STUDIES REGARDING THE PHOTOCATALYTIC TRANSFORMATION OF ERYTHROSINE B

Laura Carmen APOSTOL1,2, Anca Florentina CALIMAN2, Maria GAVRILESCU2,3

1 “Stefan cel Mare” University of Suceava, Faculty of Food Engineering, 13 Universitatii Street, 720229 Suceava, Romania; laura.apostol@fia.usv.ro
2 “Gheorghe Asachi” Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Ph. D. D. Mangeron Street, 700050 Iasi, Romania
3 Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania

*Corresponding author

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Abstract: Heterogeneous photochemical processes using semiconductors as a photocatalyst have gained wide interest in the treatment of dyes effluents from industries, where biological methods did not succeed, i.e. especially because of dyes toxicity on sludge. Experiments concerning the photocatalytic degradation of Erythrosine B xanthene dye were conducted in the presence of different semiconductor catalysts (TiO2-P-25, TiO2-Rutile, ZrO and Sb2O3). The experiments showed that TiO2-P-25 exhibited the best removal efficiency. Photocatalytic degradation rate decreased from 0.9 to 0.01 mg L⁻¹ min⁻¹ when Erythrosine B concentration increased from 30 mg L⁻¹ to 300 mg L⁻¹. The addition of hydrogen peroxide leads to increase of the reaction rate from 0.06 mg L⁻¹ min⁻¹ to 0.14 mg L⁻¹ min⁻¹. Photocatalytic degradation of Erythrosine B led to a complete detoxification of compounds, but the complete mineralization was not achieved.

Keywords: food dye degradation, reaction rate, slurry reactor

1. Introduction

Synthetic organic pollutants in wastewater can generate serious environmental problems in the aquatic system when these pollutants are improperly disposed and treated. The wastewater containing dyes can induce eco-risk, beside the dyes themselves, by toxic by-products which can be formed naturally trough oxidation or reduction pathways. To overcome the problems that dye effluents can induce when they are released into receivers, a wide range of biological and chemical treatments have been applied in order to decrease the environmental effects that can appear in these conditions.

Advanced Oxidation Processes (AOP) represent a chemical procedure designed to remove particularly the toxic and non-biodegradable organic pollutants from wastewater. The objective of the wastewater treatment using AOP is the minimization of the pollutants concentration and toxicity so that the cleaned wastewater may, nevertheless, be dumped into a conventional sewage treatment [1]. Heterogeneous photochemical processes using semiconductor as a photocatalyst have gained wide interest in the treatment of dyes effluents from industries, where biological methods did not succeed, especially due to dyes toxicity on sludge [2, 3].
The method can result in the mineralization of the hazardous pollutants rather than transferring them to another phase, such as in the case of adsorption on different materials [4, 5]. Biodegradation of recalcitrant dyes is an inefficient method due to the dyes resistance to reductive processes [6, 7]. The majority of the researchers reported that the process can generate the break of the dye, but rarely complete mineralization can be achieved in an economically and environmental friendly ways [8]. From the semiconductors tested by different researchers, the statistics showed that TiO₂ has received the biggest interest for wastewater purification [9]. The conversion of organic pollutants by TiO₂-P-25 represents an effective and economical method due to the rapidity of its electron transfer to molecular oxygen for decomposition of pollutants, chemical stability and nontoxicity [10]. The biggest challenge of TiO₂ as a photocatalyst is its wide band gap, which limits its photoactivity under visible light and the work in slurry system. Erythrosine B is authorised as a food additive in the EU and is a water-soluble dye of xanthene class used in different industries such as a colorant in foodstuffs (baked goods, fruits cocktails), cosmetics (lipsticks, bubble baths) or drugs (tablet, capsule). The large majority of the dyes from this class are toxic, carcinogenic or mutagenic for humans and animals [11]. The amount of Erythrosine B used in food products is between 150 and 200 mg kg⁻¹ [12, 13].

Hasnat et al. published in 2007 two papers containing preliminary studies regarding Erythrosine B photodegradation [14, 15]. In their papers it is presented the influence of two catalysts: TiO₂ and ZnO on Erythrosine B photodegradation for a low dye concentration comparing with the concentration used in the industries starting with aspects regarding the adsorption of the dye on the catalysts.

Erythrosine B (Ery B) has a complex chemical structure which showed to be toxic for the mixed culture of microorganisms (i.e. anaerobic granular sludge) [2]. The purpose of this study was to evaluate further the photocatalytic degradation of Erythrosine B, the influence of UV in the presence of the catalyst Degusa TiO₂ Aerioxide P25, on Erythrosine B removal from aqueous solution was tested. Experiments were conducted to evaluate the influence of different parameters (catalyst type, pH, catalyst loading, initial dye concentration, charge-trapping species - H₂O₂ and reactor type) on the removal efficiency of the dye.

2. Materials and methods

2.1. Materials
The compound investigated in this study was chosen because of its use in different industries despite the toxic and carcinogenic effects. The Erythrosine B is a red odourless powder or granules with a calculated Log P (octanol-water) of 4.95 at 25°C [16], soluble in water (≤ 9% w/w) and ethanol. The chemical was purchased from Sigma–Aldrich (C.I. Acid Red 51, 45430). A stock solution of 1000 mg L⁻¹ was prepared by dissolving an accurately weighed amount of Erythrosine B in 500 mL distilled water. For the experimental assays, dilution of the stock was done to achieve the desired concentration.

The semiconductor used in this study Degusa TiO₂ Aerioxide P25 was purchase from Aerosil; the physico-chemical properties are presented in Table 1.

2.2. Experimental procedures and analysis
The experiments were conducted in a close Pyrex cell, with a capacity of 500 mL, (9 cm diameter, 15 cm height) provided with hole for bubbling air (Fig. 1). The reaction mixture was maintained in suspension using a magnetic stirrer and the pumped air.
In order to achieve the sorption equilibrium of the dye onto the semiconductor catalyst surface the mixture was kept in dark for 15 minutes. The irradiation was performed with a 9W central lamp. The spectral response of the irradiation source (OsramDulux S 9W/78 UV-A) according to the producer is ranged between 350 nm and 400nm with a maximum at 366nm and two additional weak lines in the visible region [17, 18, 19]. The photon flow per unit volume of the incident light was determined by chemical actinometry using potassium ferrioxalate [20]. The initial light flux, under exactly the same conditions as in the photocatalytic experiments, was evaluated to be $6.46 \times 10^{-4}$ Einstein L$^{-1}$ min$^{-1}$ [17, 21].

Specific quantities of samples were withdrawn at periodic intervals and filtered through a 0.2 μm filter in order to remove the catalyst particles. In order to assess the extent of color removal, changes in the concentration of the dye were observed from its characteristic absorption band using a T60 UV–VIS Spectrophotometer. Solutions of H$_2$SO$_4$ 0.1 N and NaOH 0.1 N, respectively were used to adjust the solution pH. The pH values of the solution were monitored with a Hanna pH-meter; the reactions were conducted at room temperature (~27ºC).

The degree of Erythrosine B removal as function of time is gived by Eq. (1):

$$\% \text{ Erythrosine B removal} = \left( \frac{C_0 - C}{C_0} \right) \times 100$$

where $C_0$ and $C$ are the dye concentration at initial and any subsequent reaction time (mg L$^{-1}$).

The photocatalytic degradation rate of most organic compounds is described by first order kinetics. Direct photocatalytic pathway can be described using Langmuir - Hinshelwood (L – H) equation, which can be applied for the heterogeneous photocatalysis is based on the formation of electrons and holes by catalyst light activation. The hole is entrapped by the adsorbed dye molecule on the catalyst surface to form a reactive radical state, which can decay as a result of recombination with an electron [1]. Langmuir-Hinshelwood expression is given by Eq. (2):

$$\frac{1}{r} = \frac{1}{k_r} + \frac{1}{k_r k_a C}$$
where \( r \) is the reaction rate of the oxidation of reactant (mg L\(^{-1}\) min\(^{-1}\)), \( k_r \) is the specific reaction rate constant for the oxidation of the reactant (mg L\(^{-1}\) min\(^{-1}\)), \( k_a \) is the equilibrium constant of the reactant L mg\(^{-1}\), \( C \) is the dye concentration.

When the pollutant concentration \( C_0 \) is a millimolar solution, the equation can be simplified to an apparent first-order equation (3):

\[
\ln(C_0/C) = k_{app}t = k_{app}t
\]

A plot of \( \ln(C_0/C) \) versus time represents a straight line, the slope of which upon linear regression equals the apparent first-order rate \( k_{app} \).

The toxicity tests were conducted in triplicate using 20 seeds for germination on each Petri dish. 3 mL solution of 25 mg L\(^{-1}\) Ery B, 50 mg L\(^{-1}\) Ery B, and the corresponded degradation products, respectively were used to wet the supported paper of the seeds. The Petri dishes were kept at room temperature (~25ºC) for 72 hours. The number of seeds germinated, formed biomass, stem length and root length were measured to determine the germination degree.

3. Study of factors influencing the heterogeneous photocatalytic process

3.1. Effect of photocatalyst type on dye degradation

Experiments concerning the photocatalytic oxidation of Erythrosine B were conducted in the presence of different semiconductor catalysts. Results of the photolysis of 50 mg L\(^{-1}\) dye solution containing 0.5 g L\(^{-1}\) TiO\(_2\)-P-25, TiO\(_2\)-Rutile, ZrO and Sb\(_2\)O\(_3\), respectively are presented in Fig. 2, where the amount of the organic molecule present in the supernatant is plotted as a function of irradiation time. TiO\(_2\) P-25 exhibited the best results.

Under the experimental conditions and in the presence of 0.5 g L\(^{-1}\) TiO\(_2\) P-25, 50 mg L\(^{-1}\) Erythrosine B was complete removed after 60 min. In the presence of other catalysts, such us TiO\(_2\)-Rutile, ZrO and Sb\(_2\)O\(_3\), the degradation was a very slower process, considering the fact that after 120 min of irradiation, around 70% of dye initial concentration remained in solution when TiO\(_2\)-Rutile, ZrO and Sb\(_2\)O\(_3\) catalysts were used. Hasnat et al. (2007) [14] and Uddin et al.(2007) [15] obtained also low decolorization efficiency for Ery B with ZnO as catalyst.

3.2. Effect of catalyst concentration on dye degradation

The effect of TiO\(_2\) P-25 on the degradation kinetics of Ery B was investigated employing different concentration of catalyst: 0.25, 0.35, 0.5, 0.75 and 1 g L\(^{-1}\). Photodegradation of dye increased rapidly with increasing the amount of TiO\(_2\). Hasnat et al. (2007) [14] specified that the optimum TiO\(_2\) loading was 2.0 g/L taking into account just the degradation rate of 22 μM Ery B and ignoring the degradation efficiency; the irradiation time is not specified.

In this study the optimum catalyst concentration was established at 0.5 g L\(^{-1}\) for 30 min of irradiation. For higher values, the removal percentage remained
constant (100%) and the degradation rate value increased (Figs. 3 and 4). The increase in the amount of catalyst rises the number of active sites on the TiO₂ surface, which widens the number of OH⁻ and O₂⁻ radicals that conducted at a growing of the degradation rate.

Fig. 3. Influence of catalyst concentration on Erythrosine B (C₀ = 40 mg L⁻¹) photodegradation on time

Fig. 4. Effect of different TiO₂ P25 concentration (30 min of irradiation) on Erythrosine B (C₀=40 mg L⁻¹) degradation

3.3. Effect of pollutant concentration on dye degradation
The photocatalytic degradation of different concentration of Ery B has been investigated in aqueous suspension of TiO₂ as a function of irradiation time (Fig. 5).

Fig. 5. Influence of irradiation time on initial Erythrosine B concentration on dye photodegradation by 0.5 g L⁻¹ TiO₂ P25

The rate of dye photodegradation was investigated by varying the pollutant concentration from 30 mg L⁻¹ to 300 mg L⁻¹. It was observed that the photocatalytic degradation rate decreases from 0.9 to 0.01 mg L⁻¹ min⁻¹ because the concentration of active site remained the same for a fixed catalyst, the number of dye molecules adsorbed on TiO₂ surface increased and free radicals reactivity decreases (Fig. 6).

Fig. 6. Rate of photocatalytic degradation of Erythrosine B by TiO₂ P25 (0.5 g L⁻¹)

Hasnat et al. (2007) [14] found that the decolorization mechanism of Ery B under their reaction condition followed zero-order kinetics over TiO₂/ZnO surface. In our case, the reaction followed first - order
kinetics for a higher dye concentration and a higher amount of oxygen (provided by the bubbled air beside the magnetic steered).

3.4. Effect of initial pH on dye degradation

The pH value is an important operational variable in wastewater treatment. In photocatalysis systems, pH value is also one of the factors influencing the rate of degradation. Different pHs were tested in order to evaluate the effect of this parameter on dye degradation. The role of pH on the rate of photocatalytic degradation of Ery B was studied in the rage of 5 – 9 for 50 mg L^{-1}Ery B (Fig. 7).

![Fig. 7. Influence of initial pH of Erythrosine B (50 mg L^{-1}) on dye photodegradation](image)

The solution pH was adjusted initially and no buffered system was used to maintain constant pH during the reaction. The pH variation in time was also monitored (Fig. 8). It can be observed that after the sorption process the pH tends to stabilize in the range of neutral field. When the photodegradation process started the pH values decreased with around two pH unit due to the products released after dye degradation.

It was observed that the degradation rate decreased with increasing in pH (Fig. 10). Since adsorption became strongly around zero charge point of TiO\(_2\) the maximum reaction rate was obtained for the pH values closely to the point of zero charge (pzc). Also, it can be estimated that because the increasing of color intensity the pH increases, the solution opacity increases and the light penetration become more difficult. Hasnat et al. (2007) [14] and Uddin et al. (2007) [15] found that, with increasing of the medium pH from 5.0 to 7.0 the degradation rate, determined for the zero order reaction, increased and remained steady up to 9.0.

![Fig. 8. Variation of the pH of the solution in photocatalytic degradation of Erythrosine B](image)

![Fig. 9. First-order kinetics of the photocatalytic degradation of Ery B at different pHs](image)

3.5. Influence of charge-trapping species – \(H_2O_2\) on dye degradation

The addition of strong powerful oxidizing agents, such as hydrogen peroxide, to TiO\(_2\) suspensions leads in many cases to an increase in the photooxidation rate through...
generation of more radicals in the presence of light. The role of H$_2$O$_2$ in the process of photocatalytic degradation is dual [22]. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation and it also forms OH$_\ast$ radicals via superoxide.

A possible reaction of H$_2$O$_2$ with the photogenerated intermediates also cannot be excluded. When H$_2$O$_2$ is in excess, it may act as hole or OH radical dot scavenger or react with TiO$_2$ and form peroxo compounds that are detrimental to the photocatalytic action. This explains the need for an optimal concentration of hydrogen peroxide for the maximum effect [23 - 25]. The photocatalytic activity increases with increasing the amount of hydrogen peroxide until it reaches a maximum at the concentration of 200 mg L$^{-1}$ oxidant (Fig. 11).

**Table 2.** Erythrosine B degradation rate obtained for different H$_2$O$_2$ concentration

<table>
<thead>
<tr>
<th>H$_2$O$_2$ concentration (mg L$^{-1}$)</th>
<th>Reaction Rate (mg L$^{-1}$ min$^{-1}$)</th>
<th>Correlation coefficient ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.05417</td>
<td>0.9978</td>
</tr>
<tr>
<td>20</td>
<td>0.06132</td>
<td>0.9932</td>
</tr>
<tr>
<td>50</td>
<td>0.0672</td>
<td>0.9824</td>
</tr>
<tr>
<td>100</td>
<td>0.09359</td>
<td>0.9977</td>
</tr>
<tr>
<td>200</td>
<td>0.1479</td>
<td>0.9963</td>
</tr>
</tbody>
</table>

The process removal efficiency increases from 50%, for the assay without H$_2$O$_2$, to 98% for the analysis conducted in the presence of 200 mg L$^{-1}$ oxidizing agent. The effect of the amount of H$_2$O$_2$ on the initial reaction rates, calculated for the first 30 min of reaction, is presented in Table 2. Under the studied conditions, the addition of hydrogen peroxide accelerates the degradation by 3 times comparative with the assay without H$_2$O$_2$. A relative high positive effect was obtained in the presence of the of charge-trapping species – H$_2$O$_2$ considering that the degradation rate increased from 0.06 mg L$^{-1}$ min$^{-1}$ to 0.14 mg L$^{-1}$ min$^{-1}$ for an increasing of H$_2$O$_2$ concentration from 25 mg L$^{-1}$ to 200 mg L$^{-1}$.
The results are in concordance with those of Hasnat et al. (2007) [14] that explained the phenomena based on the activity of •OH radicals that are the major oxidant for dye decolorization. Therefore, the excess •OH radicals added to the system can accelerate the decolorization rate.

The reduction of chemical oxygen demand (COD) reflects the extent of degradation or mineralization of an organic species (Eq. 4). Therefore the percentage change in COD was studied for 50 mg L⁻¹ Erythrosine B under optimized conditions (catalysts dose 0.5g L⁻¹, pH = 5) as a function of irradiation time using UV (Table 3). The percentage of COD removal was 22 %, after 2 h concentrated UV irradiation treatment.

\[
\text{C}_{20}\text{H}_{16}\text{I}_4\text{Na}_2\text{O}_5 + 18 \text{O}_2 \rightarrow 20\text{CO}_2 + 4\text{H}^+ + 4\Gamma + 2\text{Na}^+ + \text{H}_2\text{O} \quad \text{(4)}
\]

Table 3.

<table>
<thead>
<tr>
<th>Irradiation Time (min)</th>
<th>COD (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>55.6</td>
</tr>
<tr>
<td>5</td>
<td>54.3</td>
</tr>
<tr>
<td>10</td>
<td>52</td>
</tr>
<tr>
<td>20</td>
<td>49.6</td>
</tr>
<tr>
<td>30</td>
<td>46.1</td>
</tr>
<tr>
<td>60</td>
<td>43.3</td>
</tr>
<tr>
<td>120</td>
<td>39.2</td>
</tr>
</tbody>
</table>

**4. Conclusions**

The experiments on the photocatalytic degradation of Erythrosine B xanthene dye conducted in the presence of different semiconductor catalysts (TiO₂ P-25, TiO₂-Rutile, ZrO and Sb₂O₃) showed that TiO₂ P-25 exhibited the best removal efficiency. Photocatalytic degradation rate decreased from 0.9 to 0.01 mg L⁻¹ min⁻¹ when Erythrosine B concentration increased from 30 mg L⁻¹ to 300 mg L⁻¹, because of
the given catalyst concentration (1 g L⁻¹), active site number being constant, the number of dye molecules adsorbed on TiO₂ surface increased and free radicals reactivity decreased. The addition of 20 and 200 mg L⁻¹ hydrogen peroxide led to an increase of reaction rate from 0.06 mgL⁻¹min⁻¹ to 0.14 mgL⁻¹min⁻¹. The presence of charge-trapping H₂O₂ decreased the irradiation time with 30 min required to achieve a removal efficiency of 99% to 69% in the absence of added H₂O₂. Photocatalytic degradation of Erythrosine B led to a complete detoxification of the compounds but the complete mineralization was not achieved.

5. Acknowledgment
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6. References