Photocatalytic degradation of salicylic acid employing TiO2 and ZNO in aqueous suspension

Degradação fotocatalítica do ácido salicílico empregando TiO2 e ZNO em suspensão aquosa

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ABSTRACT
The photocatalytic degradation of salicylic acid (SA) in reduced concentration (14.5 µmol L⁻¹) was investigated using TiO₂ and ZnO as photocatalysts under irradiation with UV light using UV-Vis spectrophotometry and HPLC analysis. The effect of different catalysts and catalyst loading, kinetic analysis, and dissolution of ZnO using the experimental conditions adopted were evaluated in acidic medium (pH = 3.0). Chronic ecotoxicity tests of the effluent from the reactions were conducted employing a concentration of 1 g L⁻¹ of photocatalysts. The results showed that TiO₂ and ZnO presented very similar performance for the SA degradation, whose profile followed first-order kinetics. The dissolution of ZnO observed was low using the experimental conditions adopted. Chronic ecotoxicity tests carried out showed that the use of ZnO/UV system for degradation of SA leads to a product with significant harmful effects on Ceriodaphnia dubia, even at reduced concentrations of the effluent from the reaction.

Keywords: salicylic acid, heterogeneous photocatalysis, kinetic analysis, ecotoxicological tests.

RESUMO
A degradação fotocatalítica do ácido salicílico (SA) em concentração reduzida (14,5 µmol L⁻¹) foi investigada usando TiO₂ e ZnO como fotocatalisadores sob irradiação com luz UV usando espectrofotometria UV-Vis e análise HPLC. O efeito de diferentes catalisadores e carga de catalisador, análise cinética, e dissolução de ZnO utilizando as condições experimentais adoptadas foram avaliados em meio ácido (pH = 3,0). Foram realizados testes de ecotoxicidade crónica dos efluentes das reacções, empregando uma concentração de 1 g L⁻¹ de fotocatalisadores. Os resultados mostraram que o TiO₂ e o ZnO apresentaram um desempenho muito semelhante para a degradação de SA, cujo perfil seguiu uma cinética de primeira ordem. A dissolução de ZnO observada foi baixa, utilizando as condições experimentais adoptadas. Os testes de ecotoxicidade crónica realizados mostraram que a utilização do sistema ZnO/UV para a degradação de SA leva
a um produto com efeitos nocivos significativos sobre Ceriodaphnia dubia, mesmo com concentrações reduzidas do efluente da reacção.

**Palavras-chave:** ácido salicílico, fotocatálise heterogénea, análise cinética, testes ecotoxicológicos.

**1 INTRODUCTION**

In recent years there has been growing contamination of surface and groundwater by hazardous organic pollutants [1-3]. Increased concentrations of these pollutants in aquatic environments can result in various toxicological effects, both direct and indirect, on the environment and on human health [4].

Consequently, there is an increasing need for different processes to treat those contaminants to reduce the potential damage both to the environment and human health [2]. Biological treatments are currently the most used, due to the low implementation and operational costs and the possibility of treating large volumes. However, this type of treatment has limitations that can restrict its efficiency in the case of certain classes of effluents with high toxicity, such as organochlorines and phenols. On the other hand, methods such as precipitation and incineration, despite being widely used, are questionable, since the first causes a simple phase change of the compounds without eliminating them, and the second has high cost and possibility of forming compounds more toxic than the effluent itself. [5].

Due to the frequent use, salicylic acid (SA), a representative soluble aromatic compound often used in industry and in households, is regularly detected in industrial wastewater and surface waters. This organic contaminant is the result of the decomposition of acetylsalicylic acid, one of the most used medicines in the world, and is biologically active, possibly causing adverse effects in nature [6-7]. It is also a relevant pollutant because of its toxicity and relatively low biodegradability [8]. Emerging pollutants like SA are persistent, so their complete elimination is difficult using conventional water treatment processes [1, 9].

Advanced oxidative processes (AOPs) are an alternative for destroying toxic organic contaminants based on the use of highly oxidizing species to promote more effective degradation of the pollutant to be treated [10-15]. Many semiconductors have enough band-gap energies to be used as catalysts in many chemical reactions. Among these semiconductors it is possible to mention TiO$_2$, WO$_3$ and ZnO [16]. One of the
semiconductors widely employed in heterogeneous photocatalysis is titanium dioxide (TiO$_2$), due to its high photocatalytic efficiency, physical and chemical stability, low cost, and low toxicity. Despite all the advantages of using TiO$_2$, its efficiency is influenced, for example, by the crystal structure (anatase or rutile) [5, 17]. The crystalline form anatase is more efficient than the rutile form because of its more open structure compared to rutile. The commercial form of TiO$_2$ (Degussa P-25) has been used in many photocatalytic degradation studies due to its chemical stability, availability, reproducibility, and activity as a photocatalyst in oxidation processes [16]. Zinc oxide (ZnO) surge as an alternative to TiO$_2$ because it presents nearly the same band gap energy and generates H$_2$O$_2$ more efficiently and has a larger number of active sites with high surface reactivity than TiO$_2$ [17]. ZnO has aroused interest in photocatalytic applications due to its high excitonic stability, high electron mobility, good transparency, and strong luminescence at room temperature. As such, ZnO is widely used in several applications, ranging from water treatment to solar cells, and has been used successfully for the degradation of organic pollutants, in many cases outperforming TiO$_2$. Despite all these advantages, its use in wastewater treatment has limitations. In acidic solutions it can be dissolved to form metal cations. In alkaline solutions, however, this oxide can form Zn oxyanions, such as zinctes. [18] Furthermore, ZnO maintained in suspension is generally unstable in illuminated aqueous solutions since photocorrosion generally occurs when illuminated by ultraviolet (UV) radiation, resulting in a decrease in photocatalytic activity. The ZnO dissolution tendency occurs in both strongly acidic and alkaline media [11].

\[ \text{ZnO} + 2 \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\text{O} \quad (1) \]
\[ \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} \quad (2) \]

Compared to TiO$_2$, a smaller number of contaminant degradation studies have been conducted using ZnO, which could be a viable alternative for some applications [16]. Most studies of SA degradation have used TiO$_2$ as a photocatalyst, applying various strategies. Among these strategies, it is possible to mention the degradation of salicylic acid on TiO$_2$ (anatase), ZnO, CuO, Fe$_2$O$_3$, Fe$_3$O$_4$ and ZrO$_2$ nanocrystals under UV-A light. During the experiments carried out, a reactor was used with eight 8W mercury lamps of wavelength of 365 nm, and a highly polished aluminum reflector was employed for the photocatalytic study [19]. Likewise, there are also reports of the use of ZnO as a photocatalyst to SA degradation. In one of these reports, the SA degradation occurred
using a low-pressure mercury vapor lamp as radiation source (6W, 18 cm long) emitting ultraviolet radiation with a peak wavelength of 253.7 nm. The degradation experiments of salicylic acid were carried out in a batch reactor system. The reactor used was composed of a rectangular tray (16 cm × 5 cm × 5 cm) of borosilicate glass, mounted on a magnetic stirrer [20]. Another study reported the photocatalytic degradation of SA on ZnO in an aqueous medium and in the presence of irradiation with solar energy and ultraviolet light. The reactor for degradation of salicylic acid in this case consisted of a unit cell in the reaction compartment made of Pyrex, which had a quartz window equipped with a mercury vapor lamp. The temperature of the system was maintained at the desired value by the passage of air through the reaction and by the circulation of water around the reaction cell [21]. It should be noted that the nature and extent of photodegradation reactions depend on the intensities and wavelengths of light employed during these reactions [22]. Furthermore, the wavelength of the light used during the degradation processes of SA can play an important role both in its degradation rate and in the formation of byproducts [23].

Thus, in the present work salicylic acid was subjected to photocatalytic degradation in the presence of TiO\(_2\), ZnO and UVC light (254 nm). The aim of this work was to determine the photocatalytic activity of TiO\(_2\) against ZnO, with emphasis on the SA degradation using the same experimental conditions for the two semiconductors in suspension. An acidic effluent containing salicylic acid (pH = 3.0) was simulated during the experiments to assess the degradation of SA at acidic pH where TiO\(_2\) reportedly has higher oxidizing activity, and to keep SA close to its non-dissociated form. At the same time, it was verified whether ZnO corrosion under the adopted experimental conditions. The photocatalytic degradation of salicylic acid (SA) was achieved in reduced concentration (14.5 µmol L\(^{-1}\)) in an attempt to simulate reduced concentrations of SA present in the environment and to limit the occurrence of back reactions. Furthermore, the degradation kinetics of SA in solution during the performance of the proposed advanced oxidative processes in the reaction medium were also assessed. Finally, the chronic ecotoxicity to aquatic life was evaluated by exposure of *Ceriodaphnia dubia* to solutions resulting from SA degradation after treatment with TiO\(_2\)/UV and ZnO/UV systems. Thus, the feasibility of using ZnO, even under unfavorable reaction conditions, was evaluated as a possible substitute for TiO\(_2\) for the degradation of SA in the experimental conditions adopted in this work, using a reactor with a simple configuration containing a UVC light (254.0 nm) source.
1.1 MATERIALS

The reagents used in this work were salicylic acid (99.5%, Synth), zinc oxide (≥ 99%, Sigma-Aldrich), titanium dioxide (99.8%, Sigma-Aldrich - 100% anatase), methanol (100%, Baker), H₂SO₄ (99.0%, Isofar) and phosphoric acid (85.0%, Tedia). All reagents were analytical grade and used without any further purification.

1.2 METHODS

Initially, the SA degradation was carried using a Shimadzu model UV-1800 spectrophotometer to determine the concentration of TiO₂ that would lead to further degradation of salicylic acid, by monitoring the absorption at λ_max of 202.5 nm, with sample in a quartz cell with a 1 cm pathlength. HPLC analyses were conducted using an Agilent 1100 Series system. A Zorbax Eclipse XDB-C8 reversed-phase (RP) column (150.0 mm × 4.6 mm i.d., 5 μm particle size) was used at room temperature. The mobile phase was methanol/water (50:50), at a flow rate of 1.0 mL min⁻¹ and absorbance detection of 210 nm. A solution of phosphoric acid (pH = 3.0) was used to control the pH. The aliquots were filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter for analysis. Under the described analytical conditions, the SA retention time was approximately 6 min. Zinc determination was performed using a SOLAAR M5 flame atomic absorption spectrometer (Thermo Scientific) with a deuterium lamp for continuous background correction. The wavelengths applied were 213.8 nm, with a working range 0.1 - 2.0 mg L⁻¹ and gas using air/C₂H₂ (fuel gas flow of 1.0 L min⁻¹), to verify the stability of ZnO after irradiation of solutions by UV light and to verify the concentration of zinc in solution.

1.3 EXPERIMENTAL SETUP

All experiments were carried out in open beakers. One hundred milliliters of solution containing SA at a concentration of 14.5 μmol L⁻¹ in deionized water was stirred to maintain homogeneity.

1.4 DEGRADATION PROCESSES

The SA degradation reactions using TiO₂ and ZnO associated with UVC light (TiO₂/UV and ZnO/UV systems) were carried out at initial pH of 3.0. H₂SO₄ (0.1 mol L⁻¹) was used to adjust the pH of the solution. A reduced SA concentration was employed
(14.5 µmol L⁻¹) during the experiments performed. The photocatalysts were used in suspension under magnetic stirring. Before the reaction start, the system was maintained in the dark for 60 min to reach adsorption equilibrium. The concentrations of TiO₂ and ZnO in the reaction medium ranged from 0.5 to 2.0 g L⁻¹. During the experiments, the SA solution containing a suspension of known weight of catalyst powder was irradiated using a monochromatic UVC lamp (254.0 nm, 15 W). Sample aliquots were taken from the aqueous solution at 0, 10, 20, 30, 40, 50 and 60 min with a 5 mL plastic syringe and were submitted to centrifugation (Daiki, 80-2B). The samples were centrifuged for 8 minutes at 2200 rpm (0.99 G) to remove the photocatalyst. All experiments were performed in duplicate to assure precision and accurate data acquisition. As a result, error bars representing standard deviation are depicted in figures. All experiments were conducted at room temperature. The SA degradation experiments were realized in purified water from Purelab Option-Q (Elga, Lane End, Wycombe).

1.5 ECOTOXICOLOGICAL EVALUATION

Chronic toxicity assays were performed according to the Brazilian standard NBR 13373 [24] to determine the whole sample toxicity by exposure of Ceriodaphnia dubia to increasing concentrations of the resulting solution, containing an initial SA concentration of 14.5 µmol L⁻¹ after treatment with the TiO₂/UV and ZnO/UV systems employing a concentration of 1 g L⁻¹ of ZnO and TiO₂. For 7 days, a control group containing only Ceriodaphnia dubia in surface water (group 1) was monitored in relation to Ceriodaphnia dubia in the presence of solutions in contact with increasing concentrations of the resulting effluent of SA degradation processes using both TiO₂/UV (group 2) and ZnO/UV (group 3) systems. The effluent concentrations used in the ecotoxicological tests ranged from 1% to 100% v v⁻¹ in relation to the resulting solution of the SA degradation process when the TiO₂/UV system was used, and from 0.01 % to 50.0 % v v⁻¹ using the ZnO/UV system. The experiments were performed at a temperature of 24 °C. Groups 1, 2 and 3 were submitted to a period of 16 h light and 8 h dark during the experiments. Chemicals added to the deionized water for the oxidation process were removed prior to the bioassay.
2 RESULTS AND DISCUSSION

2.1 CHOICE OF REACTION CONDITIONS

In order to achieve the best photocatalytic activity in the degradation of a contaminant, important reaction parameters must be controlled. One of these parameters is the pH of the reaction. The effect of this parameter needs to be considered since industrial wastewater has pH that can be either basic or acidic. Thus, the zero-charge point ($\text{pH}_{\text{zpc}}$) of the catalyst (pH at which that surface has a net neutral charge) can be used to consider the ideal pH to carry out the degradation reaction of a contaminant using heterogeneous photocatalysis. [25]

When the pH of the solution changes, the surface charge of the TiO$_2$ particles also changes. Thus, in acidic or alkaline conditions, the titanium surface can be protonated or deprotonated, respectively, as shown in reactions 3 and 4:

$$\text{TiOH} + \text{H}^+ \rightarrow \text{TiOH}_2^+ \quad (3)$$

$$\text{TiOH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O} \quad (4)$$

In this way, the surface of the titanium in an acid medium will remain positively charged and negatively charged in an alkaline medium. It has been reported that titanium dioxide has a higher oxidizing activity at a lower pH, but the excess of H$^+$ ions can decrease the reaction rate [26].

Setting the pH at which the reaction will take place is important because it affects the interactions between the substrate and the photocatalyst, as well as the acid/base speciation of the TiO$_2$ hydroxyl groups and the reactivity of the photoformed oxidizing species on the surface of the photocatalyst. The pH = 3 was chosen in the degradation processes employed because at that pH, the interactions between positively charged TiO$_2$ and negatively charged salicylic acid would be maximized. A reduced SA concentration was employed (14.5 $\mu$mol L$^{-1}$), in an attempt to simulate reduced concentrations of SA present in the environment and to decrease the occurrence of the back reactions. The TiO$_2$ concentration was optimized in order to obtain the greatest possible degradation of SA and limit problems related to substrate adsorption in the photocatalyst and light scattering using the experimental conditions adopted. [27].

2.2 EFFECT OF CATALYST CONCENTRATION

The concentration of TiO$_2$ present in a photocatalytic process directly influences the overall photocatalytic reaction rate. When an excess of TiO$_2$ particles is used in a
photocatalytic process, a light screening effect can occur. This effect reduces both the surface area of the catalyst exposed to illumination and the efficiency of the photocatalytic process [28, 29]. Thus, any photoreactor chosen must be operated below the saturation level of the TiO$_2$ photocatalyst, to avoid excess of catalyst and to ensure efficient photon absorption. Most of these results are independent so a direct comparison between them cannot be made since working geometry, radiation fluxes, intensity and wavelengths used are different. One study showed that the optimum catalyst loading varies in the photocatalytic processes and that this variable is mainly dependent on the dimension of the photoreactor employed [28].

Thus, the degradation of SA by the TiO$_2$/UV and ZnO/UV systems was investigated by UV-Vis spectrophotometry in order to carry out an initial assessment of the concentration of catalyst leading to highest SA degradation utilizing TiO$_2$ (100% anatase). Figure 1 presents the change of absorbance for SA with irradiation time. The optimum loading of catalyst until 50 min was found to be 2.0 g L$^{-1}$ of TiO$_2$. However, after 50 minutes of reaction, there was a decrease in the rate of the degradation using a TiO$_2$ concentration of 2.0 g L$^{-1}$. After 60 min of reaction, slightly less SA degradation was observed using a TiO$_2$ concentration of 2.0 g L$^{-1}$. Thus, all SA degradation experiments were carried out using TiO$_2$ at the concentration of 1.0 g L$^{-1}$ to avoid lower efficiency of the photocatalytic process due to the light screening effect.

Figure 1 – Effect of catalyst weight on photocatalytic degradation of SA in deionized water. Catalyst = TiO$_2$; [SA] = 14.5 µM; pH = 3.0, catalyst load = 0.5 – 2.0 g L$^{-1}$ (A = 0.5 g L$^{-1}$, B = 1.0 g L$^{-1}$, C = 2.0 g L$^{-1}$).
A concentration of 1.0 g L⁻¹ of ZnO was used in the degradation experiments for evaluation of the SA degradation employing the ZnO/UV system as an alternative to TiO₂/UV system. Figure 2 presents the change in absorbance of solutions containing SA under the same conditions employed in the experiments using TiO₂ as catalyst. Figure 2 shows that monitoring the degradation of SA by UV-Vis spectrophotometry indicated degradation values of 88% and 80% after 60 min of reaction when the TiO₂/UV and ZnO/UV systems were used, respectively. Thus, it was possible to visualize the efficiency of both systems in the photodegradation of SA.

Figure 2 – Influence of catalyst on degradation of salicylic acid in deionized water. Catalyst load = 1.0 g L⁻¹; [SA] = 14.5 µM; pH = 3.0.

![Photocatalytic degradation of SA monitored by HPLC](image)

After obtaining the preliminary results for the SA degradation by monitoring with UV-Vis spectrophotometry in aqueous medium, the SA degradation was also monitored by HPLC, using TiO₂ and ZnO concentration of 1.0 g L⁻¹ in deionized water.

To illustrate the HPLC results for SA degradation during reaction, Figure 3 contains the chromatograms observed after 0, 10, 30 and 60 min of monitoring, showing both the decrease of the characteristic peak of SA and the appearance of degradation products in the interval between 2 and 3 min. Importantly, after 50 min of reaction (not shown), when the TiO₂/UV system was employed, the remaining characteristic SA peak was little intense and similar to that observed after 60 min of reaction (Figure 3a), so that the integration of this peak impaired determination of a reasonable value for its area. However, when the ZnO/UV system was employed (Figure 3b), after 40 min of reaction (not shown), the characteristic SA peak was also no longer observed.
Observing Figure 3, it is possible to notice two characteristic peaks of SA degradation products when using the TiO2/UV system (Figure 3a). In contrast, only one peak is observed between 2 and 3 min in the chromatogram resulting from SA degradation when the ZnO/UV system (Figure 3b) was used. Thus, the differences observed in Figure 3a and 3b suggest that different SA degradation mechanisms may occur when the TiO2/UV and ZnO/UV systems are used.

Figure 3 – Decay of the characteristic SA peak and formation of degradation products throughout the reaction over time monitored by HPLC in deionized water. a) Catalyst = TiO2; catalyst load = 1.0 g L\(^{-1}\). b) Catalyst = ZnO; catalyst load = 1.0 g L\(^{-1}\).

When TiO2 is used as a semiconductor in the SA degradation, after the generation of the electron-hole pairs, the holes that survive recombination can react with salicylic acid through two possible reaction pathways: (i) direct electron-transfer (DET) oxidation of substrates interacting with the oxide surface - charge transfer reactions; and (ii) reactions induced by free or trapped hydroxyl radicals \(-\cdot OH-like induced\). Previous studies have reported that the degradation of salicylic acid mainly undergoes direct electron-transfer (DET) oxidation when TiO2 is used as a photocatalyst [27]. Thus, SA forms a charge transfer complex on the TiO2 surface [23].

However, when ZnO is used as a semiconductor for the degradation of SA, another reaction pathway after the generation of the electron-hole pairs occurs. So, in this case, reactions induced by free or trapped hydroxyl radicals \((-\cdot OH-like induced\) prevail [21].

Figure 4 shows as the SA peak area changed as a function of time, which shows complete degradation of SA after 60 min in both cases. However, complete elimination of the SA in aqueous medium occurred after 40 min of reaction when ZnO was used and after 50 min when TiO2 was used, since the peak area corresponding to the SA was
considered to be zero due to the impossibility of reliable integration. Thus, it can be stated that under the same reaction conditions, SA degradation was effective after 60 min using both TiO\textsubscript{2} and ZnO as photocatalysts.

The values of pH\textsubscript{pzc} (pH at the point of zero charge) of ZnO and TiO\textsubscript{2} were reported to be 8.6 and 6.8, respectively [11, 30]. The surface of both catalysts is positive below of pH\textsubscript{pzc}. Salicylic acid exists as its anion when pH > pKa (pKa = 2.97) [17]. Since the photocatalytic degradation experiments were performed at a pH slightly above the pKa of SA, apparently there was electrostatic attraction between the catalysts and SA sufficient for its adsorption on the surface of ZnO and TiO\textsubscript{2}, leading to efficient degradation of SA, as observed in Figure 4 after 60 minutes of reaction.

2.3 KINETIC ANALYSIS

In order to verify the order of reaction for the degradation of SA, the corresponding equations for first-, second- and zero-order of reaction were adjusted to the absorbance versus time data from Figure 1 when TiO\textsubscript{2} was used as catalyst, and from Figure 2 when ZnO (1g L\textsuperscript{-1}) was used as catalyst. As can be observed in Table 1, the best fit obtained was for the first-order reaction for TiO\textsubscript{2}, but for ZnO it was not possible to obtain a clear distinction between the reaction orders. Although for ZnO the best linear fit was not clear because the correlation factor values of the first- and second-order fits were close to each other, it is reasonable to consider a similar degradation mechanism for...
both catalysts. Therefore, first-order kinetics was also chosen for ZnO. All parameters of the linear fit for ZnO can also be observed in Table 1.

Figure 5 - First-order rate graph of salicylic acid degradation in deionized water. Catalyst = TiO$_2$; catalyst load = 0.5, 1.0 or 2.0 g L$^{-1}$

To illustrate the change in the slope of the first-order kinetics data, linear plots of $\ln(A/A_0)$ versus irradiation time $t$ for SA degradation using different concentrations of TiO$_2$ as catalyst are shown in Figure 5. Considering first-order reactions, the UV-Vis results for the 1.0 g L$^{-1}$ TiO$_2$ catalyst indicated a rate constant of $(5.79 \pm 0.25) \times 10^{-4}$ s$^{-1}$. For the same concentration of ZnO, a rate constant of $(5.38 \pm 0.97) \times 10^{-4}$ s$^{-1}$ was obtained. According to these results, considering the experimental uncertainties, it can be assumed that the TiO$_2$ and ZnO catalysts presented similar performance for the degradation of SA.

The HPLC results for the degradation of SA using either TiO$_2$ or ZnO as catalyst confirmed the first-order degradation of both semiconductors (Figure 6 and Table 1). On the other hand, there was also similar efficiency of SA degradation using both ZnO and TiO$_2$, as indicated by the UV-Vis results (Table 1). The results of both UV-Vis spectrophotometry and HPLC techniques were compatible regarding the reaction order, but there was some change considering the rate constants calculated by the two techniques, since the rate constants obtained by HPLC were 2-3 times larger than those obtained from UV-Vis spectrophotometry. The larger rate constants obtained from HPLC results may be attributed to the possibility of measuring more than one absorbing species using UV-Vis spectrophotometry, unlike HPLC, a separation technique that can only measure the SA signal during the degradation process.
Table 1. $R^2$ and first-order rate constant values for the degradation of salicylic acid.

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<tr>
<th>Technique</th>
<th>Photocatalyst (g L$^{-1}$)</th>
<th>Correlation ($R^2$)</th>
<th>First order rate values $k$ ($\times 10^4$ s$^{-1}$)</th>
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Figure 6 - HPLC results: First-order rate graph of salicylic acid degradation in deionized water. [SA] = 14.5 µM; pH = 3.0.

2.4 PHOTOCORROSION OF ZNO SURFACE

ZnO is susceptible to dissolution, so it is important to determine the amount of zinc present in the solution after the degradation process of SA. The data obtained by atomic absorption spectrometry revealed that after 60 min of reaction there was a small loss of ZnO after exposure to ultraviolet radiation. The dissolution of ZnO observed was low (0.3% loss of zinc) using the experimental conditions adopted.

2.5 ECOTOXICOLOGICAL EVALUATION

After exposure of Ceriodaphnia dubia to even higher concentrations of the resulting solution obtained from the treatment of SA by the TiO$_2$/UV photocatalytic system, it was observed that at concentrations up to 70% v v$^{-1}$ of this solution, there were no significant deleterious effects on the survival and reproduction of the organisms.
studied. Significant noxious effects were only observed at a concentration of 100 % v v⁻¹ of this resulting solution. However, when the solution with the product of SA degradation was evaluated using the ZnO/UV photocatalytic system, no harmful effects were observed at a concentration of only 0.01 % v v⁻¹ of this solution. The resulting solution was considered significantly toxic to *Ceriodaphnia dubia* at a concentration of only 0.05 % v v⁻¹. The ecotoxicological evaluation of the effluent obtained from using the ZnO/UV photocatalytic system for the degradation of SA was performed in duplicate to confirm the results obtained.

These results can be understood more clearly when observing the chromatograms resulting from the degradation process of salicylic acid monitored by HPLC (Figure 3). Figure 3a, which shows a chromatogram resulting from the degradation process using the TiO₂/UV system, between retention times of 2 and 3 min, reveals the formation of two degradation products as SA degradation progressed. Meanwhile, in the chromatogram resulting from the degradation process using the ZnO/UV system (Figure 3b), it is possible to observe the formation of only one degradation product between the retention time of 2 and 2.5 min. From this information, even without identification of the degradation products formed, it was possible to observe differences at the end of 60 min of SA degradation when TiO₂/UV and ZnO/UV systems were employed. This difference in degradation products has direct repercussion in the chronic ecotoxicity tests performed. Therefore, the chronic toxicity test showed that using the ZnO/UV system for SA degradation had very harmful effects on the microcrustaceans evaluated even at very low concentrations, with negative consequences for the environment.

**3 CONCLUSIONS**

In this study, the effects of using two different commercial photocatalysts on the SA degradation were evaluated. The results obtained revealed that initially their use in the studied degradation processes provided an efficient SA degradation under the experimental conditions evaluated employing the TiO₂/UV and ZnO/UV systems. Thus, both catalysts are viable alternatives for SA degradation.

The use of commercial oxides in heterogeneous photocatalysis is interesting because of the possibility of their application in processes of degradation of contaminants on a larger scale. However, it is important to note that in the case of the use of such oxides, non-selective degradation of organic compounds occurs, so the development of new
photocatalysts may be more interesting when there is a need for its application in the selective photocatalytic activity for a given class of contaminant.

A first-order reaction was observed for the SA degradation both by UV-Vis spectrophotometry and by HPLC after the evaluation of the data obtained.

The concentration of zinc present in the solution after the degradation process of SA was low using the experimental conditions adopted.

The chronic ecotoxicity tests that used the ZnO/UV photocatalytic system for degradation of salicylic acid lead to a degradation product with significant harmful effects on the studied microcrustacean (*Ceriodaphnia dubia*) even at low concentrations in the effluent resulting from the reaction. This fact prevents the use of this system for degradation of the organic contaminant studied.

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