

Decolorization and aromatic ring degradation kinetics of Direct Red 80 by UV oxidation in the presence of hydrogen peroxide utilizing TiO_2 as a photocatalyst

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Abstract

Textile industry consumes considerable amounts of water during various processes such as dyeing. The existence of color and aromatic rings in the form of aromatic amines in textile wastewater is a very important problem. In this paper, photocatalytic decolorization and aromatic ring degradation of Direct Red 80 in a fixed bed photocatalytic reactor, utilizing a very simple analytical method, direct UV–vis spectrophotometric detection, has been investigated. Photocatalytic decolorization and aromatic ring degradation processes performed using a 5 l solution containing Direct Red 80. The initial concentration of Direct Red 80 was 50 mg l^{-1} . The radiation source was two 15 W UV-C lamps. A batch mode immersion photocatalytic reactor was utilized. The effect of variables such as pH and H_2O_2 concentration were studied. Bench scale simulated colored textile wastewater was completely decolorized in a relatively short time after UV irradiation with a low concentration of hydrogen peroxide. The lack of any absorbance in the UV–vis spectra was indicative of the complete aromatic ring degradation. Kinetics analysis indicates that the dye photocatalytic decolorization rates can usually be approximated pseudo-first-order model. UV/ TiO_2 / H_2O_2 process proved capable of the complete degradation of the Direct Red 80.

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1. Introduction

Textile dyes are of environmental interest, because 700 000 t of them are produced in the world annually while, about 50% among them are azo dyes [1]. About 15% of the total world production of dyes is lost during textile dyeing which is released in textile effluents [1–3].

Azo dyes, which contain one or more azo bonds ($-\text{N}=\text{N}-$), are among the most widely used synthetic dyes and usually become major pollutants in textile wastewaters [4]. It has been documented that some azo dyes are toxic and even mutagenic to living organisms in aquatic environment [5,6]. The release of these colored wastewaters in the ecosystem is a dramatic source of aesthetic pollution, eutrophication and perturbation

of aquatic life [3]. In addition, the stability of their molecular structures renders them resistant to biological or even chemical degradation [7,8].

Over the last two decades semiconductor photocatalysis has been shown to be potentially advantageous and useful for the treatment of wastewater pollutants [9,10]. This process has several advantages over competing processes such as: (1) complete mineralization, (2) no waste-solids disposal problem, and (3) only mild temperature and pressure conditions are necessary [11,12].

Several studies related to application of photocatalytic degradation of various organic compounds exist nowadays [13–27].

Many catalysts like TiO_2 , ZnS , ZnO , ZrO_2 , WO_3 , SrO_2 and CdS have been utilized for the photocatalytic degradation of a wide variety of environmental contaminants [28]. Among these photocatalysts, TiO_2 as a durable photocatalyst has been applied to a variety of environmental cases [10]. The advantages of application of TiO_2 as a photocatalyst are: (1) TiO_2 is environmentally

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acceptable by being biologically and chemically fairly inert, (2) TiO_2 is inexpensive and reusable, and (3) degradation of major classes of organic pollutants can be achieved at ambient conditions [4].

Research efforts for understanding the fundamental processes and to enhance the photocatalytic efficiency of TiO_2 have been performed by chemists, physicists and chemical engineers [29].

Semiconductor can act as sensitizer for light-reduced redox processes due to their electronic structure, which is characterized by filled valence band and an empty conduction band. When a photon with energy of $h\nu$ matches or exceeds the band gap energy, E_g , of the semiconductor, an electron, e_{cb}^- , is promoted from the valence band, VB, into the conduction band, CB, leaving a hole, h_{vb}^+ behind. Excited state conduction band electrons and valence band holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface [10]. The h_{vb}^+ is a strong oxidant, which can either oxidize a compound directly, or react with electron donors like water or hydroxide ions to form hydroxyl radicals, which react with pollutants such as dyes. One efficient electron acceptor is molecular oxygen (O_2), which forms a superoxide anion radical ($\text{O}_2^{\bullet-}$) after capturing the electron. In addition, photocatalytic degradation process can be accelerated by hydrogen peroxide (H_2O_2). During the reaction, H_2O_2 can produce hydroxyl radical by reacting with $\text{O}_2^{\bullet-}$ or by direct photolysis. Besides, it can act as a conduction band electron acceptor like O_2 and form hydroxyl radicals subsequently [4]. Hydroxyl radicals react with organic pollutants leading to the total mineralization of most of them [2].

Photocatalytic degradation is promoted by a photocatalyst, which is dispersed in solution or immobilized on a surface. However, the use of a suspension solution requires the separation and recycling of the photocatalyst particles. The above problem can be avoided in a fixed bed photocatalytic reactor. To our knowledge there is not any paper dealing with the complete disappearance of UV–vis absorption in photocatalytic decolorization and aromatic ring degradation of Direct Red 80 in a fixed bed photocatalytic reactor using a very simple analytical method, such as direct UV–vis spectrophotometric detection. In the present study, we investigated the photocatalytic decolorization and aromatic ring degradation of a polyazo dye, Direct Red 80, using direct UV–vis spectrophotometric detection. The dye is water-soluble and can be used for dyeing silk, wool, cellulose and cotton. The effects of various factors on the photocatalytic degradation of the dye were studied and the results were monitored.

2. Experimental

2.1. Reagents

Direct Red 80 ($98\% \leq$ purity) was obtained from Ciba Ltd. and was used without further purification. The chemical structure of this dye is shown in Fig. 1. Analytical grade H_2O_2 (30% (w/w), Merck) was used. Titanium dioxide (Degussa P25) was utilized as a photocatalyst. Its main physical data are as follows: average primary particle size around 30 nm, purity above 97% and with 80:20 anatase to rutile.

2.2. Fixed bed photocatalytic reactor

Experiments were carried out in a batch mode immersion rectangular fixed bed photocatalytic reactor made of Pyrex glass, which is shown in Fig. 2. The radiation source was two UV-C lamps (15 W, Philips) which were protected by quartz tubes.

The photocatalyst (TiO_2) powder was immobilized by a UV resistant polymer in the inner surface of the reactor. Inner surfaces of reactor walls were cleaned with acetone and distilled water to remove any organic or inorganic material attached to or adsorbed on the surface and was dried in the air. A pre-measured mass of TiO_2 pellets were attached on the inner surfaces of reactor walls using a thin layer of a UV resistant polymer. Immediately after preparation, the inner surface reactor wall – polymer – TiO_2 system was placed in the room temperature (25°C) for at least 60 h for complete drying of the polymer.

A water pump and air pump were utilized for the transferring and aeration of dye solutions respectively. The UV irradiation onto the photocatalyst surface causes the photocatalytic oxidation of a dye with O_2 in the absence of H_2O_2 . The existence of dissolved O_2 is an important factor which increases the photocatalytic degradation of a dye. Hence, we used an aquarium air pump for the aeration of the dye solutions.

2.3. Methods and analyses

The photocatalytic experiments were performed using a 5 l solution containing Direct Red 80. The initial concentration of Direct Red 80 was 50 mg l^{-1} . Samples were withdrawn from a sample point at certain time intervals and analyzed for decolorization and degradation of Direct Red 80 dye. Decolorization of dye solutions and aromatic ring destruction were checked and controlled by measuring the absorbances of dye solutions at different intervals using a UV–vis CECIL2021 Spectrophotometer. The maximum absorbances of the dye were at 225, 290 and 543 nm. Absorbance measurements of the samples at

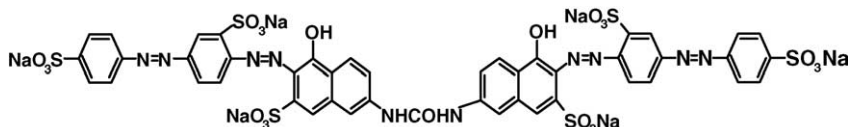


Fig. 1. Chemical structure of Direct Red 80.

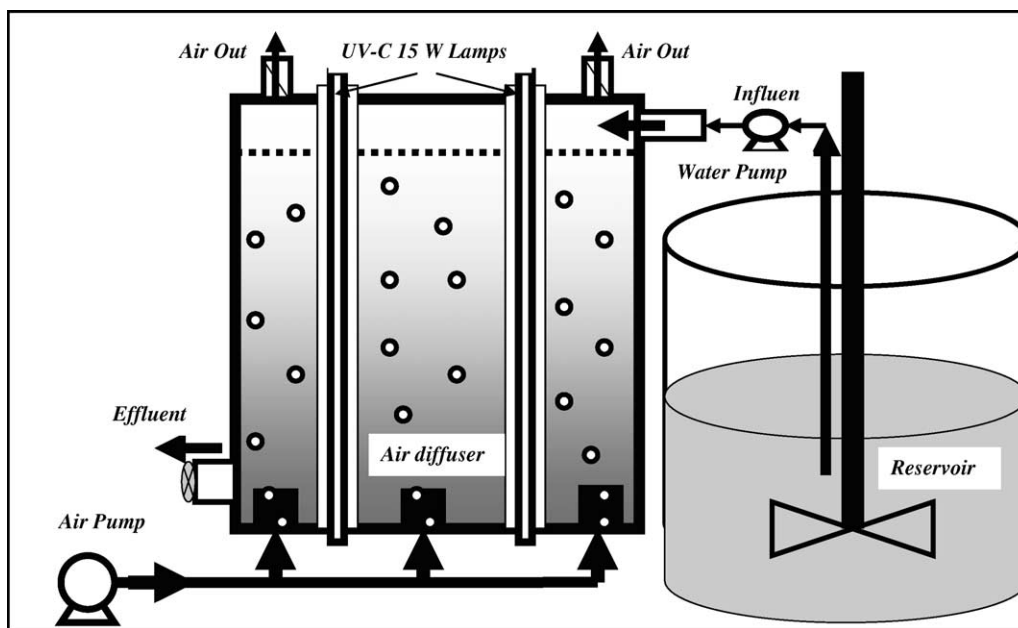


Fig. 2. Scheme of the fixed bed photocatalytic reactor for photocatalytic dye degradation.

254 nm were taken as an indication of the aromatic compound content [30]. A pH-meter (Hach) was utilized for the adjustment and investigation of pH variation during the process. The pH of the dye solutions was adjusted prior to irradiation by NaOH or H_2SO_4 .

3. Results and discussion

3.1. Decolorization and aromatic ring destruction

Direct Red 80 is a tetrakis azo dye, which has a strong absorbance in the UV–vis region. The chromophore part containing azo linkage has an absorption in the visible region while benzene and naphthalene rings in the UV region; naphthalene ring absorption wavelength is higher than that of benzene ring [31,32]. The absorbance peaks at 225, 290 and 543 nm are, respectively, attributed to benzene, naphthalene rings [31,32] and azo linkage. Moreover, changes in the absorption spectra of Direct Red 80 (50 mg l^{-1}) with H_2O_2 (300 mg l^{-1})/ TiO_2 /UV at different time intervals of irradiation and pH 6 are shown in Fig. 3.

With a time elapse of 15 min, the spectral height at 543 nm decreased rapidly. This wavelength indicates the $-N=N-$ bond of the dye which is the most active site for oxidation attack [33,34]. The absorbance at 290 and 225 nm decreased from 0.78 to 0 and from 0.5 to 0, respectively, after 35 min of experiment. The destruction of the aromatic rings becomes evident in Fig. 4. All initial absorbance disappeared after 40 min.

3.2. H_2O_2 effect

Hydrogen peroxide has different effects on dye decomposition depending on its concentration and nature of reductants [4,32]. At optimal concentration, H_2O_2 increases the formation

rate of hydroxyl radicals in two ways. Firstly, the reduction of H_2O_2 at the conduction band would produce hydroxyl radicals. Secondly, the self-decomposition by illumination would also produce hydroxyl radicals [32]. As seen in Fig. 5, the decolorization rate increased when H_2O_2 concentration changed from 0 to 300 mg l^{-1} . No changes were observed at decolorization time when the concentration further increased to 1200 mg l^{-1} . A concentration of 300 mg l^{-1} appears to be optimal. However, when present at high concentration, H_2O_2 can also become a scavenger of valence bond holes and hydroxyl radicals [4,20,35].

3.3. pH effect

The wastewater from textile industries usually has a wide range of pH values. Generally, pH plays an important role both in the characteristics of textile wastewater and generation of

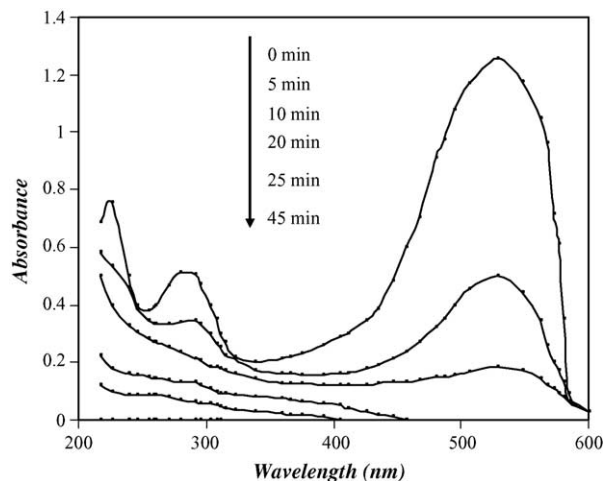


Fig. 3. Changes in the absorption spectra of Direct Red 80 (50 mg l^{-1}) with H_2O_2 (300 mg l^{-1})/ TiO_2 /UV at different time intervals of irradiation.

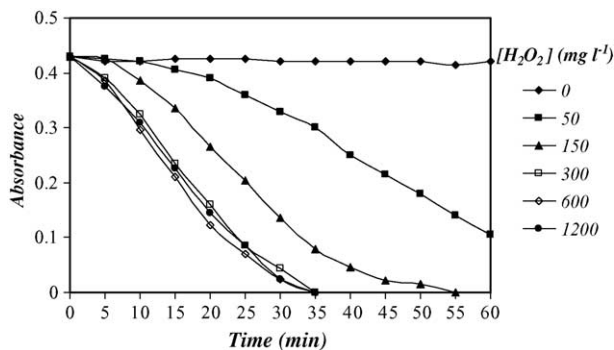


Fig. 4. Photocatalytic aromatic ring destruction of Direct Red 80 at different concentrations of hydrogen peroxide at 254 nm and pH 6.

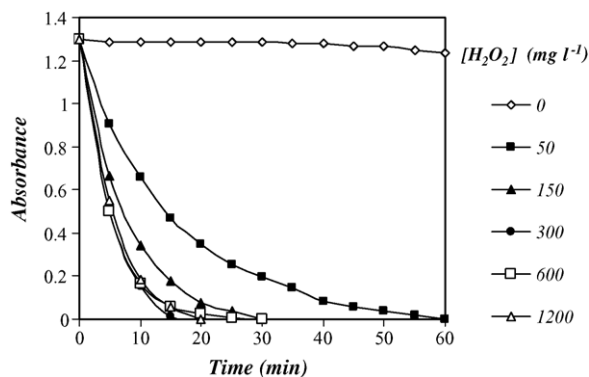


Fig. 5. Photocatalytic disappearance of Direct Red 80 with different concentrations of hydrogen peroxide at 543 nm and pH 6.

hydroxyl radicals [36]. Hence, the photocatalytic degradation of the dye was studied in a pH range between 2 and 10. The pH of dye solutions was adjusted by NaOH or H₂SO₄ before irradiation. Fig. 6 shows the effect of pH on the decolorization rate of Direct Red 80. It can be seen that percentage decolorization decreases with decreasing initial pH of the dye solutions. The possible explanation for this behavior is that as the initial pH of dye solution decreases, TiO₂ presents a positive charge in surface which may highly promote the adsorption of dye since it contains negative sulfonate groups. This phenomenon hinders the photon absorption by the photocatalyst. Consequently, the decolorization rate of dye was decreased. Different optimal pHs (6–7) have also been observed for other sulfonated azo dyes [37,38]. However, the interpretation of pH effects on the efficiency of the photocatalytic degradation process is a very difficult task,

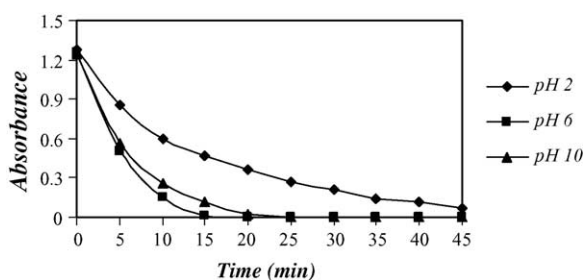


Fig. 6. Effect of pH on the photocatalytic decolorization of Direct Red 80 (543 nm and H₂O₂ (300 mg l⁻¹)).

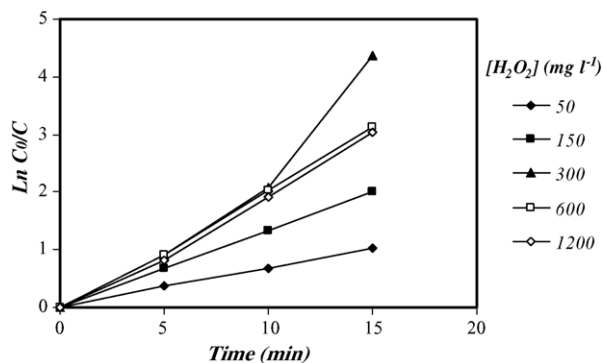


Fig. 7. The pseudo-first-order decay rate constants of Direct Red 80 decolorization at different H₂O₂ concentrations.

Table 1

Parameters for the effect of different H₂O₂ concentrations on the decolorization rate of Direct Red 80 after 15 min of irradiation

H ₂ O ₂ (mg l ⁻¹)	<i>k</i> (min ⁻¹)	<i>R</i> ²
50	0.0676	0.9993
150	0.1337	1.0000
300	0.2976	0.9435
600	0.2096	0.9983
1200	0.2046	0.9952

because the different reaction mechanisms such as hydroxyl radical attack, direct oxidation by positive hole and direct reduction by the electron in the conducting band can contribute to dye degradation. The importance of each one depends on the substrate nature and pH [37,28]. In this study pH 6 was found to be the optimal pH under the given experimental conditions. All dye solutions become slightly acidic after photocatalytic degradation process as it has also been observed elsewhere [30].

3.4. Kinetics of dye disappearance

The kinetics of disappearance of Direct Red 80 is represented in Fig. 7. First-order kinetic model was utilized as follows:

$$\ln C_0/C = kt \quad (1)$$

where *C*₀, *C*, *t* and *k* are the initial dye concentration, dye concentration in *t*, decolorization time (min) and the global reaction apparent rate constant (min⁻¹), respectively.

The linear fit between the ln *C*₀/*C* and irradiation time under pH 6 and different concentrations of H₂O₂ can be approximated as pseudo-first-order kinetics. The parameters *k* (rate constant, min⁻¹) and *R*² (correlation coefficient) of decolorization process are shown in Table 1. The order of rate constants was pH 6

Table 2

Parameters for the effect of different pH values on the decolorization rate of Direct Red 80 after 15 min of irradiation (H₂O₂ 300 mg l⁻¹)

pH	<i>k</i> (min ⁻¹)	<i>R</i> ²
2	0.066	0.9912
6	0.2976	0.9435
10	0.1587	0.9998

(0.2976 min^{-1}) > pH 10 (0.1587 min^{-1}) > pH 2 (0.066 min^{-1}) (Table 2).

It is apparent that the photocatalytic degradation is more favored in neutral solutions.

4. Conclusions

In this research, a very simple analytical method, direct UV–vis spectrophotometric detection, has been investigated for the examination of decolorization and aromatic ring destruction of Direct Red 80. Direct Red 80 could be successfully decolorized and degraded by UV/TiO₂/H₂O₂ process in a novel fixed bed photocatalytic reactor. The effect of different variables such as H₂O₂ concentration and pH was studied. The decolorization rate goes through a maximum when the concentration of hydrogen peroxide increases from 0 to 300 mg l⁻¹. The photocatalytic decolorization kinetics follows a pseudo-first-order model. In this study pH 6 was found to be the optimal pH under the given experimental conditions. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain a high degradation rate, which is essential for any practical application of UV/TiO₂/H₂O₂ process. Thin-film coating of photocatalyst may resolve the problem of decolorization. Hence, this technique may be a viable one for the treatment of large volumes of textile wastewater. The experimental results confirmed that photocatalysis appears as a subdivision of heterogeneous catalysis, which is able to convert Direct Red 80 to minerals such as CO₂, H₂O and etc. without using high pressure of oxygen or heating. This manuscript has discussed the photocatalytic decolorization and aromatic ring destruction experiments of only one dye (Direct Red 80) but this method could be use for the degradation of other dyes such as Direct Red 23, Direct Red 31, Direct Red 81 and Direct Orange 108 that have very similar chemical structures with Direct Red 80 (Figs. 8–11, respectively).

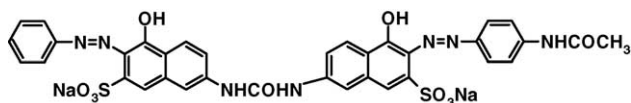


Fig. 8. Chemical structure of Direct Red 23.

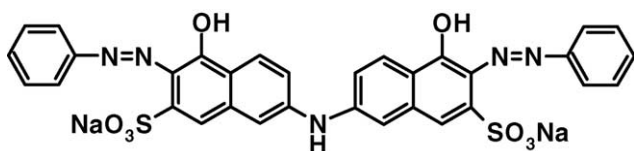


Fig. 9. Chemical structure of Direct Red 31.

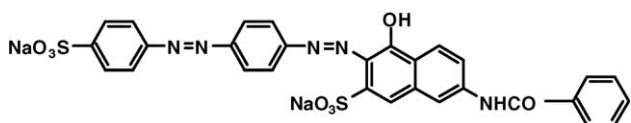


Fig. 10. Chemical structure of Direct Red 81.

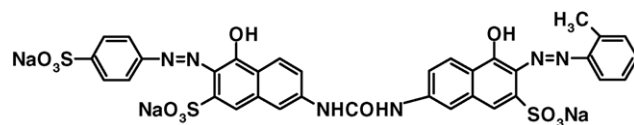


Fig. 11. Chemical structure of Direct Orange 108.

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