KINETIC STUDIES OF THE PHOTOCATALYTIC DEGRADATION OF TARTRAZINE

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Abstract—Kinetic studies of the photocatalytic degradation of tartrazine are carried out in a batch stirred reactor built in quartz at laboratory scale using TiO2 as catalyst and irradiating the photoreactor with ultraviolet light. An experimental design is performed using as independent variables or factors the catalyst concentration, the calcination temperature of the catalyst and the initial concentration of tartrazine. The obtained kinetic model indicates that the value of the kinetic constant, k, for a first order reaction is high, in the operating conditions studied. This is consistent with the low value of the adsorption constant, K. The experimental data fitted, with the Langmuir-Hinshelwood model, lead to an equation that, in the range of concentrations studied, allows the evaluation of photodegradation and describes well the photoreactivity results.

Keywords—tartrazine, photocatalysis, kinetics.

I. INTRODUCTION

Tartrazine is an artificial dye that is present in a wide variety of foods and drugs, having been reported to cause health problems at the level of bronchia and skin, in case of intensive ingest for the human (Colins-Wiliams, 1985; Dipalma, 1990; Giri et al., 1990; and Hess, 2002). It has been found as a contaminant of wastewaters that can not biodegrade quickly or easily. One of the processes that can be used to eliminate this contaminant is heterogeneous photocatalysis. This process is based on the direct or indirect absorption by a solid, usually a semiconductor, of photons of visible or UV light. When this semiconductor is illuminated, it can generate electron-hole pairs by promoting an electron from the valence band to the conduction band, thus leaving a gap in this band. These holes can absorb H2O or hydroxyl groups from the reaction medium and produce highly reactive hydroxyl radical species.

On the other hand, the electrons promoted to the conduction band, can reduce the molecular oxygen to peroxide anion to form hydrogen peroxide or organic peroxides in presence of organic compounds (Akpan and Hameed, 2009).

Radical hydroxyls are strong oxidizing agents that can degrade organic compounds or their intermediaries to reach final products such as CO2, H2O, N2. The photocatalysis process can be defined, then, as the acceleration of a chemical reaction by the presence of a catalyst which, when activated by absorption of light, accelerates the reaction process by interaction of the reactive with the electron-hole (e-, h+) pairs, being this a characteristic of semiconductor materials. In particular, for water recovery, the best catalyst is titanium oxide, TiO2. Bekbolet et al. (2002) in their studies of humic acid photocatalytic degradation performed the kinetic analysis in terms of a pseudofirst order kinetics (at low substrate concentrations) and a Langmuir-Hinshelwood kinetics (at high substrate concentrations). They showed that the reaction rate does not depend on the specific surface of the catalyst and that the morphological and crystallographic properties of the TiO2 can play an important role in the photocatalytic efficiency. Sobczynski et al. (2004) studied the photocatalytic decomposition of phenol by TiO2. They recommend the use of the initial reaction rate for kinetic studies, due to the existence of many competing reactions in the suspensions of TiO2 illuminated, and present a mechanism for the complete mineralization of phenol. Wu et al. (2006) studied basic dyes decomposition kinetics by nano-sized TiO2 suspension, at a pH of 9.8, by varying the agitation speed, TiO2 suspension concentration, initial dye concentration, temperature, and UV power intensity. They developed a kinetic model, based on the Langmuir–Hinshelwood model and the Lambert–Beer’s law, to successfully correlate the initial rates. Furthermore, Gondal et al. (2007) applied the photocatalysis process to compare the catalytic activity of four photocatalysts for the phenol degradation in water, irradiating with laser: WO3, NiO, Fe2O3 and TiO2. They obtained the maximum degradation using a WO3 catalyst and showed that the degradation process follows a first order kinetics. Moreover, Sham et al. (2009) performed the kinetic study of the photocatalytic degradation of the 2-chlorophenol, determining that the kinetics of the organic compound degradation fits satisfactorily with the Langmuir-Hinshelwood (L-H) model. Farias et al. (2009) focused their study on the kinetic modeling of the Fenton and photo-Fenton degradation of a pollutant (formic acid) in aqueous solution, for low iron concentrations. They derived a reaction rate expression from an accepted reaction mechanism by having explicitly into account the local volumetric rate of photon absorption. Friedmann et al. (2010) discussed the relevance of the parameters affecting the kinetics and mechanisms of photocatalysis for TiO2 water treatment. They determined that there is a strong interplay between pollutant structure, reactivity, and mode of interaction with cata-
lyst surface. They also determined that for each pollutant, a unique set of conditions may be needed for optimal performance. Zhang et al. (2011) studied the photocatalytic degradation kinetics of rhodamine B (RhB) by TiO$_2$-coated activated carbon (TiO$_2$/AC) catalyst under different reaction conditions (light intensity, TiO$_2$ content in TiO$_2$/AC and initial content of contamination). They found that the kinetics of RhB photodegradation follows the first-order rate law and could be described for a modified Langmuir–Hinshelwood model.

To our knowledge, literature on the subject does not account for reported studies of the kinetics of photodegradation of tartrazina over TiO$_2$. Consequently, the objective of this work is to study the kinetic of photocatalytic degradation of tartrazina, analyzing the effects of factors such as catalyst concentration, calcination temperature of the catalyst and initial concentration of tartrazina. The kinetic parameters were determined: kinetic constant $(k)$ and adsorption constant $(K)$.

II. METHODS

A. Kinetic Modeling

The kinetics of the photocatalytic degradation of many organic compounds in suspensions of TiO$_2$ under illumination has been modeled using the equation of Langmuir-Hinshelwood (L-H) (Valente et al., 2006). This model considers that the reaction rate is proportional to the photocatalyst surface fraction covered by the substrate ($\theta$).

$$r = -dC/dt = k \theta$$

with:

$$\theta = KC/(1+KC)$$

where $k$ is the reaction kinetic constant and $K$ is the constant of the reactant adsorption on the particles of TiO$_2$.

Substituting Eq. (1) in Eq. (2) yields:

$$r = -dC/dt = k KC/(1+KC)$$

Integrating Eq. (3):

$$\ln\left(C_o/C\right) + K(C_o - C) = k K t$$

where $t$ is the irradiation time.

Equation (3) is zero order when the concentration $C$ (mol/L) is high ($C > 5 \times 10^{-3}$). When the solution is diluted ($C < 10^{-3}$) the reaction is an apparent first-order reaction:

$$r = -dC/dt = k KC = k_{app} C$$

where $k_{app}$ is the apparent kinetic constant of a pseudo-first order reaction.

Integrating Eq. (5) is:

$$\ln\left(C_o/C\right) = k_{app} t$$

Plotting $\ln\left(C_o/C\right)$ versus $t$ it is possible to determine the apparent kinetic constant $(k_{app})$.

B. Experimental

The tartrazine solution was prepared using an Aldrich 99% reactive and H$_2$O of osmosis, in order to obtain a concentration of $4 \times 10^{-4}$ M. The aqueous solution was kept in a dark recipient, to avoid the contact with light.

The photocatalytic degradation of tartrazine was carried out in a quartz batch stirred reactor with a capacity of 150 cm$^3$, with side lighting using an Ultra Vitalux lamp of 300 W. TiO$_2$ synthesized in the laboratories of the National University of Salta and identified as Ti(II) was used as photocatalyst.

The catalyst was prepared by means of the sol-gel technique, using titanium isopropoxide (Aldrich 97%) as precursor. Hydrolysis of a 1M solution of titanium isopropoxide in isopropyl alcohol (Ciccarelli P.A) was carried out, using ultrapure H$_2$O (pH=6) as hydrolyzing media. The 1M solution of titanium isopropoxide was slowly added to the constantly stirred hydrolysis media. The used H$_2$O/Ti ratio used was 4. The addition of alcoxide produced the formation of titanium oxohydroxide, finally generating a whitish dispersion in the reactive medium. This suspension was stirred for 24 hours and the solid was then separated and washed by centrifugation.

The solid was calcined at 300 and 500 °C and was characterized by BET N$_2$ specific surface area and X-Ray Diffraction.

BET Nitrogen Specific Surface Area (SSA) measurement was made at a degassing temperature of 100ºC for 1 hour and was performed on a Flow Sorb II Micromeritics.

The phase identification of the samples was conducted with powder X-ray diffraction (XRD) Phillips PW-1140/00, using Cu Kα radiation.

The tartrazine solution and the photocatalyst were kept agitated by a magnetic stirring bar located at the bottom of the reactor, while the experiment lasted. The reaction temperature was kept constant at 35ºC.

Preliminary experiments were conducted to determine whether the sample could be degraded by the photocatalytic process and determine the levels of catalyst concentration, reaction time and initial concentration of organic compound. Two types blank of experiments were carried out, one non-illuminated with the addition of TiO$_2$ and another in absence of TiO$_2$ with illumination of the tartrazine solution. The experiments were programmed being selected as factors (independent variables) the following: concentration of the catalyst $(C_o)$, calcination temperature of the catalyst $(T_{calc})$ and initial concentration of the tartrazine $(C_o)$. Table 1 shows the levels of the factors used in the experiments.

Tarttrazine concentration used in the studies was chosen taking into account the average concentration normally used in commercial juice soft drinks.

The stirring speed was kept constant at 600 rpm after verifying that it has no significant effect on the degradation rate of the organic matter. The pH of the solution remained constant with an approximate value of 5 during the whole experiment.

$X$ was chosen as the only system response, the amount of degradation that experiences the organic compound with regard to its initial concentration, $C_o$, and was defined as:
Table 1: Factors and their values used in the experiments

<table>
<thead>
<tr>
<th>Factor</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of TiO₂ (g/L):</td>
<td>Cₛ</td>
</tr>
<tr>
<td></td>
<td>0.05; 0.1; 0.125; 0.25; 0.5; 1; 1.5</td>
</tr>
<tr>
<td>Calcination temperature of TiO₂ (°C): T_cal</td>
<td>300; 500</td>
</tr>
<tr>
<td>Initial concentration of tartrazine (mol/L): C₀</td>
<td>1x10⁻⁵; 2x10⁻⁵; 4x10⁻⁵</td>
</tr>
</tbody>
</table>

Figure 1. Effect of the photocatalyst concentration

\[
X = \frac{C₀}{C} - C
\]  

(7)

where C is the concentration of the dissolved organic compound in the solution at the given time. The definition of X given by Eq. (7), was the one used to follow the course of degradation. In order to accomplish this, at pre-programmed reaction time samples were taken from the reaction mixture, centrifuged to separate the catalyst and analyzed by UV spectrophotometry at a wavelength of 275 nm.

C. RESULTS AND DISCUSSION

**Characterization of TiO₂**

The specific surface area for samples calcined at 300°C was 154 m²·g⁻¹, and decreased to 46 m²·g⁻¹ when it was calcined at 500°C.

XRD studies show that samples treated at 300°C and 500°C were constituted by only one well identified phase, anatase, being more crystalline at 500°C. These results could explain the difference in reactivity of the solid calcined at different temperatures. With increasing firing temperatures (500°C), the intensity and sharpness of the TiO₂ anatase peaks grow, indicating an increase in the crystallinity and in the particle size, which is in accordance with the results of specific surface area. Our results show that photocatalytic increases with calcination temperature, that is to say with the increase of the crystalline degree.

**Effect of the concentration of TiO₂**

Figure 1 shows the effect of the concentration of the photocatalyst (TiO₂), calcined at 500 °C, on the tartrazine degradation of initial concentration 4 x 10⁻⁵ mol/L.

The effect of the photocatalyst concentration begins to become important when increasing the solid concentration. For example to reach 85 % degradation of the organic compound it takes 120 min when the photocatalyst concentration is Cₛ = 0.05 g/L, 105 min when Cₛ = 0.1 g/L, 50 min when Cₛ = 0.2 g/L, 20 min when Cₛ = 1 g/L and 15 min when Cₛ = 1.5 g/L.

**Effect of the initial concentration of the organic compound**

The data to analyze the influence of the initial concentration of the tartrazine on its degradation rate are plotted in Fig. 2, for a TiO₂ concentration of 0.2 g/L, calcined at 500°C.

It can be observed that increasing the initial concentration of the organic compound, its conversion degree decreases for a given time. For example, when the initial concentration of tartrazine is 2 x 10⁻⁵ its photodegradation is 33 % lower than when the initial concentration is 1 x 10⁻⁵, 10 minutes after starting the process. This agrees, essentially, with the general theoretical aspects of the photocatalytic reactions.

**Effect of the calcination temperature of the TiO₂**

The influence of the calcination temperature of TiO₂ on the degradation of the organic substance, at a TiO₂ concentration of 0.1 g/L is shown in Fig. 3.

It can be seen that although an increase in the calcination temperature of TiO₂ increases the degradation of the organic component, this effect is not very significant, perhaps because at 300 and 500°C of calcination temperature the crystalline structure does not change, being the anatase phase the only one detected.
Table 2: Values of the kinetic constant ($k_{ap}$)

<table>
<thead>
<tr>
<th>$C_a$ (g/L)</th>
<th>$C_a \times 10^{-3}$ (mol/L)</th>
<th>$k_{ap}$ (L/min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>1</td>
<td>0.156</td>
<td>0.9615</td>
</tr>
<tr>
<td>0.250</td>
<td>1</td>
<td>0.163</td>
<td>0.9674</td>
</tr>
<tr>
<td>0.250</td>
<td>2</td>
<td>0.127</td>
<td>0.9891</td>
</tr>
<tr>
<td>0.500</td>
<td>1</td>
<td>0.140</td>
<td>0.9976</td>
</tr>
<tr>
<td>0.500</td>
<td>2</td>
<td>0.153</td>
<td>0.9870</td>
</tr>
<tr>
<td>1.500</td>
<td>4</td>
<td>0.131</td>
<td>0.9966</td>
</tr>
</tbody>
</table>

Table 3: Kinetic Parameters

<table>
<thead>
<tr>
<th>$C_a$ (g/L)</th>
<th>$C_a \times 10^{-3}$ (mol/L)</th>
<th>$r_o$ (mol/min)</th>
<th>$K$ (L/mol)</th>
<th>$k$ (mol/min)</th>
<th>$K_a$ (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>1</td>
<td>0.156</td>
<td>0.156</td>
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<tr>
<td>0.250</td>
<td>1</td>
<td>0.163</td>
<td>0.163</td>
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<tr>
<td>0.250</td>
<td>2</td>
<td>0.127</td>
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<tr>
<td>0.500</td>
<td>1</td>
<td>0.140</td>
<td>0.140</td>
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</tr>
<tr>
<td>0.500</td>
<td>2</td>
<td>0.305</td>
<td>0.153</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.500</td>
<td>4</td>
<td>0.523</td>
<td>0.131</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Eq. (3) Since the initial concentrations are very low, the product $KC<<1$ and the equation becomes:

$$r_o = k K C_a = k_{ap} C_o$$  \hspace{1cm} (10)

This equation describes the degradation rate for a first order reaction. Consequently it is possible to infer that, since the initial reaction rate ($r_o$) increases with the initial concentration ($C_o$), the increase in concentration in the product $k_{ap} C_o$ is more significant than the variation in the values of $k_{ap}$.

**III. CONCLUSIONS**

Heterogeneous photocatalysis is an alternative for the degradation of organic compounds such as tartrazine. Degradation rate is high and the process shows good efficiency. Increasing the initial concentration of the photocatalyst and its calcination temperature increases the degradation rate, being the initial concentration of TiO$_2$ the most significant effect. This is because although both catalysts have the same phase, the degree of crystallinity is very different being more crystalline catalysts calcined at 500 °C.

Kinetic studies results show that the kinetic model for the photodegradation of tartrazine corresponds with that of an L-H model and the equation for the theoretical evaluation of photodegradation, under the operating conditions studied is $1/r_o = 6.11/C_a + 0.477$. When increasing the initial concentration of tartrazine, a significant increment in the initial reaction rate happens. This effect is true for various concentrations of photocatalyst studies. The obtained kinetic model indicates that the kinetic constant, $k$, of the first order reaction, is high. It is consistent with the law value of the adsorption constant, $K$.

**REFERENCES**


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