure 5, show that at pH values of 5, 7 and 10, decolorization efficiency of -, - and - wer obtained respectively.
5. As Figure 6 shows, removal efficiency at concentrations of 25, 50 and 100 mg/L, is 94.29%, 82.22% and 62.64% respectively.
6. As Figures 7 and 8 show, DR 80 decolorizatin

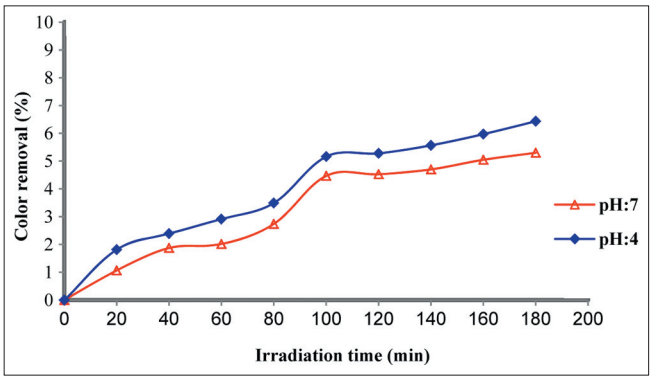

Figure 3: The effect of UV alone on the percentage of DR 80 decolorization at dye's initial concentration, 50 mg/L

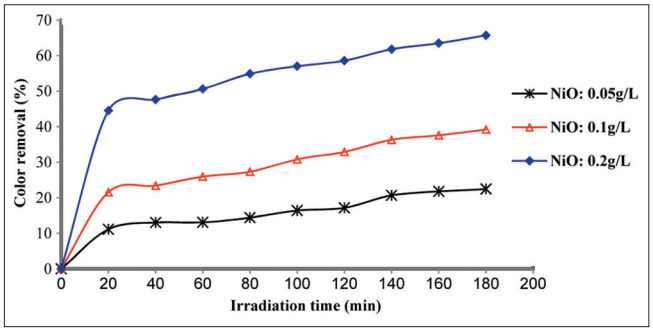

Figure 4: The effect of differenet NiO concentrations on the percentage of DR 80 decolorization in UV/NiO process (C_0:50 mg/L, pH:7, UV:11W)

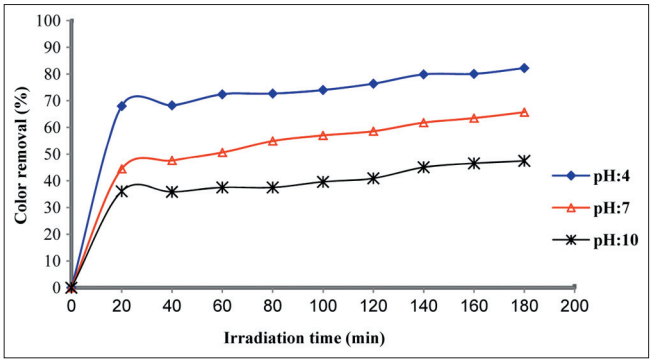

Figure 5: The effect of differenet pH on the percentage of DR 80 decolorization in UV/NiO process (C_0: 50 mg/L, NiO_{opt}: 0.2g/L, UV:11W)

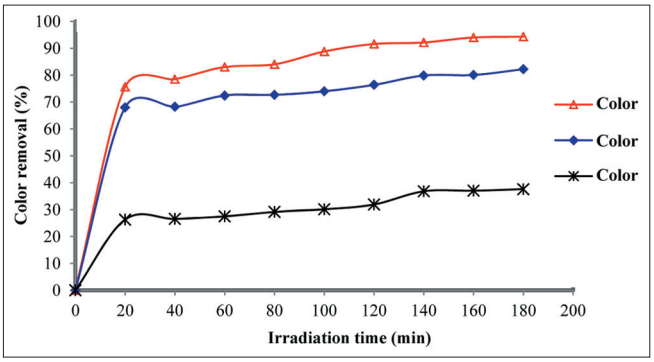

Figure 6: Decolorization percent in optimum condition and different initial dye concentrations (DR 80) in UV/NiO process (NiO_{opt}: 0.2g/L, pH_{opt}:4, UV:11W)

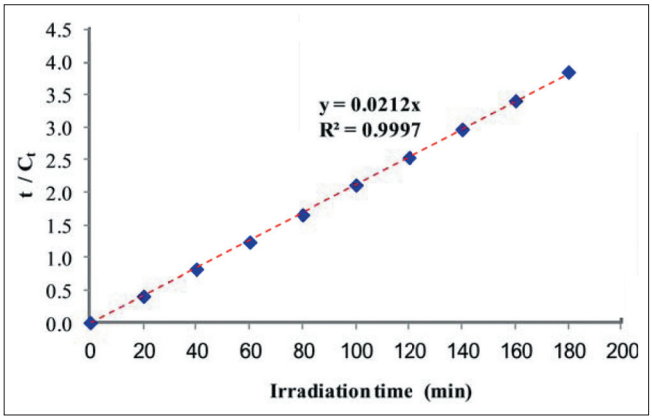

Figure 7: determination of reaction order in UV system alone under optimal conditions (C_0: 50 mg/L, pH_{opt}:4, UV:11W)

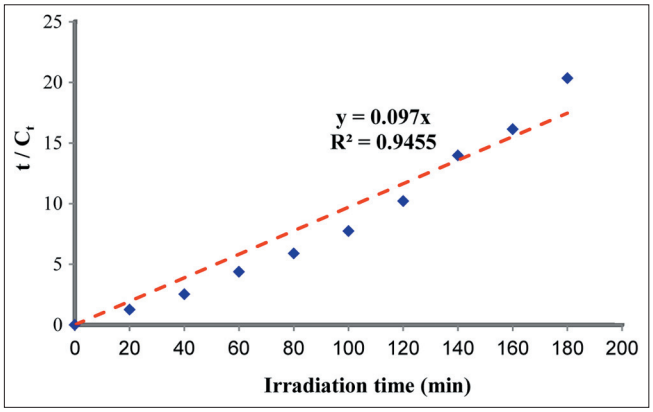

Figure 8: determination of reaction order in UV/NiO system under optimal conditions (C_0: 50 mg/L, NiO_{opt}: 0.2g/L, pH_{opt}:4, UV:11W)

equations with UV and UV/NiO process follow pseudo-second-order reaction kinetics and reaction rate constants for UV and UV/NiO are 0.021 and 0.097, respectively.

DISCUSSION

Evaluation of the effect of nio content alone in the decolorization process

To discover the effective role of NiO as a catalyst in decolorization, these experiments were done (performed) with initial concentration of dye (50 mg/L) and at about 2 hours with different concentrations of NiO. According to Figure 2 decolorization efficiency for NiO with concentrations of 0.2, 0.4, 0.5 and 1 g/L was 40.7%, 85.5%, 95%, 99.5%, respectively. Thus the results indicate that NiO at concentrations of 0.4 to 1 g/L, is very effective for DR 80 decolorization. While its absorption decreases at concentration of 0.2 g/L and less, after 40 minutes only 33% of dye is adsorbed by NiO. To confirm the results, Zhi Song and *et al.* introduced NiO as an efficient and recyclable adsorbents for different dyes.[17]

Examining the effect of uv ray alone on decolorization process

According to Figure 3, the results of the experiment show that within 3 hours of UV light radiation alone, at neutral and optimum pH of UV/NiO systems, (obtained in later stages), only 5.3% and 6.4% of the dye concentration has decreased, respectively.

The effect of the nio catalyst content on decolorization process

In order to measure the effect of initial concentrations of nickel oxide in UV/NiO system, different concentrations of nickel oxide (0.2 – 0.1 – 0.05) in terms of g/L, at a fixed dye concentration and neutral pH range at different times of radiation, were used. According to Figure 4, the results of experiments show that the amount of DR 80 catalysis has increased from 0.05 to 0.2 g/L with the increase of NiO loading. That is, the amount of decolorization increases with the increase of catalyst's active surface.[15] Therefore, the value of 0.2 g/L NiO was selected as optimum concentration of NiO. Decolorization efficiency in UV/NiO, NiO and UV11W systems, only after 40 minutes, is 68%, 33% and 2.4% respectively, which indicates the effective catalytic role of NiO in poly Azo decolorization with UV/NiO process. Under these conditions, the maximum adsorption of photons is completed by the catalyst [18] and oxidation agent, and bonded hydroxyl radicals or free holes are produced which oxide dye molecules at interface of solid-liquid.[19]

pH Effect in decolorization process

Wastewater of textile industries usually includes a wide range of pH. Generally, pH has an important role in the characteristics of textile wastewater and production of hydroxyl radicals. In other words, pH of the environment is one of the important parameters in photocatalytic reactions occuring at the particles surface and affecting the speed of chemical reactions. The environment's pH affects the properties of the surface charge of photocatalytic particles.[16] Therefore, the photocatalytic degradation of DR 80, was studied at the pH rang of acidic, netural and basic. The pH of dye solutions were adjusted by NaOH and H_2SO_4 before irradiation. The results presented in Figure 5, indicate that oxidation and percentage of decolorization are affected by pH, and the highest decolorization efficincy for UV/NiO systems was 82.22% which obtained at the optimum pH of about 4. The results show that the efficiency of Poly Azo (DR 80) decolorization increases with the decrease of pH. At low pH, direct reduction by electrons in the conduction band may play an important role in dye degradation leading to the creation of reviver gap in azo bonds.[15] So far, no studies are found in which the UV/NiO system is used for removing organic matter. However, Mahvi and *et al.* reported an acidic pH as optimum for RO 16 decolorization with UV/TiO_2 system.[15]

The effect of initial dye concentration in decolorization process

For this purpose, different dye concentrations of about 20-50-100 mg/L were studied. To investigate this part of the research, the best effect point of optimal pH and concentration of NiO obtained from the previous steps along with different dye concentrations was used. As Figure 6 shows, decolorization rate decreases with the increase of initial dye concentration from 25 mg/L to 100 mg/L, so that the removal efficiency at concentrations of 25, 50 and 100 mg/L, is 94.29%, 82.22% and 62.64% respectively. Generally, the point is that the level of dye degredation increases with the increase of dye concentration to a specific level, or the amount of dye degredation decreases with more increase in dye concentration. The rate of degredation is related to the possibility of formation of OH° radicals on the surface of the catalyst and the possibility of OH° radicals reaction is related to dye molecules. Thus, the increase of the initial dye concentration increases the possibility of reaction between dye molecules and oxidants which increases the amount of decolorization. Dye degradation efficiency decreases with further increase in dye concentration.[20] The possible reason is that at high dye concentrations, catalyst active sites are covered with dye ions and thus the production OH° radicals on the catalyst surface decreases. Another reason for such results is the UV-Screening effect of dye.[20] The number of produced hydroxyl radicals remains fixed with the increase of dye concentration and the stability of catalyst concentration and UV radiation, thus decreasing the decolorization rate. Moreover, intermediate products formed due to the pigment degradation increase with the increase of the initial dye concentration, thus there is the possibility of competition between produced intermediate products and mother dye molecules for degradation.[21-23]

Decolorization procedure and reaction kinetics

In order to examine the amount of DR 80 decolorization in different photo catalytic processes and to compare them with each other, the reaction kinetics was studied, and the results were interpreted based on the constants of reaction rate and extracted decolorization efficiencies of them. As shown in figures 7 and 8, the linearity of t/C_t changes in terms of time and high linear correlation of curves, and we can conclude that DR 80 decolorization equations with UV and UV/NiO process follow pseudo-second-order reaction kinetics; and, reaction rate constants for UV_{11W} and UV/NiO are 0.021 and 0.097, respectively. Other researchers have also achieved the same results.[17,24]

CONCLUSIONS

This study was done to assess the usage of photo catalytic system in DR 80 degradation and decolorization. The results show that UV/NiO process is an effective technique for decolorization of poly azo dye DR 80 from aqueous solutions, and the amount of decolorization is affected by NiO amount, pH of the solution, initial dye concentration and irradiation durations; however, efficiency of UV alone in not sufficient and does not yield the desired results. The percent of decolorization achieved by using the nano photo catalytic process is a function of the catalyst concentration in solution, and the decolorization efficiency increases with the increase in the amount of the catalyst loading. The results show the effective catalytic role of NiO in decolorization. The optimal NiO concentration for decreasing dye in UV/NiO system is 0.2 g/L. The amount of DR 80 degradation in all of studied processes depends on the ph of the environment. The results show that decolorization efficiency increases with a decreasing pH value, the optimum pH value being at 4.

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