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# Photocatalytic Degradation of Orange II in Aqueous Solutions by Immobilized Nanostructured Titanium Dioxide

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This paper deals with the degradation of an organic dye by photocatalysis. The examined compound is Orange II. The adopted photoreactor consists of a bed of glass spheres coated by TiO2, immobilized located in an inclined half pipe and irradiated at the top by an UV lamp. The nanostructured titania used for the glass coating was previously produced by wet chemical synthesis. The experimental work investigated the effect on the dye degradation of the following operating conditions: feed flow rate, coating procedure and UV wavelength. At the optimal operating conditions it was possible to reduce the organic content of the wastewater of 96% in 24 h residence time.

## 1. Introduction

The degradation of organic matter in wastewater streams of industrial origin is often a difficult task by conventional operations, as evaporation, electrolysis, distillation, and adsorption, because of the high unit cost to get the purification grade required for the water disposal. Photocatalysis is a promising technique to degrade organic matter in wastewater streams in a cheap and efficient way (Fernandez et al., 2004). The breakthrough of this technique was reached in the '90, when it was possible to produce a very efficient catalyst such as nanostructured titanium dioxide. This latter material may be used as catalyst nanoparticles, suspended in the solution to be treated, or as coating of a solid support. In the first case, the photocatalysis is performed in a stirred vessel, the nanoparticles catalyze the organic degradation of wastewater when exposed at the liquid surface, but after the treatment the nanoparticles recovery is troublesome (Sungmin et al., 2010). In the second case, the immobilized catalyst has a relatively low surface per unit volume and the reactor consists of a fixed catalytic bed irradiated by UV light, which penetrates through a relatively thin layer of the wastewater stream flowing over the catalyst itself.
In this work the efficiency of photocatalysis assisted by immobilized nanostructured titanium dioxide is investigated. The adopted model system is the degradation of Orange II in aqueous solutions, a dye used in the textile industry as pigment and present in the textile wastewater at a concentration ranging from 40 mg/l up to 100 mg/l. This dye is typically used to evaluate photocatalysis for the degradation of organic

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compounds present in wastewater streams from textile industry (Fernandez et al., 2004; Mu et al., 2004).

## 2. Experimental Setup

The adopted photoreactor consists of a bed of catalytic particles situated at the bottom of a slightly inclined channel, irradiated by an UV lamp (see Figure 1). The wastewater is continuously re-circulated from a feed vessel to the photocatalytic reactor by means of a volumetric pump. Each experiment was carried out in batch mode by using 2 litres of wastewater.

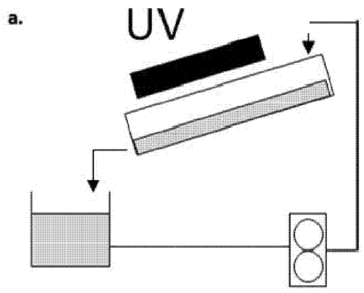


*Figure 1: The adopted photoreactor set-up.*

The used catalyst consists of glass spheres, 2 mm in diameter, coated by a micrometric nanostructured layer of titanium dioxide.

The suspension of titanium dioxide nanoparticles used for coating was prepared as follows. First of all, $TiO_2$ nanoparticles were produced by the reaction between titanium isopropoxide and a 0.1 M nitric acid solution in the ratio of 1:10. The reaction-precipitation operation was accomplished by using a spinning disc reactor, 300 mm in diameter, rotating at 1500 rpm (Baffi et al., 2002). The applied operating conditions are reported in more details by Stoller et al. (2009). The obtained suspension was, then, concentrated at 80°C during 8 h and submitted to a hydrothermal process at 200°C for 6 h. Finally, in order to re-disperse the agglomerated particles the suspension was stirred for 1 h in presence of $HNO_3$ 0.1 M. The particles size distribution was measured by a DLS instrument supplied by Brookhaven. The size distribution was narrow and the average value was 80 nm.

The coating operation was carried out over the surface of glass spheres, 2 mm in diameter. Firstly, the spheres were immersed in the obtained titania particles suspension for some minutes under a gentle agitation; then they were removed from the solid suspension, dried at ambient temperature and calcinated at 450 °C to transform $TiO_2$ dioxide almost completely to anatase phase. Calcination avoided any loss of $TiO_2$ during the treatment. The coating procedure was repeated to obtain more coating layers.

Experimental runs were performed in batch mode by using the above mentioned catalyst. During each run samples of liquid were withdrawn and their absorbance was measured by means of the spectrophotometer LASA 100 by Hach-Lange. A calibration curve, absorbance vs. Orange II concentration, was used to estimate the dye concentration. The photocatalytic reaction enabled a progressive degradation of Orange II, clearly shown by the degradation of the solution colour, initially orange and quite transparent at the run end.

## 3. Results and Discussion

The examined aqueous solutions contained 56 mg/l of Orange II. Some series of runs were devoted to investigate on the effects of the following variables on the organic degradation:

- flow rate of the recirculation stream (in the range 2.5 l/h - 14.0 l/h)
- wavelength of the UV lamp ( 254 nm or 365 nm)
- temperature (in the range 25°C - 40°C)
- number of coating layers of titanium dioxide over the glass spheres (1 layer or 3 layers).

For all the runs a mass of coated glass spheres equal to 300 g was used.
First of all, the best recirculation stream flow rate was chosen by performing runs at 25°C, by using one layer coating on glass spheres and UV lamp, 365 nm in wavelength.

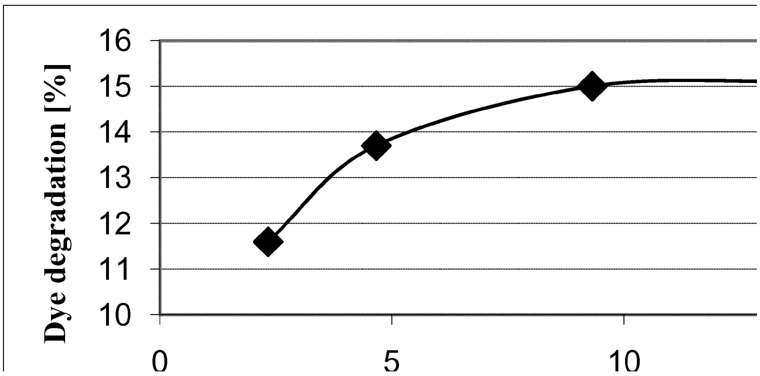


*Figure 2: Orange II degradation at different flow rates of the recycled stream.*

The obtained results, reported in Figure 2, show that the degradation percentage increases as well as the flow rate of the recirculation stream increases and a plat point of the curve is attained at a flow rate value equal to 10 l/h. The results are interpreted as the effect of hydrodynamics on the mass transport of Orange II from the liquid to the catalytic surface. The mass resistance becomes negligible at a flow rate higher than 10 l/h, accordingly a flow rate equal to 14 l/h was adopted in the subsequent runs. The adopted flow rate corresponds to a Re value equal to 19365. This Re value should be considered in case of scale up from pilot or lab plant experiments to industrial applications. Runs were then carried out, with a three hours time duration, to evaluate the process efficiency by using glass spheres with one layer (C-1) and three layers (C-2) coating. The results, reported in Figure 3, shows that the use of a multiple coating remarkably increases the effectiveness of the process, because of a more rough coating, and, as a consequence, a larger catalytic surface.
The influence of wavelength was examined by using UV lamps with different wavelengths. In particular runs were carried out with: three lamps, 365 nm in

wavelength (UV1); three lamps, 254 nm in wavelength (UV2) ; two lamps, 254 nm in wavelength, and a third one, 365 nm in wavelength (UV3). From the obtained results shown by Figure 4, it may conclude that the best lamp configuration is that one with three lamps, 254 nm in wavelength. It has to be noticed that the use of a wavelength of 254 nm entails a quite expansive case made by quartz, whereas for a wavelength of 365 nm lamps with a glass made case can be adopted.

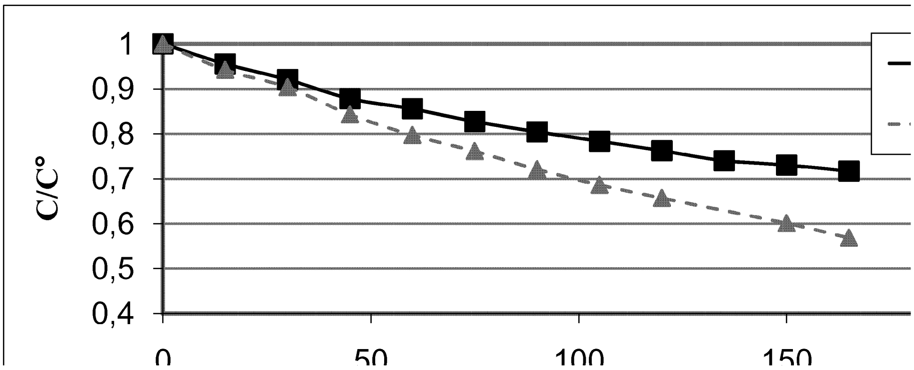


*Figure 3:Organic degradation by using a single layer coating (C-1) and a triple layer coating (C-2).*

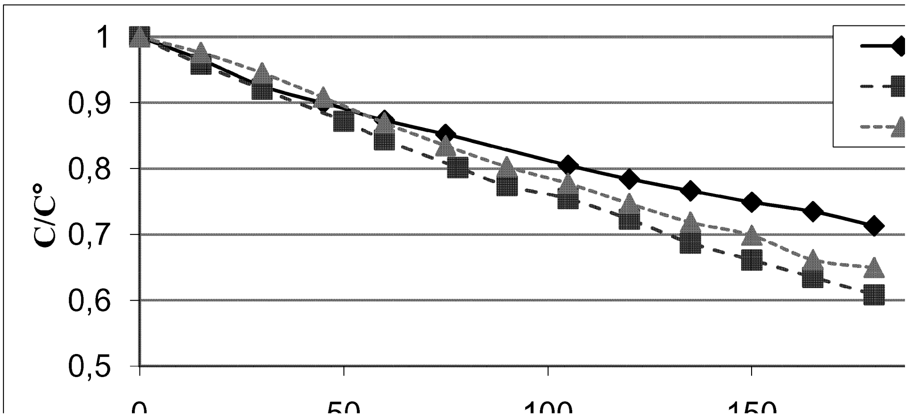


*Figure 4: Organic degradation by using UV lamp with different wavelength.*

In all the runs, a reduction of the catalyst efficiency was observed after its use. The worsening of the degradation process due to the catalyst deactivation is shown in Figure 5, reporting the obtained degradation grade for progressive runs performed by using the same catalyst.

The efficiency reduction was not caused by any reduction of the catalyst mass, since its constancy was experimentally ascertained, but it was due to adsorption of Orange II by $TiO_2$. In fact, the efficiency of the used catalyst was restored by a simple washing procedure with an aqueous NaOH solution at pH 10.

Figure 6 reports the Orange II decrease obtained in two subsequent runs by a fresh catalyst and the same catalyst re-used after the regeneration procedure. The very good reproducibility of the process performances obtained in the two runs represents a validation of the adopted catalyst regeneration procedure and, at the same time, supports the hypothesis of catalyst deactivation due to Orange II adsorption.

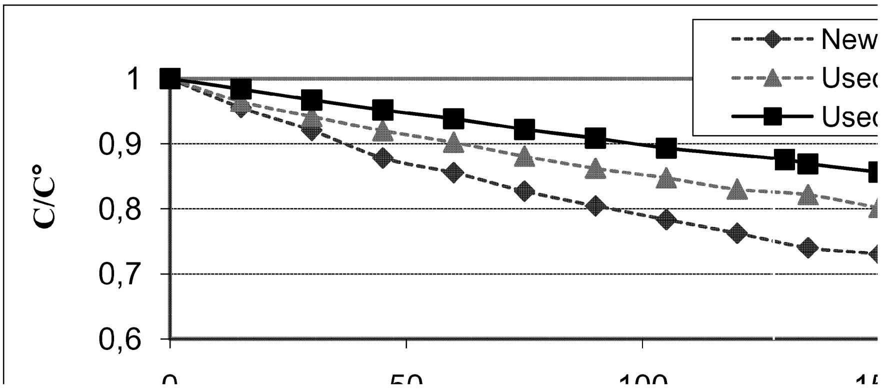


*Figure 5: Orange II degradation with re-used catalyst.*

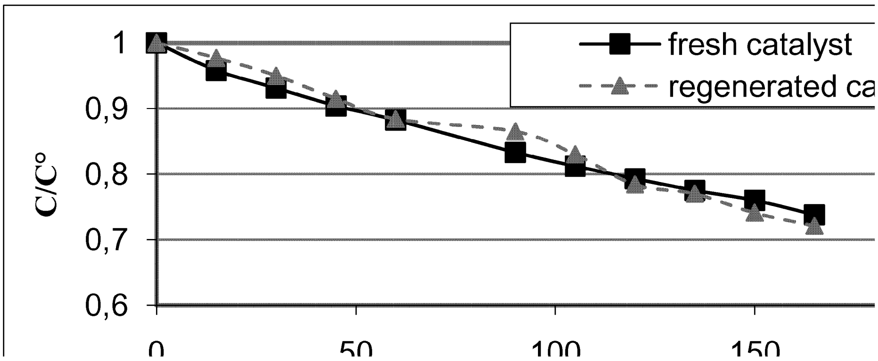


*Figure 6: Comparison of the Orange II degradation for the fresh and the regenerated catalyst.*

Summarizing, for the examined wastewater the best performances were obtained for the following operating conditions: feed flow rate higher than 10 l/h, 3 layers of titanium dioxide coating and irradiation by UV lamps, 254 nm in wavelength. From other runs, a negligible effect was ascertained for the temperature change between 25 °C and 40 °C, therefore a temperature of 25 °C appeared the best choice.

*Table 1: Orange II degradation at optimal operating conditions.*

| Time | COD | COD reduction |
|---|---|---|
| 0 h | 90.0 mg/l | 0 % |
| 1 h | 76.5 mg/l | 15 % |
| 2 h | 68.4 mg/l | 24 % |
| 4 h | 49.5 mg/l | 45 % |
| 6 h | 33.3 mg/l | 63 % |
| 24 h | 3.6 mg/l | 96 % |

By applying these optimal operating conditions in a run of 24 h an almost complete degradation of the Orange II dye was observed (see Table 1). The obtained solutions appeared quite transparent, thus we may exclude the occurring of any reaction of polymerization of the examined dye along the photocatalytic process.
The obtained results are comparable with those reported by Fernandez (2004) in spite of the more severe operation conditions adopted in this work (use of pure $O_2$, addition of $H_2O_2$, higher electrical power of UV lamps, etc.).

## 4. Conclusions

In this work nanostructured $TiO_2$ immobilized over glass spheres was used as catalyst for the degradation of Orange II dye in aqueous solutions. The obtained results were comparable with those reported in the literature, where more severe oxidation conditions where applied. The adopted reactor was very simple, since it consisted of a catalytic bed, situated in an inclined channel, irradiated by an UV lamp.
In order to face the catalyst deactivation occurring during the process, a procedure based on a washing operation of the catalyst particles with an NaOH solution was successfully applied. In conclusion, the proposed process for its easy procedure and the satisfactory achieved results appears very suitable to purify wastewater streams with COD values up to a few grams per litre.

## 5. Acknowledgment

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