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Municipal wastewater treatment by photocatalysis: comparison between UV lamp and solar radiation using TiO_2 and ZnO/TiO_2 synthesized catalysts

Tratamiento de aguas residuales municipales por fotocatálisis: comparación entre lámpara UV y radiación solar

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Abstract

To reverse the negative impacts on water resources caused by industries, advanced oxidation processes (AOP's) have been developed as an alternative for the treatment of effluents. This work evaluates the photodegradation of organic, inorganic oxidizable compounds and the inactivation of microorganisms in municipal wastewater, from the effluent of a Wastewater Treatment Plant (WWTP). The efficiency of two light sources, a UV lamp and solar radiation, and two catalysts synthesized through the sol-gel method, TiO_2 with a crystallite size of 20 nm and ZnO/TiO_2 with a crystallite size of 8 nm, were compared. The results obtained showed that photocatalytic treatments reduced TSS levels by 91%, COD by 69%, and BOD_5 by 73%, in the best of cases. Besides, 10 of the 11 organic compounds present were degraded, most of which are of hospital origin. It was also possible to inactivate some microorganisms such as *Enterobacter*, *pseudomonas*, and *Klebsiella*, in the order of 3.6×10^8 CFU to 1.63×10^4 CFU in the best of results. It was found that both photocatalytic processes represent a viable option for polishing the treatment of wastewater discharges from conventional WWTPs. However, the ZnO/TiO_2 catalyst with solar radiation showed the best result.

Keywords: municipal wastewater, photodegradation, solar radiation, UV radiation, ZnO/TiO_2.

Resumen

Para revertir los impactos negativos sobre los recursos hídricos provocados por las industrias, se han desarrollado los procesos avanzados de oxidación (PAO's) como una alternativa para el tratamiento de efluentes. En este trabajo se evalúa la fotodegradación de compuestos orgánicos, inorgánicos oxidables y la inactivación de microorganismos en aguas residuales municipales, a partir del efluente de una Planta de Tratamiento de Aguas Residuales (PTAR). Se comparó la eficiencia de una lámpara UV y radiación solar, y dos catalizadores sintetizados a partir del método sol-gel, TiO_2 con un tamaño de partícula de 20 nm y ZnO/TiO_2 con un tamaño de partícula de 8 nm. Los resultados demostraron que los tratamientos fotocatalíticos redujeron los niveles de SST en un 91%, la DQO en un 69% y la DBO_5 un 73%, en el mejor de los casos. Además, fueron degradados 10 de los 11 compuestos orgánicos presentes. También fue posible inactivar microorganismos como *Enterobacter*, *pseudomonas* y *Klebsiella*, en un orden de 3.6×10^8 UFC a 1.63×10^4 UFC. Se encontró que ambos procesos fotocatalíticos representan una opción viable para pulir el tratamiento de las descargas de aguas residuales de las PTAR convencionales. Sin embargo, el catalizador ZnO/TiO_2 con radiación solar mostró el mejor resultado.

Palabras clave: agua residual municipal, fotodegradación, radiación solar, radiación UV, ZnO/TiO_2.

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1 Introduction

For the World Health Organization (WHO), the innocuity and quality of water are essential for human development and welfare. For the water to be appropriate for human consumption, a series of treatments is required according to its initial quality. (Iqtedar *et al*., 2020).

Treatment of water contaminated with residues of organic compounds has been very difficult to make in recent years. The presence of emerging contaminants such as pharmaceuticals, antibiotics, biocides, pesticides, and personal care products has been increasingly constant in the effluents of Wastewater Treatment Plants (WWTP) (Soriano-Molina *et al*. 2019), daily all over the world are downloaded large volumes of water contaminated with residues of these medications and their metabolites down drain domestic and hospitable, unfortunately, conventional WWTP are not designed to eliminate this type of contaminant (Luna-Sánchez *et al*., 2013).

All treatments have limitations and advantages depending on the field of application. The research focused on Advanced Oxidation Processes (AOP's) for the destruction of synthetic organic compounds or species resistant to conventional methods. AOP's is based on the generation of highly oxidative species, such as hydroxyl radicals (·OH), which degrade polluting compounds (Domingues *et al*. 2019). On the other hand, in the last three decades, research has increased on the use of AOP's in the inactivation of microorganisms present in water and wastewater. Additionally, UV radiation eliminates bacteria, viruses, bacterial spores and is an effective technique in the disinfection of wastewater, especially for the reuse of wastewater irrigation water (Pantoja-Espinoza *et al*., 2015).

The photocatalytic process starts when a semiconductor absorbs light energy with equal or greater energy than that of its forbidden band, it promotes an electron (e^-) from the valence band to the conduction band with the simultaneous generation of a positive hole (h^+) in the valence band. Some electrons (e^-) and holes (h^+) migrate to the surface of the catalyst where the reactions of oxide-reduction. In aqueous suspension, the holes (h^+) react with the adsorbed water and with the OH^- groups to generate the HO· radicals. The general reaction indicates that HO· radicals react with organic pollutants leading to the mineralization of these compounds (Luna-Sánchez *et al*., 2013).

These treatments then make it possible to reduce the high organic load by lowering the Chemical Oxygen Demand (COD) and the Biochemical Oxygen Demand (BOD) of the effluents, which is why it has been applied to the disinfection of water by deactivating bacteria and viruses, and especially attractive application for the purification of water. Water in regions with scarce water resources and limited access to adequate sanitation (Valencia Sánchez *et al*., 2013) (Carbajo, 2013).

Photocatalysts that are active in the visible light region can be very useful as they efficiently break down harmful organic compounds under indoor light or sunlight (Belver *et al*., 2016). Sunlight is direct, primary, abundant, and cheap energy that in many cases is absorbed by chemical compounds to produce photolytic processes. The interaction of light with molecular systems occurs on a molecular scale where it interacts with a photon, in which A represents the ground state of the molecule, hν is the absorbed photon and A^o the molecule in the excited state (Garcés *et al*., 2004):

$$A + h\nu \rightarrow A^o \tag{1}$$

In recent years, much effort has been directed to the design and manufacture of visible-light-driven photocatalysts, and various advanced photocatalytic materials have been developed for antibiotic wastewater treatment (Li & Shi, 2016). There are several materials with suitable properties to act as catalysts: TiO_2, ZnO, CdS, iron oxides, WO_3, ZnS, etc. (Vásquez *et al*. 2010) however, of the many different photocatalysts, TiO_2 has been the most studied (Nakata & Fujishima 2012).

The connection between TiO_2 and other materials can produce a visible light absorption by the added material with the load separation provided by TiO_2 (Dahl *et al*. 2014). The number of investigations where TiO_2 is used as a catalyst for the degradation of various pollutants has increased in recent years. Illuminated suspensions containing TiO_2 are effective in killing *Escherichia coli*, a finding that spurred research towards the development of photocatalytic methods to kill bacteria and viruses using TiO_2 in aqueous media. However, most of these works have been carried out on a laboratory scale and using lamps for the generation of UV light.

The inorganic zinc oxide nanoparticles have peculiar semi-conducting, photocatalytic, electrical, antibacterial, dermatological, and optical properties. As compared to other nanoparticles, zinc oxide

nanoparticles are inexpensive, have a relatively high catalytic efficiency, low cost, chemical stability, and have less toxicity; therefore, they have many applications (Souza *et al*. 2017) (Iqtedar *et al*., 2020). For this reason, ZnO/TiO_2 compounds have been used as photocatalysts, presenting improved photocatalytic activity, since both oxides have a similar bandgap (~3.37 for ZnO and 3.2 for TiO_2) absorb in the UV portion of the electromagnetic spectrum (Dahl *et al*. 2014). Although several studies are using ZnO/TiO_2 composites, the photocatalytic properties of this catalyst remain largely unexplored.

This work is therefore focused on preparing and examining the applicability of TiO_2 and ZnO/TiO_2 catalysts for photocatalytic degradation of organic, inorganic oxidable pollutants and the deactivation of microorganisms in the effluent of municipal WWTP. The synthesis of the two catalysts was carried out using the sol-gel method, obtaining a fine white powder for the case of the TiO_2 catalyst and a fine beige powder for the case of the ZnO/TiO_2 catalyst.

When comparing the photodegradation technique with UV lamps and with sunlight, clarity is obtained when choosing which method represents the greatest advantages. Although the photocatalysis technique using UV lamps has indeed been shown to be highly efficient in the degradation of pollutants, it is also true that it becomes a not so cheap technique, due to the high energy consumption, so if it is verified that photocatalysis using sunlight is just as efficient would be a fairly profitable alternative to be used on large scales.

The first part of the work focuses on the synthesis and characterization of the catalyst to later be able to use it in photodegradation tests. The tests were carried out in a batch reactor and in a solar collector to compare the efficiency of UV light and sunlight in the degradation of organic and inorganic compounds, as well as the inactivation of microorganisms present in real water samples, coming from the effluent from a WWTP.

2 Materials and methods

2.1 Water samples

Five mixed samples were taken in total, in the months of March, July, and December 2017 and in February and April 2018. During each sampling, a 6 L sample was taken from the effluent of the municipal WWTP San Francisco, from Puebla City, Mexico.

2.2 Catalyst synthesis using the sol-gel method

The methodologies proposed by Khairy & Zakaria 2014 and Moradi *et al*. 2016 were taken as a reference and modified for the development of catalysts.

2.2.1 Preparation of TiO_2 catalyst

For the preparation of the TiO_2 catalyst, titanium tetrabutoxide (TTB) (Sigma-Aldrich, reactive grade, 97%) was dissolved with ethanol (Merck) to obtain the precursor solution, that solution was added to a mixture of ethanol, glacial acetic acid (Merck, 100%) and deionized water in a 10:6:1 M ratio to obtain the sol; the final solution was aging for 24 hours. Finally, a heat treatment was applied at two-step, 350°C for 10 minutes and after at 500°C for 5 hours.

2.2.2 Preparation of ZnO/TiO_2 catalyst

For the preparation of the ZnO/TiO_2 catalyst, TTB was dissolved in ethanol in a molar ratio of 1:9 respectively and left in agitation for 15 minutes to obtain the precursor solution. A 10:6:1 M mixture of ethanol, acetic acid, and deionized water was slowly added to the precursor solution, kept in vigorous and continuous agitation until the sol (transparent/yellow) was obtained. On the other hand, a solution of hexahydrated zinc nitrate and ethanol was prepared in a 1:110 M ratio, stirred for 15 minutes, and a mixture of ethanol, diethanolamine (stabilizer), and deionized water was added to the solution in a ratio of 10:2:1 M. The mixture was kept in constant agitation for 15 minutes to obtain the ZnO sol. The obtained ZnO sol is added directly into the sol from TiO_2. This new mixture was left to age for 24 hours, then heat-treated 350°C for 10 minutes, and then 500°C for 5 hours.

2.3 Characterization of catalysts

The catalyst's surface is the place in which heterogeneous catalytic or photocatalytic reactions occur. Therefore catalyst surface area, pore size, particle size (and their distribution), and adsorption/desorption phenomena of the species on the catalyst surface are very important parameters for the catalytic reactions to proceed with an assessment of the catalytic activity and to investigate the reaction mechanisms (Yurdakal *et al*., 2019).

The focal purpose of the characterization work is to describe the nature of the active centers suitable to catalyze a definite chemical reaction. It is easy to comprehend that a single characteristic taken alone cannot explicate all the characteristics of the catalyst behavior during the catalytic reaction. That means that the object of the characterization work must be the achievement of complete knowledge of the catalyst and the process (Leofanti *et al*., 1997).

2.3.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects (Bunaciu *et al*., 2015).

The analysis of both catalysts was carried out by X-ray diffraction (XRD) with a Brucker D8 Discover equipment, which has an Eye Lince detector that measures the incidence angles from 5° and up to 90°, with this technique the phases of the oxides were identified.

2.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is one of the most versatile techniques used for the observation and analysis of the microstructure morphology of catalysts (Yurdakal *et al*., 2019).

The Scanning Electron Microscopy (SEM) was made with the JEOL JSM-6610 LV equipment that has tungsten filament and operates at 15 V; with which are obtained the images of the morphology of the catalysts. The elemental chemical composition was carried out through the average Energy Dispersive Spectroscopy (EDS) after obtaining the microscope images with the microscope of the JEOL JSM-6610 LV equipment that has the detector that allows this determination. We analyzed 3 different points of the sample to get the average compositions.

2.4 Physico-chemical characterization of water samples

The physicochemical characterization of the effluent before applying the photochemical treatments was carried out to determine the initial conditions under which the effluent was present when the sample was taken. After applying the photochemical treatments, the physicochemical parameters were measured again to compare them with the initial values and to evaluate the efficiency of the photocatalytic process in the degradation of pollutants present in wastewater.

Each parameter analyzed was determined using the corresponding Mexican standards (NMX), NMX-AA-004-Determination of settleable solids in wastewater - Imhoff cone method, NMX-AA-006-Determination of floating matter - Visual method with specific mesh, NMX-AA-007-Determination of temperature - Visual method with a thermometer, NMX-AA-008-Determination of pH - Potentiometric method, NMX-AA-034-Determination of solids in water - Gravimetric method. On the other hand, methods 113 and 139 of the MERCK SQ 118 spectrophotometer were used to determine turbidity and color. For the determination of the Chemical Oxygen Demand (COD) the photometric method was used with the kit COD cell test brand Merck in a range of 25-1500 mg/L, analyzed in the NOVA 60A spectrophotometer, and for the determination of the Biochemical Oxygen Demand BOD_5 the OXITOP measuring system of the brand WTW was used. Each measurement was performed 5 times.

2.5 Degradation tests

Degradation tests of the contaminants present in the effluent of the WWTP were carried out using heterogeneous photocatalysis with two types of light, artificial and solar, and two synthesized catalysts. Each experiment was assigned an identification key, which varies with each type of catalyst and light used (Table 1). Each test was performed in triplicate.

2.5.1 Degradation tests with UV light

Mostly, most current UV disinfection systems employ tubular germicidal lamps surrounded by a quartz tube submerged in a chamber through which the fluid flows. Several parameters can impact the rate of inactivation of microorganisms such as the physic-chemical parameters (pH, temperature, etc.), the UV dose applied, the UV water contact time, the number and the type of microorganisms existing in the water (Ouelhazi *et al*., 2017).

For this research, the tests were performed on a batch photoreactor (Fig. 1). The reactor has a capacity of 850 mL and is composed of a medium pressure mercury vapor lamp, because medium-pressure lamps have approximately 15 to 20 times the germicidal UV intensity of low-pressure lamps, disinfects faster, and has greater penetration capability because of

Table 1. Key assigned to each experiment.

Assigned key	Description
FS	Batch photoreactor without catalyst
FT	Batch photoreactor with TiO_2
FZ	Batch photoreactor with ZnO/TiO_2
SS	Solar collector without catalyst
ST	Solar collector with TiO_2
SZ	Solar collector with ZnO/TiO_2

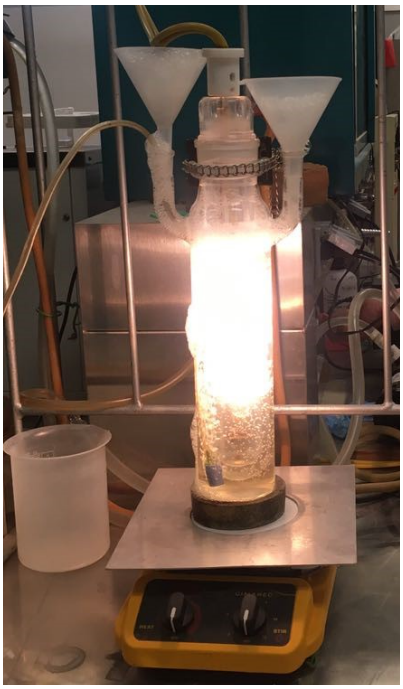

Figure 1. Photoreactor batch.

his higher intensity (EPA, 1999). However, these lamps operate at higher temperatures with higher energy consumption, because of that the lamp operates at a power of 1000 W, a voltage of 145 Volts, and a current of 7.5 Amperes.

Furthermore, as the optimal wavelength to effectively inactivate microorganisms is in the range of 250-270 nm (EPA, 1999), so this lamp emits ultraviolet radiation in a region between 200-400 nm.

The reaction vessel is made of Pyrex glass, which has at the top two ground inlets and at the bottom an inlet for the air stream supplied by an Elite 801 compressor (2000 mL/min), which corresponds to a supply of 400 mL/min of O_2.

Figure 2. Solar reactor.

The reactor has a demineralized water recirculation system for temperature regulation.

For each experiment, 850 mL of the effluent of WWTP and 0.03 g of catalyst were deposited into the photoreactor and kept in continuous agitation for 30 minutes. During photocatalytic processes samples of 10 mL were taken every 5 minutes and analyzed in a Perkin Elmer Lambda 20 UV-VIS spectrophotometer in a range of 200 nm to 450 nm.

2.5.2 Degradation test with solar light

Ultraviolet light is characterized by wavelengths between 100 and 400 nm. The UV strip UVC range from 200 to 280 nm, where the wavelengths are the most effective for disinfection. The maximum efficiency of UV disinfection corresponds to an energy output of 253.7 nm which represents the peak absorption of UV radiation by microorganisms (Ouelhazi *et al*., 2017).

The solar reactor (Fig. 2) consists of a Pyrex-branded ball flask made of borosilicate with 95% UV transmission and 1000 mL capacity. Within this flask, 850 mL of the sample to be treated with 0.03 g catalyst were deposited. The flask was placed on a stirring plate with the aid of universal support and a clamp, the flask was placed at an angle of 19° concerning the plate and kept at a constant speed, the plate with the flask was placed on top of a work table, in the open air so that

solar radiation would hit the reactor directly. Every test was performed for 5 hours (10:00 h -15:00 h) and each hour a sample of 10 mL was taken and analyzed in the UV-VIS spectrophotometer Perkin Elmer model Lambda 20 in a range of 200 nm to 450 nm.

2.6 Determination of organic compounds

A gas chromatography-mass spectrometry (GC-MS) was performed. One liter of WWTP effluent sample and one liter of treated effluent were collected with each photocatalytic treatment and with both catalysts. Each liter of the sample was performed a liquid-liquid extraction process with chloroform and later another with hexane to ensure the separation, purification, and identification of organic species.

The GC-MS system consisted of a GC HP-7890 equipped with a mass spectrometer 5973N and the column used with the following specifications: column DB-5ms, J & W GC Agilent J & W Ultra Inert, film 30 m length 0.25 mm ID 0.25 μm (5% Phenyl) - methylpolysiloxane. The injected volume was 1 μl of the sample after having passed through the liquid-liquid extraction process, (it was injected in splitless mode) the automatic auto-injector of liquid samples ALS 7683 was used in the injection port of the GC system. The furnace temperature was adjusted to 56 °C (4 min retention) and increased to 194 °C at a speed of 12°C per minute (10 min retention) to 270 °C for 20 min. The injector and the GC system detector were maintained at 180 °C and 290 °C, respectively. Helium was used as the carrier gas and the flow rate was set at 1 mL per minute. Once the chromatograms were obtained, they were compared with the NIST08 library database.

2.7 Microbiological test

This test was performed before and after photodegradation treatments to calculate the efficiency in the inactivation of microorganisms from photochemical treatments. For this assay, the platelet counting methodology was used, which is a methodology widely used. For this assay, the BIOXON Nutrient Broth was used, which is a liquid medium in which a wide variety of microorganisms can develop; the BIOXON Agar MacConkey medium is used to isolate and selectively identify Enterobacteria. Then, the decimal dilution method was used, in which 6 progressive dilutions were made from a sample to allow subsequent microbial counts.

Table 2. Identification proposed in the BIOXON manual.

Characteristic of the colony	Bacteria
Red to pink, not mucoid, may surround an opaque precipitate of bile salts	*Escherichia coli*
Large pink nonmucoid	*Enterobacter*
Large pink mucoid	*Klebsiella*
Colorless to greenish-brown. Characteristic sweet smell	*pseudomonas*

The next step was the sowing by striae in the plates, 6 plates for each sample, which was done with a loop of 10 μL and then proceeded to incubation for 24 h to 37°C. Finally, the count of the Colony Forming Units (CFU) was done. For the identification of microorganisms, we consulted the Bioxon manual in which we found the interpretations to characterize each colony according to its size, color, and texture (Table 2).

3 Results and discussion

3.1 Synthesis of the photocatalysts

The synthesis of the two catalysts was carried out using the sol-gel method, obtaining a fine white powder for the case of the TiO_2 catalyst and a fine beige powder for the case of the ZnO/TiO_2 catalyst.

3.2 Catalyst characterization

3.2.1 XRD

The identification of the peaks obtained was made by comparison with standard values of the International Centre for Diffraction, Data's Powder Diffraction File (JCPDS). Figure 3A shows the X-ray diffractogram of the synthesized TiO_2 nanoparticles and Figure 3B shows the ZnO/TiO_2 catalyst. The characteristic values of 2θ determined and the planes [hkl] for the two catalysts are 25.354° (101), 38.507° (112), 48.077° (200), 53.922° (105), 55.115° (211), 62.074° (204), 68.596° (116), 70.359° (220) and 75.094° (215) which correspond to the JCPD Card No. 21-1272 belonging to the anatase phase of TiO_2 (Figure 3C).

The diffractogram of the ZnO/TiO_2 catalyst shows the same characteristic values of 2θ as those of TiO_2, although the characteristic peaks of zinc in its zincite form (2θ signals at 31°, 47°, 54°, 57°, 63°, 67°, 69°)

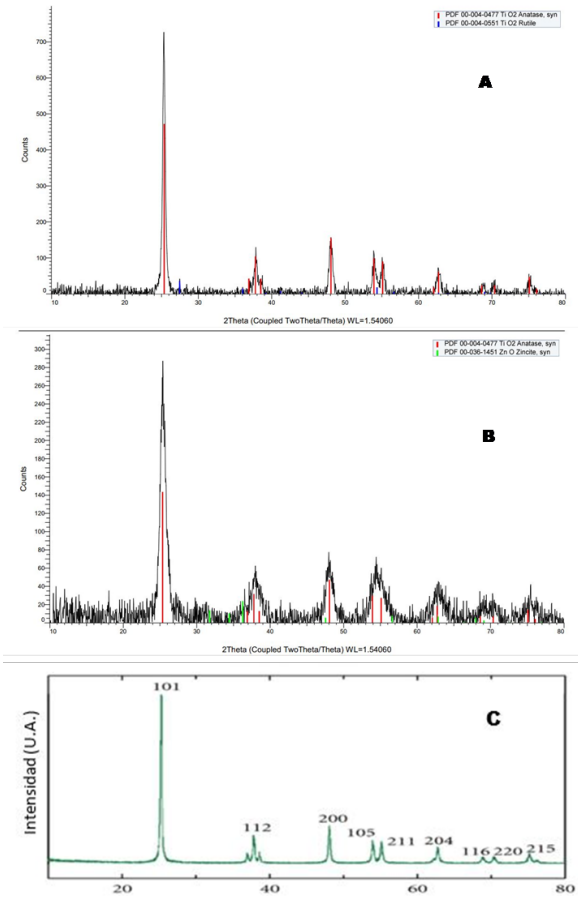

Figure 3. A) Diffractogram of the TiO_2 catalyst, B) Diffractogram of the ZnO/TiO_2 catalyst, C) JCPD Card No 21-1272, TiO_2 in anatase phase.

are also appreciated so it can be concluded that zinc was properly incorporated during synthesis however there is also increase in the width of the peaks and less defined, which translates into an immersion of Zn within the structure of TiO_2. The size of crystallites, as well as their shapes, also contribute to the widening of X-ray diffraction peaks (Vargas *et al*., 1983; Moradi *et al*., 2016). In addition to this, we can say that the characteristic peaks of the ZnO (Figure 3C) are of a very small size since the relationship between the ZnO and the TiO_2 is 10:50 M.

This indicates that the procedure of synthesis and treatment of the catalysts was adequate.

3.2.2 *Calculation of the size of crystallite using the Scherrer equation*

The technique of X-ray diffraction by the powder method has an increasing use in the determination of the size of crystallites and its correlation with different properties of the solid (Vargas *et al*., 1983). From the XRD patterns, the grain size was calculated by Debye-Scherrer equation (2), which states that the crystallite size (T) is inversely proportional to the average width of the maximum diffraction peak and the cosine of the maximum peak angle, such that:

$$T = \frac{K\lambda}{\beta \cos\theta} \text{Å} \tag{2}$$

where the average size of the crystallite is considered to be the form factor (K) = 0.9, λ as the wavelength of the incident beam which in this case is equal to 1.5406 Å, β is the average width of the maximum peak, β_{TiO_2} = 0.4138 and β_{ZnO/TiO_2} = 1.0346, finally, θ is the angle between the incident beam and the crystal plane, with a value of 12.6770 for both catalysts.

The nanoparticle sizes prepared were 20 nm for pure TiO_2 and 8 nm for ZnO/TiO_2.

This size variation can be explained by the fact that doping ions (Zn^{2+}) retard the grain growth of TiO_2 nanoparticles (Khairy & Zakaria, 2014). The crystallinity of the materials varies depending on the thermal treatment in the crystallization stage during the synthesis, and that the synthesis method is also dependent on the crystal size, which could favor photocatalytic activity since it has been reported that the anatase phase of TiO_2 with a small crystal size has greater photocatalytic activity (Zarazua-Aguilar *et al*., 2017). While, (Savi *et al*., 2012) mentions that the size of the crystallite is a function of the type of precursor and the synthesis temperature.

The crystallite size of the ZnO/TiO_2 catalyst is close to the size range cited in other studies like by (Colonia *et al*., 2013) who synthesized ZnO nanoparticles by the sol-gel method using sonochemical radiation as an external agent, with particle sizes between 9-14 nm.

In our case, both synthesized catalysts, TiO_2 and ZnO/TiO_2 are in the 1-100 nm range so they are considered nanocrystalline solids.

3.2.3 *Scanning Electron Microscopy*

Micrographs of TiO_2 (Fig. 4a and 4b) show agglomerations with an almost spherical shape with a size greater than 10 μm, when zooming in at 10,000X (b) it can be observed that the particles are joined together, giving a similar appearance. to the bunch of grapes. These agglomerations were formed due to the high viscosity of the sun, which reduced the dispersion of particles (Moradi *et al*., 2016). The conventional sol-gel method, by reflux, promotes the morphology

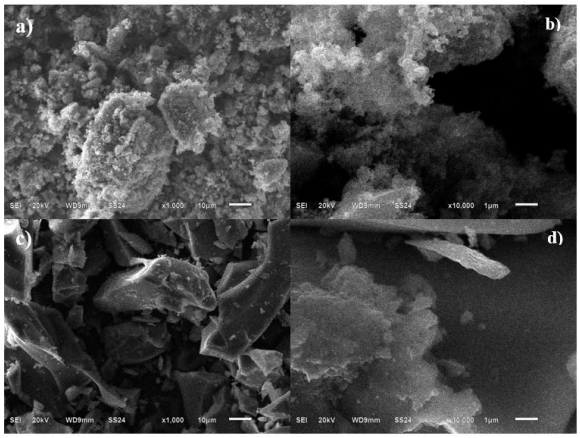

Figure 4. Micrography of catalysts. a) TiO_2 to 1,000 X, b) TiO_2 to 10,000 X c) ZnO/TiO_2 to 1,000 X and d) ZnO/TiO_2 10,000 X.

integrated by lobular agglomerations according to Zarazua-Aguilar *et al*., 2017.

While the micrographs of the ZnO/TiO_2 catalyst show that after doping with Zn the morphology of the catalyst changes to an irregular polygonal geometry of size greater than 10 μm that resemble aggregated plates as can be seen in Figures 4c and 4d.

Nanostructured or microstructured TiO_2 spheres generally have a high specific surface area and a high volume and pore size, increasing the size of the accessible surface area and the mass transfer rate for the adsorption of organic pollutants. In general, they result in better photocatalytic performance because photocatalytic reactions are based on chemical reactions on the surface of the photocatalyst (Nakata & Fujishima 2012).

3.2.4 Energy-dispersive spectroscopy

The results obtained from the EDS can be seen in Figure 5A, showing that in the case of the TiO_2 catalyst titanium is the element most frequently found followed by oxygen and carbon, this percentage of carbon in the sample may be because the adhesive strip on which the sample is deposited is made of carbon fiber. In the case of the ZnO/TiO_2 catalyst (Fig. 5B), the element that is in the highest percentage is also titanium followed by oxygen, carbon, and zinc, it is important to remember that zinc is in a very small proportion because the ratio compared to titanium is lower, ZnO/TiO_2 catalyst is produced in a 10:50 M ratio.

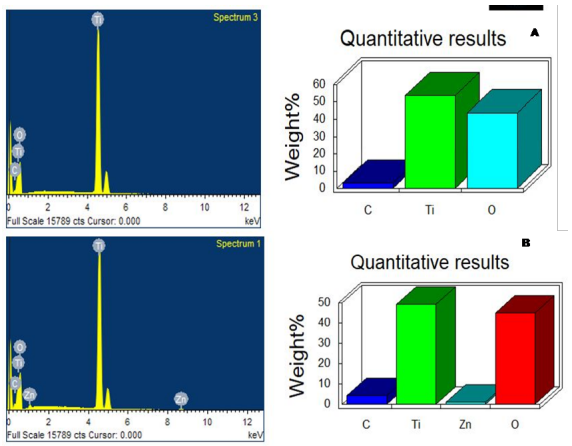

Figure 5. Graphs of EDE results for the (A) TiO_2 and (B) ZnO/TiO_2 catalysts.

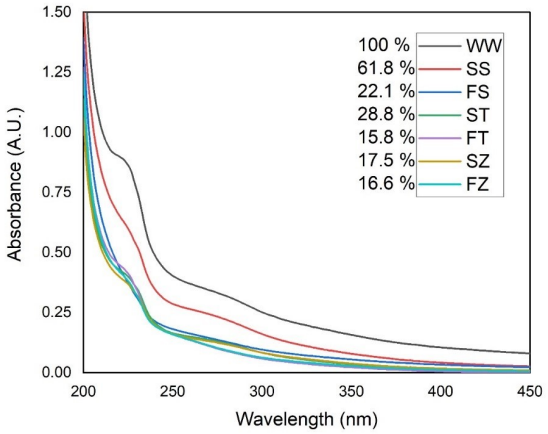

Figure 6. UV spectra of photodegradation tests for wastewater (WW), solar collector without catalyst (SS), batch photoreactor without catalyst (FS), a solar collector with TiO_2 catalyst (ST), batch photoreactor with TiO_2 catalyst (FT), a solar collector with ZnO/TiO_2 catalyst (SZ) and batch photoreactor with ZnO/TiO_2 catalyst (FZ). The percentages of reduction of pollutants in each process are shown, considering the initial sample (WW) as 100%.

3.3 Degradation tests

As can be seen in Figure 6, after the photochemical treatments there was a notable decrease in the concentration of the pollutants, both catalysts accompanied by the photoreactor being the ones that obtained the best results. It can also be seen that tests without a catalyst degrade contaminants due to the presence of UV radiation, however, with catalysts better results are obtained.

By making an approximation of the measurement of the area under the curve of the spectra shown in Figure 6 for each test, the following percentages of decrease in contaminants are obtained. In such a way, that if the area under the curve is considered as 100 percent of contaminants present in the initial wastewater sample (WW), the processes that achieve a greater reduction in these are the FT and FZ, up to 15.8 and 16.6 percent, respectively.

3.4 Physicochemical characterization of the effluent

The physicochemical characterization was carried out before and after the photochemical treatments, the value of the physicochemical parameters analyzed are shown in Table 3.

Within the results obtained from the physicochemical characterization before the photocatalysis, all the parameters analyzed in the wastewater exceed the allowable ranges by Mexican regulations even after they have been treated at the WWTP. According to Mexican regulations, the effluent from this WWTP is not suitable for agricultural use, nor public use, and it is not sufficient for the protection of aquatic life. While the results obtained after the photocatalysis treatment with both catalysts (TiO_2 and ZnO/TiO_2) and both types of light (UV light and sunlight) show that all the parameters decreased in considerable amounts to the point of being acceptable by the Mexican regulations.

According to the surface water quality classification scale proposed by the National Water Commission (CONAGUA), water quality can be established based on the biochemical oxygen demand at 5 days (BOD_5), the chemical oxygen demand (COD), and total suspended solids (TSS) (CONAGUA, 2018). Using the SST parameter, the best results of the treatments are found since the effluent from the WWTP is in the range classified as heavily contaminated by having more than 400 mg/L and after the treatments, it can be classified as good quality water since the values obtained are in the range of 25-75 mg/L.

Figure 7 shows clearly the difference in the degradation percentages of the parameters: total suspended solids, BOD_5, and COD. For the total suspended solids, it can be seen that the highest degradation percentage was carried out with UV light and both catalysts, since both showed a degradation percentage equal to 91%, while for COD and BOD the highest degradation was carried out with the TiO_2 catalyst and UV light with 69% and 73% respectively. This shows that in the case of the physicochemical parameters, the TiO_2 catalyst plus UV light show the best results.

Table 3. Physicochemical characterization before and after photochemical treatments.

Parameter analyzed	Before treatment	After treatment				MEXICAN REGULATIONS NOM-001-SEMARNAT-1996		
	Effluent WWTP	Photoreactor batch		Solar collector		Rivers		
		TiO_2	ZnO/TiO_2	TiO_2	ZnO/TiO_2	Agricultural Irrigation	Public use	Protection aquatic life
pH	7.67	8.56	8.22	8.28	8.05	5-10	5-10	5-10
Settleable solids (mg/L)	5.0	< 5.0	< 5.0	< 5.0	< 5.0	2	2	2
Total suspended solids (mg/L)	636.00	59.0	57.0	96	92.0	200	125	60
COD (mg/L)	360	112	118	127	120	N.S	N.S	N.S
BDO_5 (mg/L)	245	67	70	76	76	200	150	60
Turbidity (NFU)	44	21	19	9	3	N.S	N.S	N.S
Color (m^{-1})	7.0	3.6	3.6	2.0	1.2	N.S	N.S	N.S

NFU= Nefelometric Units

N.S = not specified

The values shown are the mean of 5 repetitions of each parameter +/- the standard deviation

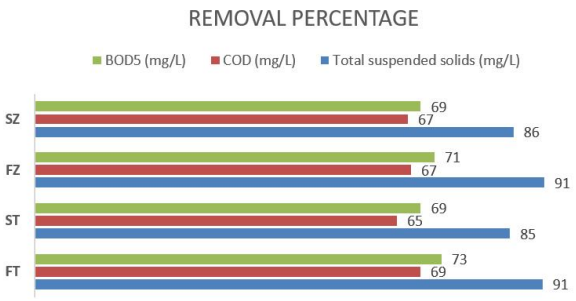

Figure 7. Removal percentage graph of BOD_5, COD, and TSS for the samples after the photochemical treatment.

Table 4. Plate count of microorganisms.

Sample name	CFU/mL	Microorganisms
Effluent WWTP	3.6×10^8	*Enterobacter Klebsiella E. coli pseudomonas*
FS	2.4×10^7	*E. coli pseudomonas*
SS	3.1×10^7	*pseudomonas*
ST	2.3×10^6	*pseudomonas*
FZ	53,000	*E. coli pseudomonas*
FT	28,000	*E. coli pseudomonas*
SZ	16,300	*E. coli*

3.5 Quantification and identification of microorganisms

After the incubation of the plates, the Colony Forming Units (CFU) were counted, obtaining the results shown in table 4.

It is well known that UV radiation eliminates, completely, bacteria, viruses, spores bacterial and is an effective technique in disinfection of wastewater, especially for the reuse of water in irrigation (Pantoja-Espinoza *et al*., 2015).

Seven *et al*., (2004), inactivated microorganisms such as *P. aeruginosa*, *E. coli*, *S. aureus* and *A. niger* in aqueous suspension with TiO_2 and ZnO (Pantoja-Espinoza *et al*., 2015), so it is not surprising that a decrease in the amount of CFU in all treated samples. However, Rincón and Pulgarín (2004), and Alrousan *et al*., (2009), reported that the presence of organic and inorganic components in water has a decisive influence on the inactivation rate of *E. coli* (Pantoja- Espinoza *et al*., 2015). That would explain why *E. coli* is still present in most samples despite being treated.

In the case of photochemical treatments (FZ and FT), carried out with artificial light and both catalysts, the results obtained can be related to the irradiation time, since there is no total inactivation of the microorganisms, the assumption is made that the exposure time of 30 min was insufficient since it has been found in similar studies that at the end of 1 h of lighting, the pathogens are completely inactivated (Kumar *et al*., 2014) although this also depends on other factors such as the power and distance of the lamp, the irradiation time is one of the determining factors for the inactivation of microorganisms. The results obtained from the photochemical treatments without catalyst (FS and SS) do not show great inactivation of microorganisms, which is not surprising since Kumar *et al*. (2014) mentions in their study that the results of photolysis show the same number of *E. coli* pathogens before and after lighting, which reveals that lighting alone does not affect bacterial growth even after 5 h.

Regarding the treatments carried out with sunlight, it can be said that the treatment carried out with the doped catalyst (ZnO/TiO_2) was the one that presented the highest efficiency in inactivating pathogens; however, some CFUs were still found because complete inactivation of microorganisms does not always occur for a variety of reasons, usually related to bad weather or turbidity conditions (McGuigan *et al*., 2012). According to several authors, the degree of bacterial inactivation after treatment depends on the dose of UV-A, which, if it is low the DNA repair mechanisms, allowing bacterial regrowth during storage (McGuigan *et al*. 2012)(Castro-Alférez *et al*., 2017).

After having performed the plate count, an additional count was carried out through the absorbance, which consisted of using aliquots of the dilutions made to analyze them in a spectrophotometer and obtain the absorbances of each sample. The decrease in absorbance is associated with the decrease in the turbidity of the sample and therefore with the decrease in the number of microorganisms present. The data of the CFU count were studied employing the Kruskal Wallis statistical analysis to determine which of all the treatments was the one that presented the highest efficiency in the inactivation of microorganisms, obtaining the results shown in Table 5, in which it can be seen that only the treatment with the ZnO/TiO_2 catalyst combined with solar radiation shows a $P < 0.05$, which refers to a statistically significant difference, making it the appropriate

Table 5. Kruskal Wallis statistical analysis of the microbiological assay.

Comparison before vs after	Mean difference	P-value
FS	12.667	ns P>0.05
FT	5.500	ns P>0.05
FZ	15.333	ns P>0.05
SS	14.833	ns P>0.05
ST	9.500	ns P>0.05
SZ	20.167	** P<0.01

ns= not significant

option to inactivate microorganisms. So, both in the plate count and in the absorbance measurement, the treatment that obtained the most favorable results for the inactivation of the microorganisms was the ZnO/TiO_2 catalyst combined with the use of solar radiation.

3.6 Identification of organic compounds

Table 6 lists the compounds that were detected in high proportions through GC-MS before photodegradation processes. For this analysis, only the samples marked with code FT, FZ, ST, and SZ were used.

It should be noted that 11 organic compounds were present in the initial sample, which means, before the treatment, most of them, pharmaceutical or chemical products used in the industry, considered as recalcitrant pollutants, all of them coming from industrial, domestic, and hospital discharges in the area. After the treatments, with the two kinds of lights and both catalysts, only one organic compound could be detected, which does not appear in the initial list, n-Hexilmetilamina ($C_7H_{17}N$), this compound was present only in the chromatogram of the ST sample.

Table 6. Organic compounds present in the WWTP effluent before & after treatment.

	Type of water	RT (min)	%	CAS	Name	Characteristics
		4.996	98	000127-18-4	tetrachlorethylene	A synthetic chemical used for dry cleaning fabrics and as a metal degreaser. Carcinogenic, dangerous for the environment.
		5.162	59	000354-28-9	Chlorodifluoroacetamide	Reagents for laboratory and substance manufacturing.
		14.918	64	000300-62-9	Amphetamine	Stimulant drugs. Creates addiction. The production of the algae stops.
		19.374	53	000084-74-2	Dibutyl phthalate	Animal experimentation shows that this substance is possibly causing toxic effects on human reproduction. Toxic to aquatic organisms.
		23.620	90	000111-03-5	(2,3-dihydroxypropyl Z) -9-octadecenoate	Skin conditioner, emollient, surfactant, and emulsifier.
Before treatment	WWT	4.723	59	054910-89-3	Fluoxetine	Antidepressant
		8.082	53	294667-75-7	Furazan	Heterocyclic aromatic organic compound
		14.014	72	014838-15-4	Phenylpropanolamine	A decongestant in anti-flu medications and appetite suppressant. It must be subjected to special treatment following official regulations. It must not be disposed of with household waste. You should not reach the sewage system.
		19.373	50	1000315-47-5	Phthalic acid	Plasticizer and as a fixative in makeup. The substance irritates the eyes, the skin, and the respiratory tract.
		24.144	55	1000332-57-2	1,2-benzisothiazol-3-amine	It has local anesthetic action and has numerous applications in human and veterinary medicine.
		31.044	90	002716-53-2	2,3-dihydroxypropyl elaidate	Lipids with polymorphic nanostructures.
After treatment	Solar collector with TiO_2 (ST)	9.307	56	035161-70-7	n-Hexilmetilamina	Laboratory reagents. Manufacture of substances.

RT: Retention time.

To reach the complete mineralization of a certain pollutant, a whole series of compounds can appear and disappear previously reaction intermediates. The appearance of detected intermediate compounds demonstrates the complexity of the photocatalytic process and suggests the existence of several degradation routes, moreover, this compound, identified as n-hexyl-methylamine presents nitrogenous structures that are among the few that present a high resistance to hydroxyl radical attack (Blanco *et al*., 2015).

Since it was not present in the initial sample, it follows that it was formed as a by-product of treatment due to radiation. However, n-Hexilmetilamina no longer represents a danger because it is non-toxic and easily biodegradable. According to the information provided by the safety data sheet of the compound, no component of this product is identified, which presents levels greater than or equal to 0.1% as carcinogenic or as a potential carcinogen by the Occupational Safety and Health Administration (OSHA).

Several studies report the conversion of organic compounds into different intermediate products, which manage to obtain a high degree of mineralization, or the ability to completely degrade organic pollutants by heterogeneous photocatalytic processes involving irradiated TiO_2 (Peralta-Zamora *et al*., 1998) (Gaya & Abdullah, 2008) (Augugliaro *et al*., 2012)(Luna-Sánchez *et al*., 2013) (Souza *et al*., 2017).

So, the photochemical treatments were successful in the transformation and elimination of organic compounds.

Conclusions

According to the characterization analysis, the synthesis was successful. Both catalysts presented a crystalline phase corresponding to the anatase phase of TiO_2, the doped catalyst also presented the crystalline phase of zincite and ZnO was incorporated into the structure of TiO_2. The synthesized nanomaterials have a crystallite size between 8-20 nm.

Both treatments and catalysts are used to reduce the concentration of the contaminants initially present in the WWTP effluent to levels permissible by the applicable Mexican regulations and show an evident degradation of contaminants. Also, they act as inactivators of microorganisms reducing the amount of CFU present in the wastewater from an order of 3.6 $\times 10^8$ to 1.6×10^4 in the case of the ZnO/TiO_2 catalyst, which was the one that presented the best results.

Photochemical treatments manage to eliminate most organic compounds, even persistent ones, however, there is still one present that, although it does not represent a risk of toxicity, it is convenient to eliminate it, so it is recommended to extend the irradiation time.

An analysis of the production cost of both catalysts was carried out and the results showed that with the amounts of reagents established in sections 2.2.1 and 2.2.2, 1.3162 g of the TiO_2 catalyst are obtained, while the ZnO/TiO_2 catalyst is obtained 3.1886 g. It was determined that to treat 1L of wastewater it was necessary to occupy 0.035 g of either of the two catalysts. The cost of manufacturing that amount of TiO_2 catalyst with our method is 3.76 Mexican pesos, the equivalent of 0.19 dollars. For the case of making 0.035g of the ZnO/TiO_2 catalyst, the cost is 1.82 Mexican pesos, the equivalent of 0.091 dollars.

In addition to the fact that the ZnO/TiO_2 catalyst is the one with the lowest production price, it is also the one that allows greater energy savings if used with the solar collector, since the only electrical energy used during the photocatalysis process it is the one used to generate agitation within the collector; while with the batch photoreactor, in addition to the cost involved in purchasing it, the UV lamp is 1000 W and consumes a considerable amount of electrical energy, which translates into increased costs during the process.

In summary, both TiO_2 and ZnO/TiO_2 catalysts with both types of light, UV and solar, represent a viable option for the polishing of the effluent from the "San Francisco" WWTP since both degrade organic matter, eliminate organic compounds, inactivate microorganisms, and do not present toxicity, however when evaluating all these aspects it is concluded that the most efficient treatment is the use of the solar collector with the doped catalyst since it showed better results and it is also a cheap and simple method that uses clean energy and so it is environmentally friendly.

The foregoing leads us to deduce that solar energy represents a cheap and effective alternative for the degradation of pollutants, however, both the country and the State of Puebla are wasting its use since it has optimal solar irradiation.

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