

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, accele-

rates 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 TiO₂-coated activated carbon (TiO₂/AC) catalyst under different reaction conditions (light intensity, TiO₂ content in TiO₂/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 tartrazine over TiO₂. Consequently, the objective of this work is to study the kinetic of photocatalytic degradation of tartrazine, analyzing the effects of factors such as catalyst concentration, calcination temperature of the catalyst and initial concentration of tartrazine. 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 TiO₂ 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 (θ).

$$r = -dC/dt = k\theta \quad (1)$$

with:

$$\theta = KC/(1+KC) \quad (2)$$

where k is the reaction kinetic constant and K is the constant of the reactant adsorption on the particles of TiO₂.

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

$$r = -dC/dt = kKC/(1+KC) \quad (3)$$

Integrating Eq. (3):

$$\ln(C_o/C) + K(C_o - C) = kKt \quad (4)$$

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:

$$r = -dC/dt = kKC = k_{ap}C \quad (5)$$

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

Integrating Eq. (5) is:

$$\ln(C_o/C) = k_{ap}t \quad (6)$$

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

B. Experimental

The tartrazine solution was prepared using an Aldrich 99% reactive and H₂O of osmosis, in order to obtain a concentration of 4×10^{-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 cm³, with side lighting using an Ultra Vitalux lamp of 300 W. TiO₂ 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 (Cicarelli P.A) was carried out, using ultrapure H₂O (pH=6) as hydrolyzing media. The 1M solution of titanium isopropoxide was slowly added to the constantly stirred hydrolysis media. The used H₂O/Ti ratio used was 4. The addition of alc oxide 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 N₂ specific surface area and X-Ray Diffraction.

BET Nitrogen Specific Surface Area (SSA) measurement was made at a degassing temperature of 100°C 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 K α 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 35°C.

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 TiO₂ and another in absence of TiO₂ with illumination of the tartrazine solution. The experiments were programmed being selected as factors (independent variables) the following: concentration of the catalyst (C_s), calcination temperature of the catalyst (T_{cal}) and initial concentration of the tartrazine (C_o). Table 1 shows the levels of the factors used in the experiments.

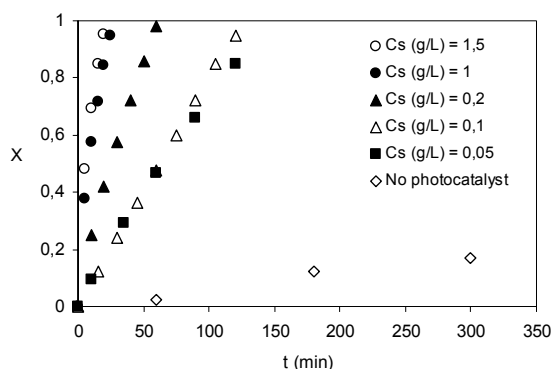
Tartrazine concentration used in the studies was chosen taking into account the average concentration normally used in commercial juice soft drinks.

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

Concentration of TiO ₂ (g/L): C _s	0.05 ; 0.1; 0.125; 0.2; 0.25 ; 0.5; 1; 1.5
Calcination temperature of TiO ₂ (°C): T _{cal}	300; 500
Initial concentration of tartrazine (mol/L): C _o	1x10 ⁻⁵ ; 2x10 ⁻⁵ ; 4x10 ⁻⁵

**Figure 1.** Effect of the photocatalyst concentration

$$X = \frac{C_o - C}{C_o} \quad (7)$$

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 photoactivity 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 C_s = 0.05 g/L, 105 min when C_s = 0.1 g/L, 50 min when C_s = 0.2 g/L, 20 min when C_s = 1 g/L and 15 min when C_s = 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.

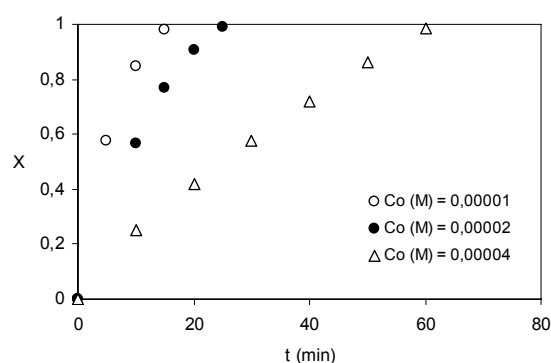
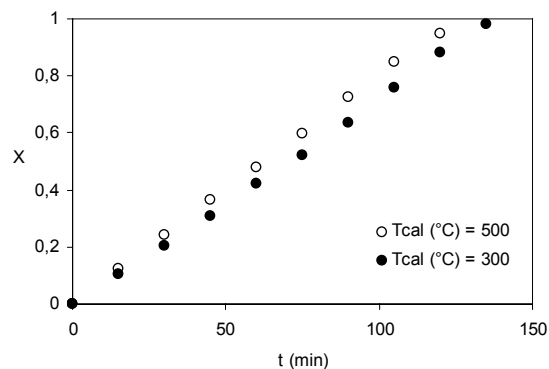
**Figure 2.** Effect of the initial concentration of the organic compound**Figure 3.** Effect of the calcination temperature of the photocatalyst

Table 2: Values of the kinetic constant (k_{ap})

C_s (g/L)	$C_o \times 10^5$ (mol/L)	k_{ap} (L/min)	R^2
0.125	1	0.156	0.9615
0.250	1	0.163	0.9674
0.250	2	0.127	0.9891
0.500	1	0.140	0.9976
0.500	2	0.153	0.9870
1.500	4	0.131	0.9966

Table 3: Kinetic Parameters

C_s (g/L)	$C_o \times 10^5$ (mol/L)	r_o (mol/min)	k_{ap} (L/min)	k (mol/min)	K (L/mol)
				2.098	0.078
0.125	1	0.156	0.156		
0.250	1	0.163	0.163		
0.250	2	0.255	0.127		
0.500	1	0.140	0.140		
0.500	2	0.305	0.153		
1.500	4	0.523	0.131		

Table 2 shows the k_{ap} values obtained for initial concentrations of tartrazine of 1×10^{-5} , 2×10^{-5} and 4×10^{-5} mol/L and concentrations of photocatalyst of 0.125; 0.250; 0.5 and 1.5 g/L, calcined at 500°C. There are also the values of R^2 for lineal regressions.

It can be observed that the system presents a lineal behavior, indicating that the reaction of photodegradation of tartrazine follows a first order kinetics.

Multiplying the reaction constant (k_{ap}) by the initial concentration (C_o) yields the initial reaction rate (r_o) of first order.

In this work the kinetic constant (k) and the adsorption constant (K) were calculated using the L-H model, considering the initial reaction rate and concentration, thus following:

$$r_o = -dC/dt = k K C_o / (1 + K C_o) \quad (8)$$

This equation can be transformed into a lineal form:

$$\frac{1}{r_o} = \frac{1}{k K C_o} + \frac{1}{k} \quad (9)$$

Plotting of $1/r_o$ versus $1/C_o$, the values of the kinetic constant (k) and the adsorption constant (K) are obtained. A summary of the obtained kinetic parameters is presented in Table 3.

As shown in Table 3, the photocatalytic degradation rate (r_o) initially increases with increasing TiO_2 dosages. However, at higher TiO_2 dosages, r_o decreases. The first effect is likely to be due to the increase of the total surface area (or number of active sites) of the photocatalysts available for photocatalytic reaction. When TiO_2 is overdosed, the intensity of light penetration is attenuated and light scattering is increased, which counteracts the positive effect coming from the dosage increment and therefore the overall performance is reduced.

It can be also observed, in Table 3, that the initial degradation rate (r_o) of tartrazine increases with the increasing initial concentration (C_o). This effect is true for the various concentrations of photocatalyst studied. A better analysis of this result may be done considering

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

$$r_o = k K C_o = k_{ap} C_o \quad (10)$$

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 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 $1/r_o = 6.11/C_o + 0.477$. 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 low value of the adsorption constant, K .

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