

Capítulo 2 Degradación de piridina con un receptor fotocatalítico de película descendente utilizando como catalizador TiO₂-Au

Chapter 2 Pyridine degradation with a falling film photocatalytic receptor using TiO₂-Au as catalyst

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Resumen

Se estudió la degradación de la piridina (C_5H_5N) utilizando nanopartículas caseras de TiO_2 dopadas con Oro en un reactor recirculante de película descendente (FRD) irradiado con luz UV y luz Natural. Las pruebas requerían encontrar las condiciones adecuadas para una degradación favorable y trabajar en diferentes condiciones para la descomposición a diferentes concentraciones. Los parámetros de operación utilizados son la concentración de piridina (5, 10, 20, 30, 40 y 50 ppm), el caudal de agua residual sintética (1 L/min, 0,5 L/min y 0,2 L/min), pH de agua residual (3-9) y el tipo de luz irradiada. (luz ultravioleta y luz natural) han sido investigados por sus efectos sobre la degradación de piridina. Se logró una degradación de piridina del 85% dentro de las 24 horas de operación; Se manipularon a un pH de 7 y un caudal de 1 L/Min, con luz ultravioleta. Los resultados experimentales revelaron que se podía observar una mejor degradación de la piridina con luz ultravioleta con el catalizador de TiO_2 dopado con Au.

Degradación, Concentraciones, Parámetros, Experimental, Condiciones, Aguas Residuales

Abstract

The degradation of pyridine (C_5H_5N) was studied using homemade TiO_2 nanoparticles doped with Gold in a recirculating falling film reactor (FRD) irradiated by UV light and Natural light. The tests required finding the right conditions for favorable degradation and working under different conditions for decomposition at different concentrations. The operating parameters used are the concentration of pyridine (5, 10, 20, 30, 40, and 50 ppm), the flow rate of synthetic wastewater (1 L/min, 0.5 L/min, and 0.2 L/min), pH of wastewater (3-9) and the type of light irradiated. (UV light and nat. light) have been investigated for their effects on pyridine degradation. Pyridine degradation of 85% was achieved within 24 hours of operation; They were handled at a pH of 7, and a flow rate of 1 L/Min, with UV light. The experimental results revealed that a better degradation of Pyridine with UV light could be seen with the TiO_2 catalyst doped with Au.

Degradation, Concentrations, Parameters, Experimental, Conditions, Wastewater.

1. Introduction

Water pollution is a problem that we all experience today since it occurs not only in industrialized or less industrialized countries but also affects every one of the sectors of each population. Many think that this resource, which is essential for us, will always be there, but the truth is that this is not the case since we are unaware of the acts or activities we carry out with this resource (Guadarrama-Tejas et al., 2016). Therefore, procedures are required to mineralize this class of contaminant completely; Among the treatment alternatives are photocatalytic processes that mineralize organic compounds to other species such as CO_2 and H_2O (Ibhadon, A. O., & Fitzpatrick, P. 2013).

Advanced oxidation processes (POA) have received increasing attention in the research and development of wastewater treatment technologies in recent decades. These processes (e.g., cavitation, photocatalytic oxidation, Fenton chemistry, ozonation) have been applied successfully for the removal or degradation of recalcitrant contaminants or used as pretreatment to convert pollutants to shorter-chain compounds that can then be treated by conventional or biological methods (JL WANG & LJ XU, 2012).

The advantages of POAs are (Giraldo *et al.*, 2004):

- Potential capacity to carry out deep mineralization of organic contaminants and oxidation of inorganic compounds to carbon dioxide and ions (chlorides, nitrates).
- Reactivity with most organic compounds, a fact that is mainly interesting if you want to avoid the presence of potentially toxic by-products present in the original contaminants that other methods ca.
- Decomposition of reagents used as oxidants into harmless products.

1.1 Heterogeneous photocatalysis

According to the IUPAC Gold Book, photocatalysis is the “change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible, or infrared radiation in the presence of a light-absorbing substance the photocatalyst is involved, in the chemical transformation of the reactants present in the reaction”. A photocatalyst is defined as a “catalyst capable of producing, upon absorption of light, chemical transformations of the reaction partners. The excited state of the photocatalyst repeatedly interacts with reaction partners to form reaction intermediates and is regenerated after each cycle of such interactions” (IUPAC, 1997). In heterogeneous photocatalysis, the photocatalyst is solid, with the reactions occurring at the interface between the phases, i.e., solid-liquid or solid-gas.

Heterogeneous photocatalysis takes place on the surface of solid semiconductor materials, which act to absorb photon energy and provide active sites for the adsorption of reagents. In semiconductor photocatalysis, the immediate reactions are oxidation or reduction electrochemical reactions that involve the transfer of holes and electrons from the photoexcited semiconductor (Byrne J. A, 2015).

1.2 Physical factors that influence photocatalytic degradation.

The processes of heterogeneous photocatalysis by oxidation-reduction methods can be influenced by various parameters (both qualitatively and quantitatively) affecting the speed and overall performance of the reaction in a determining way (Blanco *et al.*, 2001); some of the most important are:

1. Absorption of light: The absorption of photons with energy greater than E_g (photoexcitation) promotes electrons from the valence band to the conduction band, and for each promoted electron, a hole is produced in the valence band (Blanco *et al.*, 2001).
2. Temperature: As the temperature increases, the speed of all the reactions that occur in the system increases (except for the photogeneration of electron-hole pairs), but on the other hand, an increase in the reaction temperature decreases the solubility of oxygen in the reaction mixture, so a low concentration of dissolved oxygen will cause a decrease in the capture of electrons from the catalyst surface (Mathews N. R. *et al.*, 2009; Aguilar *et al.*, 2012).
3. PH: Studies show that pH has a notable impact on the degradation of the organic compound, which can be achieved through its manipulation, a higher reaction speed, and a higher percentage of degradation, among other modifications to the system (Candal *et al.*, 2001).
4. Radiant energy flow: Where the reaction speed (r) is proportional to the radiant flow, which confirms the photoinduced nature of the activation of the catalytic process (Hermann, 2005).
5. Catalyst: Since a catalytic reaction occurs at the fluid-solid interface, a large interface area may be helpful or essential to achieving a significant reaction rate. In the case of many catalysts, this area is due to a porous structure; the solid contains many delicate pores, and the surface of those pores provides the area needed to have a high reaction rate (Krysa J *et al.*, 2006; Fogler, 2011).

2 Description of the method

2.1 Pyridine

The contaminant to be studied in the degradation mechanism is pyridine, an essential chemical compound with tremendous applications in various fields. Therefore, it seeks to study the degradation mechanism of a said polluting compound; with this proposed method, several beneficial factors will be combined, such as the use of sunlight and catalysts, to study the degradation parameters and advantageous kinetics for the degradation of the pyridine. The pyridine solution was prepared in a 6 L container with different pyridine concentrations of 5, 10, 20, 30, 40, and 50 ppm. The procedure is as follows in a test tube, up to 1 L of water, then take 20 ppm of a pure pyridine solution using a micropipette, pour it into the test tube that contains 1 L of water, and deposit it in a 6 L container. Said procedure is repeated until the 6 L container is filled, giving a proportion that in each 1 L of water that is poured into the container, there is 20 ppm of pyridine. Once the container is complete, it is shaken manually to mix the water-pyridine.

2.2 TiO₂-Au catalyst

For the preparation of the TiO₂-Au catalyst, the procedure was carried out in the following way, a solution of titanium oxide was prepared with 20 g of titanium oxide with 200 ml of water; it was impregnated using a brush the key to the clay plates. The resulting material was dried at room temperature for one h; then, the material was calcined at 550 °C for 4 hours in a muffle. Gold deposition on TiO₂ was performed, making a solution of 0.003 g of gold in 3 L of water. TiO₂-impregnated plates were placed in a falling film reactor with recirculation. The gold key is deposited in the reactor and is allowed to recirculate for 1 hour under UV light. After gold deposition on TiO₂, it is left to dry at room temperature for one h to calcinate the plates at 550 °C for 1 hour in a muffle.

2.1 Recirculating Falling Film Reactor (FFR)

For the degradation of pyridine, a falling film reactor with recirculation (FFR) was used, whose system structure is rectangular in stainless steel that works as a support for the FFR; this is a support 120 cm high, 80 cm wide. long and 30 cm wide.

The FFR has a container with a maximum capacity of 10 L located below the plates where the solution for the degradation tests is deposited. This container is connected to a pump to let the solution to be degraded flow over the descending plates. After the solution flows through the plates, it passes through an outlet that will recirculate it to the container so that this solution can be recirculated in the system. Clay plates placed on a support inclined at an angle of 25° are impregnated with TiO₂ and Au metal nanoparticles. Above the plates is a stainless-steel lid containing 2 natural light lamps and one U.V light lamp below it, connected to a plug circuit to alternate their uses.

Table 2.1 Reactor characteristics

Stainless steel bracket	
Height	120 cm
Length	80 cm
Width	30 cm
Clay plates	
Length	56 cm
Width	30 cm
Thickness	1.2 cm
Plate area	1.68 m ²
Generalities	
Number of natural light lamps	4
Number of UV light lamps	2

2.4. Degradation tests

The degradation tests were carried out in a falling film reactor with a recirculation solution of 5, 10, 20, 30, 40, and 50 ppm in 6 L of water. The tests require finding the right conditions for favorable degradation, so they will work at different conditions before starting to degrade them at different concentrations.

The conditions to be carried out are the following:

Flow: 1 L/min, 0.5 L/min and 0.2 L/min

pH: Natural, Base: 3, Acid 8.5 (nat. light) and 9 (UV light)

Light: Natural and UV

The pyridine degradation test was carried out for 24 continuous hours. During the reaction time, samples were taken every 3 hours, starting with time 0; the samples were taken directly from the recirculation tube of the reactor.

2.5. Degradation runs

In this stage, the experimental runs of pyridine degradation were carried out using the Falling Film Reactor with recirculation. The initial conditions of the first degradation run were a concentration of 20 ppm of pyridine, with a flow rate of 1 L/min, pH: Natural, with natural light.

The conditions will change depending on which is more favorable during the first degradations, the flow being first with the conditions of 1 L/min, 0.5 L/min, and 0.2 L/min once the best flow for recirculation in the reactor has been observed. Proceed to pH with pH conditions: Nat, Base: 3, Acid 8.5 (Natural light), and 9 (UV light). Once the previous conditions have been evaluated, the degradations will be carried out with several concentrations of pyridine (5, 10, 30, 40, 50); this procedure will be repeated for natural and UV light.

2.6. Sample analysis

During the degradation, the samples were taken and stored in clean, dry, and labeled plastic vials for later analysis in the UV–VIS spectrometer. Initially, a pyridine sample was scanned to identify the maximum absorption peak and wavelength. Scans were made of each sample taken from 200 to 400 nm wavelengths.

3. Results and discussion

Figure 3.1 shows the variation in concentrations suffered by pyridine when exposed to degradation with Nat. light and the use of $\text{TiO}_2\text{-Au}$ as a catalyst in a falling film reactor. How can we observe these conditions if they affect the initial concentration of pyridine concerning the reaction time. In the 24 h of reaction, the initial concentration of the 50-ppm concentration begins to vary significantly with degradation of 80.3% of the total concentration.

If we compare Figure 4.15, the degradation percentage of the first 24 h of the reaction, the concentration of 50 ppm begins to degrade up to a degradation percentage of 82.5% with UV light with stopping it with natural light was 80.2% of the concentration 50 ppm.

So, in the case of concentrations, the difference in the percentage of light degradation with UV was slightly more significant than that of more considerable light, but it indicates the. Still, the catalyst is a good option for pyridine degradation for both diffusion conditions.

Figure 3.1 Degradation of pyridine with different initial concentrations exposed to natural light against time using $\text{TiO}_2\text{-Au}$ as a catalyst

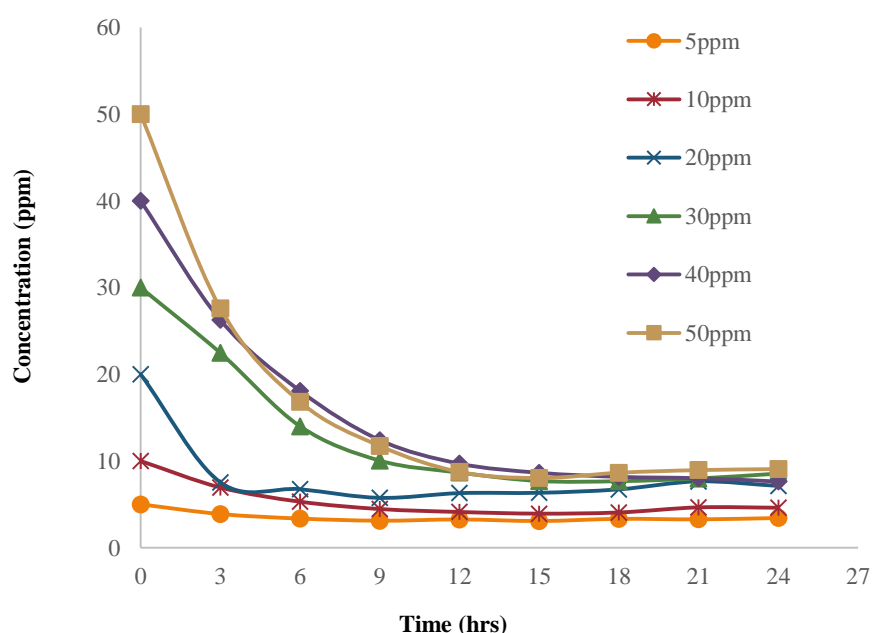
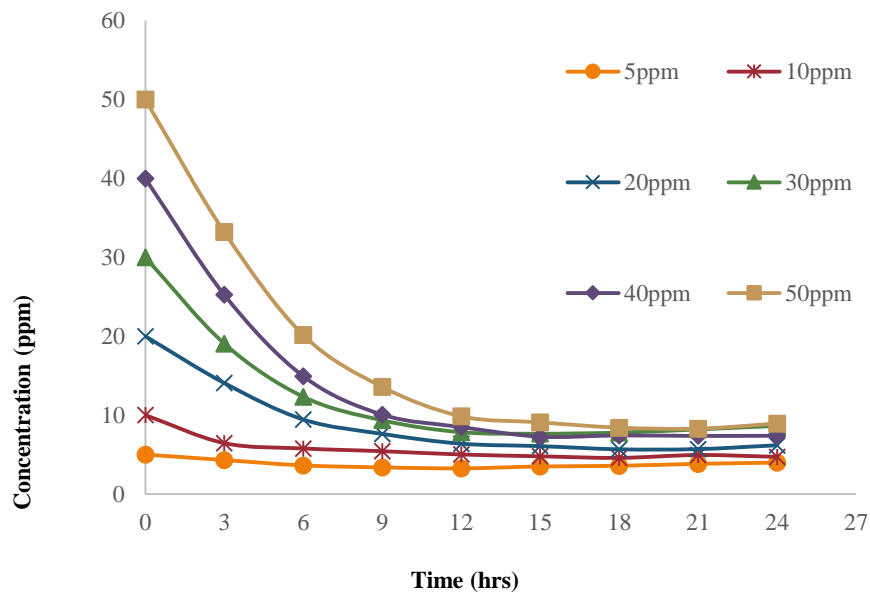


Figure 3.2 Degradation of pyridine with different initial concentrations of exposure to UV light. Against time using TiO₂-Au as a catalyst



Various studies show that the first step in the photocatalytic degradation of organic compounds follows first-order or zero-order kinetics. The results clearly show that the reaction rate depends fundamentally on the concentration of the reactant, so it can be said that it follows first-order kinetics or is similar to first-order kinetics:

$$r_a = -\frac{dca}{dt} = Kc \quad (3.1)$$

By integrating the velocity equation, the following function is obtained:

$$\ln(C/C_0) = -K_{apparent}t \quad (3.2)$$

Which is equivalent to:

$$C = C_0 e^{-K_{apparent}t} \quad (3.3)$$

Then in Figure 3.3 - 3.4, the logarithms of the log of the normalized concentrations (C/C_0) were plotted against reaction time. The values of the apparent reaction constant were obtained by linear regression.

Figure 3.3 Kinetics of the pyridine reaction using TiO₂-Au as a catalyst with natural light.

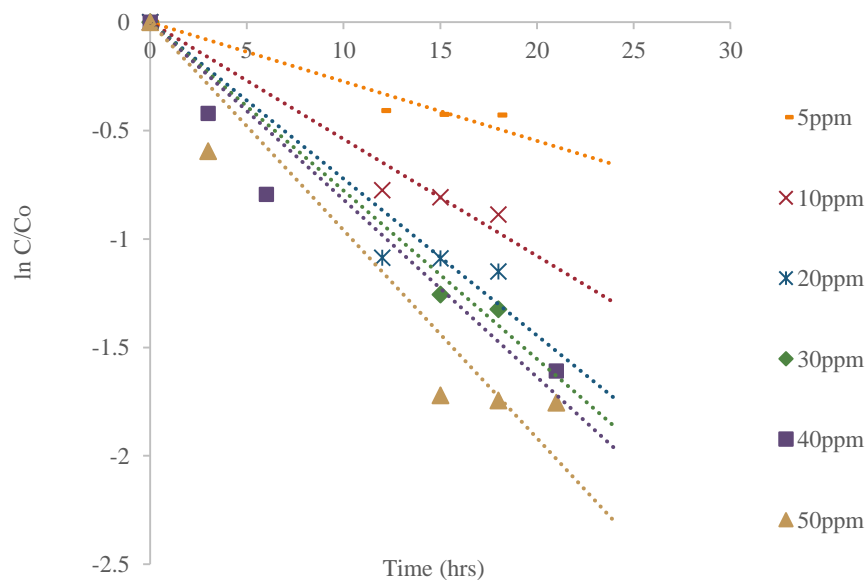
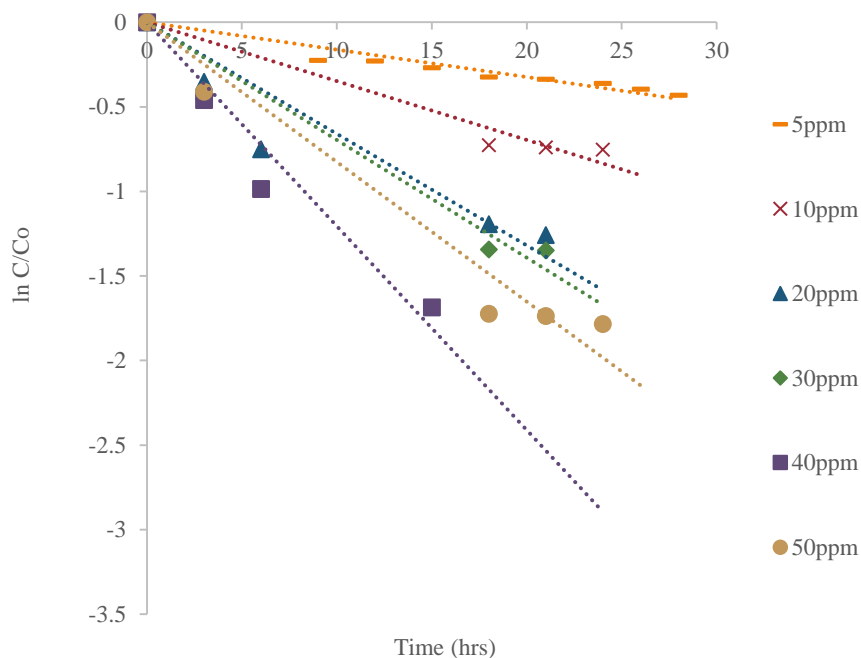


Figure 3.4 Kinetics of the pyridine reaction using TiO₂-Au as a catalyst with UV light



These data are necessary to obtain the kinetic constants $K_{apparent}$ obtained from the line equation. Figures 3.5 - 3.6 show the photocatalytic degradation of pyridine, and this follows a zero-order reaction since the reaction rate is lower as the concentration increases, according to the Langmuir-Hinshelwood model.

Figure 3.5 Graphic representation of $1/Co$ vs $1/ra|_{t=0}$ according to the linearization of the Langmuir-Hinshelwood model (TiO₂-Au with natural light)

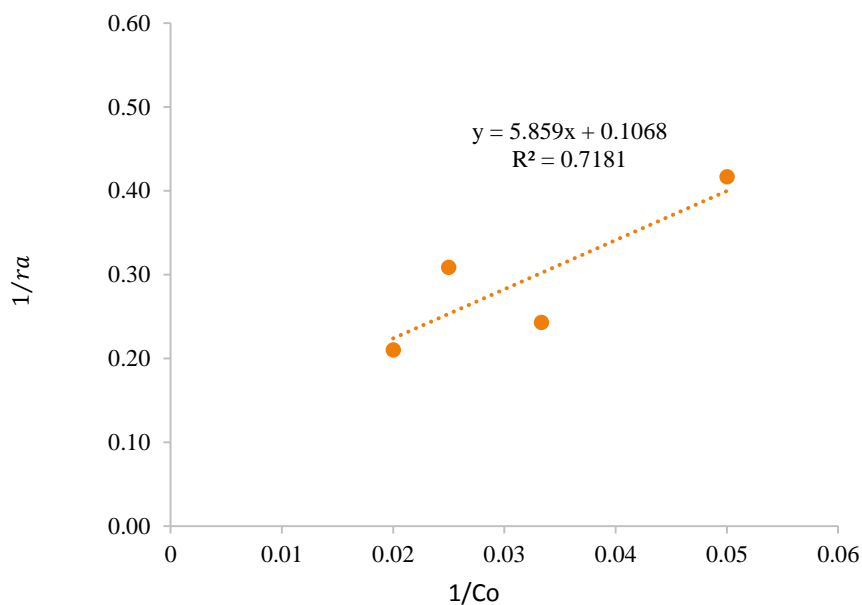


Figure 3.6 Graphic representation of $1/Co$ vs $1/ra|_{t=0}$ according to the linearization of the Langmuir-Hinshelwood model (TiO₂-Au with UV light)

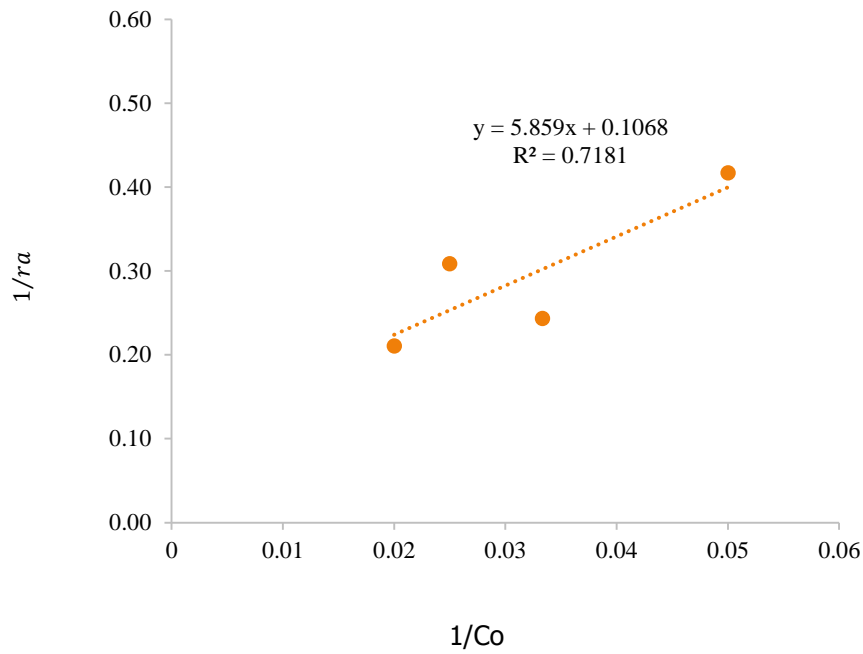


Figure 3.7 - 3-8 shows the experimental data for the initial reaction rate as a function of the initial concentration. The velocity versus Co curve obtained from equation 3.4 is also shown. As can be seen, there is a good prediction of the experimental data from equation 3.4 (Fogler, 2001; Moctezuma *et al.*, 2006; Mathews N. R. *et al.*, 2009) of the form:

$$\frac{1}{r_{a|t=0}} = \frac{1}{K_1 C_0} + \frac{K_2}{K_1} \quad (3.4)$$

Figure 3.7 Graphic representation of the evaluation of the Langmuir-Hinshelwood model, having calculated k_1 and k_2 (with natural light)

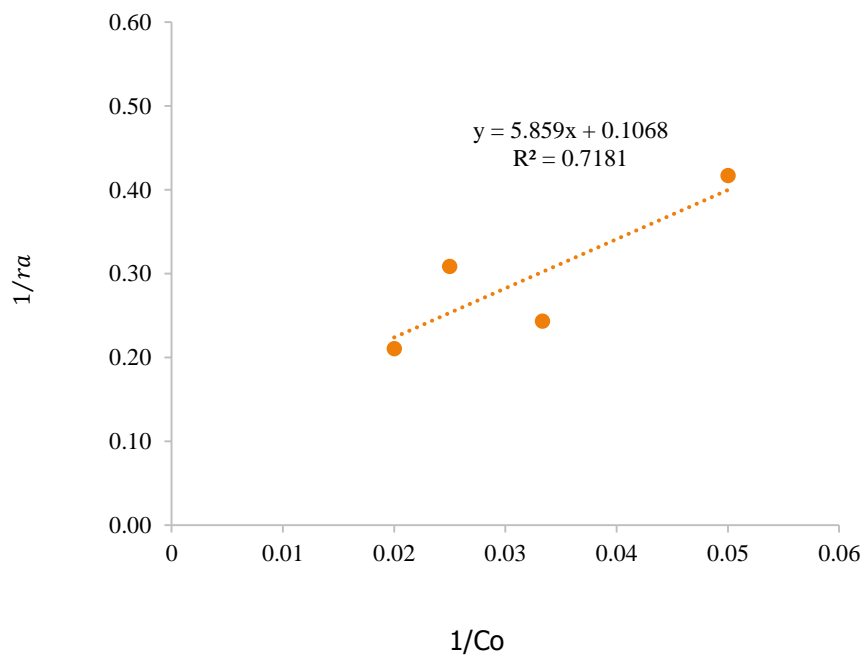
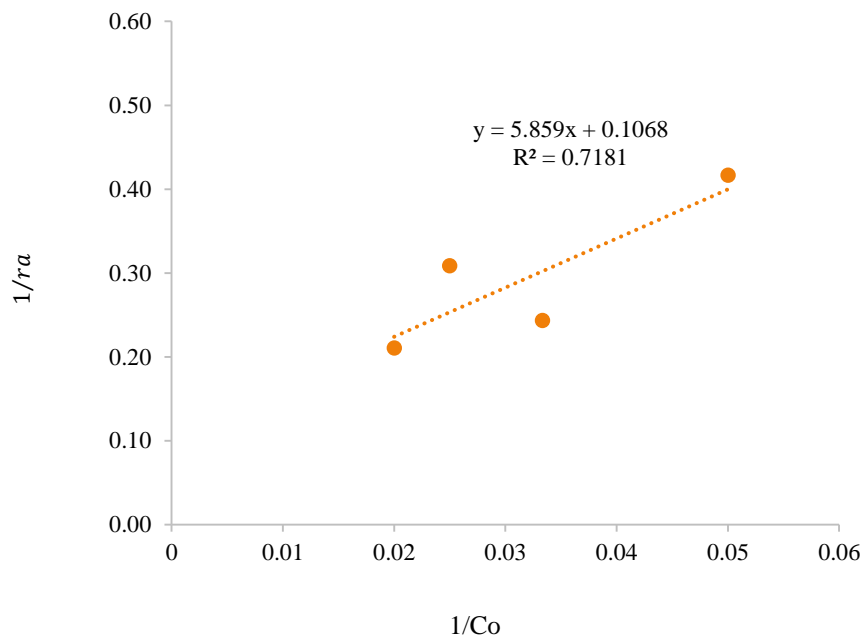


Figure 3.8 Graphic representation of the evaluation of the Langmuir-Hinshelwood model, having calculated k_1 and k_2 (with UV light)



4. Conclusions

According to the results obtained, it can be concluded that using photo deposition can obtain better results with $\text{TiO}_2\text{-Au}$ as a catalyst in this research, and it is effective in the degradation of recalcitrant pollutants. Regarding the comparison with similar works, it can be specified that the works carried out in the photocatalytic treatment using waste or residual contaminants obtained maximum degradation percentages of 70-90% using TiO_2 elaborated in those investigations, which, compared to this thesis, a degradation of 74-85% was obtained, which is within the parameters of the results obtained. Given the approach and development of the thesis, the results obtained using Au/TiO_2 in photocatalytic reactions with contaminants in the liquid phase, are a series of investigations that contribute to providing solutions to water pollution problems. Demonstrating the efficiency in the removal of pyridine is highly considerable at low concentrations, so it can be deduced that this process is highly viable for the removal of organic compounds at low concentrations and that the $\text{TiO}_2\text{-Au}$ catalyst has a high efficiency when degrading compounds. Organics at low concentrations with high volumes of solution

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