

EVALUATION OF PHOTOCATALYTIC REACTORS FOR DEGRADATION OF REACTIVE BLACK DYE 5 IN THE PRESENCE OF TiO₂

Gabrielle Gonçalves de Moura

Department of Engineering, ``Universidade
Federal de Lavras``
Lavras – MG, Brazil

Stéfany Gonçalves de Moura

Department of Chemistry, ``Universidade
Federal de Lavras``
Lavras – MG, Brazil

Natália Maira Braga Oliveira

Department of Engineering, ``Universidade
Federal de Lavras``
Lavras – MG, Brazil

Fabiano Magalhães

Department of Chemistry, ``Universidade
Federal de Lavras``
Lavras – MG, Brazil

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Abstract: In this work, two types of reactors were evaluated (tubular and tank) under different experimental conditions (with and without aeration and temperature control) to degrade the textile dye Reactive Black 5 (PR5), using TiO₂ as a photocatalyst. A jacketed tubular reactor made of PVC and a glass cylinder was used, equipped with a 36 W Hg lamp (submerged in the contaminant solution), temperature control and aerator, and a second tank-type reactor equipped with two Hg lamps (15 and 36 W) located above the contaminating solution. In experiments carried out in the tubular reactor without temperature control, discoloration results were 99% (with aeration) and 87% (without aeration). The values obtained for reactions with temperature controls were 55% (10 °C), 95% (25 °C) and 99% (35 °C). PR5 photolysis reactions showed that the dye discolored by approximately 4, 25 and 35% in experiments carried out at 10, 25 and 35°C, respectively. For the reactions in the tank reactor, the discoloration of PR5 during the photocatalytic reactions carried out with and without aeration was around 22%, while the dye photolysis reactions did not reach 1% discoloration. Therefore, it can be concluded that the tubular reactor is more efficient for the degradation of PR5, since the UV lamp immersed in the dye solution and the design of the reactor favor the reaction and aeration of the system, which are important factors for the best performance of a photocatalytic reactor.

Keywords: Titanium dioxide. Jacketed reactor. Textile industry. Photocatalysis.

INTRODUCTION

Industrial advancement is fundamental for human development, but it contributes to several environmental problems. This is because, in industries, there is the consumption and manufacture of products that are highly

toxic to living beings and the environment (REDDY et al., 2016). In Brazil, a sector that stands out as a source of contamination through its industrial effluents is textiles. The country has the fifth largest textile industry in the world, is the second largest producer of denim and third in knitwear, according to data from the Brazilian Association of the Textile and Clothing Industry (ABIT, 2022).

One of the most common effluents from this industry are dyes, including reactive ones. Those classified as azo dyes have complex aromatic structures, toxic effects and are not biodegradable, as is the case with Reactive Black 5 (PR5). Furthermore, inadequate disposal of these in waterways can result in non-absorption of light, which causes a major imbalance in this ecosystem (BERKTAŞ; KARTAL, 2022).

One way to degrade these dyes is through Advanced Oxidative Processes (POA's). One of these processes is photocatalysis, which consists of the formation of hydroxyl (OH•), hydroperoxyl (OOH•) and superoxide (O₂•-) radicals (LIMA et al. 2017). Such oxygenated radicals are generated from the incidence of ultraviolet radiation on the photocatalyst, which can be classified as a semiconductor (LI; LYU; LANG; 2021). These radicals are highly reactive and non-selective and, therefore, oxidize most non-biodegradable organic compounds present in effluents. Thus, there is the formation of less toxic molecules or the mineralization of contaminants into CO₂ and water (LIMA et al. 2017).

Radical species are obtained in photocatalysis from the absorption of photons by the semiconductor, which cause electronic excitation from its valence band to the conduction band. This excitation is sufficient to react with the water and oxygen in the medium, forming radicals for the oxidation of the contaminant (LUGO-VEIGA; SERRANO-ROSALES; LASA, 2016

and HAYYAN; HASHIM; ALNASHEF, 2016).

A good semiconductor, to be used as a photocatalyst, therefore, must be chemically and biologically inert, have high mechanical and thermal resistance, be accessible, abundant, easy to handle, demonstrate high oxidative power and absorb in the visible region. Titanium dioxide (TiO₂) meets almost all of these requirements, with the exception of the last one. Another limitation is the fact that it is made up of fine particles and, consequently, is difficult to recover. However, it is widely studied in photocatalytic processes, due to its proximity to a semiconductor determined to be good (MOURA et al., 2021).

However, the type of semiconductor is not the only parameter that affects the photocatalytic reaction. The performance of the process can be directly related to factors such as the intensity of the UV light used, the amount of oxygen dissolved in the medium, the type of pollutant, temperature, pH, among others. Furthermore, the type of reactor used in degradation will also influence, since its characteristics are extremely relevant to the efficiency of photodegradation (SUNDAR; KANMANI, 2020). In this context, the objective of this work was to evaluate two types of reactors for the degradation of the Reactive Black 5 dye using titanium dioxide as a photocatalyst.

MATERIALS AND METHODS

MATERIALS

The materials used in this experiment were: reactive black dye 5 (Sigma-Aldrich), TiO₂ P25 (Evonik), thermostatic bath (Biofoco), submersible atmospheric air pump, silicone tip, syringe attached to this silicone tube, stem thermometer long stainless-steel tube, centrifuge (Fanem) and UV-vis spectrophotometer (Genesys)

The reactors used were as represented in

Figure 1, being a tubular reactor (Figure 1A) made with a 500 mL beaker, a 10 cm diameter PVC tube, two 10 cm PVC plugs, silicone for sealing and two connectors for the bath. The PVC shell acts as a heat exchange jacket for the reactor, making temperature control possible. The UV radiation source used was a 36 W UVC low pressure Hg lamp (Philips).

The second reactor (Figure 1B) is of the tank type. It was placed in an MDF box covered in laminated paper. The low-pressure Hg lamps (Philips) used total 51 W (15 and 36 W) of power and are located at the top of the box. The reaction solution was placed in a glass container located below the lamps.

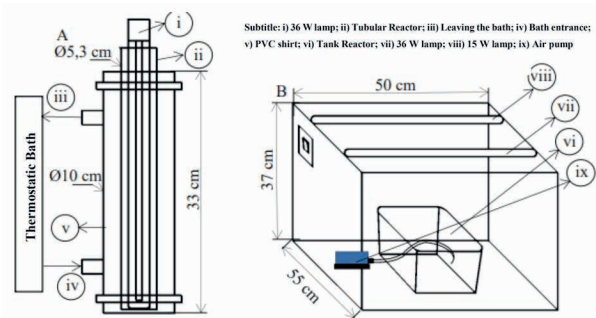


Figure 1 – Representation of the reactors used: (A) Tubular and (B) Tank.

Source: From the author (2023).

METHODS

DISCONTINUOUS TUBULAR REACTOR

The experiments were carried out using 400 mL of 40 mg/L PR5 solution and 10 mg of TiO₂. The atmospheric air was bubbled using an air pump with a submersible nozzle and the temperature control of the tubular reactor was carried out using a thermostatic bath, for reactions in which the presence of oxygen and temperature control were present.

To evaluate adsorption, PR5 and TiO₂ were placed in contact for 30 minutes. Aliquots of 5 mL were withdrawn (0, 15 and 30 min.) with the aid of a syringe attached to a silicone

tube. Then, the photocatalytic reaction was started and monitored for 20 minutes by collecting aliquots every 2 minutes. Under these conditions, reactions were carried out with and without aeration. Photolysis was carried out without the presence of TiO₂. The temperature was monitored using a stainless-steel thermometer.

The experiments in the tubular reactor were also evaluated at the following temperatures: 10, 25 and 35 °C. Before starting the reactions, the system was left to cool for 30 minutes. After each aliquot collected during the experiments, the samples were centrifuged and the absorbance was quantified using a UV-visible spectrophotometer at a wavelength of 598 nm.

TANK REACTOR

The experiments carried out in the tank reactor followed the same amounts of solution and concentration of the PR5 dye and mass of TiO₂, used for the reactions in the tubular reactor. Four reactions were carried out: two photolysis and two photocatalysis, both with and without aeration. In the case of the tank reactor, the available structure did not make it possible to carry out reactions at different temperatures, but it was monitored during the reaction time.

Adsorption was also evaluated in this reactor for 30 minutes of contact of the PR5 and TiO₂ solution, with aliquots removed at the same time intervals. Then, photocatalysis began, with 51 W UVC irradiation being turned on for a period of 20 minutes, with samples collected every 2 minutes with the aid of a Pasteur pipette. Photolysis was evaluated at the same time, with sampling intervals of 2 minutes. The centrifugation and UV-visible analysis procedures were carried out as described in the previous item.

RESULTS AND DISCUSSION

ADSORPTION TESTS AND PHOTOLYSIS AND PHOTOCATALYSIS REACTIONS

The results of the adsorption tests (Figure 1) show that TiO₂ adsorbed less than 1% of PR5 during 30 minutes of contact. This value is very low and does not significantly affect the results of the photocatalytic reactions that were carried out.

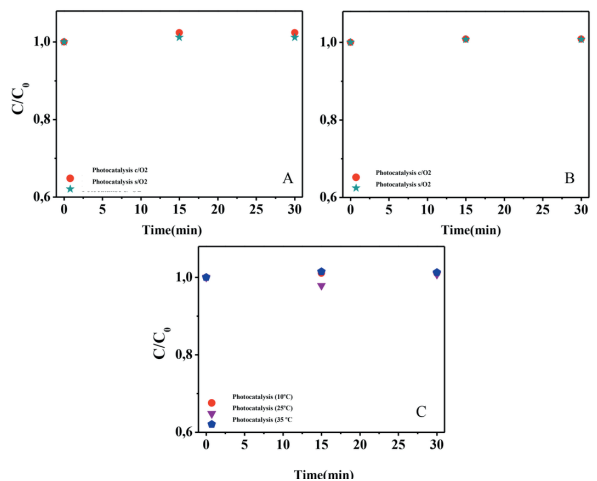


Figure 2 – Adsorption graphs for: A) tubular reactor without temperature control; B) tank reactor without temperature control; C) tubular reactor with temperature control and aeration.

Source: From the author (2023).

The results of the photocatalytic reactions were subjected to kinetic treatment for pseudo-zero-order, pseudo-first-order and pseudo-second-order reactions, according to Equations 1, 2 and 3, respectively (where, CA = concentration of reactant A, C0 = concentration of reactant A at time zero, K = kinetic rate constant, t = reaction time). The results obtained showed that they fit better into the pseudo-zero order treatment, in range limits where the drop-in concentration was more pronounced.

$$\frac{C}{C_0} = 1 - \left(\frac{k}{C_0}\right) * t \quad (1)$$

$$\ln\left(\frac{C_A}{C_0}\right) = -kt \quad (2)$$

$$\frac{1}{C_A} = \frac{1}{C_0} + kt \quad (3)$$

This evaluation was carried out by linearizing all data and obtaining R² values, which served as an evaluation parameter. From these linearizations it was also possible to obtain the values of the speed constants(k).

The values of the k constants can be seen in Table 1 for pseudo-zero-order reactions. It is possible to notice that the k values are greater than the corresponding photolysis values. Furthermore, it can also be noted that the values increase when the reactions were carried out in the presence of aeration in the tubular reactor, while in the tank reactor, it is not possible to notice the same effect. It is also noted that the values of k increase with temperature when the reactions were carried out in the tubular reactor in the presence of aeration.

The graphs obtained from data processing for pseudo-first order and pseudo-second order kinetics can be analyzed in Appendix A.

The graphs of the kinetics of reactions with UV light can be seen in Figure 3.

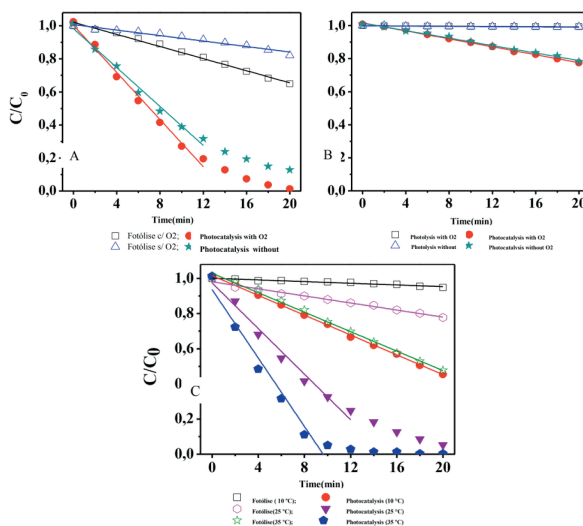


Figure 3 – Monitoring dye degradation for: (A) tubular reactor without temperature control; (B) tank reactor without temperature control; (C) tubular reactor with temperature and aeration control.

Source: From the author (2023).

Figure 3A represents the results of the reactions carried out in the tubular reactor without temperature control, with and without aeration. It is possible to note that the results of photolysis reactions, with and without oxygen, present a certain linearity between the points obtained. This result indicates that the kinetics of these reactions are pseudo-zero order, governed by Equation 3.

It is also noted that both reactions are less efficient than the corresponding reactions in the presence of TiO₂. This result shows that the dye has good stability when exposed to UV radiation and that the photocatalyst is active for dye degradation.

It is also noted in Figure 3A that the results of the photocatalytic reactions show kinetic behavior of pseudo-zero order up to approximately 12 minutes, an interval in which the points show good linearity. After this time, the reaction slows down and the kinetics tend to change to pseudo-first order. In order to facilitate calculations and analyses, k values were obtained considering

Type of reaction	Reactor description	k (gL ⁻¹ min ⁻¹)	R ²
Photolysis	Tubular, with aeration, without temperature control	0,01835	0,99155
Photocatalysis		0,07136	0,98824
Photolysis	Tubular, no aeration, no temperature control	0,00831	0,95914
Photocatalysis		0,05893	0,9863
Photolysis	Tank, with aeration, without temperature control	3,2639x10 ⁻⁴	0,91235
Photocatalysis		0,01206	0,99729
Photolysis	Tank, no aeration, no temperature control	4,43095x10 ⁻⁴	0,83321
Photocatalysis		0,0113	0,99368
Photolysis (10 °C)		0,00238	0,94715
Photocatalysis (10 °C)		0,02822	0,99917
Photolysis (25 °C)	Tubular, with aeration, with temperature control	0,01006	0,98435
Photocatalysis (25 °C)		0,06492	0,97838
Photolysis (35 °C)		0,02772	0,99474
Photocatalysis (35 °C)		0,09742	0,96156

Table 1 – Rate constants (k) of pseudo-zero order and coefficient of determination (R²) for each reaction.

Source: From the author (2023).

linearization in the pseudo-zero-order region.

Another factor that could be observed during the experiments in the tubular reactor was the gradual increase in temperature throughout the reaction (from 25 to 40 °C), which occurred due to the submersion of the UV lamp in the medium. This is because the lamp heats up when it is turned on and, as there is direct contact between it and the solution, heat transfer is favored. The increase in temperature increases the efficiency of the reaction. When comparing all the data for this reaction conformation (Figure 3A), it is possible to notice that the reactions in the presence of aeration were better at degrading PR5 when compared to those without aeration. This is because the increase in the dissolved oxygen content in the reaction medium favors the formation of radicals (•OH, O2•- and •OOH), since the probability of the electron present in the TiO2 conduction band being transferred to the dissolved O2 increases considerably.

Figure 3B shows the degradation data obtained in the tank reactor, with and without aeration. All reactions carried out are pseudo-zero order, as can be seen from

the linear format of the results obtained. The results of the photolysis reactions show that there was practically no degradation of PR5. Although the photocatalytic reactions showed an efficiency of 22%, they were still not satisfactory, showing the need for a longer reaction time to obtain complete degradation of the dye. It is also possible to see that the aeration of the reactions carried out in the tank reactor did not influence the degradation of the dye. This result is certainly related to the low efficiency of the reactor, as the more efficient the reaction, the greater the consumption of O2 and, consequently, the more necessary and important it is to have an aerated system. Regarding the temperature of the reactions carried out in the tank reactor, it can be said that it remained constant at room temperature throughout the 20 minutes of reaction.

When comparing the results in Figures 3A and 3B, both without temperature control, but using different radiation (36 W for the tubular reactor and 51 W for the tank reactor), it is noted that the reactions carried out in the tubular reactor are more efficient, even with lower incidence of UV radiation.

In addition to the fact that oxygenation is more efficient in the tubular reactor, two other factors that may have contributed to the advantage of this model are the incidence of direct radiation and the increase in the temperature of the reaction medium. In the tank reactor, the radiation only affects the surface of the solution containing the dye and in the tubular the radiation source is immersed in the dye solution, which increases the efficiency in the use of light by the TiO_2 particles.

Figure 3C presents the results of reactions conducted with temperature control (10, 25 and 35 °C) and aeration, carried out in the tubular reactor. The results obtained show that photocatalytic reactions carried out at 25 and 35 °C present pseudo-zero-order kinetics up to approximately 12 and 10 minutes, respectively. After this time the rate of degradation decreases. These reactions were approximated to pseudo-zero order at the respective times for calculating k , since they demonstrated better R^2 values with these considerations. The results of the other reactions show good linearity between times 0 and 20 minutes.

As expected, the efficiency of the reactions improved with increasing temperature, the best of which was photocatalysis at 35 °C, which degraded all the dye after 10 minutes of reaction. The reaction carried out at 25 °C also completely degraded the dye, however it took around 20 minutes. The reaction carried out at 10 °C, presented a similar result to the photolysis at 35 °C, degrading around 56% of PR5.

A comparison between Figures 3B and 3C allows us to identify that, even at a lower temperature (10 °C), the tubular reactor presents better photocatalytic degradation of the contaminant, when compared to the tank reactor. This may have occurred because, even with a lower temperature than the ambient

temperature, there was still better use of radiation with the lamp submerged.

When comparing the results in Figures 3A and 3C, it is clear that the photocatalysis reactions in the presence of oxygen without temperature control (Figure 3A) and with temperature control at 25 °C (Figure 3C) were efficient in practically degrading the entire PR5 with 20 minutes of reaction. Therefore, it can be said that the efficiency of temperature control will influence temperatures greater than 25 °C, which is confirmed by the reduction in degradation time when evaluating the photocatalytic reaction at 35 °C.

Figure 4A represents the percentages of discoloration and the kinetic constants for the reactions in the tubular reactor without temperature control.

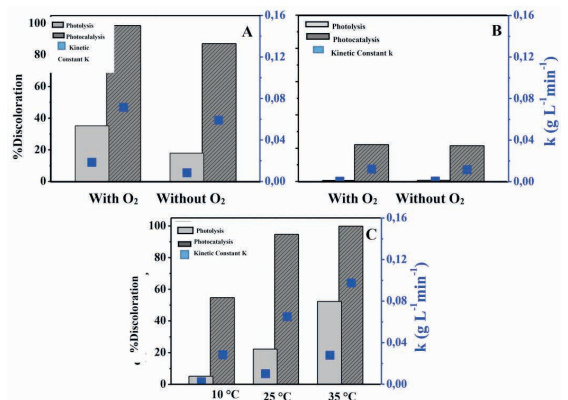


Figure 4 – Discoloration percentage data and kinetic constant for: (A) tubular reactor without temperature control; (B) tank reactor; (C) tubular reactor with temperature and aeration control.

Source: From the Author (2023).

It is possible to observe in Figure 4A that the final discolorations, after 20 minutes of reaction in the presence of aeration, from both photolysis (35%) and photocatalysis (99%), were better than those without the addition of O_2 (without aeration). While the photolysis efficiency practically doubled with aeration, the presence of gas in the photocatalysis reaction improved the conversion by 11.5%, almost completely discoloring the solution

within 20 minutes.

Figure 4B shows the results of the reactions carried out in the tank reactor, with and without aeration (O₂). In aerated reactions, the percentages of PR5 degradation were 0.6 and 23% for photolysis and photocatalysis, respectively. These values are very similar to those obtained for reactions without aeration, where photolysis and photocatalysis had efficiencies equal to 0.8 and 22%, respectively. These results show that the aeration of this reactor is insignificant for the final result.

Figure 4C, in turn, presents data on the reactions carried out in the tubular reactor with temperature and aeration control. It is noted that the efficiency for dye degradation increased with temperature, where the photocatalytic reactions carried out at 10, 25 and 35 °C showed efficiencies of 55, 95 and 99%, respectively. On the other hand, the photolysis reactions carried out at 10, 25 and 35 °C showed efficiencies equal to 5, 22 and 52%, respectively. It is noted that efficiency also increased with temperature, but those reactions carried out in the presence of TiO₂ performed much better, which proves its high photocatalytic activity.

When evaluating all the systems and conditions presented in Figure 4, it is possible to see that the discoloration of PR5 at 35°C and without temperature control, both with oxygenation, were very close. Therefore, it is possible to state that photocatalysis carried out without temperature control represents an intermediate scenario between photocatalytic reactions at 25 °C and 35 °C. This is because the degradation of the dye is improved when using the tubular reactor with natural and gradual heating offered by the transfer of heat from the lamp to the medium (without temperature control). As the aeration process was carried out in a simple way, with low cost, it can be considered advantageous for the process.

In the literature it is possible to find several experiments involving TiO₂ and the photocatalytic degradation of dyes, including PR5. They vary according to the type of reactor used, whether or not the photocatalyst is doped, the dye concentration, type and power of radiation, among others. In order to validate the experimental results of this work, it is possible to compare them with data obtained by other authors.

Lucas et al. (2013) compared the degradation of PR5 in a cylindrical reactor made of borosilicate, with a lamp in an axial position being inserted into a quartz shield. The efficiency of commercial TiO₂ and combined with magnetic nanomaterial consisting of Fe₃O₄ and SiO₂ were evaluated. Under these conditions, it was possible to obtain almost complete degradation of the model dye in 120 minutes of reaction, with most of it being removed in the first 90 minutes.

Gark, Sangal and Bajpai (2016) in turn, carried out the degradation of the dye with mercury lamps positioned above the reactor, like the tank reactor experiment carried out in this work. Almost 100% discoloration of PR5 was obtained with approximately 1h of reaction.

Finally, Copete-Pertuz et al. (2018), evaluated different amounts of TiO₂, concentration of PR5 and pH of the medium, in an aluminum photoreactor with the lamp positioned over the beakers and with constant stirring. The authors found that, after 10 hours of reaction, the highest percentage of discoloration was obtained with 50 mg/L of PR5 and 0.5 g/L of TiO₂.

The main data from the previously mentioned works are briefly presented in Table 2.

It is possible to see, therefore, that there are several ways to evaluate the degradation of reactive black 5 using TiO₂. Comparing the best degradation scenario identified in this

Author	Reactor	Variables	Photocatalyst	Radiation	Better discoloration
Lucas et al. (2013)	Cylindrical (borosilicate) with axial lamp (500 mL)	Types of photocatalyst	Commercial pure TiO ₂ and doped with Fe ₃ O ₄ /SiO ₂	Hg lamp UVC 15W	120 min (Mostly 90 min)
Gark, Sangal and Bajpai (2016)	Tank reactor with lamp positioned above (variable volume 500, 750 and 1000 mL)	TiO ₂ concentration and PR5, pH, area/volume ratio, UV intensity and time	commercial pure TiO ₂	Hg lamp UVC (30W x 8)	150 min (Almost complete 60 min)
Copet-Pertruz et al (2018)	Aluminum reactor with lamp positioned above (100 mL)	TiO ₂ and PR5 concentration and pH	commercial pure TiO ₂	Hg lamp UVC (30W x 5)	10 hours

Table 2 – Data from some works in the literature where photocatalytic reactions were carried out under different experimental conditions for degradation of the PR5 dye using TiO₂ as photocatalyst.

Source: From the author (2023).

work, it can be stated that in just 20 minutes of reaction it was possible to discolor 99% of the PR when the following conditions were used: tubular reactor with (reaction carried out at 25°C) and without temperature control and with aeration. This result is much better than those obtained by previously presented literature works. Therefore, this actively contributes to the hypothesis that this reaction system is efficient, as immersing the lamp and adding oxygen to the medium makes the reaction much faster.

CONCLUSION

It is possible to conclude that photocatalysis is an efficient process for degrading organic contaminants present in an aqueous medium and that its efficiency

depends on several factors, some of which are: temperature, incidence of radiation, aeration of the medium and the type of reactor. These parameters play an extremely important role in the speed of contaminant degradation. The results obtained also showed that the tubular reactor where the Hg lamp is submerged in the contaminant solution and the presence of aeration are extremely important factors for having an efficient system in photocatalytic reactions. The results also showed that this type of reactor has much higher efficiency than the tank-type reactor, where the radiation source is located just above the contaminating solution.

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ANNEX A

Graphs with pseudo-first order (Figure I-A) and pseudo-second order (Figure II-A) regressions for photolysis and photocatalysis reactions.

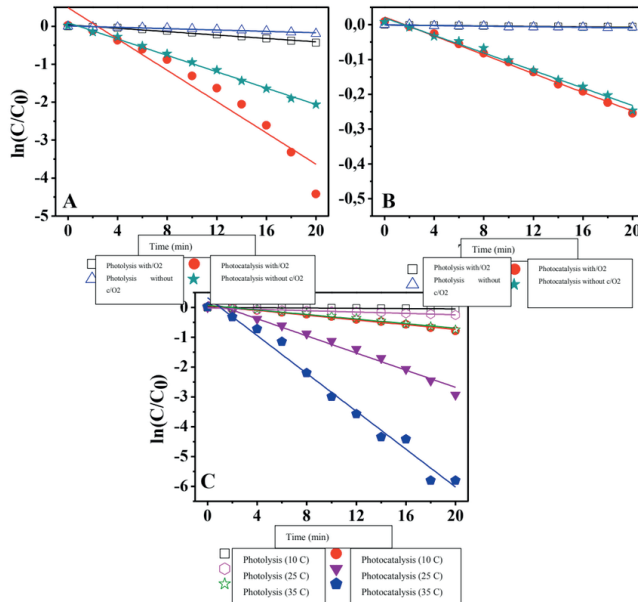


Figure I-A – Pseudo-first order regressions for: (A) tubular reactor without temperature control; (B) tank reactor without temperature control; (C) tubular reactor with temperature and aeration control.

Source: author (2023).

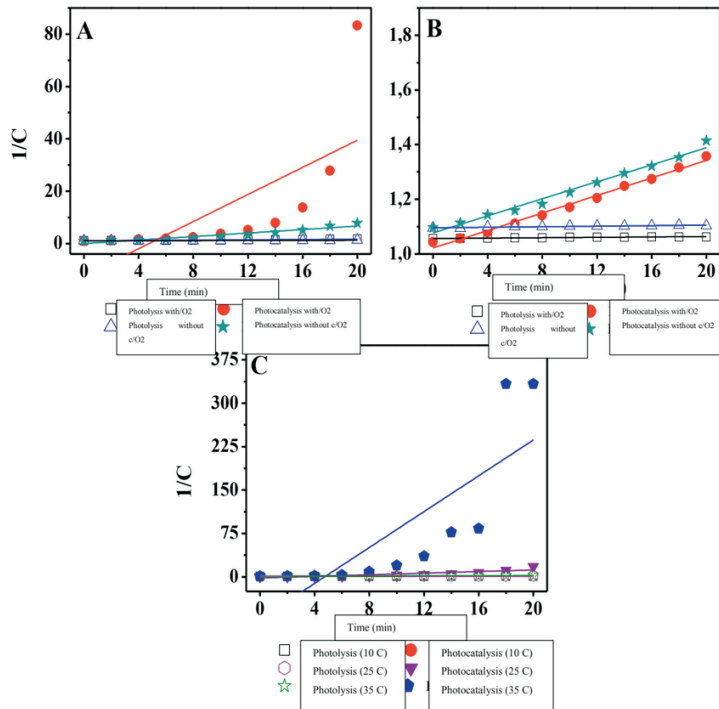


Figure II-A – Pseudo-second order regressions for: (A) tubular reactor without temperature control; (B) tank reactor without temperature control; (C) tubular reactor with temperature and aeration control.

Source: Author (2023).