Chapter 191

Synthesis and characterization of photocatalyst from titanium dioxide and zinc oxide supported on laponite clay RD

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ABSTRACT

The industrial and agricultural expansion together with the growth of cities has raised environmental questions about the disposal of effluents and their possible treatments. Organic wastes with industrial phenolic compounds and pesticides are not treated properly in WTPs, where the methods used as flocculation and decantation are inefficient for this class of compounds. In the last decades, ways of eliminating such compounds from effluents have been studied, one of these techniques being the Advanced Oxidative Processes (POA). In POA, through a generated radical, it is possible to mineralize harmful compounds to innocuous compounds such as CO2 and H2O. The present work aimed to synthesize and characterization of two photocatalysts based on titanium dioxide and zinc oxide capable of degrading organic molecules using POA, through natural solar irradiation. The synthesis was performed using titanium dioxide (TiO2) and zinc oxide (ZnO), which in their crystalline forms have photocatalytic properties. TiO2 and ZnO were supported on a synthetic clay (Laponite RD), which has a large adsorptive capacity. The characterization of the composites was performed utilizing infrared spectroscopy (FTIR) and X-ray fluorescence (XRF), where morphological and composition characteristics of the synthesized composites were obtained. To understand the photocatalytic behavior of the materials, a study of the speed of degradation of the methylene blue organic dye (AM) in the presence of sunlight was performed. The photodegradation kinetics was accompanied by the UV-visible spectroscopy technique, where the efficiency of the new photocatalysts increases about 4 times the degradation speeds.

Keywords: Photocatalyst, Photocatalysis, Titanium oxide, Clay.

1 INTRODUCTION

The use of industrial products and their unbridled disposal without proper treatment has been in recent decades one of the greatest concerns when it comes to the environment and development of contemporary society. Even with the adoption of new legislative norms, these have not proved efficient to solve the problem of waste generated by industries and cities in general. As a way to treat this problem, researchers have been looking for methods and alternatives that enable the treatment of effluents. Currently, the treatment processes for industrial and domestic tailings are incineration, biological treatment and activated carbon treatments. Therefore, because they present a high cost, most of this waste is not disposed of adequately [1,2].

Environmental problems in recent years have become increasingly critical and more frequent, promoted by population growth and increased agro-industrial activities. Changes in soil, water and air quality are observed as a reflection [3].

The contamination of natural waters (rivers, streams, ponds, lakes, springs, groundwater, aquifers) has required great attention to sectors that consume large volumes of water and generate high volumes of effluents, such as the agricultural sector (irrigation of crops) and the textile sector (effluents) that if not treated properly cause serious damage to the environment [3,4]. The agricultural sector, in addition to using natural waters for irrigation, has as an aggravating factor effluent containingtoxic substances, the so-called phytosanitary or agrochemical pesticides, derived from the washing of machinery or incorrect disposal of packaging. They are toxic recalcitrant compounds (highly stable, resistant to natural chemical composition) that can accumulate in the environment [4]. The effluents of the textile industry have the characteristic of being highly colored because they contain dyes that did not attach to the fiber during the processing process. The molecule of a dye can be divided into two main parts, the chromophore group responsible for the coloration of the pigment and the second part of the structure responsible for the fixation in the fiber [3].

The pollution of natural waters with these compounds, agrochemicals and dyes, cause changes in biological cycles affecting the process of photosynthesis. Por being recalcitrant are not biodegraded by the organisms present in biological treatment systems , and with the accumulation, their concentration can reach the lethal dose in organisms such as invertebrates and fish. Studies show a remarkable carcinogenic and mutagenic potential inthese compounds and their derivatives [3-5].

Techniques such as coagulation, flocculation separation, flotation and/or sedimentation, present a high efficiency when used in the removal of particulate matter, however, in processes involving a dissolved organic compound and color removal, these techniques are ineffective. Processes using activated carbon as an adsorbent present a considerably higher efficiency, however for cationic dyes this technique is inefficient due to the surface of activated carbon ifr positive [3,4]. Therefore, it is necessary to develop research to find alternative low-cost technologies with better performance.

1.1 ADVANCED OXIDATIVE PROCESSES

In recent years the Advanced Oxidative Processes (AOP) have been studied for the treatment of effluents, as a means of reducing or eliminating molecules harmful to living beings and ecosystems. The AOPs are an alternative of moderate cost with other methods of environmental contamination, considering, for example, the use of ultraviolet lamps for the generation of ozone in the aqueous environment, being the long-term method more sustainable. The technique is based on the formation of the hydroxyl radical (OH•), where its high reactivity (standard reduction potential 2.6 V) can mineralize molecules to inert compounds such as CO2 and H_2O [1,2].

The AOPs are divided into two classes, heterogeneous and homogeneous. The homogeneous processes involve the use of ozone (O_3), hydrogen peroxide (H 2 O 2), and the decomposition of H_2O_2 by acid catalyse, the nde the medium itself is responsible for generating the OH• radical. In heterogeneous or photo-Fenton processes, semiconductors such as iron oxide II (FeO), zinc oxide (ZnO) and titanium dioxide (TiO_2) are used, which when irradiated by a certain wavelength generate the OH• radical in the reaction medium [2,6].

Processes involving O_3, such as O_3/UV, O_3/H_2O_2, O_3/TiO_2, have been alternatives in the treatment s of organic compounds, such as dyes, showing efficiency in environmental decontamination. The processes can react with a large class of organic compounds, given their high oxidation potential (E° = 2.08 eV). However, the cost of these techniques is not cheap, as their instability prevents storage. It is therefore necessary to generate the reaction *in situ*, which raises the cost of operation [5].

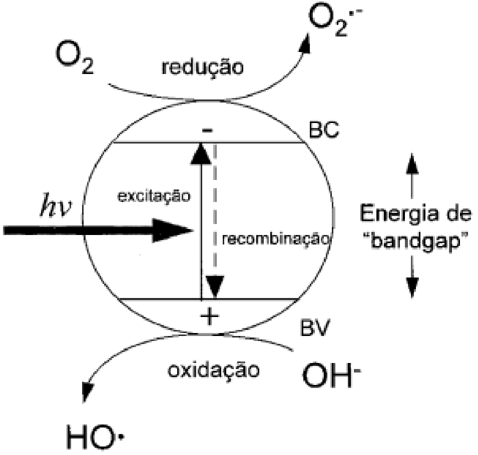
Fenton reactions have been used in the decontamination of soils and groundwater in aqueous effluents containing pollutants such as atrazine, ethylenediamine tetrahedral acid (EDTA), phenols and others [7].

1.2 PHOTOCATALYSIS

Among the AOPs, heterogeneous photocatalysis has been widely studied in the last five decades with the use of several semiconductors for the degradation of organic compounds present in effluents. The first studies on heterogeneous photocatalysis took place around the year 1970 when in one of the Fujishima and Honda experiments, the oxidation of water into oxygen and hydrogen was observed. Several studies have been done in this area, involving a semiconductor to generate the hydroxyl radical (OH•).

A semiconductor that has been widely studied for photocatalysis in water and wastewater treatment because it shows promise are titanium dioxide (TiO_2) and zinc oxide (ZnO). Compared to other semiconductors, they are highly photo-reactive, low-cost, photo-stable, non-toxic and can be used in a wide pH range. When irradiated with a wavelength of less than 380 nm, (energy greater than band *gap* 3.2 and 3.7 eV respectively), electrons (and $_{bc}^{-}$) are generated in the conduction band and gaps (h_{bv}^{+}) in the valence band (Figure 1) . The gaps are generated to interact with the organic molecule generating R^+ or with the aqueous medium generating OH•. By interacting with the gaps the chemical bonds of the molecules are fragmented, forming radicals and thus generating an instability that leads to a chain reaction. This reaction happens in semiconductors as long as there is enough surface for the formation of radicals. The hydroxyl radical (OH•) has a great importance in the reaction action, because its size and its low selectivity makes it able to degrade most of the organic compounds presented in the literature [2,6,8,26].

Figure 1: Representative scheme of a semiconductor particle, where BV valence band and BC conduction band.



Source: Adapted from [6].

$_{TiO2}$ has three crystalline forms in the study of photocatalysis: brookite, rutile, and anatase. The anatase phase has characteristics that make it more widely used, such as high surface area (50 m^2/g), high density of active adsorption sites and lower speed in electron/gap recombination. This last property is extremely important for the conferral of a longer time for stabilization of the surface of the catalyst, thus promoting a greater number of radicals in the reaction medium and greater mobility of electrons. Its *band gap* is 3.2 eV, corresponding to a wavelength of 388 nm. Irradiation with this range of ultraviolet spectrum can be obtained by exposure to sunlight, even though this range of the electromagnetic spectrum is less intense than the range corresponding to the visible [9].

ZnO has a wurtzite-like hexagonal structure, has alternating planes composed of tetrahedrically ordered Zn^+ and O2, which provides piezoelectric and pyroelectric properties when doped with a specific metal. By having a relatively open structure, ZnO enables the incorporation of dopants, contaminants and impurities into its crystal lattice. It has a band gap energy of 3.4 eV, an energy corresponding to a wavelength of 365 nm. Like TiO_2, this wavelength can be reached by sunlight, which makes it possible to use ZnO for photodegradation [26].

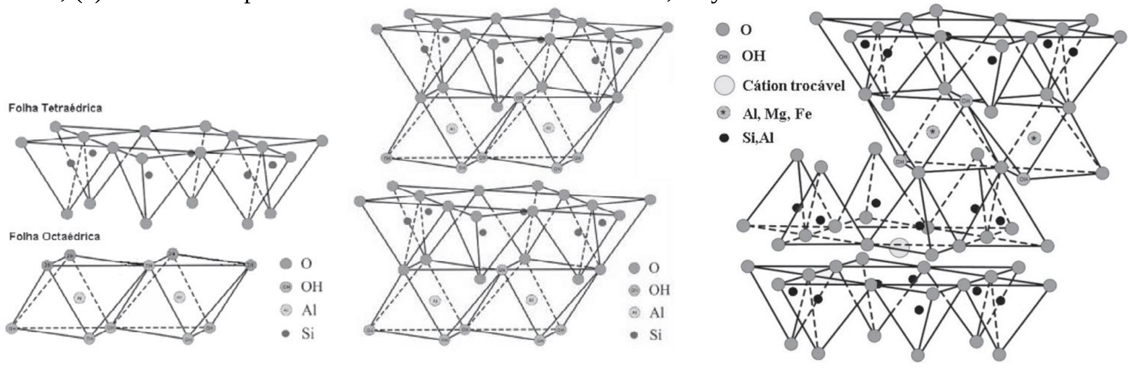
Even with these properties that give advantage over other semiconductors, it has been found as obstacles to full application: the removal of the catalyst and electron/gap recombination, the latter being the main limiting factor in the photodegradation process. To solve these problems, it has been proposed the use of supported semiconductors, in which the support has no photocatalytic activity. The implementation of clay as a support presents advantages that help in the recovery of the photocatalyst, in addition to the possibility of using the adsorptive properties of these in the process [2, 6,10].

1.3 CLAYS

The use of clays dates back to the beginning of civilizations in the manufacture of ceramic utensils, bricks and tiles. Recently several relatively new technological applications are being developed and applied, such as adsorbents in bleaching processes in the textile and food industry, transportation of drugs, support for catalysts, paints and as adjusters of rheological properties in fluids of petroleum drilling, cosmetics and paints. [11].

The structures of the clays in the solid phase are made up of crystalline lamellae mostly at the micrometric scale, with some at the nanometer scale, stacked as playing cards. The lamellae can be formed by two types of crystalline leaves, with octahedral or tetrahedral structure. According to the arrangement of the leaves are defined the clay groups; where the bond of a tetrahedral sheet with an octahedral one forms the 1:1 structure, and the 2:1 structure is conceived with an octahedral sheet between two tetrahedral sheets (Figure 2). As the most abundant of 1:1 clays we have kaolinite and among the clays 2:1 is smectite [11].

Figure 2: (a) schematic representation of tetrahedral and octahedral leaves, (b) schematic representation of kaolinite structure, 1:1 clay mineral; (c) schematic representation of the structure of smectite, clay mineral 2:1.



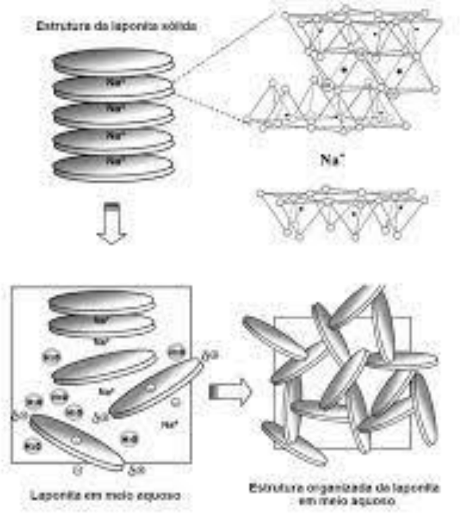
(a) (b) (c)

Source: Adapted from [17]

The adsorption property of clays is linked to their cation exchange capacity (CTC) and interplanar distancing. CTC is defined by the exchange of charges on the surface of the lamellae, where an excess of negative charge is formed by the isomorphic replacement of ions of $Si^{4}+$ by cations of $Mg^{2}+$ and Al^{3+}. This substitution has this name because the sizes of these ions are similar, which does not interfere with the structure of the tetrahedral s sheets. This exchange generates a deficiency of charges, making the lamellar surface negatively charged. The other important feature is the tendency to expand the distancebetween the lamellae, such as the adsorption of water molecules by smectites. In this case, one can expand the interlamellar space up to 40 Å, with the original being 9.5 Å an increase of 421% [12].

Laponite RD, belongs to the class of synthetic clays, with lamellar structure 2:1; it has two tetrahedral layers s and an octahedral intersperseds apresenting the molecular f... Laponite also forms colorless colloidal dispersionses and estáveis. Possui also hydroxyl groups on its surface, which provides electrostatic interactions with ions and polar molecules dispersed in solution.

Figure 3: Laponite structure. Source: Adapted from [31]



1.4 SUPPORTED PHOTOCATALYSTS

The use of clay as a support seeks to solve the problem of separating the photocatalyst from the medium for possible reuse in different degradation cycles. As described by Lopes, et. al [13], the use of clays as support for TiO2 and showed efficiency in the discoloration of organic dyes [13].

The process of modifying clay through the incorporation of substances on its surface and interlamellar regions (in clays that have interlamellar regions such as bentonites) followed by calcination is called pillarization. The compound inserted in the interlamellar region forms a kind of pillar, providing an increase in the space between the layers of clay, giving a configuration similar to zeolites, which are naturally porous due to the spacing between the gills, an interbasal distance of 7 to 20 Å [14].

Merg. J., et al.demonstrated that the incorporation of titanium dioxide in zeolites for application in heterogeneous photocatalysis was efficient. Improvement in semiconductor performance was observed when exposed to UV-vis irradiation. The material presented uniform granulometry, facilitating the removal of the photocatalyst from the medium. This material presents an industrial alternative for the treatment of effluents [15].

The development of new photocatalysts has already been studied in recent years. However, research and development of high-performance and low-cost materials with improved properties such as the ability to withstand various degradation cycles is still needed. The photoactive properties of$_{TiO2}$ and the properties of Laponite-RD added together may be promising in these aspects.

1.5. SYNTHESIS OF SUPPORTED PHOTOCATALISERS

The synthesis of photocalisers has been studied as a way to treat effluents and contaminants in waterways, reservoirs and wells. There is more than one way to synthesize a photocatalyst [13, 14, 22, 25, 29], among them dispersion in solution and doping with some other metal, clay or polymer as seen in Lopes et. al. [13]. Mostly using a metal to dope a polymer or clay, noting that the metal used must necessarily have a low band-gap, so that there is the photochemical effect.

In cases where clay is used, it can be of natural or synthetic origin, in the first case some treatment is done totivate the sites of activity, eliminate impurities and / or increase the interlamellar distance.

The use of support has shown that the photochemical properties of metals have been improved. In search of materials that have better performance, the doping technique with another material also promotes better recovery of photocatalysts being used in other cycles.

2 OBJECTIVE

Andthis work aimed to synthesize a new photocatalyst using Laponita RD clay as support for TiO_2 and ZnO. The viability of the photocatalyst was tested in degradation assays of the methylene blue dye and the kinetics of the process were monitored by UV-VIS spectroscopy.

Specifically, the objectives were:

- Synthesize a titanium oxide photocatalyst supported on Laponita RD synthetic clay.
- Characterize the composite through techniques such as: infrared spectroscopy, X-ray fluorescence.
- To study the photocatalytic activity in an organic dye (methylene blue) through irradiation in visible light, with monitoring of kinetics by the technique of ultraviolet-visible spectroscopy.

3 MATERIALS AND METHODS

3.1 PHOTOCATALYST SYNTHESIS

3.1.1 Dispersion of titanium dioxide and zinc oxide

The synthesis of the compound is based on Cervantes et. al. [6], where a solution containing 0.5 m L of hydrogen peroxide, 0.5 m L of ammonium hydroxide, 0.10 g of oxide is prepared in a volume of 40.0 m L of deionized waterkept in agitation for 24 hours.

3.1.2 Preparation of the oxide/clay catalyst

A suspension of Laponita-RD clay was prepared at a concentration of 2.5 g. L-1 under magnetic stirring for 24 hours, for a total dispersion of the clay in the aqueous medium.

5.0mL of titanium oxide solution was added to 150.0mL of clay suspension, keeping the system in magnetic agitation for 24 hours followed by calcination at 600°C for 2 hours.

3.2 DISCOLORATION TESTS WITH METHYLENE BLUE (AM)

For the experiment involving the discoloration of methylene blue, 1000 mL of an aqueous solution containing methylene blue dye with a concentration of 3.0x 10-5 mol $^{L-1}$ was prepared. This solution was distributed in beakers with a volume of 50.0 ml of solution. To each beaker 0.5g of the synthesized photocatalyst was added. The samples were irradiated by natural solar lighting (INS). A sample was kept in the dark for adsorption study.

3. 2.1 UV-Visible Spectroscopy

The bleaching kinetics of the solution was accompanied by UV-visible spectroscopy measurements. The technique is the observation of the absorption of electromagnetic radiation in the visible and ultraviolet regions of the spectrum. It is among the most widely used techniques for studying compounds and their reactions. Using the technique and Lambert's Law - Beer (Equation 1), it is possible to follow the decrease or increase of concentration in the analyzed solutions, thus being able to determine the kinetics of the reactions [22].

Figure 5 (Results and Discussions section) shows the graph of the concentration curve for AM at concentrations constructed for Lambert-Beer calibration and to identify the best concentration and wavelength where absorption is maximum to work with the photocatalysts.

3.3 CHARACTERIZATION

To verify the modification of the clay and understand the morphology of the photocatalyst, the following analyses were made: for the determination of the amount of material incorporated in the clay will be used the technique of X-ray fluorescence (XRF). Fourier transform infrared spectroscopy (FTIR) providesu information about the chemical groups present in the sample.

3.3.1 X-ray Fluorescence

X-ray fluorescence is a non-destructive and multi-elemental analytical technique capable of identifying elements with an atomic number equal to and greater than 12, through the characteristic X-rays kα, kβ or Lα, Lβ of the elements contained in a sample. A beam of X-rays is applied to the sample, which interact with the atoms causing ionization of the inner layers of the atoms. The filling of the resulting vacancies, by more peripheral electrons, induces the emission of X-rays characteristic of each element of the sample, thus being able to determine qualitatively and quantitatively the presence of the elements [20]. The analysis was performed in an EDX equipment – 720 SHIMADZU for the quantitative determination of the incorporation of oxide in the clay structure.

3.3.2 Infrared Spectroscopy (FT-IR)

Infrared spectrometry is a technique that uses the absorption of energy in the infrared region to identify a compound or investigate the composition of a sample. The technique is based on the fact that the bonds of substances have specific vibration frequencies. Thus, the infrared spectrum serves molecules as fingerprints serve humans [18].

For mid-infrared analysis , the JASCO infrared spectrometer model 4100 with Fourier Transform (FT-IR) and triglycine sulfate detector (TGS) was used. The spectra were obtained in the range of 4000-400 cm−1, with a resolution of 4 cm^{-1} and 64 scans. The samples were supported on KBr tablets.

The clay, TiO_2, ZnO and photocatalyst samples were macerated in mortar and quartz pstyle, with a ratio of 3% m/m dried at 150 °C for 1 hour and supported on KBr tablets**.**

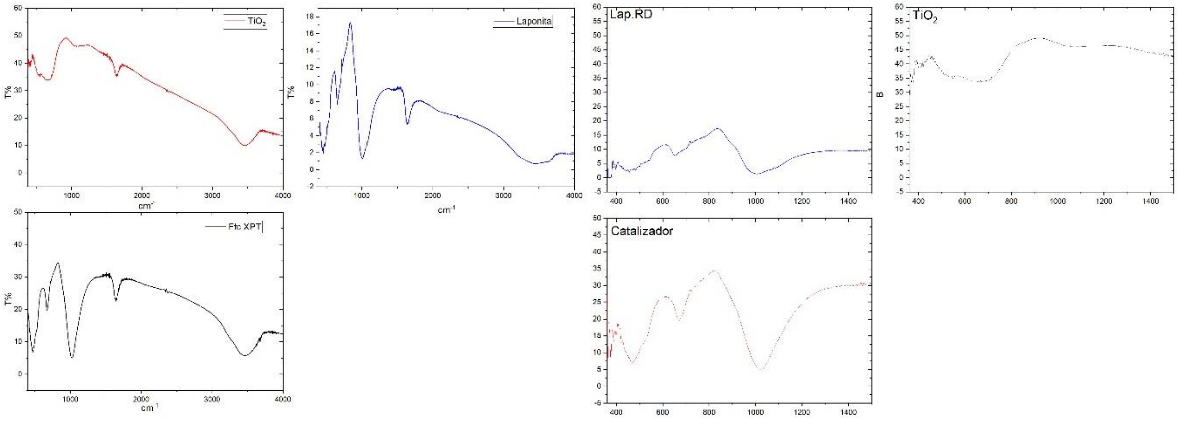
4 RESULTS AND DISCUSSIONS

The synthesized material was characterized by XRF and (FT-IR) to determine the incorporation and percentage of TiO2 and ZnO in the lamellar structure of the clay. Figure 4 shows the infra-red spectrum of the samples, before and after the synthesis. For operational reasons, the data of (FT-IR) for the ZnO were not entered in this study.

4.1 CHARACTERIZATION BY FT-IR

The results obtained for the infrared spectroscopy technique can be seen in Figure 4. The characteristic peaks of Laponite are observed, such as the characteristic bands of 480 cm-1 (Si-O-Mg), 949 cm-1 (Si-OH), 1003 cm-1 (Si-O), and 1645 cm-1 (O-OH) [27]. It was noticed that peaks do not present a good definition, and can be attributed to a band overlap as in the case of 949 cm-1, where it may have been added to the peak 1003 cm-1 and 1645 $^{cm-1}$ where the equipment presented a noise attributed to the excess $_{CO2}$ during the development of the analyses.

Figure 4: FT-IR spectra of the samples, where transmittance T(%) is represented as a function of the wavelength ($^{cm-1}$). Right: Shows the entire spectrum of the samples, Left: shows the part of interest.



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According to Costa *et. al.* [28] The characteristic peaks for TiO2 in anatase form are between 450 and 600 $^{cm-1}$. It was evidenced in the photocatalyst spectrum a peak in the region of ~450 cm-1 and another peak in ~650 cm-1 that can be attributed to TiO_2 or a Mg-O-Mg bond of laponite as described in Aguiar A. S. [27].

4.2 CHARACTERIZATION BY XRF

The verification of the incorporation of TiO_2 and ZnO in the Laponite clay was observed through the technique of X-ray, and the result iflorecences presented in Table 1. The data are also presented after the degradation/discoloration of the AM solution, to observe the wear of the photocatalyst. The catalysts were defined as XPT for the embedded photocatalyst with TiO_2 and XPZ for the photocatalyst embedded with ZnO.

An increase in the percentage of $TiO2$ and ZnO oxides is observed concerning their quantities in the clay before synthesis (pure), confirming the incorporation of the oxides in the photocatalyst. It is also observed that in the case where fluorescence was measured after the photodegradation experiment, there was not a very large variation in the relative amounts of oxides, which may indicate that the synthesized photocatalyst does not undergo considerable degradation during the process. This fact indicates that the photocatalyst can be applied in more than one photodegradation cycle, facilitating its future application.

Table 1: Quantitative XRF results. Source (owned)

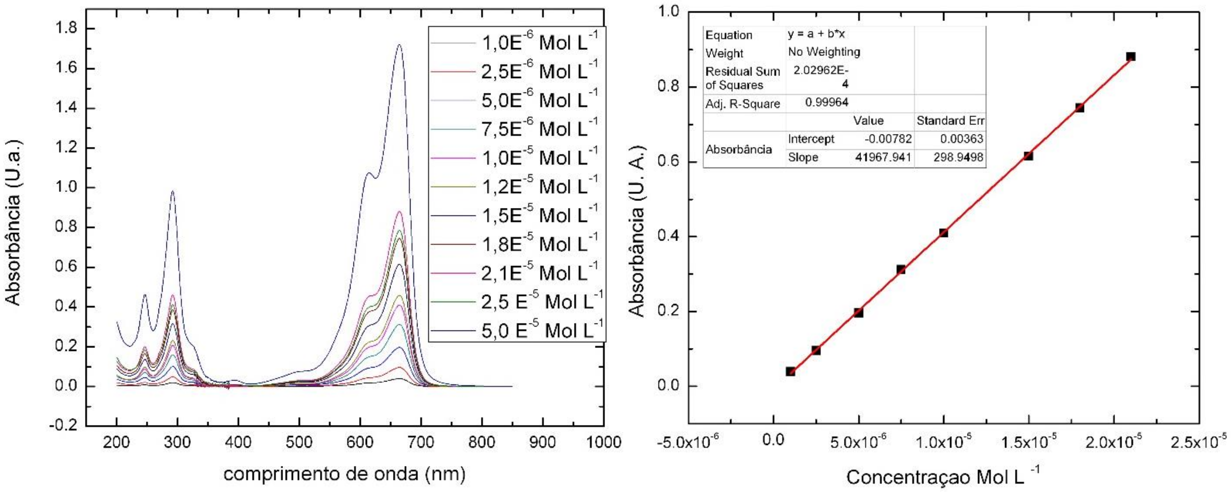
Oxide	Laponite RD	XPT	XPT_{EX}	XPZ	XPZ_{EX}
	%	%	%	%	%
SiO_2	97,467	94,595	94,860	98,126	95,741
OS_3	1,999	3,166	3,342	0,774	2,922
CaO	0,369	0,376	0,364	0,232	0,337
Fe_2O_3	0,074	0,106	0,138	0,120	0,102
$Uncle_2$	0,053	1,089	0,988	0,031	0,055
K_2O		0,584	0,230	0,268	0,283
Cr_2O_3		0,025		0,018	
ZnO		0,003	0,025	0,382	0,490

4.3 PHOTODEGRADATION OF DYE

The samples were submitted to photodegradation via natural solar irradiation (INS), for 6 hours in the afternoon, with absence of clouds, on the Campus of the Federal University of Jataí in June. A methylene blue solution was used in water with a concentration of 3.3 x 10-5 mol. $^{L-1}$ divided into two aliquots of 50.0 mL, being added 0.015g of the prepared photocatalysts. Two samples were prepared with each reagent and one containing only AM. And these samples were divided into two groups, those that would receive INS and those that would be kept in the dark, to verify the adsorptive or degradation effect without the presence of light. The analyses were initiated from the preparation of the samples, the first being zero time. The experiment was carried out with equal intervals of 60 minutes between the análysis, to verify the kinetics of degradation/discoloration.

The curves obtained were also used for the application of Lambert-Beer law, taking the absorption at most of the band of 665 nm. Figure 5 Left shows the BF curves in different concentrations (calibration curve), which was used to determine which would be the best concentration range to be worked. Figure 5 Right is a linear adjustment of the variation of BF concentration versus absorbance.

Figure 5: *Left* graph of the absorbance of AM concentrations obtained by UV-vis, *Right* linear fit of the variation of the concentration of BF.



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The evaluation of the discoloration was performed utilizing the UV-visible spectroscopy technique, where small aliquots of the sample were analyzed with periodic intervals observing the absorbance (Abs) and by Lambert Beer's Law, calculating the concentration of dye still existing during degradation, according to equation 1:

$$A = \varepsilon l[AM] \qquad (1)$$

Where: A is absorbance, c is the concentration of the solution, l is optical path, ε is molar absorptivity.

Figure 6 Left compares the Abs of the AM samples to the experiment time. There was a decrease in the concentration of BF in the sample that was exposed to the INS, confirming the bleaching effect. It was also observed that there was no considerable change in absorbance for the sample kept in the dark. Figure 6 Right shows the ln of the Abs of the sample exposed to the INS, according to the kinetic treatment to determine the velocity constant of a first-order reaction (equation 2). The results obtained for the kinetic constants are presented in Table 2.

$$kt = ln[AM] - ln\,[AM_0] \qquad (2)$$

Where: [AM] are the concentrations of methylene blue, k is the kinetic constant of the reaction, and t is the reaction time to the concentration [AM].

For the verification of the effects in the absence of light (chemical catalysis and adsorption), all experiments were divided into two groups, one of which was maintained in the absence of INS. The results were compared with the experiments performed in the presence of INS, being the results for the samples containing only the oxides without modification presented in Figure 7 and for the samples where the photocatalyst synthesized in Figure 8 was used.

Figure 6: Absorbance versus time to that of the AM solution with initial concentration of 3.3 x 10-5 mol. L-1 during 6 hours of experiment, *Left:* sample kept in the dark compared to that exposed to INS. *Right:* ln of absorbance versus time of exposure to INS of AM

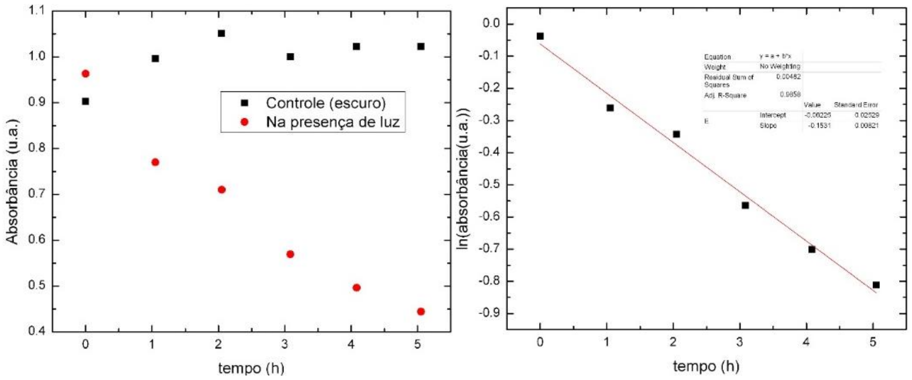

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Figure 7 Left shows that the Abs of the AM samples containing only oxides kept in the dark does not presenta significant variation, indicating that adsorption or catalysis can be disregarded. Figure 7 Right shows the ln of Abs versus the reaction time, according to first-order kinetic treatment (equation 2) to determine the reaction velocity. It is observed that the system fits well to the linear adjustment applied, indicating the suitability for first-order treatment.

Figure 7: Absorbanceversus time to that of the AM solution with initial concentration of 3.3 x 10-5 mol. L-1, in the presence of zinc and titanium oxides. *Left:* sample kept in the dark. *Right:* ln of absorbance versus time of exposure to INS of AM

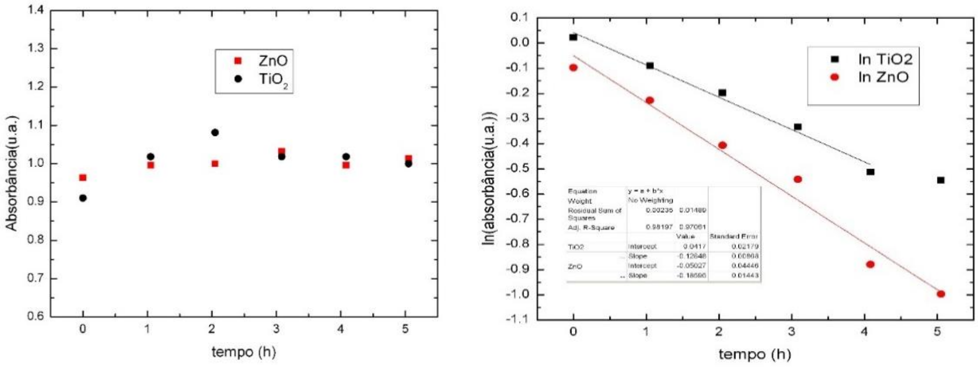

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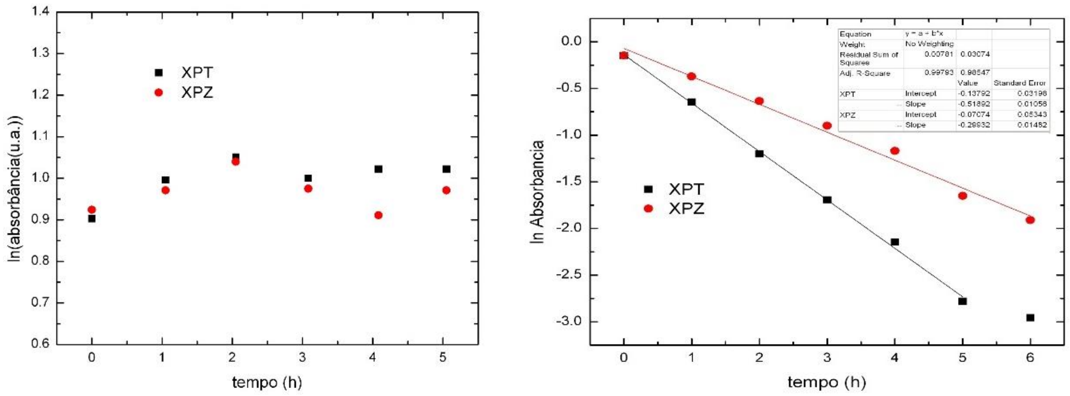
Figure 8 shows the test performed for methylene blue samples in the presence of photocatalysts XPT (TiO_2 incorporated in Laponite) and XPZ (ZnO incorporated in Laponite) in the absence (left) and presence of sunlight (INS) (Right). It is observed that the AM samples containing XPT and XPZ photocatalysts did not present significant variation of Abs. when maintained in the absence of INS, indicating that as for pure oxides it is possible to disregard the adsorptive and catalysis effect as a bleaching agent of the sample. Figure 8 Right shows the ln of Abs versus the reaction time (according to kinetic treatment for first order) for AM in containing the XPT and XPZ photocatalysts in the presence of light. It was observed that the systems fit well regarding the proposed linear adjustment, indicating the agreement for the first-order treatment. It is also observed that the slope of the XPT photocatalyst line is greater, indicating a higher reaction speed.

Figure 8: Absorbance versus time to that of the AM solution of initial concentration of 3.3 x 10-5 mol. L-1, in the presence of XPT and XPZ photocatalysts. *Left:* sample kept in the dark. *Right:* ln of absorbance versus time of exposure to INS of AM



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It is observed that both pure oxides and synthesized photocatalysts have the capacity to degrade AM at a speed above the natural effect of INS (as shown in Figure 6). Table 2 presents the values of the reaction velocity constants for each oxide and photocatalyst used, according to the treatment proposed by equation 2. It was observed that ZnO without clay has a higher degradation rate with TiO_2, however when they were modified it was noticed a 4-fold jump in the speed of the XPT photocatalyst compared to the oxide. Such an effect may indicate a greater synergistic effect between Laponite and TiO2 with the ZnO system, and the reason for this is to be determined in future studies.

Table 2: Pseudo-first-order velocity constant for samples exposed to INS.

System	***k/***$^{h-1}$
Methylene blue	0,1531
AM +TiO2	0,1265
AM + ZnO	0,1859
AM + XPT	0,5190
AM + XPZ	0,2993

In the three cases in which the samples were kept in the dark for evaluation of the desorption, no significant decrease dto Abs of the samples was observed, thus demonstrating that the adsorbed portion on the clay and oxide surface was not significant to the point of interfering in the experiment.

For the analysis of kinetic data, it is not possible to state that all the variables that affect the reaction mechanism were controlled. However, by the good mathematical adjustment obtained for the first-order kinetics, it is possible to affirm that the concentration of the dye is the determining point for the photodegradation mechanism. If important, other possible interfering factors are likely in large concentrations, forcing the system to respond with first-order kinetics. Given the lack of certainty of the influence of possible interferents, we chose the denomination of pseudo first order for the determined constants.

When compared with pure oxides, the photocatalysts synthesized in this work showed better performance. It was observed that the velocity for the experiments with ZnO doubled after the modification, and for TiO2 the increase was 4 times s when compared to pure oxide. The XPT and XPZ photocatalysts presented a performance similar to those described in the literature [13, 14, 22, 25, 29], significantly decreasing the initial concentration of the dye in solution.

5 CONCLUSION

The photocatalysts based on TiO_2 and ZnO supported in Laponite clay were synthesized and characterized, obtaining an improvement in photocatalytic activity against unsupported oxides. During the XRF analyses, the incorporation of oxides into the clays was observed. The analyses also showed that there is no significant degradation of the photocalisers after the methylene blue dye degradation assay. The system's pseudo-first-order velocity constants were determined, reflecting the relative velocity variation between conditions.

It was observed that the TiO2 photocatalyst (XPT) increased the bleaching speed of the solution by 4 times when compared to pure oxide, and the photocatalyst composed of ZnO inco rporado in Laponite increased the bleaching speed of the solution by 2 times when compared to pure oxide. With these results, these catalysts can be considered promising prototypes for the development of effective methods for the discoloration and degradation of organic agents in effluents as a possible alternative method for water treatment. In later stages, the effect of synthesized photocatalysts on the degradation of hormones and pesticides may be tested.

The present work culminated in the publication of an article in 2018, *Revista Processos Químicos*, entitled *Photodegradation of Methylene Blue by Oxides Incorporated in Synthetic Clay* [30].

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