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Heterogeneous Photodegradation for the Abatement of Recalcitrant COD in Synthetic Tanning Wastewater

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Abstract: Tannery wastewater is considered one of the most contaminated and problematic wastes since it consists of considerable amounts of organic and inorganic compounds. These contaminants result in high chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total suspended solids (TSS). In this work, the heterogeneous photodegradation of recalcitrant COD in wastewater from the tanning industry was investigated, in particular the recalcitrant COD due to the presence of vegetable tannins extracted from mimosa and chestnut and from synthetic tannins based on 4,4′ dihydroxy phenyl sulfone. TiO_2 Aeroxide P-25 was employed to study the photodegradation of model molecules in batch conditions under different parameters, namely initial concentration of COD, temperature, and catalyst dose. The maximum COD abatement reached was 60%. Additionally, preliminary kinetic investigation was conducted to derive the main kinetic parameters that can be useful for process scale-up. It was found to be independent of the temperature value but linearly dependent on both catalyst loading and the initial COD value.

Keywords: advanced oxidation processes; tanning industry; vegetable and synthetic tannins; wastewater treatment

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1. Introduction

The leather industry plays an important role in the economy of many countries around the world, with more than USD 80 billion per year worth of global leather trade [1]. In fact, raw leather processing operations lead to the production of solid, liquid, and gaseous by-products and waste. Since a large part of the production process is conducted in aqueous media, the major waste is made up of wastewater [1]. The produced wastewater from the tanning industry can cause serious health and environmental problems, as it has high concentrations of organic and inorganic hazardous effluents [2–4]. In the various stages of tanning, many compounds are used, such as acids, alkalis, chromium salts, tannins, solvents, dyes, oils, resins, and synthetic tannins, that are not completely fixed on the skin and remain in water without being treated. Thus, high values of chemical oxygen demand (COD), biochemical oxygen demand (BOD), sulfate, chloride, heavy metals, and various organic substances characterize the discharged wastewaters [5–8].

COD is one of the main parameters used to evaluate the quality of wastewaters; in particular, it can provide indications on the content of organic matter. We can distinguish two fractions of the COD: the biodegradable one, represented by all those compounds that are removed from urban or industrial wastewater through traditional biological purification processes, and the not-biodegradable fraction, represented by all those substances defined

as "recalcitrant", that is, they resist microbial degradation and persist in the environment for a long time [6,8,9].

In the last few years, alternative tanning processes have been developed, defined as chrome free when the chromium salts are replaced with vegetable and synthetic tannins [10]. These tannins have some advantages and disadvantages. On one hand, they are defined as eco-friendly. On the other hand, they are known to be poorly biodegradable, since they show BOD_5/COD ratios lower than 0.4, indicating a low biodegradability [11]. Furthermore, their presence can determine inhibitory conditions for biomass in biological treatment. Therefore, they are not completely degraded by the traditional wastewater treatment processes, leading to COD values that exceed the limits imposed by law [6,12,13].

The conventional treatments of effluent from the leather industry are equalization, neutralization, sedimentation, coagulation, flocculation, and biological treatment with activated sludges, but these treatments show low efficiency in removing recalcitrant compounds [9,14,15]. The increase of these compounds in wastewaters and the concern about the unknown long-term effects of their accumulation in the environment have led to growing awareness among researchers about the need to improve existing technologies and to develop new strategies for the removal of this class of pollutants from wastewater. Therefore, advanced technologies, such as advanced oxidation processes (AOPs), adsorption, membrane separation processes (MSPs), and hybrid treatments, are widely investigated in the literature nowadays to overcome the conventional technologies' drawbacks [16]. Among the advanced technologies proposed for wastewater treatment, we considered AOPs, which involve the use of oxidizing agents (O_3, H_2O_2) and catalysts (TiO_2, Fe), often supported by a radiation source (UV light), electrochemical oxidation, etc. These processes are designed to produce hydroxyl radicals, which act with high efficiency to degrade organic compounds [6,17]. Semiconductors are used to generate hydroxyl ions in the solutions, which leads to the degradation of the organic matter present. Particularly, when UV light with an energy equal to or greater than the band energy gap is incident on the surface of a semiconductor, such as titanium dioxide (TiO_2), the photons transfer their energy to the electrons, allowing them to jump into the conduction band, generating an equivalent vacancy in the valence band [18].

In the last few years, several studies have been conducted on the AOPs applied for the treatment of wastewater from the tanning industry because they are considered environmentally friendly [6,19]. This is due to the fact that these processes promote green chemistry aspects by providing high reaction rates and efficiencies with minimal dangerous by-products [20]. In the comprehensive systematic review of Hansen and coworkers [21], the different treatment technologies applied to the post-tanning effluents were addressed. The authors concluded that further studies on AOP processes should consider the cost and the toxicity of by-products generated. Furthermore, they reviewed the studies that considered both real and synthetic wastewater effluents, such as syntan, azo dyes, leather dye red Red2BN, fat liquor, benzidine, and Cr (VI). Trojanowicz et al. [22] presented the recent advancements in AOP technologies and the limitations of the removal of organic pollutants from wastewater in terms of extended contact times for the destruction of pollutants, which can reach several hours to achieve 90% removal. However, none of these studies focused on the photodegradation of vegetable and synthetic tannins in wastewater [19]. Hence, this study deals with the recalcitrant COD abatement processes derived from the use of vegetable and synthetic tannins in the tanning processes and catalyzed by TiO_2 Aeroxide P-25. The effect of several operating parameters was evaluated, such as the initial concentration of COD, temperature, and catalyst dose. Moreover, kinetic investigation was conducted to derive the main kinetic parameters that are useful for prospective process scale-up.

2. Materials and Methods

2.1. Materials

Synthetic tanning wastewater was prepared with the vegetable and synthetic tannins that are mostly used in the tanning process. In particular, we used the vegetable tannin extract derived from mimosa and chestnut and a condensation polymer of 4,4′ dihydroxyphenylsulfone as a synthetic tannin (BiagioSiani, Solofra, Italy). Chestnut and mimosa extracts had tannin contents of 80% and 70%, respectively. TiO_2-P25 was supplied by Evonik Industries (Essen, Germany).

2.2. Photodegradation Experimental Set-Up

The system used for photodegradation consists of a glass-lined reactor with a capacity of 1.5 L closed with a lid with three necks: in the center of the reactor was inserted the UV lamp (Toshiba FL4BLB 15 cm × 1.5 cm, with a power of 4 W, emission at the wavelength of 365 nm, and 220 V); in the other the thermocouple for reading the reaction temperature; and in the third a digital flow-meter regulator (supplied by Bronkhorst), connected to a sintered filter used as gas sparger, to warrant a good gas–liquid interface in the mass transfer of air to the liquid phase. Synthetic wastewater containing tannins was prepared using the vegetable extracts of chestnut, mimosa, and synthetic tannin based on hydroxyphenylsulfone at a different concentration of COD. The different solutions prepared were inserted inside the reactor, which was closed and was connected to the thermostat at the desired reaction temperature. The air flow was adjusted to the pressure of 1 bar, the UV lamp was turned on, and finally the catalyst added. The experiment lasted a total of 5 h. Every 30 min, aliquots of the sample were taken from the reactor and centrifuged at 3300 rpm for 15 min. The photodegradation efficiency was evaluated by determining the parameters pH, COD, and TOC. For determination of pH, potentiometric methods were used (Mod 856/867, Metrohm, Zofingen, Switzerland). The COD was measured by oxidative acid digestion followed by colorimetric methods (Hach, DR 3900, Düsseldorf, Germany), and the TOC was determined by sample combustion coupled with an NDIR detector (TOC-V–Shimadzu, Kyoto, Japan). The quantification of COD and TOC was performed using an external calibration curve. The detection limit (LOD) and the limit of quantification (LOQ) were calculated using the blank method. The calculated average values of LOD and LOQ in the matrix were 0.12 and 0.5 mg/L for TOC and 1.5 and 5 mg/L for COD. The data quality was ensured by proficiency testing (PT-AQ-11, LGC Standard). The experiment was conducted at different conditions of temperatures and catalyst concentrations (ρ_B). The scheme of the different conditions is reported in Table 1.

Table 1. Different conditions of temperature and catalyst dose used for the experiments at fixed values of $Q_{air} = 1.0 \times 10^{-6}$ m^3/s and $v = 500$ rpm.

Experiment No.	Temperature (K)	ρ_B (g/L)	pH	TOC (mg/L)	COD (mg/L)
1	293	0	5.2	88.7	200
2	293	0.5	4.6	74.1	200
3	293	0.5	5.5	44.9	100
4	293	0.5	5.5	27.7	50
5	293	1.0	4.9	71.2	200
6	293	1.5	4.9	75.3	200
7	313	0.5	4.8	73.7	200
8	323	0.5	4.6	66.6	200

2.3. Kinetic Modeling

The experimental data collected by varying the reaction temperature were interpreted to obtain the activation energy value. The Arrhenius law was applied:

$$ln(k) = ln(k_0) - \frac{E_a}{RT} \quad (1)$$

where k is the rate constant of the reaction, k_0 is the frequency factor, E_a is the activation energy, R is the ideal gas constant, and T is the temperature.

In particular, a first-order rate expression was adopted for simplicity. The assumption is valid as we are analyzing the data collected at t_0, where the linear trend can be approached to a first-order kinetics.

$$r_{obs} = -\frac{d\text{COD}}{dt}\bigg|_{t\to 0} = k_{obs}\text{COD}_0 \quad (2)$$

where r_{obs} is the observed rection rate and k_{obs} is the observed rate constant.

3. Results and Discussion

3.1. Photodegradation Experimental Results

In this preliminary study, different experiments were conducted to verify the influence of the temperature, the quantity of the catalyst, and varying the initial concentration of COD. The influence of the reaction temperature was investigated (Figure 1). It was observed that as the temperature increases, there is a reduction in COD up to a maximum value of 40%.

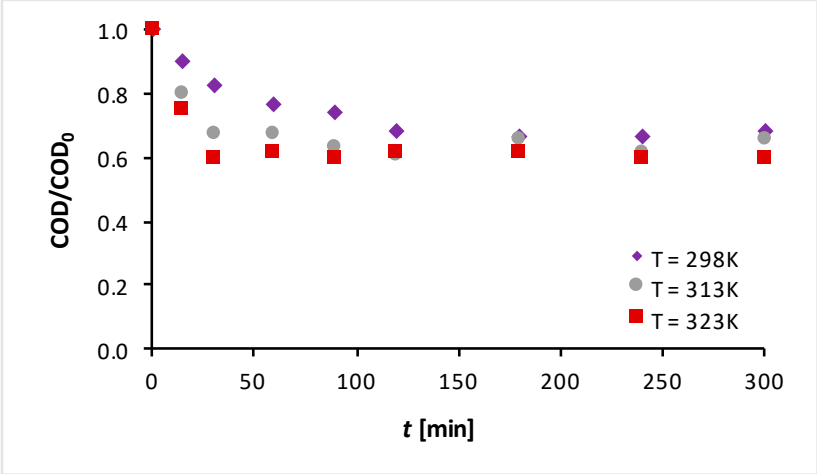

Figure 1. COD/COD_0 profile vs. reaction times for experiments conducted at different temperatures. The tests were conducted by fixing the following operation conditions: COD_0 = 200 mg/L, ρ_B = 0.5 g/L, $Q_{air} = 1.0 \times 10^{-6}$ m^3/s, and v = 500 rpm.

Furthermore, it was observed that after 100 min from the beginning of the reaction, the COD concentration reaches a stable plateau value. This effect has already been observed in the literature, where Jouali et al. attributed the phenomenon to the shield effect due to the tanning residual content [23]. The assumption is valid, considering the chemical complexity of the matrix that could undergo a more difficult photodegradation at a certain level of decomposition.

The influence of the different quantities of the catalyst was investigated. The first experiment was conducted in the absence of the catalyst, to verify eventual photodegradation due to the UV irradiation (Figure 2), but no substantial decrease in COD concentration was observed. Figure 2 shows that by increasing the catalyst concentration, an increase in COD photodegradation was measured, suggesting a dependency of the photodegradation rate on the catalyst load. A reduction in the COD concentration of about 60% was observed at ρ_B = 1.5 g/L.

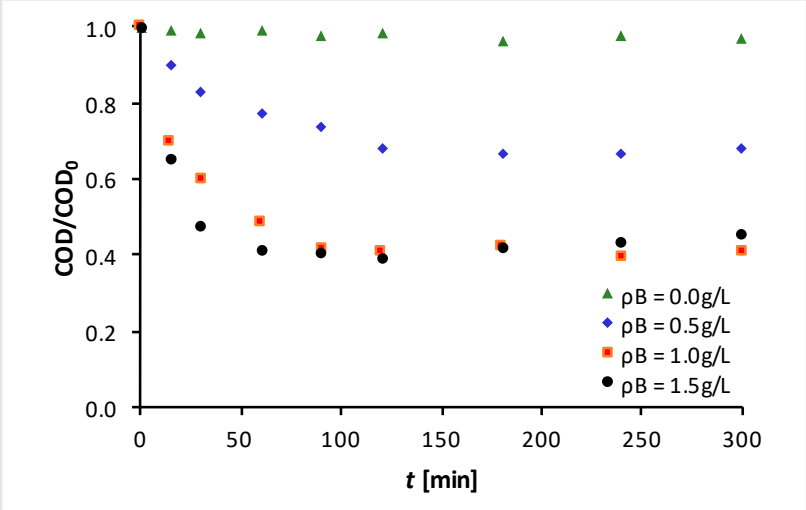

Figure 2. Effect of the catalyst loading on the photodegradation of tanning. The experiments were carried out by fixing the following operation conditions: COD_0 = 200 mg/L, T = 298 K, Q_{air} = 1.0 × 10^{-6} m^3/s, and v = 500 rpm.

Therefore, no significant differences were observed when using either ρ_B = 1.0 g/L or 1.5 g/L, probably due to the shield effect of the solid phase. This phenomenon has been addressed by different researchers in the field of wastewater treatment [24–27]. Moreover, after about 100 min from the beginning of the reaction, the COD concentration reached a stable plateau value.

Finally, experiments were carried out at different values of COD_0 (Figure 3). The effect of this parameter was evaluated by varying its value from 50 to 200 mg/L. The results showed a degradation efficiency of about 60% for COD concentrations of 50 mg/L, while for concentrations above 100 mg/L, the efficiency decreased by up to 40%. The effect of the high concentrations could be due to the absorption of the tannin molecules on the surface of the catalyst, inhibiting the catalytic activity [24,28,29]. The results showed that the higher the initial content of the COD, the faster is the reaction rate, suggesting a reaction order different than 1.

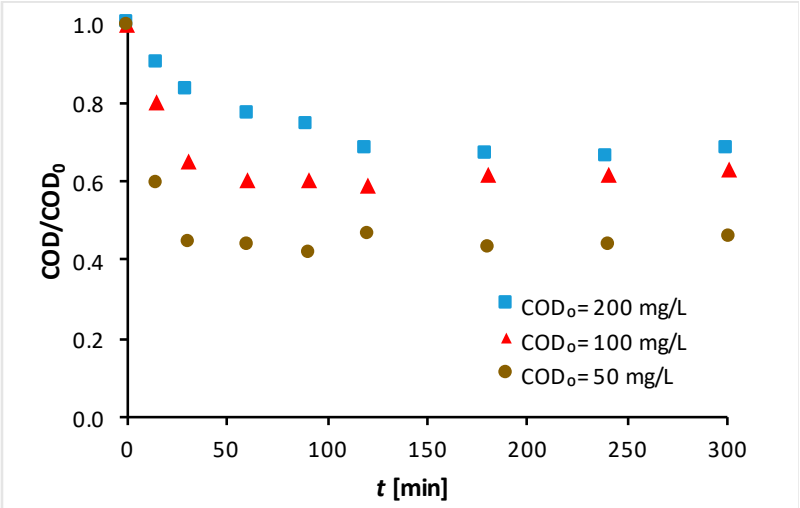

Figure 3. COD/COD_0 profile vs. reaction times for experiments carried out at different initial concentrations of COD. The experiments were conducted fixing ρ_B = 0.5 g/L, T = 298 K, Q_{air} = 1.0 × 10^{-6} m^3/s, and v = 500 rpm.

3.2. Kinetic Modeling

Performing a chemical reaction kinetic study is an important pillar for the prospective scale-up of AOPs [30]. Studying experimentally the reaction rate, the rate constant, and the activation energy, which are independent of the scale, will be insightful in terms of the progress of the reaction and thus the predicted reaction time. Starting from the experimental observations, the experimental data were interpreted with a preliminary approach to retrieve useful kinetic information to allow the scale-up of the photodegradation operation. The experimental data collected varying the reaction temperature were interpreted to obtain the activation energy value. In particular, the linearized plot reported in Figure 4 allowed one to calculate an activation energy value of E_a = 28 ± 2 kJ/mol, value of the order of magnitude for the photodegradation of complex organic molecules [31,32].

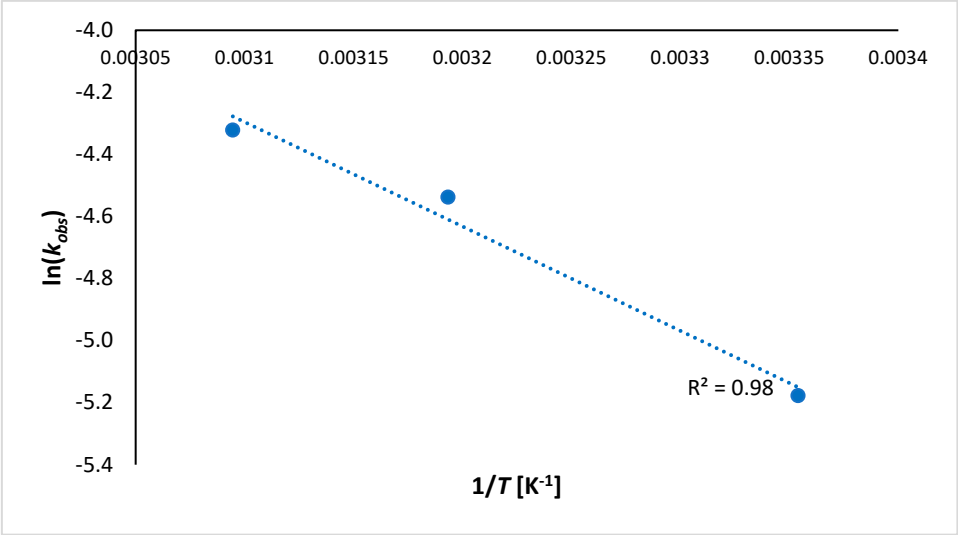

Figure 4. Arrhenius plot obtained using the experiments conducted at different temperatures.

As revealed, the R^2 value is more than satisfactory and the confidence interval associated with the activation energy value is low, showing high reliability and statistical significance of the obtained parameter. These experiments lead all to the same COD final plateau value, that is dependent only on the catalyst loading and on the initial COD value, as will be seen below.

The effect of catalyst loading was interpreted both on the initial slope of the kinetic curves, proportional to the observed reaction rate (r_{obs}), and the final plateau value of COD. The results are reported in Figure 5A,B.

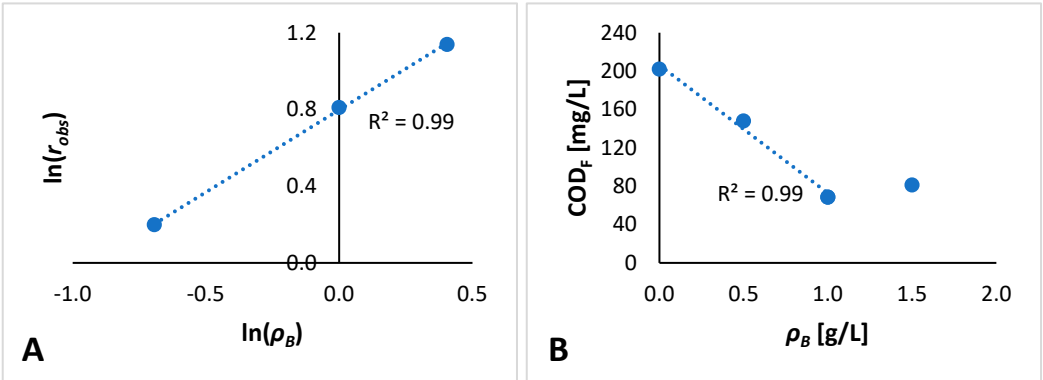

Figure 5. Effect of the catalyst loading on (**A**) the observed reaction rate, r_{obs}, and (**B**) the COD plateau value, COD_F.

It is evident that the reaction rate is promoted by the amount of catalyst, showing a linearity coefficient near unity (0.9); Figure 5A. Moreover, the final COD value linearly decreases till 1 g/L of catalyst, becoming then invariant with the catalyst loading, Figure 5B. This fact can be always explained by the shield effect obtained, as previously discussed, when adopting a high catalyst concentration.

The effect of ρ_B on the apparent first-order rate constant and the COD removal % is presented in Figure 6A,B, respectively. The influence of the dose of TiO_2 Aeroxide P-25 is linearly proportional to the rate constant (Figure 6A), which is in agreement with the apparent first-order reaction rate. However, increasing the dose of TiO_2 Aeroxide P-25 beyond 1 g/L leads to a decrease in the COD removal %, as shown in Figure 7B. This could be attributed to the decrease in UV light penetration, so the photocatalytic degradation rate would decrease [26], as discussed in Figure 2.

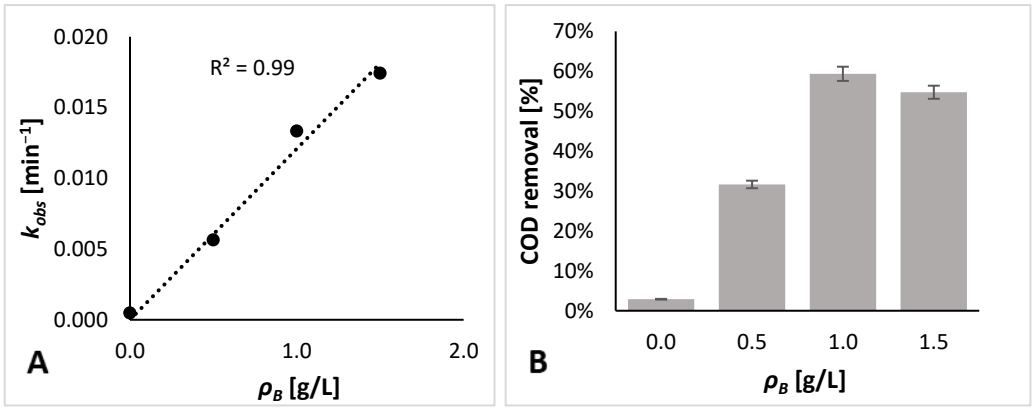

Figure 6. The effect of ρ_B on (**A**) the observed reaction rate constant, k_{obs}, and (**B**) the COD removal.

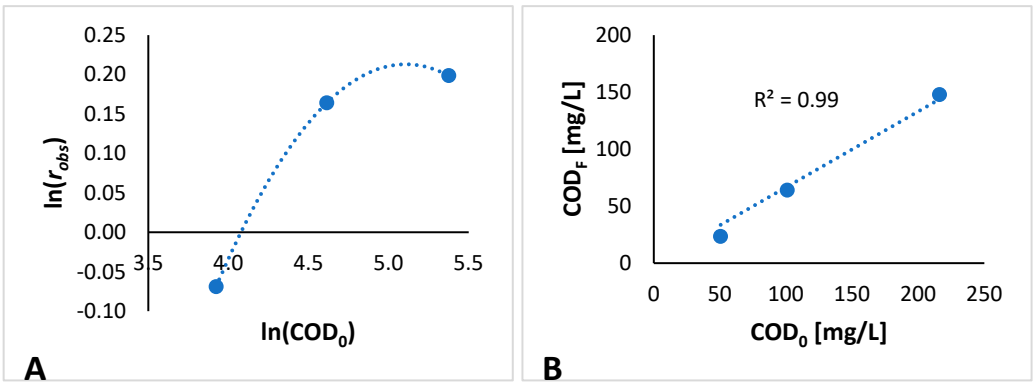

Figure 7. Effect of the initial COD value on (**A**) the observed reaction rate, r_{obs}, and (**B**) the COD plateau value, COD_F.

Finally, the effect of the initial COD value on the photodegradation kinetics was interpreted, concerning both the observed reaction rate and the final plateau value (Figure 7A,B). It can be seen that the increase in the COD_0 value corresponds to a non-linear increase in the reaction rate value, suggesting the occurrence of a more complex mechanism involving also superficial adsorption phenomena (Figure 7A). Figure 7B shows an important result, as the final COD value linearly depends on the initial one, with a linearity coefficient of 0.7. This clearly indicates that the higher the contaminant quantity, the higher is the residual. Thus, its value is a matter of optimization.

4. Conclusions

The present study can be considered a preliminary investigation of the photodegradation vegetable tannins of chestnut and mimosa and synthetic tannins, mostly used in

the tanning industry. The experiments were conducted with model solutions, simulating industrial wastewater at different concentrations of COD in the range of 50–200 mg/L. TiO_2 Aeroxide P-25 was used and demonstrated to be an effective catalyst for COD abatement, with a maximum value of 60%. From the collected evidence, an activation energy of Ea = 28 kJ/mol was obtained, which is comparable with the literature values obtained for persistent organic molecules. In every experiment, the COD reached a plateau value, independent of the temperature value but linearly dependent on both the catalyst loading and the initial COD value. The higher the catalyst load, the more efficient is the photodegradation process, while using high values of COD_0 could lead to non-optimal reaction conditions as it inhibits the reaction itself, suggesting a surface mechanism. This work paves the road for future studies on the AOPs applied for the treatment of real and synthetic tannin wastewater using TiO_2 Aeroxide P-25. However, the cost, scalability, and toxicity of any possible by-products generated in these processes should also be further investigated and assessed. It can also be concluded that this process can be promising for short-term applicability through coupling photocatalytic processes with other physical, chemical, or biological systems in tanning wastewater treatment.

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