Photocatalytic degradation of Remazol Red F3B using ZnO catalyst

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Abstract

The photocatalytic degradation of aqueous solution of a commercial azo-reactive textile dye, Remazol Red F3B, has been investigated in a batch slurry reactor, in the presence of ZnO catalyst using two different UV light sources emitting at 254 nm and 365 nm. The effects of various process variables on degradation performance of the process have been investigated. The results showed that decolourization and total organic carbon (TOC) removal are both affected in the same manner by the solution pH in the pH range 6–10, showing maxima at pH 7 and pH 10. They are inversely related to the dye concentration, they increase in power-law with the light intensity. Decolourization is faster with 365 nm UV. TOC removal is not affected by UV wavelength in the initial period up to 20 min, after which it progresses faster under 365 nm UV radiation. These results indicate that the UV wavelength influences especially the degradation rate of the intermediate products generated during the initial period of the photocatalytic process. Finally, catalyst loading affects both efficiencies in the same trend, which are maximized at about 2 g/l catalyst loading.
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1. Introduction

Large quantities of coloured dye effluents discharged from manufacturing and processing processes in the textile industry, create severe environmental pollution problems due to their negative impact on photosynthetic activity [1]. Conventional methods used to treat dye effluents are classified as physical, biological or chemical methods [2–4], each having its own drawbacks. Physical methods such as chemical or electro-flocculation, reverse osmosis and adsorption are not destructive and mainly create pollutant concentrates. Activated sludge process does not work efficiently due to high solubility of synthetic dyes and their resistance to aerobic degradation. Furthermore dyes, although not directly toxic, may generate carcinogenic compounds such as aromatic amines from azo dyes during their anaerobic treatment [4]. On the other hand, chemical treatment using strong oxidants chlorine or ozone, has led to more successful results, but they

are not found economically feasible due to the required high dosages [2].

Thus, new treatment methods are necessary for the removal of persistent dye chemicals or converting them into harmless compounds in water. Advanced oxidation processes (AOPs) offer new routes for the oxidative degradation of organic compounds. UV radiation in the presence of oxidants such as H_2O_2 [5–7] or Fenton reagent [8] has been found promising for the degradation of azo-reactive dyes. Heterogeneous photocatalysis is another important destructive technology leading to the total mineralization of most of the organic pollutants to CO_2, water and mineral acids [9–16]. The process uses atmospheric oxygen as the oxidant and is carried out under ambient conditions utilizing a semiconductor catalyst. Electrochemically assisted photocatalytic process is also investigated to degrade reactive azo dyes [17,18].

TiO_2 [19–23], and ZnO [24–30] especially in recent years, are used as effective, inexpensive and nontoxic semiconductor photocatalysts for the degradation of a wide range of organic chemicals and synthetic dyes. Moreover,

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visible light-induced degradation of an azo dye on coupled TiO$_2$/CdO–ZnO nanoporous films was also investigated to show higher photocatalytic activity [31]. Studies performed with ZnO powders with different morphologies indicated that the particle crystallinity, rather than the surface area, significantly affects its photocatalytic activity [32].

This study deals with the comparative investigation of the photocatalytic degradation of the reactive azo dye Remazol Red F3B using two different UV light sources emitting at 254 nm and 365 nm. Experiments were conducted to investigate the effects of various process variables on the process performance, which is assessed in term of total organic carbon (TOC) removal and decolourization.

2. Experimental

2.1. Materials

Remazol Red F3B (C.I. Reactive Red 180) was provided by DyStar. The dye structure in azo tautomeric form is shown in Fig. 1. The commercial sample, which contains inorganic salts and organic formulating agents, was used without further purification.

The photocatalyst ZnO is obtained from Merck (BET, <5m^2/g) and is used as received.

2.2. Apparatus

The experimental set-up was described previously [28]. The quartz photoreactor was designed in column shaped in 25 cm height and 4.5 cm diameter. Air was blown into the reaction medium by an air pump at a flow rate of 150 ml/min, to saturate the solution with oxygen during the course of the reaction. Stirring was applied at 600 rpm to ensure a complete suspension of catalyst particles. The reactor was surrounded by six UV lamps located on the corners of a hexagonal which predominantly emit at 365 nm (6W, General Electric F6T5/BLB) or 254 nm (6W, Philips TUV G6T5). Blowing cooled air between the lamps and the quartz reactor eliminated heat effect of the lamps, maintaining the temperature of the reaction medium constant at 25 ± 0.2 °C. The intensity

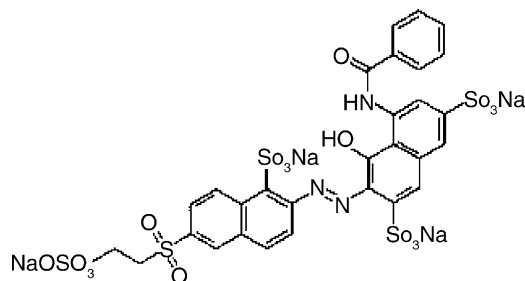of irradiation entering the quartz reactor was measured by a chemical actinometric method using potassium ferrioxalate (K$_3$Fe (C$_2$O$_4$)$_3$) [33]. The actinometer solution was irradiated under conditions similar to those used for photoreaction. Light intensity of all six lamps measured using 300 ml of the actinometer solution was found as 1.66×10^{-6} Einstein/l s (365 nm), and 1.60×10^{-6} Einstein/l s (254 nm).

2.3. Experimental procedure and analysis

The batch experiments were carried out with 300 ml dye solutions prepared in appropriate concentrations using deionized water. Prior to the runs, dye solutions were stirred in the dark for 30 min after the addition of the catalyst to allow the physical adsorption of dye molecules on catalyst particles to reach the equilibrium. During the experiments, 6 ml samples of suspension were withdrawn at regular intervals and were immediately centrifuged at 3500 rpm for 10 min to completely remove catalyst particles.

Solution pH, dye concentration, UV light intensity, UV wavelength and catalyst loading were investigated for their effects on the photocatalytic degradation performance in terms of TOC removal and decolourization, defined as

$$\text{Performance} \% = \frac{C_0 - C}{C_0} \times 100 \qquad (1)$$

where C_0 is the initial TOC or dye concentration. TOC was measured with SIEVERS 2244 AP Analyzer, and dye concentration with UV–vis GBC CINTRA 20 spectrophotometer by measuring the absorbance of the solution samples at $\lambda_{max} = 531$ nm. The pH of the solution was adjusted initially by adding 0.01N NaOH or 0.01N H$_2$SO$_4$ for exploring the effect of the pH, otherwise the experiments were carried at the original pH of the solution.

3. Results and discussion

In this preliminary process analysis, base values of the process parameters are selected as: catalyst loading = 1.5 g/l, pH = 7.0, dye concentration = 150 mg/l, light intensity = 24 W, light wavelength = 365 nm. The effect of each process variables is presented at three different reaction times 10, 30 and 60 min.

3.1. Solution pH

The role of pH on the decolourization is studied in the pH range limited to 6–10 by considering the solubility of ZnO in acidic as well as in highly basic solutions. The pH of the solution is adjusted initially and it is not controlled during the course of the reaction. A slight decrease, approximately 0.5 pH unit, is usually noted at the end of the experiments, depending of the reaction time. As seen in Fig. 2(a) and (b), the solution pH affects decolourization and TOC removal,
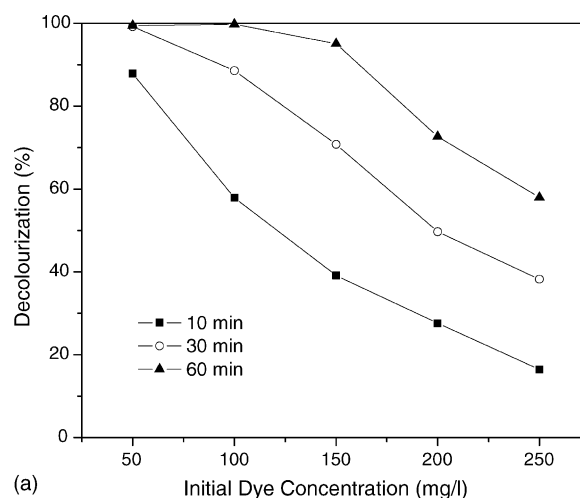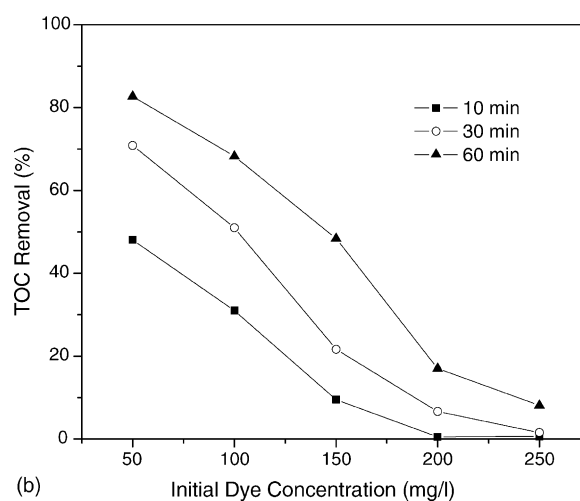

Fig. 1. Remazol Red F3B.
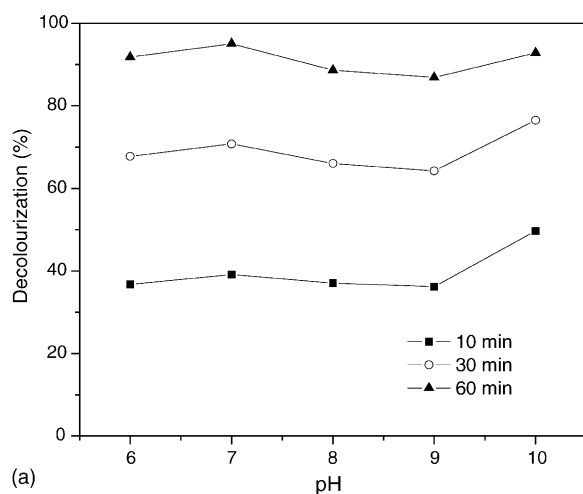
(a)
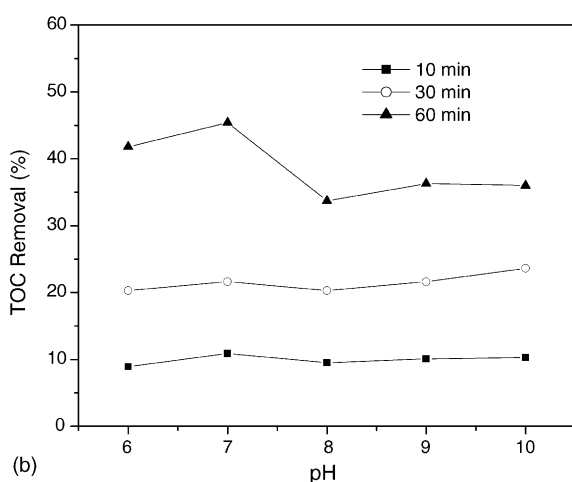
(b)

Fig. 2. Effect of initial pH (a) on the decolourization (%) (b) on the TOC removal (%) (catalyst loading, 1.5 g/l; dye concentration, 150 mg/l; light intensity, 24 W; light wavelength, 365 nm).
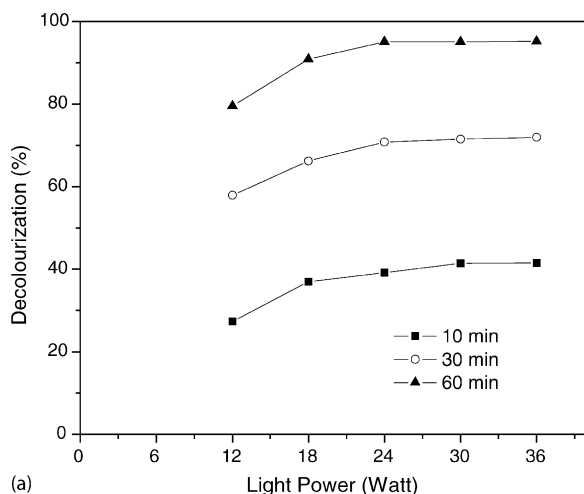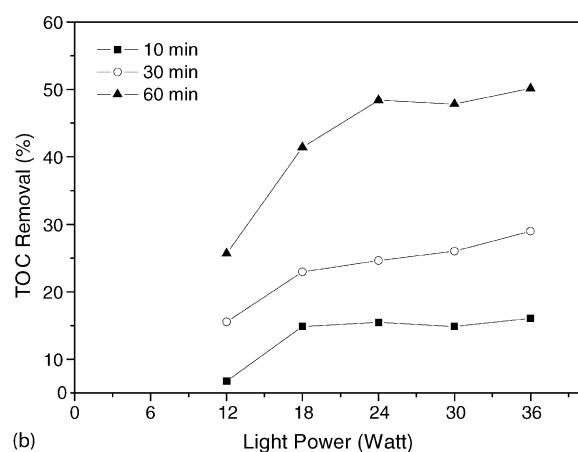

(a)

(b)

Fig. 3. Effect of initial dye concentration (a) on the decolourization (b) on the TOC removal (%) (catalyst loading, 1.5 g/l; pH, 7.0; light intensity, 24 W; light wavelength, 365 nm).

but not very appreciably, in the pH range studied. In both figures, a maximum is seen near pH 7. By increasing pH further, process performances decrease slightly and increase again at pH 10. Similar situations have been observed by Akyol et al. [28] using Remazol Red RR, and also by other authors [22,23]. The pH of zero point of charge for ZnO is about 9 [26]. Below pH 9, active sites on the positively charged catalyst surface are preferentially covered by dye molecules bearing four sulfonate anions (see Fig. 1), thus, surface concentration of the dye is relatively high, while those of OH^- and hydroxyl radical ($^\bullet OH$) are low. Above pH 9 on the other hand, catalyst surface is negatively charged by means of metal-bound OH^-, consequently the surface concentration of the dye is low and that of hydroxyl radical is high. In conclusion, by increasing pH, surface concentration of the dye decreases while that of hydroxyl radical increases. Surface reaction rate, which depends on the concentration of these principal reactants, creates extreme points seen in Fig. 2.

3.2. Initial dye concentration

The effect of initial dye concentration was investigated by varying the initial concentration from 50 to 200 mg/l and results are shown in Fig. 3. As seen, the decolourization and TOC removal are both inversely affected by the dye concentration. TOC removal is more strongly dependent on this parameter. Clearly, the dye concentration affects adsorptive and reactive processes in various manners; first of all, increasing initial dye concentration will enhance the rate of the liquid phase reaction, and surface reaction as well, at least of the initial steps of the complex degradation mechanism. Meanwhile, the experimental results show that the negative effects of the dye concentration depresses the positive ones; the adsorption of dye molecules on the catalyst surface hinders competitive adsorption of OH^- ions, thus it lowers the formation rate of hydroxyl radicals, and consequently it affects negatively all the steps of the mechanism. Furthermore, as the initial dye concentration

Fig. 4. Effect of light power (a) on the decolourization (%) (b) on the TOC removal (%) (catalyst loading, 1.5 g/l; pH, 7.0; dye concentration, 150 mg/l; light wavelength, 365 nm).

increases, the path length of photons entering the solution decreases according to the well-known Beer–Lambert law, this means obviously lower photonic absorption on catalyst particles and slower photocatalytic reaction rates.
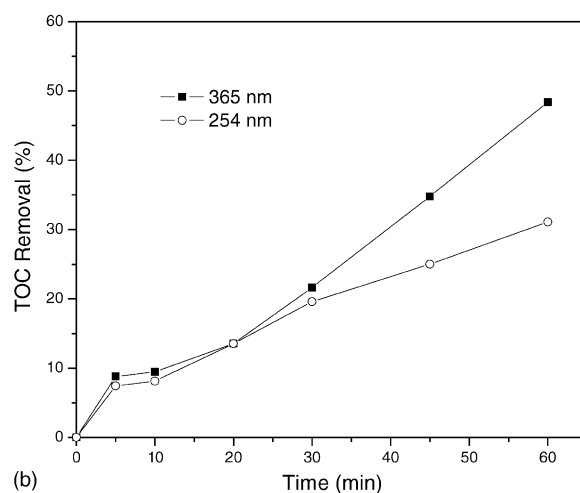
3.3. Light intensity

The influence of light intensity has been examined by varying nominal light power between 12 and 36 W. As seen in Fig. 4, the decolourization and TOC removal are not linearly, but power-law dependent on the light power, probably square root dependent, which means that the reactions are surface controlled to various extents.

3.4. Light wavelength

The light wavelength experiments were carried out with two different UV lamps emitting at 254 nm and 365 nm. Fig. 5 depicts the time progresses of decolourization and TOC removal, which are both faster when the solution is irradiated with 365 nm UV source. For a reaction time of 60 min, the
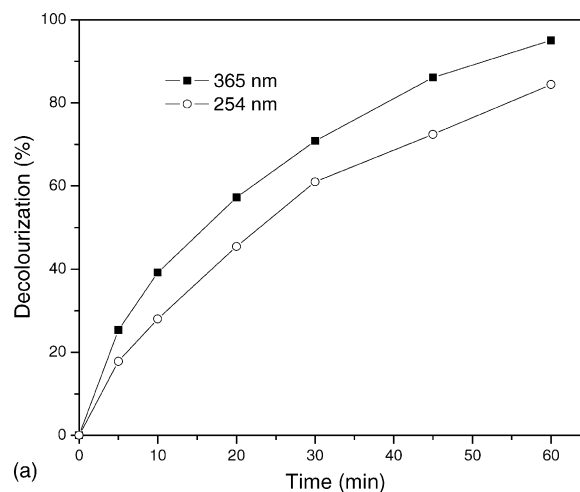
Fig. 5. Effect of wavelength (a) on the decolourization (%) (b) on the TOC removal (%) (catalyst loading, 1.5 g/l; pH, 7.0; dye concentration, 150 mg/l; light intensity, 24 W).

extent of decolourization is 10% higher than with 254 nm. Furthermore, in the case of TOC removal, a different situation is observed; TOC is not affected by the UV wavelength in the initial period up to 20 min, after which it progresses clearly faster under 365 nm UV radiation. These results indicate that the impact of the UV wavelength is especially on the degradation rate of the intermediate products generated during the initial period of the photocatalytic process, which is faster under 365 nm UV irradiation.

3.5. Catalyst loading

To determine the effect of the catalyst loading, a series of experiments were carried out by varying the amount of catalyst from 0.5 to 2.5 g/l. Decolourization and TOC removal are depicted in Fig. 6(a) and (b). Both efficiencies show similar trends and they are maximized at the same catalyst loading of about 2 g/l. This extreme point results from the conflicting effects of this parameter on the photocatalytic process; at lower loading levels, such as 0.5 g/l, photonic adsorption
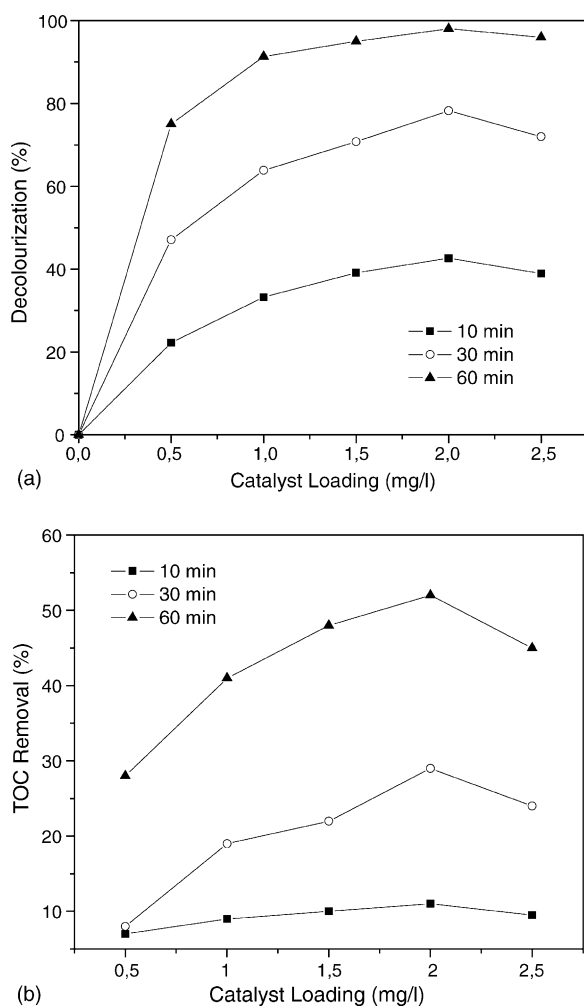
Fig. 6. Effect of catalyst loading (a) on the decolourization (%) (b) on the TOC removal (%) (pH, 7.0; dye concentration, 150 mg/l; light intensity, 24 W; light wavelength, 365 nm).

controls the reaction extent due to the limited catalyst surface area, and an increase in catalyst loading greatly enhances the process performance. On the other hand, at higher loading levels, light scattering by catalyst particles attenuates light absorption inside the reaction medium [28,29].

The initial decolourization rate is very fast and decreases exponentially with time. In contrast, TOC removal proceeds very slowly initially; at the end of 10 min, only 11% of TOC is removed, while the decolourization reaches up to 42%. The mechanism of the photocatalytic degradation of dyes is of very complex nature, but it may be greatly simplified as

Dye $\rightarrow$ Organic intermediates

$$\rightarrow CO_{2(gas)} + (\text{Inorganic C, N})_{solution} \qquad (2)$$
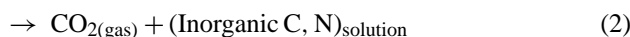
Initially, dye molecules adsorbed on the photocatalyst particles react with surface-bound hydroxyl radicals (or surface-trapped holes) to break preferentially the chromophore azo group, assuring rapid decolourization without any appreciable mineralization. The half life ($t_{1/2}$) of the

azo dye is approximately 15–20 minutes at the end of which a noticeable increase in TOC removal rate occurs; various naphthalene and benzene derivatives intermediates, generated during initial steps, are further degradated progressively to di-carboxylic acid derivatives (saturated or unsaturated), simple carboxylic acids such as acetic acid, formic acid, and finally to $H_2CO_{3(liq)}$ or $CO_{2(gas)}$. Meanwhile, the total mineralization of the dye is a slower process than the decolourization; with 2 g/l catalyst loading and reaction time of 60 min, the dye solution is decolourized almost totally, while 53% of TOC is removed.

4. Conclusion

In this study, photocatalytic decolourization of an azo-reactive textile dye, Remazol Red F3B, has been investigated using ZnO powder catalyst. The following conclusions have been obtained about decolourization and TOC removal:

- They are affected by the solution pH in a similar manner, exhibiting maxima at pH 7 and 10.
- They are inversely related to the dye concentration.
- They are power-law dependent on the light, intensity, probably square root dependent, which means that the reactions are surface controlled to various extents.
- Decolourization is faster under 365 nm UV radiation. Furthermore, TOC removal is not affected by the UV wavelength in an initial period of about 20 min, after which it proceeds clearly faster under 365 nm UV radiation; UV wavelength affects especially the degradation rate of the intermediate products generated during the initial period of the photocatalytic process.
- Catalyst loading exhibits conflicting effects on the photocatalytic process; at lower loading levels, photonic adsorption controls the reaction extent due to the limited catalyst surface area, while at higher loading levels, light scattering by catalyst particles predominates over photonic adsorption. Due to these adverse effects, decolourization and TOC removal reach their maximum values at about 2g/l catalyst loading.

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