

PHOTODEGRADATION STUDIES ON C.I. REACTIVE RED 158

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Abstract:

Dye-containing wastewater generated from textile industries is a major source of environmental pollution. Azo dyes, which are the largest group of coloring agents, are widely used in industry.

Advanced Oxidative Processes are very promising for effluent treatment mainly due to their high efficiency and simplicity of operation. Our group became interested on photocatalytic methods (included in the AOP's), using TiO₂, for degradation of dyes, started with simpler structures and continued with commercial dyes. Titanium dioxide (TiO₂) has proven to be the most effective and suitable catalyst for photocatalytic reaction due to its low cost economical, chemical stability, and insolubility.

In this paper, the effects of UV light irradiation in the presence of TiO₂ particles at various pH's (3, 6, 8 and 10) on the photodegradation of an azo dye, Reactive Red 158, were investigated. The photocatalytic degradation was carried out either in aqueous solutions or in a synthetically prepared dyebath effluent, under UV irradiation, in the presence of Degussa P25 TiO₂ as the catalyst. Reactive dyes of the pyrimidinyl type partly hydrolyse during dyeing in basic medium; RR 158 was hydrolysed and this solution was also irradiated. The fastest degradation was obtained with an acid solution (14 minutes, 95.53% loss of colour), but the hydrolysed dye took longer to be decolourised.

Keywords: Photodegradation, Titanium dioxide, Decolourisation, Azo dye, Reactive dye, C. I. Reactive Red 158.

1. Introduction

More than 30.000 commercial dyes based on ca 8.000 different chemical structures are used in textile, food, pharmaceutical, paper and ink industries, and usually they are discharged in waste water [1].

The textile industry is the largest consumer of dyes (60%), using them in conjunction with a wide range of auxiliary reagents for various dyeing, printing and finishing processes. Irrespective of dye or fibre class, mill effluents are invariably deeply coloured by unabsorbed dyes, the extent of which varies according to the dye-fibre system [2]. Azo dyes, represent the most common dyes actually employed in textile industries, and a relevant problem is related to the presence of these products in the environment. By the year 2004, the forecast is that the use of reactive dyes will increase to about 50%. As a result of the chemical reactions involved in the fixation of reactive dyes to fabrics, as much as 20 to 50 % of the reactive dye can be released into waterways depending upon dyestuff type, the application route and depth of shade required.

Waste water derived from industrial plants that use dyes in their processes needs suitable treatments before its release in order to avoid dangerous increase of BOD and COD in rivers or in drainage areas. Moreover, effluent streams coming from textile plants contain toxic or carcinogenic residues together with their by-products. The treatments are focussed not only to solve the environmental impact but also to allow water and dyes reuse.

The effluents are usually treated by physico-chemical, oxidative or, most commonly, active sludge biochemical processes. The main drawback of the above processes is that they generally produce secondary pollution due to the introduction of chemicals and/or the possible accumulation of other bio-resistant species in the environment.

Since azo dyes are intentionally designed to resist degradation, traditional methods such as flocculation, carbon adsorption, reverse osmosis and activated sludge process have low mineralization (i.e. conversion to inorganic species) efficiency for this class of xenobiotics. These alternative methods, such as activated carbon adsorption and dissolved air flotation, are not only costly, but result in phase transfer of pollutants.

As an alternative or an integration to the conventional processes, advanced oxidation technologies have been proposed. Bleaching of dyes has been carried out by using ozone [3], photo-Fenton type reactions [4] or a reduction followed by a photo-oxidation process [5]. They are generally referred to as advanced oxidation processes (AOP) [6]. The AOP processes involve the oxidation of organic pollutants by the combination of ultraviolet light, oxidants (H_2O_2 , O_3 , etc) and/ or a catalyst (such as TiO_2) and in most cases imply the generation of hydroxyl radicals and their subsequent reactions with pollutant molecules. This will remove the organic impurities by converting them into harmless inorganic products (CO_2 , H_2O , etc). The combination of UV irradiation with photocatalysts such as TiO_2 is one of such methods which has attracted considerable attention in recent years, due to its effectiveness in mineralization of organic compounds [1, 2, 6, 7]. TiO_2 semiconductor is a very good photocatalyst for the elimination of pollutants from air and water due to its low cost, chemical stability, nontoxicity, high photocatalytic reactivity and insolubility. A further important advantage is the fact that the process can be powered by natural sunlight [8,9], thus reducing significantly the electrical power requirements and operating costs. It should be noted that with visible light, the photodegradation processes proceed by different routes, involving for example electron transfer from the excited state of the dye molecules adsorbed on the TiO_2 surface into the conduction band of TiO_2 . Such processes are less efficient than those occurring with UV light [2].

For the photocatalytic oxidation (TiO_2/UV) the semiconductor absorbs UV light and OH^\cdot radicals are generated mainly from the absorbed H_2O and hydroxide ions. The mechanism of the TiO_2/UV degradation has been described using the band-gap model [10]. It is well established that by irradiation of an aqueous TiO_2 suspension with light energy greater than the band gap energy of the semiconductor conduction band, electrons and valence band holes are generated [6]. These will act as strong oxidising agents that can easily attack any organic molecules adsorbed on, or located close to, the surface of the catalyst, thus leading to their complete degradation into small inorganic species (Figure 1).

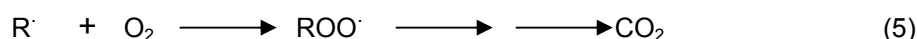
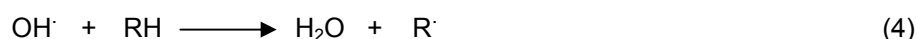
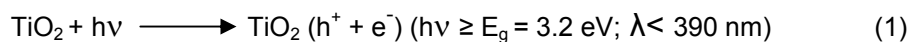
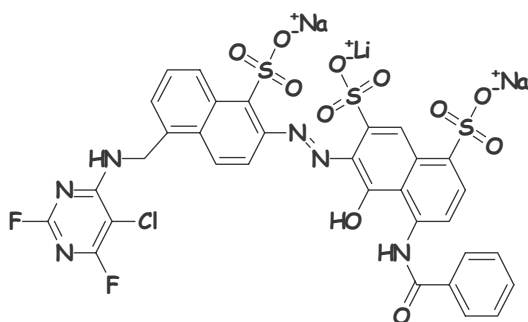


Figure 1: Mechanism of the TiO_2 -catalysed UV oxidative degradation of organic species.

Our group became interested on photocatalytic methods for degradation of dyes, started with simpler azo dye structures (model dyes) [11], and continued with commercial dyes such as C.I. Reactive Red 2 [12], and C. I. Reactive Orange 4 in the last case studying a simulated dyeing bath as well [2].

Our previous studies on photocatalytic degradation of dyes with TiO_2 [13], have now been extended to include the important reactive dye C. I. Reactive Red 158 (6). This dye is applied to cotton at about 50 °C in the presence of common salt (sodium chloride or sulfate), and sodium carbonate (final pH 10,5-11). The present paper describes the effects of UV light irradiation in the presence of TiO_2 particles on the photodegradation of an azo dye, Reactive Red 158 at various pH values (3, 6, 8 and 10). The photocatalytic degradation was carried either in aqueous solutions or in a synthetically prepared dyebath (only for cotton dyeing) effluent, under UV irradiation, in the presence of TiO_2 as the catalyst. Reactive dyes of the pyrimidinyl type partly hydrolyse during dyeing in basic medium; RR 158 was hydrolysed and this solution was also irradiated.



(6)

2. Experimental

2.1. Materials

A commercial sample of C.I. Reactive Red 158 (from Dystar) was used in this study, without further purification. The catalyst employed was technical grade TiO₂ Degussa P-25. Additives for the preparation of simulated dyebath effluent were from Bayer (Diadavin ANE) and all other chemicals were of technical grade.

2.2. Apparatus

UV-vis spectra were recorded on a Unicam UV2 spectrophotometer.

UV irradiation experiments were carried out using an annular laboratory immersion UV Reactor System 2, Heraeus Noblelight was equipped with medium pressure arc mercury lamp Heraeus TQ 150 (efficiency ca 150 W).

2.3. Irradiation of dye solutions

The photocatalysis of Reactive Red 158 (0.2 g/L) was carried out in a UV reactor in the presence of TiO₂ (0.4 g/L) in media of different pH (3, 6, 8 and 10) with a maximum irradiation time of 150 minutes at room temperature. The reaction mixture (800 mL) was vigorously stirred during irradiation. The starting reaction mixture was ca 20 min sonicated before use and kept 30 min conditioned in the dark under stirring to equilibrate. Samples of reaction mixtures (1 mL) were withdrawn diluted to 10 mL flasks, centrifuged and the absorption at 512 nm determined. For the rate determinations, calibration curves for the dye in water were obtained at λ_{max} (512 nm) at pH values of 3, 6 (pH of distilled), 8, 10 and 11.2.

Table 1: Composition of the simulated dyebath effluent.

Component	Concentration	Function
Dye	0.019 g/L	-----
NaCl	5 g/L	Promotes exhaustion of the dye onto cotton
Na ₂ CO ₃	1.5 g/L	Adjustment of the final dyeing pH (10.5-11.0) to cause further ionisation of the cellulose and dye-fibre reaction
Diadavin ANE	0,15 mL/L	Detergent for washing off

Blank experiments were also conducted (without TiO₂) under UV light irradiation.

Conversion of the reactive dye into its hydrolysed form was ensured by heating the solution at 50 °C for 2 hours, in the presence of NaOH (0.03 M). The composition of the simulated dyebath (only for cotton dyeing) effluent and the function of the additives in the mixture are described in Table 1.

3. Results and discussion

3.1. Influence of pH on decolourization of Reactive Red 158

Reactive dyes of the pyrimidinyl type partly hydrolyse during dyeing in basic medium, reacting with water or hydroxide ions, thus being part of the waste.

The degradation studies were performed in aqueous solutions of the dye, as marketed, at different pH values.

The pH dependence of the rate of decolourization for the dye solutions was examined by carrying out UV-irradiated experiments with TiO₂ catalyst (0.4 g/L), at pH values of 3, 6, 8 and 10. The influence of pH on degradation of hydrolysed dye was also studied. The kinetic results are summarised in Figure 2.

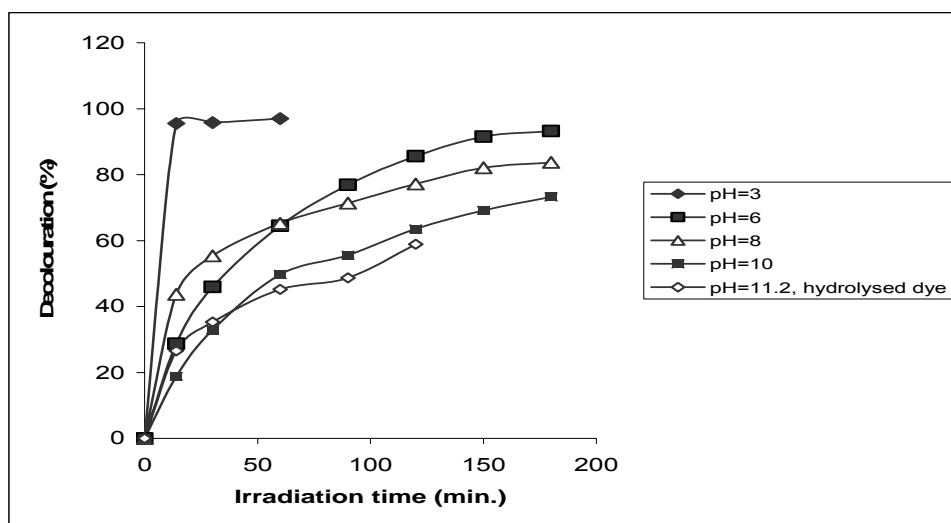


Figure 2: Influence of pH on UV-induced decolourisation of dye in the presence of TiO₂ (0,4 g/L).

The fastest degradation was obtained with an acid solution (14 minutes, 95.53% loss of colour), but the hydrolysed dye took longer to be decolourised. In the case of the pH=6, after the photolysis it was obtained a value of pH=2.2, which suggest that possibly acids, had already formed. In the case of the photocatalytic degradation of dye-only solution, without TiO₂, at pH=6, the behaviour is similar, that is, after the photolysis it was obtained a value of pH=3.4.

3.2. Kinetic analysis

Initial decolourisation rate constants were determined from the slope of $\ln(C_0/C)$ vs t (min) plots, where C_0 and C are the dye concentration at zero time and time t , respectively.

In the experiments the degradation of the dye during the first 14 minutes of irradiation followed pseudo first order kinetics. Relevant first order rate constants are indicated in Table 2.

Table 2: Pseudo first order rate constants for the degradation of solutions of Reactive Red 158 (0.2 g/L).

Solution ^a	pH	R ^{2b}	K (min ⁻¹) ^c
Aqueous	3	0.9405	0.3294
Aqueous	6	0.9853	0.0454
Aqueous	8	0.9806	0.0532

^a "Aqueous" refers to a solution of the dye in water with no other additives.

^b Correlation coefficient of the straight line.

^c Pseudo first order rate constant determined for the first 14 minutes of irradiation.

3.3. Photodegradation of simulated dyebath effluent

In an attempt to relate our present study to the real situation arising with effluent from the commercial dyeing of cotton with Reactive Red 158, it was decided to formulate a simulated spent dyebath and to test its response to photocatalytic decolourisation.

The rinsing and soaping processes which follow the reactive dyeing of cotton (namely the reactive red 158) result in a considerable dilution of the dyehouse effluent [14].

The results for the photocatalysed degradation reaction are presented in Figure 3.

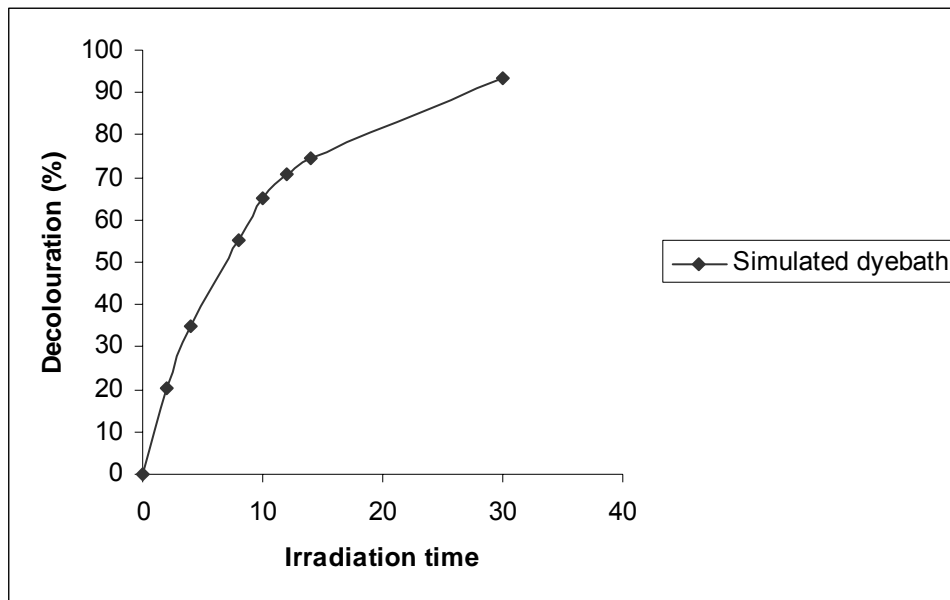


Figure 3: Decolourisation (%) of the simulated dyebath effluent (pH=10,74, Dye 19mg/L, TiO₂ 0,4 g/L).

The simulated dyebath effluent shows to degrade reasonably fast. However it may be remembered that the relative concentration dye /catalyst is, in this case, lower than in the studies previously carried out.

3. Conclusion

We have shown that photodegradation using UV light in conjunction with TiO₂ is a promising method for degrading C. I. Reactive Red 158 either alone in water, or in its hydrolysed form in spent dyebath liquor.

The fastest degradation was obtained with an acid solution (14 minutes, 95.53% loss of colour), but the hydrolysed dye took longer to be decolourised. It may be concluded that the photocatalytic method is feasible for dyehouse wastewater treatment. However further experiments must be carried out in order to obtain the best results.

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