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Influence of Operating Conditions in the Photo-Fenton Removal of Tartrazine on Structured Catalysts

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Organic dyes in wastewater negatively affect aquatic life by impeding light penetration and they can eventually results in carcinogenic and genotoxic effects on human health. Tartrazine is a commonly not-biodegradable dye used in food industries. The aim of this work was to evaluate the influence of operating conditions in the heterogeneous photo-Fenton process for the removal of tartrazine on structured catalysts. In particular $LaFeO_3$ or Pt/$LaFeO_3$ perovskite supported on honeycomb monoliths have been tested. The process efficiency was evaluated in terms of both dye discoloration and mineralization. The influence of initial dye concentration, H_2O_2 dosage, and initial pH of solution has been evaluated. Experimental results evidenced that the presence of the platinum allows the removal of the colour already in dark condition, enhancing the adsorption phase. Moreover, the highest photo-Fenton performances were obtained at natural solution pH (6), reaching the complete discoloration and mineralization after about 30 and 40 min of irradiation, respectively. No formation of sludge in the whole pH range investigated was observed.

1. Introduction

Dyes are one of the most used raw materials in food, pharmaceutical and textile industries and consequently related wastewaters contain residual dyes, which are not readily biodegradable. The generation of dye containing wastewater has a negative impact on receiving water bodies because colour impedes sunlight penetration in water, negatively affecting photo synthesis process(Gupta and Suhas, 2009). Photo synthesis is the first step of the food chain, and if impeded a general misbalance takes place in the ecosystems, because zooplankton and fish species feed from algae which cannot grow anymore, thus compromising the fishing based economy of villages and towns located at water shores (Arroyave Rojas et al., 2008).

Organic dyes in wastewater cause also carcinogenic and genotoxic effects on human health. Moreover, these compounds, because of their chemical nature, are considered as persistent in the environment (Arroyave Rojas et al., 2008). One of them is tartrazine, which is an azo dye whose presence in foods and drugs has been reported as a possible cause of asthma, urticaria, and angioedema (Modirshahla et al., 2007) and potentially phototoxic (Daneshvar et al., 2007).

Conventional treatments of dye effluents include biological oxidation and adsorption. But adsorption onto activated carbon only transfers the contaminant from the wastewater to the solid phase, thus requiring a subsequent sludge disposal (Golder et al., 2005).

Dyes removal using conventional oxidation methods is difficult, because a lot of pollutants, such as tartrazine, are bio-recalcitrant (Gupta et al., 2011). An interesting alternative for the removal of dyes from wastewater is represented by advanced oxidation processes, such as heterogeneous photocatalysis (Salem et al., 2009) and in particular the photo-Fenton process. The Fenton´s reaction is known as one of the most classic and powerful oxidation reactions in water. This reaction takes place without UV light, but its oxidation power can be increased by using UV or UV/visible irradiation (Photo-Fenton reaction).

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The oxidizing activity of the Fenton process results from the reaction between hydrogen peroxide and ferrous ion (Fe^{2+}) which subsequently produces free hydroxyl radicals (HO•) and the ferric ion (Fe^{3+}). Typically the process is carried out in homogeneous phase, and, as a consequence, the recovery of iron ions from the solution through additional separation steps is needed. Moreover, drawbacks of the homogeneous process, such as low pH (3) operating conditions, production of Fe containing sludge, and deactivation may be overcome by the use of structured catalysts (Vaiano et al., 2014). $LaFeO_3$ perovskite supported on honeycomb monoliths has been successfully investigated in photo-Fenton treatment of organic contaminants such as acetic acid (Sannino et al., 2011b).

In this work the influence of operating conditions in the heterogeneous photo-Fenton process with structured catalysts for the removal of tartrazine has been investigated. Reaction products were monitored by discoloration in liquid phase and total organic carbon (TOC) analysis.

2. Experimental

2.1 Structured catalysts characteristics

$LaFeO_3$ was supported on honeycombs by impregnation method starting from metal nitrate precursors. Thin walls (0.25 mm) of corundum monolithic support (triangular channels size = 2.5 mm) were treated with solutions of nitrates salts in the presence of citric acid and ethylene glycol. After drying at 110 °C, samples were calcined in air at 900 °C for 4 h inducing the formation of a grainy porous $LaFeO_3$ supported layer (Sannino et al., 2011a). The final $LaFeO_3$ content was 10.64 wt% (10La). Pt was supported on 10La by wet impregnation from H_2PtCl_6 aqueous solution. The final Pt loading was equal to 0.1 wt% (0.1Pt10La). These structured catalysts correspond to an optimized formulation obtained studying the photo Fenton removal of other contaminants, such as acetic acid (Sannino et al., 2011b).

2.2 Photo Fenton tests

The evaluation of the photo-Fenton activity was carried out by following the reaction of discoloration and mineralization of tartrazine. In a typical photo Fenton test, 160 ml of solution are continuously stirred inside a cylindrical photoreactor. Model aqueous solutions containing different initial concentration of tartrazine equal to 40, 60 and 80 ppm, corresponding to 17, 20 and 28 ppm of TOC respectively, at the spontaneous pH of the solution (pH 6), were used. An 8 W Hg vapors lamp emitting at 254 nm was used as light source. 13 g of the monolith catalysts were placed in the reactor. The system was kept in dark conditions for 3 h to reach the adsorption/desorption equilibrium of tartrazine on catalyst surface. After this time, the lamp was switched on. During the irradiation time, H_2O_2 was continuously added to the reactor (0.076 mol h^{-1}, 0.038 mol h^{-1} or 0.019 mol h^{-1}) through a peristaltic pump (Gilson). Photo-Fenton tests at different initial pH of solution (3, 6 and 9) were also performed.

The liquid samples were collected at fixed time and analyzed to determine the change of colour of aqueous samples, measured with a Perkin Elmer UV-Vis spectrophotometer at λ_{max} = 426 nm. TOC of the collected aqueous samples was measured from CO_2 obtained by catalytic combustion at T = 680 °C.

3. Results and discussion

The behaviour of tartrazine discoloration and mineralization for UV+10La+H_2O_2, UV+0.1Pt10La+H_2O_2 and UV+H_2O_2 is represented in Figure 1.

Dye discoloration has been reported as A/A_0 where A is the absorbance at reaction time t and A_0 is the initial absorbance, respectively. To quantitatively characterize the mineralization of azo dye, the TOC content of solution used in this study is defined as TOC/TOC_0 where TOC and TOC_0 are the TOC values at reaction time t and 0, respectively

In the case of UV+H_2O_2 alone the discoloration (Figure 1a) after 60 min of irradiation was 90 % and didn't change at higher irradiation time. In the presence of catalyst, a decrease of A/A_0 and TOC/TOC_0 (Figure 1b) was observed in dark conditions, during the first 2 h of the test and it was unchanged during the third hour, indicating that the adsorption equilibrium of dye on catalyst surface was reached.

From the Figure 1 it is clear the influence of the presence of platinum in the discoloration of the sample. In fact 0.1Pt10La sample allows to obtain a higher removal of the colour already in dark condition, enhancing the adsorption phase. Furthermore, with the same sample, the removal of colour is improved during the irradiation time.

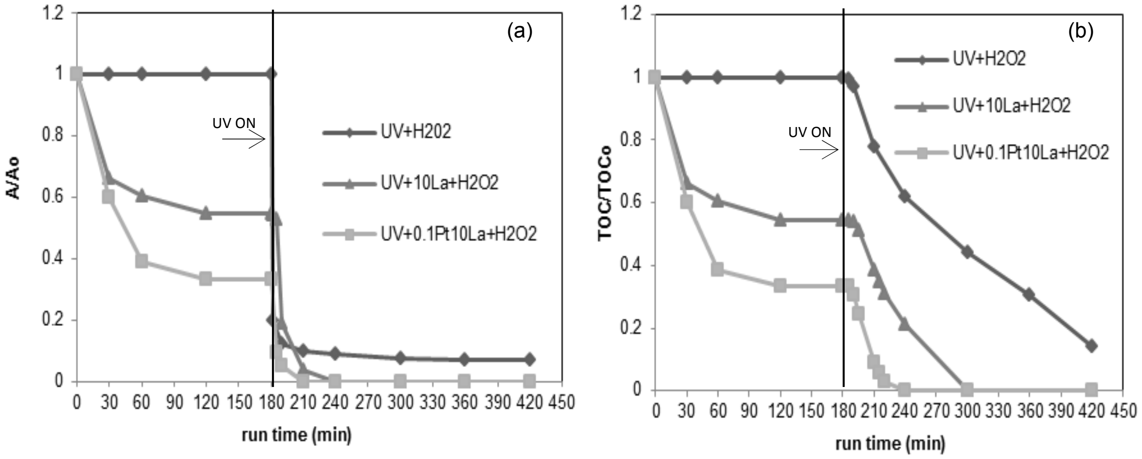

Figure 1: Behaviour of tartrazine discoloration (a) and mineralization (b) for different systems (UV+H_2O_2, UV+10La+H_2O_2, UV+0.1Pt10La+H_2O_2); initial dye concentration: 40 ppm; initial pH of solution: 6; H_2O_2 dosage: 0.038 mol h^{-1}

In Figure 1b it is reported the behaviour of tartrazine mineralization. Also in this case the presence of the platinum plays an important role in the removal of the organic substance, enhancing the potentiality of the catalyst in dark condition and assuring a total TOC removal after about 40 min of irradiation time. The efficiency improvement obtained in presence of Pt can be explained considering that $LaFeO_3$ is a semiconducting material (Tijare et al., 2012). Adding small amount of noble metals on the surface of a semiconductor, it is possible to suppress to some extent the charge carriers recombination rate by forming a Schottky barrier (Linsebigler et al., 1995). For this reason, the presence of Pt determined an increase of photo Fenton activity.

It is very important to underline that in the absence of catalyst the TOC removal rate is lower that means that oxidation intermediates still persist in the water solution (Rizzo, 2011).

The influence of initial dye concentration has been evaluated with 0.1Pt10La catalyst (Figure 2). The results show that 0.1Pt10La catalyst is able to bleach the aqueous sample for all the tartrazine concentration investigated (Figure 2a). The TOC removal (Figure 2b) started to decrease after about 5 min, when the discoloration degree is higher.

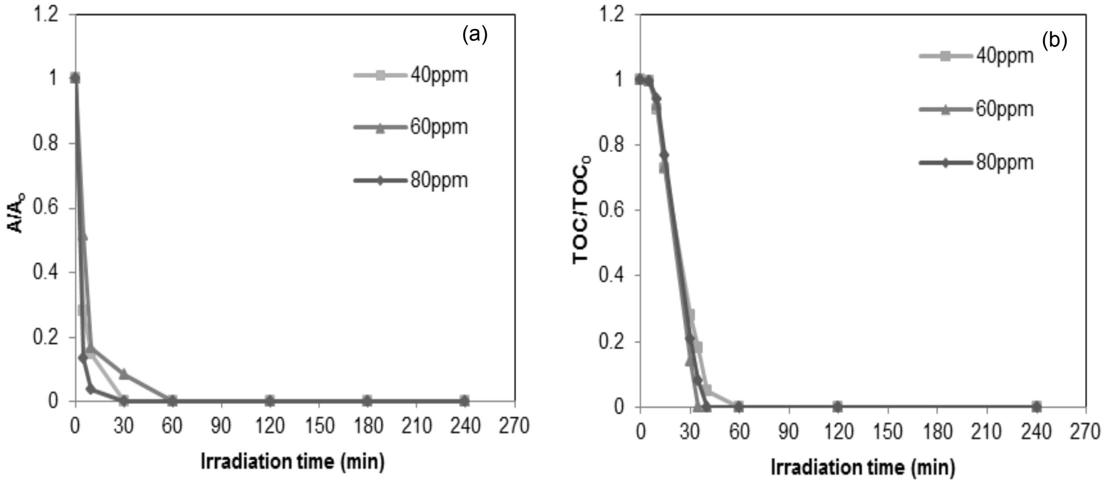

Figure 2: Influence of initial dye concentration on tartrazine discoloration (a) and mineralization(b); catalyst: 0.1Pt10La; initial pH of solution: 6; H_2O_2 dosage: 0.038 mol h^{-1}

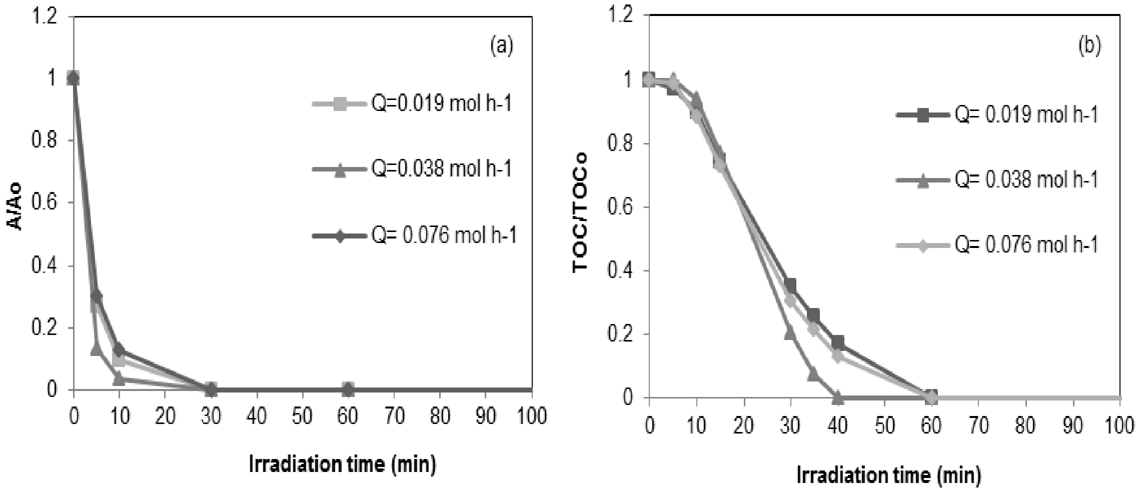

Figure 3: Influence of H_2O_2 dosage on tartrazine discoloration (a) and mineralization (b); catalyst: 0.1Pt10La; initial dye concentration: 80 ppm; initial pH of solution: 6

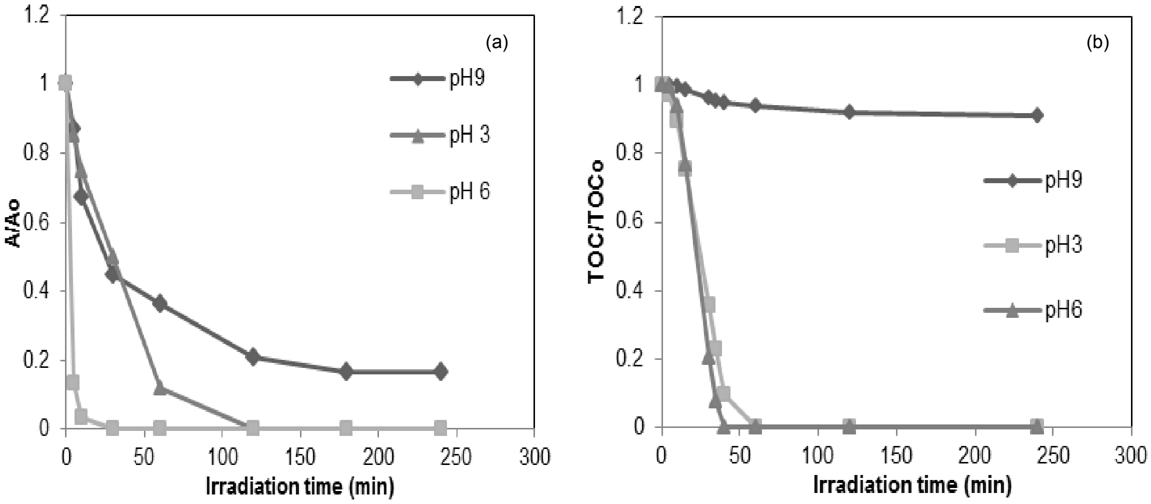

*Figure 4: Influence of different initial pH of solution on tartrazine discolora*tion (a) and mineralization (b); *catalyst: 0.1Pt10La; initial dye concentration: 80 ppm; initial pH of solution: 6; H_2O_2 dosage: 0.038 mol h^{-1}*

This phenomenon is due to the degradation of chromophore group (at λ_{max} = 426 nm), determining the discoloration of solution and the formation of reaction intermediates (dos Santos et al., 2014). After 5 min, TOC removal rate is similar for all the test conditions, indicating that also the reaction intermediates are converted into CO_2 and water.

As reported in literature, H_2O_2 dosage is one of the most important parameters controlling the efficiency of the photo-Fenton treatment of organic pollutants (Sannino et al., 2013). To understand the effect of H_2O_2 dosage on the decomposition of tartrazine, photo-Fenton test was carried in the presence of different H_2O_2 continuous dosage (Q) in the range of 0.019-0.076 mol h^{-1} (Figure 3).

Increasing the flow rate of H_2O_2 from 0.019 to 0.038 mol h^{-1}, an improvement in discoloration (Figure 3a) and mineralization (Figure 3b) of dye was achieved.

A further increase of H_2O_2 flow rate of (up to 0.076 mol h^{-1}) resulted in a worsening of the performance. These last results could be explained considering that, with the increase of H_2O_2 concentration, more hydroxyl radicals are generated which attack the dye molecules (Oancea and Meltzer, 2013).

However, higher concentration of H_2O_2 scavenges the radicals, making the process less effective (Vaiano et al., 2014).

In the photo-Fenton reaction, the pH value influences the generation of HO• and the oxidation performance of the process (Lu et al., 2010). In this study, the experiments were carried out under different pH values (3, 6 or 9), in the presence of 0.1Pt10La and with H_2O_2 continuous dosage (0.038 mol h^{-1}).

The effects of initial pH on discoloration and TOC removal are shown in Figure 4a and Figure 4b, respectively. The results demonstrate that the discoloration (Figure 4a) was 100 % after 30 min of irradiation at spontaneous pH of solution (pH=6).

On the contrary, the discoloration was 50 % under acidic condition (pH 3) and 55 % under basic condition (pH 9), after 30 min of irradiation.

Moreover, total TOC removal was achieved in 40 min under natural pH. At the end of the same time, 77 % TOC removal was obtained at pH 3, whereas it was about 5 % at pH 9.

The result obtained under acidic conditions is likely due to the fact that under the excess of H^+, i.e. at low pH condition, H^+ ions react with HO• and produce water subtracting hydroxyl radicals useful for the degradation of dye (Chiou et al., 2006). In basic condition, H_2O_2 accumulated in liquid medium increased with the irradiation time because under alkaline conditions H_2O_2 has a very high stability (Li et al., 2012), limiting in this way the production of hydroxyls radicals. As a consequence, photo-Fenton performance decreased (Vaiano et al., 2014).

In summary, experimental data at different initial pH of solution indicated that pH close to the neutral value is the better operating condition for the photo-Fenton removal of tartrazine.

4. Conclusions

In this work it has been evaluated the influence of operating conditions in the heterogeneous photo-Fenton process for the removal of tartrazine on structured catalysts. In particular, $LaFeO_3$ or $Pt/LaFeO_3$ perovskite supported on honeycomb monoliths have been tested. The results showed that the process is effective both for discoloration and mineralization of the dye.

It was also found that the presence of Pt/LaFeO3 dispersed on the monolithic structure enhances the removal of the colour already in dark condition, through the adsorption phase.

An interesting result was obtained by tuning the H_2O_2 dosage, a critical parameter controlling the efficiency of the photo-Fenton treatment for organic pollutants. Higher discoloration and mineralization rate has been achieved with a continuous H_2O_2 dosage of 0.038 mol h^{-1}.

A higher H_2O_2 flow rate has worsened the photo-Fenton performances because a high concentration of H_2O_2 scavenges the OH radicals, making the process less effective.

With respect to the effect of the initial pH of solution we found that at the spontaneous pH of the solution (pH 6), the complete discoloration and mineralization of tartrazine is achieved after 30 and 40 min of irradiation, respectively.

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