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PHOTODEGRADATION OF METHYL ORANGE DYE USING TITANIUM AND TUNGSTEN OXIDES FIBERS AS SEMICONDUCTORS

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ABSTRACT
Photodegradation is a good economical alternative for removing organic pollutants from water, and several semiconductor metal oxides have been used in the photodegradation of organic compounds. The use of TiO_2, as a semiconductor most commonly used in heterogeneous photocatalysis, is relevant, due to its efficiency in the decomposition of pollutants from water, air, toxic organic compounds, bacteria, etc. However, the photocatalytic capabilities of TiO_2 are active only in 3% of the solar spectrum, a fact that limits its greater use. Based on this, this work proposes to synthesize TiO_2, and TiO_2 fibers doped with H_2WO_4, by electrospinning, relating the optical and photocatalytic properties of these elements. The X-ray diffraction technique (XRD) was used to determine the phases present. The morphology was observed through scanning electron microscopy (SEM). And photodegradation tests over time, by analyzing the discoloration of 125 mL of a 20 ppm solution of the orange methyl dye, in the presence of the synthesized fibers, when irradiated by UVA-visible light. The results show that the fibers containing tungsten were more efficient in the photodegradation of the methyl orange dye, indicating a greater photoactivity of this material in comparison with the standard P25 catalyst. This is possibly due to the existing synchronization between the chemical and physical properties of titanium and tungsten oxides, and the position of the valence band and the conduction band of WO_3 in relation to TiO_2, which inhibits the recombination of the electron pair/gap allowing the transfer of charges between the two semiconductors, increasing the efficiency of the process.
Keywords: Fibers, Photodegradation, Orange Methyl Dye.

1. INTRODUCTION

Photodegradation, in addition to being a good economic alternative for the removal of organic pollutants from water, also allows the generation of the electron/hole pair, during the

oxidation of the pollutant, and of oxygen-containing radicals. It is part of the advanced oxidative processes that, through the action of a photocatalyst, increase the rate of a reaction. These chemical reactions are caused by the absorption of photons of ultraviolet, visible or infrared light by compounds (photocatalysts) that are capable of generating free radicals, such as hydroxyl radicals (•OH) (SEDGHI, 2017).

These can be generated through the use of photochemical processes with ultraviolet radiation, in association with the absorption of radiation by a semiconductor, generating the electron/hole pair [(e)/(h^+)] in its electronic structure. Photogenerated species give rise to the formation of redox reactions (JIANYU, 2013, DONG, 2011) .

Several semiconductors can be used as photocatalysts, among which, among others, TiO_2, CdS, ZnO, WO_3, and ZnS stand out (NOGUEIRA, 1998). TiO_2 is one of the most used due to its excellent photoactivity, abundance in nature, being economically viable and easy to process (FIOREZE, 2014). The catalytic properties of these materials are directly related to morphology, crystalline phase, surface area, particle size and electronic structure. Therefore, studies related to the increase in the absorption range by the catalysts have attracted great interest from researchers, since most semiconductors absorb photons in the ultraviolet region, which ends up making photocatalytic processes more expensive. The doping of the material with other metals, aiming to expand the absorption spectrum to the visible region, appears as an option to minimize the costs of the process (DONG, 2011).

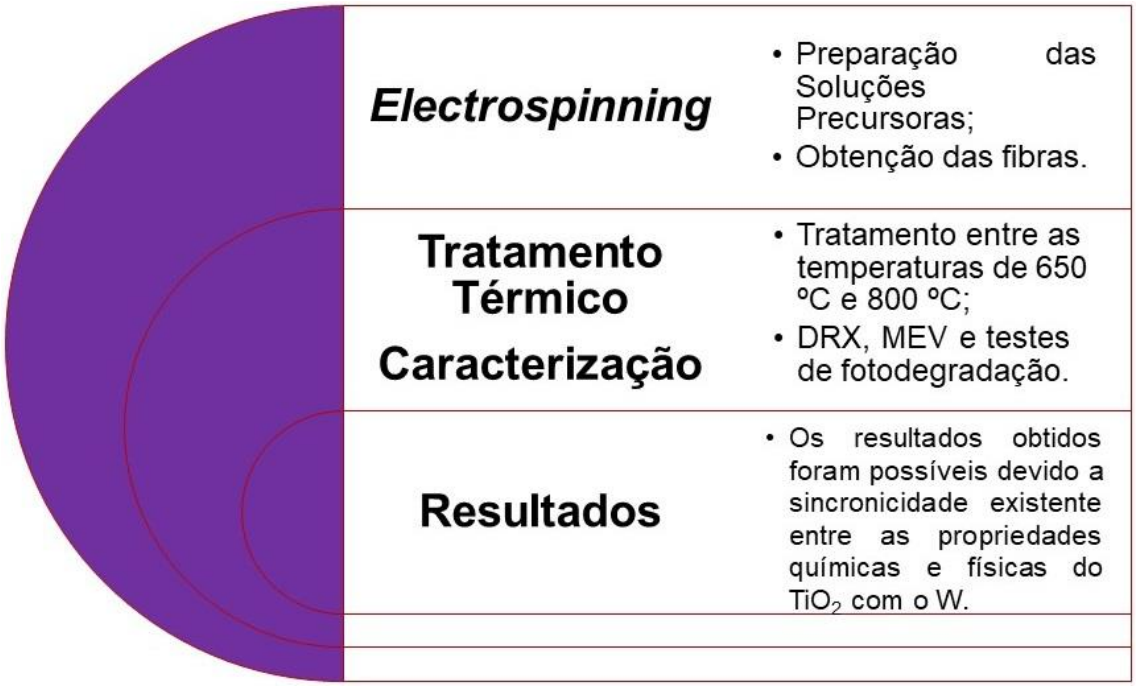
Heterogeneous Photocatalysis using TiO_2 as a semiconductor has also been successfully used to destroy some classes of compounds, such as alkanes, haloalkanes, aliphatic and aromatic alcohols, phenols, 6 surfactants, herbicides, pesticides (*DDT*), dyes (Rhodamine B, methyl orange and methylene blue) (DONG, 2011).

Therefore, in this work, we evaluated the photocatalytic activity of fibers synthesized by *electrospinning* . The synthesized fibers were used as semiconductors during photodegradation tests under UV-visible lighting. Methyl orange was the organic compound chosen for the photodegradation tests because it is an organic dye, characterized by the presence of the N=N azo bond between the aromatic rings (Ar−N=N−Ar) and molecular formula $C_{14}H_{14}N_3O_3SNa$, widely used in heterogeneous photocatalysis (CADORIN, 2016).

2 METHODOLOGY

Figure 1 presents an illustration of the steps involved in the development of this work.

Figure 1. Illustration of the steps involved to perform the work.
Source. Authors of the work.



The main steps for the production of the 2 types of fibers included:

i) Preparation of precursor solutions (without heating):

$TiO_{2\ solution}$ – 2.5 mL of titanium propoxide (TiP) were mixed ; 2 ml of glacial acetic acid and 5 ml of an alcoholic solution containing 10% by weight of polyvinylpyrrolidone (PVP). This solution was obtained by mixing 10 g of the polymer (PVP) in a beaker containing 100 ml of ethyl alcohol, without heating and, under constant magnetic stirring, until all the polymer was completely dissolved .

TiO_2/WO_3 solution – To the previously prepared solution containing titanium, 1 mL of hydrogen peroxide and 0.10 g of H_2WO_4 were added , which were kept under magnetic stirring for 15 minutes.

ii) *Electrospinning*

To obtain fibers by the *electrospinning process* , a 5 mL plastic syringe connected to a 1 mm internal diameter stainless steel hypodermic needle was filled with the precursor solution. The needle was connected to the high voltage source. The distance between the needle tip and the rotating cylindrical collector covered with aluminum foil was 12 cm. A voltage of 13.5 kV was applied between the needle and the collector. An infusion pump (KD

Scientific) controlled the flow of the precursor solution (1.8 mL/h). Fibers were collected every 30 minutes during the 4-hour period for each formulation.

iii) Heat treatment of fibers obtained by *electrospinning* :

The fibers obtained were subjected to heat treatment in an electric oven (Sanchis) at temperatures of 650 °C, 700 °C, 750 °C and 800 °C, with a 1-hour threshold and a heating rate of 1.4 °C/min, in order to remove polymeric material and form crystalline phases.

2.1 CHARACTERIZATION

A PHILIPS diffractometer with CuKα radiation, with a voltage of 40 kV and 40 mA, equipped with the X'PERT HightScore software, was used to identify the phases present in the fibers. A scanning electron microscope (SEM, JEOL 6060) equipped with EDS (energy dispersive spectroscopy), used to assess fiber morphology and identify the presence of W, Ti and O atoms in the samples, depending on fiber composition.

The photodegradation tests were carried out in a photocatalytic reactor , made of *pyrex* glass , where the radiation was provided by 12 UV-A black lamps, of 8 W each, model Fluor BLB T5 and brand *Sadokin* . The lamps are arranged in two semi-cylinders, which have a reflective inner surface. The other components of the photocatalytic reactor comprised a magnetic stirrer, a compressed air aeration system and a thermostatic bath. Samples were taken from the reactor flask through a channel closed by a silicone septum. The water circulation was carried out in a constant way, through the external part of the flask, thus making it possible to keep the test temperature fixed at 30 °C. The bottle also has a cap with a porous tip extension for bubbling compressed air into the liquid. To carry out the photocatalysis tests, 125 mL of a solution containing 20 ppm of methyl orange dye was used, transferred to a photocatalytic reactor and the UV light system was turned on. Before the beginning of each assay, a 4 mL aliquot of the solution was collected, defined as the initial reference sample (absorbance indicative of a concentration equal to 100% methyl orange; reaction time of zero minutes). This first aliquot was removed before the application of the light system, water circulation and air bubbling. After the beginning of each assay, 4 mL aliquots were removed with a syringe, filtered through a 0.2 µm filter, and transferred to polymethylmethacrylate (PMMA) cuvettes at 15-minute intervals. Then, the aliquots were analyzed by a spectrophotometer (Cary 5000, Agilent, with UMA accessory).

3 RESULTS AND DISCUSSION

Before heat treatment, the fibers were amorphous for all formulations. TiO_2 fibers (Figure 2a) treated up to 700 °C showed the majority presence of the anatase crystalline phase (JCPDS 010782486), with the first characteristic peak at approximately 2Θ = 25.271 °. Fibers treated from 750 °C formed, in addition to the anatase phase, the rutile phase (JCPDS 01-077-0442), with the first characteristic peak at approximately 2Θ = 27.294 °, the result of a transition from the anatase to the rutile phase, after increasing the calcination temperature. The literature reports that this TiO_2 phase transition occurs after heat treatment between 350 and 1175 °C, which can vary depending on the synthesis method used to obtain the samples. In the TiO_2/WO_3 fibers treated up to 650 °C, the phases anatase (JCPDS 01-078-2486) and brookite (JCPDS 01-075-1582) were identified for TiO_2 with characteristic peaks at approximately 2θ = 25.271º and 25.425 º, respectively. For WO_3 the monoclinic phase (JCPDS 00-032-1393) appeared at all heat treatment temperatures, with the first characteristic peak at approximately 2Θ = 23°. Fibers treated at 700 °C showed the rutile phase (JCPDS 01-077-0442), the latter with the first characteristic peak at 2Θ = 27.294 ° for TiO_2 in addition to the anatase and brookite phases.

Figure 2. Diffractogram of fibers synthesized by *electrospinning* (a) TiO_2 and (b) TiO_2/WO_3. Source. Authors of the work.

(a) (B)

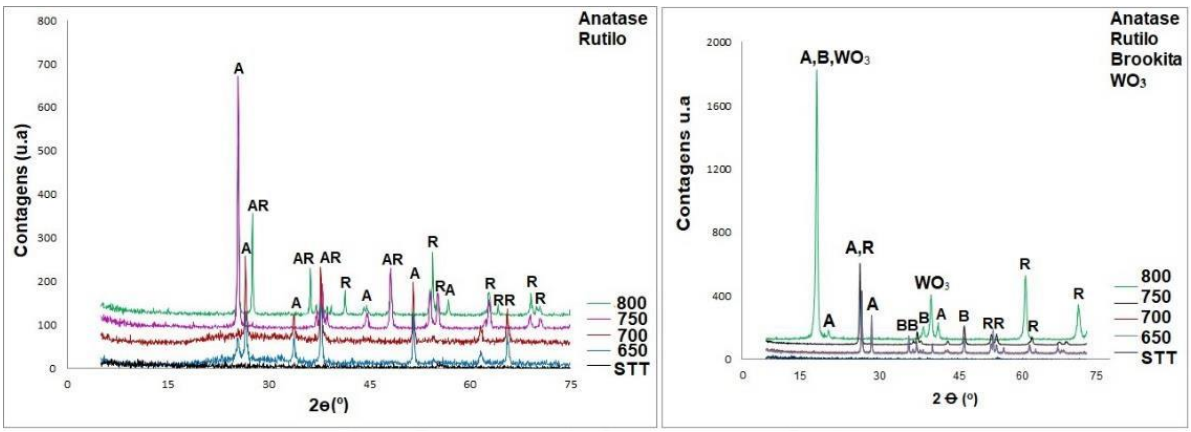


Figure 3 (ab) presents the (SEM) images of the surface of TiO_2 and TiO_2/WO_3 fibers. Analyzing these images, the fibers do not appear to have a preferential orientation, appearing to have an elongated and continuous microstructure .

Figure 3. Images of (SEM) of TiO_2 and TiO_2/WO_3 fibers heat treated at 650 ºC.
Source. Authors of the work.

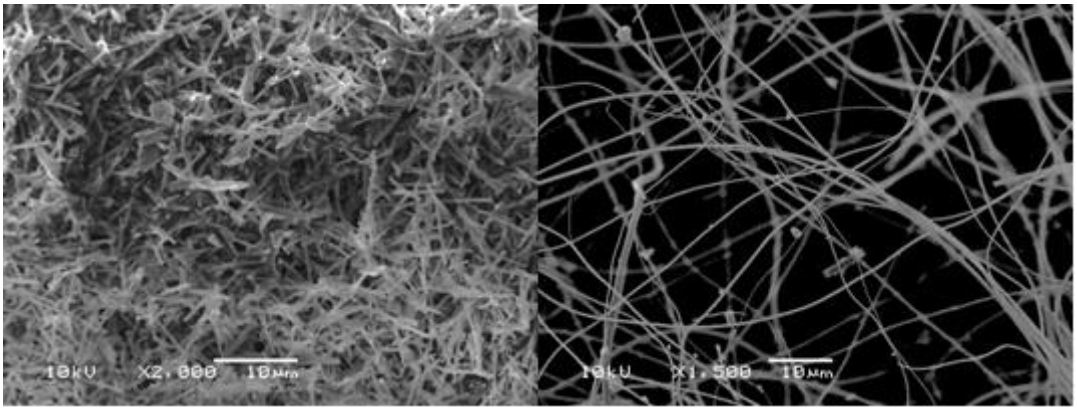


Figure 4 shows the catalytic activity of TiO_2 fibers in the photodegradation of methyl orange dye during 135 minutes of exposure to UV-A light (λ = 365 nm). It can be seen from the graph that all samples were able to degrade the methyl orange dye. The determination of photocatalytic activity was performed based on the C/C_o ratio , where C is the molar concentration of the aqueous dye solution in the presence of the catalyst at the time of analysis and C_o is the initial molar concentration of the aqueous dye solution without the presence of the catalyst. For the TiO_2 fibers , the most photoactive were those that received heat treatment at 650 ºC, degraded approximately 52% of the methyl orange dye, being more effective even than the standard P25-TiO_2 that had a degradation capacity of approximately 36 %. Fibers treated at 700°C and 750°C degraded approximately 32% and 27% of the dye, respectively. Finally, the fibers treated at 800 ºC degraded 22% of the dye. This decrease observed in the photoactivity of the samples is the result of the formation of the rutile phase, which in the case of synthesized fibers arises from treatments above 700 ºC. The rutile form is less photoactive than the anatase form and, for this reason, its appearance reduces the photocatalytic activity of the synthesized fibers (FELTRIN, 2013).

Figure 4. Photocatalytic activity of $TiO_{2\ fibers}$ in the photodegradation of methyl orange dye.
Source. Authors of the work.

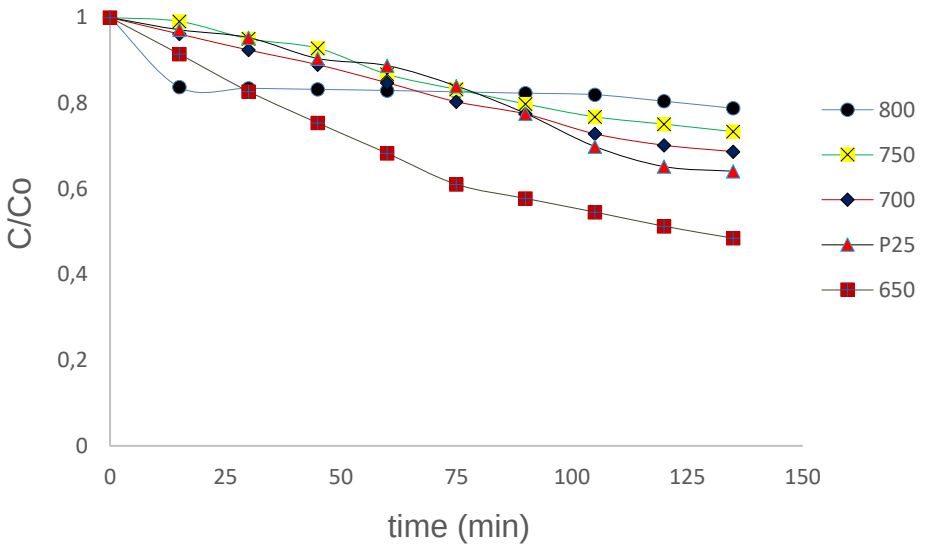
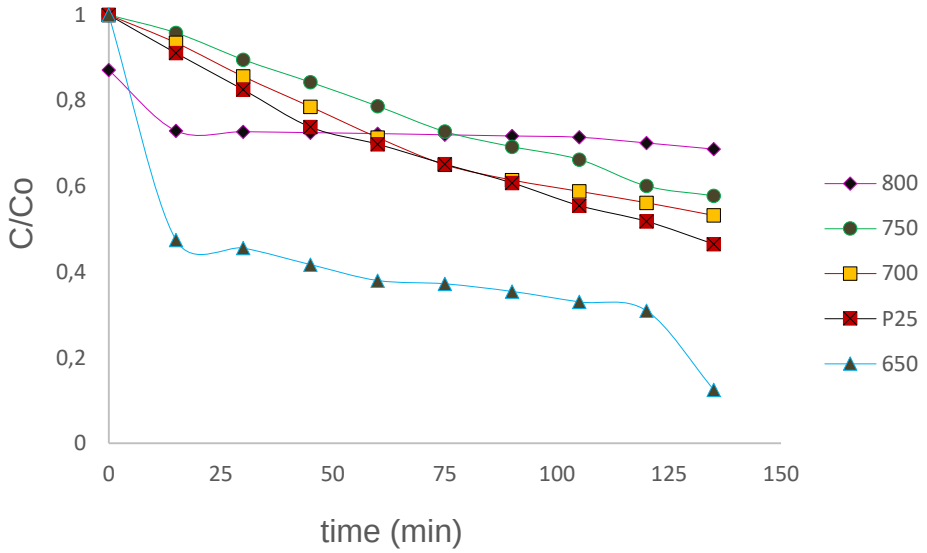


Figure 5 shows the catalytic activity of $TiO_{2\ fibers}$ in the photodegradation of methyl orange dye during 135 minutes of exposure to UV-A light (λ = 365 nm). It can be seen from the graph that the photocatalytic activity of all fibers synthesized in the photodegradation of the methyl orange dye increased considerably, due to the presence of tungsten in the samples, which allowed a greater transfer of charges between the two semiconductors (titanium and tungsten dioxide) , inhibiting the recombination of the electron/hole pair, increasing the efficiency of the process. The determination of photocatalytic activity was performed based on the $C/C_{o\ ratio}$, where C is the molar concentration of the aqueous dye solution in the presence of the catalyst at the time of analysis and C_o is the initial molar concentration of the aqueous dye solution without the presence of the catalyst. For the $TiO_2/WO_{3\ fibers,}$ the most photoactive were those that received heat treatment at 650 ºC, degraded approximately 88% of the methyl orange dye, being more effective even than the standard P25-TiO_2 that had the ability to degrade approximately 54%. Fibers treated at 700°C and 750°C degraded approximately 47% and 43% of the dye, respectively. Finally, the fibers treated at 800 ºC degraded 32% of the dye.

Figure 5. Photocatalytic activity of $TiO_2/WO_{3\ fibers}$ in the photodegradation of methyl orange dye.
Source. Authors of the work.



4 CONCLUSIONS

electrospinning technique was efficient in the production of synthesized fibers. Among the $TiO_{2\ fibers}$ studied, the ones that showed the highest photoactivity in the degradation of the methyl orange dye, when irradiated with UV-A light, were the fibers treated at a temperature of 650º C. Because the photoactivity of the fibers is directly associated with the crystalline phase formed , and at this temperature the fibers showed the majority presence of the anatase phase, which is clearly the most photoactive phase of TiO_2. Heat treatments above 700 ºC presented, in addition to the formation of the anatase phase, the presence of the rutile phase, which caused a reduction in the photocatalytic activity of the fibers. Even with the decrease in photoactivity presented by the fibers treated from 750 ºC, the results obtained indicate that all synthesized fibers showed catalytic activity in the photodegradation of the methyl orange dye. As for $TiO_2/WO_{3\ fibers}$ the most photoactive were those that received heat treatment at 650 ºC, degraded approximately 88% of the methyl orange dye. The increase in the photoactivity of the samples is directly related to the presence of tungsten, since the presence of this oxide allowed a greater transfer of charges between the two semiconductors (titanium dioxide and tungsten), inhibiting the recombination of the electron/hole pair, increasing the efficiency of the process.

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