



PHOTODEGRADATION OF ERIONYL DYE IN AQUEOUS MEDIUM BY SUNLIGHT AND PALLADIUM CATALYSTS

FOTODEGRADACIÓN DEL COLORANTE AZUL ERIONYL EN AGUA MEDIANTE LUZ SOLAR Y CATALIZADORES DE PALADIO

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Abstract

In this investigation, the degradation of blue dye erionyl was evaluated in aqueous medium by photocatalysis with solar radiation. Six catalysts of palladium supported on combinations of aluminum-cerium-zirconium oxides were synthesized by the sol-gel method and impregnation. Materials used as supports were characterized by XRD, meanwhile catalysts were analyzed by SEM and EDS techniques. The Degussa TiO₂ commercial was used as reference for evaluating the performance of the palladium catalysts in the photocatalytic processes, since is widely used as an efficient catalyst for photodegradation of pollutants in water. The photocatalytic processes were carryout in a system with borosilicate reactors and high reflectance aluminum foil compound parabolic collectors. The six palladium catalysts achieved a percentage degradation of erionyl blue dye higher than 60%, having the best performance the palladium supported on alumina with 97% degradation after 5 hours of photocatalytic process. It is noteworthy that this catalyst showed a better performance than the TiO₂ catalyst reached up to 81% degradation.

Keywords: Photocatalysis, blue dye erionyl, water pollution, solar radiation, palladium catalyst.

Resumen

En esta investigación se evaluó la degradación del colorante azul erionyl en agua mediante fotocatalisis con radiación solar. Se sintetizaron seis catalizadores de paladio soportados en combinaciones de óxidos de aluminio-cerio-zirconio obtenidos por el método sol-gel e impregnación. Los soportes se caracterizaron por XRD, mientras que los catalizadores se analizaron por SEM y EDS. Se utilizó Degussa TiO₂ comercial como referencia para evaluar el desempeño de los catalizadores de paladio en el proceso fotocatalítico, debido a que es el catalizador más utilizado para la fotodegradación de contaminantes en agua. El proceso fotocatalítico se realizó en un sistema con reactores de borosilicato y láminas de aluminio de alta reflectancia que actúan como colectores parabólicos. Los seis catalizadores de paladio lograron una degradación del colorante mayor al 60%, mostrando el mejor resultado la alúmina con 97% de degradación después de 5 horas del proceso fotocatalítico. En este caso se destaca el hecho de que se logró una degradación mayor a la del TiO₂, el cual alcanzó sólo el 81%.

Palabras clave: Fotocatalisis, colorante azul erionyl, contaminación del agua, radiación solar, catalizadores de paladio.

1 Introduction

The textile industry has a high environmental impact, given the large water consumption and the use of

dyes which generates wastewater discharges with a significant amount of chemicals substances difficult to transform, degrade or remove (Krizanec and Majcen, 2001; Blackburn and Burkinshaw, 2002; Lacasse and Baumann, 2004).

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The dyes are known as very stable chemicals, when added to a substrate grants color to this, this occurs by the absorption process or by ionic or covalent bond forming, which make them resistant when subjected to conditions as exposure to light, water, or detergents, directly affecting the water quality standards because the treatments supplied to the discharges of these industries do not completely eliminate these chemicals, they leave the appearance and the smell of the water unpleasant and they avoid the passage of sunlight causing the low photosynthesis of oxygen inhibiting the growth of microorganisms (Ghalay and Ananthashankar, 2014).

Due to the high stability of the dyes (azo-compounds), conventional processes for treating wastewater such as adsorption, flocculation and processes using activated carbon cannot efficiently remove such compounds or generate secondary pollutants; sludge is toxic to the environment and requires further treatment (Scott and Ollis, 1995). The development of technologies to reduce or remove contaminants from water has been important, especially for the treatment of these dyes (García-Montano *et al.*, 2006; Ahmed *et al.*, 2011). Most of the processes are aimed to reach complete mineralization of these pollutants in water. Photocatalysis is a process that presents an important alternative to remove contaminants from water, is promoted by energy as light and the use of catalysts is based on the transfer of charge through the interface between the semiconductor and the contaminated aqueous solution (Legrini and Braun, 1993; Huang *et al.*, 1993, Chong *et al.*, 2010). In various investigations, UV radiation is used for photocatalysis processes; however, the focus of others is to use solar energy as a source of clean energy (Malato *et al.*, 2009). The most used catalyst for this advanced oxidation process is TiO₂ (Fujishima *et al.*, 2008, Vulliet *et al.*, 2013, Ibrahim and Halim, 2008, Dette *et al.*, 2014). The TiO₂ catalyst has shown high efficiency in the degradation of recalcitrant compounds such as phenol (97%), but in these cases UV light and high doses of catalyst (2g/L) are required (Moctezuma E. *et al.*, 2016). In that sense, some disadvantages of the use of TiO₂ are the high doses required for the photocatalysis processes and the increase in turbidity. Therefore, recent research focuses on evaluating the catalytic performance of other materials, such as metal oxides that have functioned efficiently in the removal of air pollutants in order to solve these problems. One option has been to use metal oxides that can simultaneously perform

reduction and oxidation reactions of contaminating molecules, such as palladium or ruthenium catalysts supported in combinations of alumina, ceria and zirconia (Pintar *et al.*, 2001). Recently, different mixed oxides have been used in photocatalysis to degrade emerging or recalcitrant contaminants present in water (as diclofenac) (Morales-Zarate *et al.*, 2018) reaching higher degradation percentage than conventional TiO₂ photocatalyst.

2 Materials and methods

2.1 Synthesis of catalysts

Supporting catalysts were prepared by sol-gel method with alumina (between 80 and 100 wt.%) and cerium and/or zirconium oxide (between 0 and 20 wt.%) from organic precursors following a procedure reported previously (Masuda *et al.*, 1999). A solution of acetylacetonate of cerium (Aldrich) and/or acetylacetonate of zirconium (Alpha Aesar) in ethanol with moderate agitation was added to a mixture of aluminum sec-butoxide (Alpha Aesar) and 2-metil-2,4-pentanediol (Alpha Aesar), staying in reflux for 3 h, with moderate agitation at 94 °C. Hydrolysis was made by adding drop by drop deionized water. The obtained gel was aged for 10 h. Samples were dried at vacuum (10⁻² Torr) and temperature of 100 °C for 12 h and then calcined in N₂ atmosphere at 450 °C for 12 h, with a later treatment in air at 650 °C for 4 h. The six palladium catalysts were obtained by support impregnation using a palladium chloride solution of 0.12 wt.% in volume, to give a concentration around of 0.3 wt.% of palladium. After impregnation, the samples were again calcined in air at 650 °C for 4 h.

2.2 Characterization of materials

Catalysts supports were analyzed by X-rays diffraction with equipment Bruker D8 Discover (1 wt.% limit detection), with this technique various phases of the mixed oxides were identified by comparison with the database of ICDD. Scanning Electron Microscopy of the six palladium catalysts and TiO₂ was performed with a JEOL JSM-6610 LV which images of the morphology and particle size were obtained. Elemental chemical composition was measure by Energy Dispersive Spectroscopy with a JEOL JSM-6610 LV microscope.

Table 1. Information of dye Acid Blue 260: erionyl. (World dye variety).

Name	Molecular	Molecular	CAS Registry	weight	number
	structure	structure	formula		
C.I. Acid Blue 260		Anthraquinones	$C_{26}H_{23}ClN_3NaO_6S$	563.99	62168-86-9

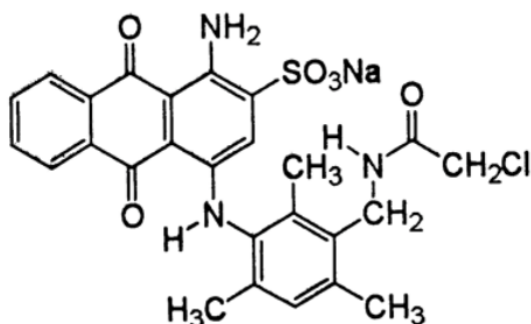


Fig. 1. Molecular structure of Acid Blue 260: erionyl.

2.3 Photocatalytic tests

The solar collection system consists of borosilicate reactors of 36 mm of diameter and 1500 mm of length (1.4 L of volume), which has a 95% UV transmission, placed in aluminum foil, used as reflecting surface (involute). The system was connected to coolants to prevent evaporation of water, a water pump coupled to the cooling system and two pumps to provide air diffusion (1800 cc/min, ELITE 801 air pump) in spite of keep dispersion catalysts. The dye solution was prepared with the dye blue erionyl mixed with demineralized water to 50 ppm. Fig. 1, shows molecular structure and Table 1 presents basic information of the Acid Blue 260 (erionyl). The solar collector was placed in an area where sunlight received completely in a north-south orientation for 5 hours, with 19 degrees of inclination (Altitude of Puebla city) respect to the Ecuador, with the dye solutions and 40 mg of every catalyst in each test. Experiments were performed at 9:00 am and were taken an aliquot of 10 mL each hour to evaluate dye degradation with a UV-vis spectrophotometer.

2.4 Adsorption tests

To determine the adsorption capacity of the catalysts in the degradation of the dye in aqueous solution, the dye was adsorbed in the dark, with the catalysts TiO_2 and Pd/Al_{100} . 500 mL of aqueous solution (50 ppm) of erionyl blue was placed in a flask, 30 mg of

catalyst was added, stirred for 4 hours and the UV-vis spectra were determined. Finally, the sample was filtered to recover the catalyst with Whatman filter paper, qualitative 1, retention of particles $11 \mu m$.

3 Results and discussion

3.1 X Ray Diffraction

X ray diffraction patterns are shown in Fig. 2, those results correspond to supports due to the amount of palladium dispersed is lower than limit detection of this equipment. In general, broad peaks are observed in palladium support catalysts, indicating that the materials obtained by sol-gel synthesis possess amorphous zones and low degree of crystallinity. In spite of, several mixed oxide phases were identified according to the reference of the ICDD (2015). Support made of 100% alumina shows three peaks with significant intensity at 2θ angles: 37° , 45.5° and 67° , corresponding to aluminum oxide cubic phase (00-029-0063, $\gamma-Al_2O_3$). Supports containing alumina and ceria, do not shows aluminum oxides peaks only have their most representative signals at 2θ angles: 28.5° , 33° , 47.5° , and 56.5° corresponding to cerium oxide cubic phase (03-065-2975).

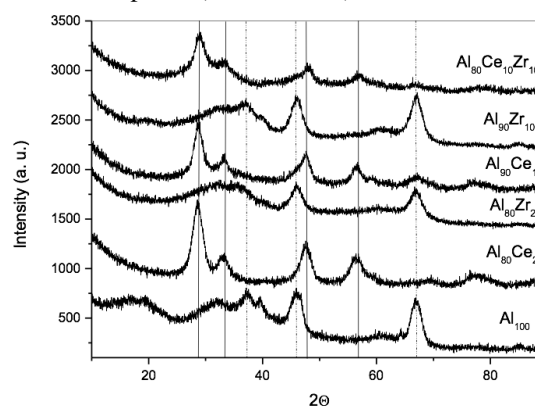


Fig. 2. Patterns of X-Ray diffraction of the catalysts supports, solid line correspond to cerium oxide signals and dotted lines correspond to alumina.

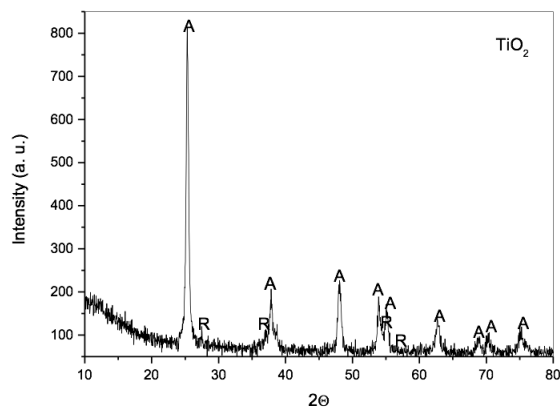


Fig. 3. Patterns of X-Ray diffraction of the TiO₂ (A: anatase phase, R: rutile phase).

The X ray diffraction patterns of supports containing alumina and zirconia, presents two signals at 46° and 67° corresponding to aluminum oxide tetragonal phase (00-056-1186, δ -Al₂O₃) and a broad signal between 20 and 40° indicating the presence of zirconium oxide orthorhombic phase. In the case of support containing alumina-ceria-zirconia, were identified peaks in the 2 θ angles: 29.5°, 34°, 49° and 57.5° corresponding to cerium zirconium oxide cubic phase (01-075-9469, Ce_{0.91}Zr_{0.09}O₂). Fig. 3; present the X ray diffraction pattern of titanium oxide where well-defined signals are observed indicating high crystallinity degree. Two phases were identified, anatase tetragonal mainly and rutile tetragonal.

3.2 SEM and EDS

Fig. 4 shows the images of scanning electron microscope of palladium catalysts at 1000 amplifications. All materials possess particles with several sizes and shapes; there is no uniformity and geometric forms.

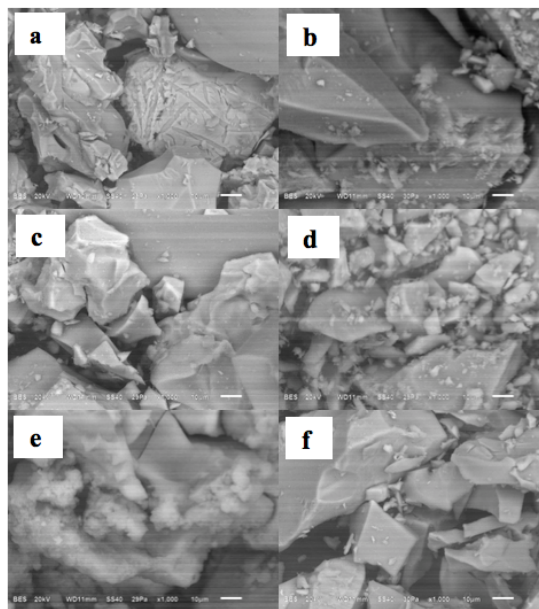


Fig. 4. Images of scanning electron microscope of palladium catalysts at 1000 amplifications: a) Pd/Al₈₀Ce₂₀, b) Pd/Al₈₀Zr₂₀, c) Pd/Al₉₀Ce₁₀, d) Pd/Al₉₀Zr₁₀, e) Pd/Al₁₀₀, and f) Pd/Al₈₀Ce₁₀Zr₁₀.

Meanwhile Fig. 5 presents SEM of titanium oxide with small, uniform and spherical shape particles. In the Table 2, elemental chemical composition in weight percentage of catalysts is presented, obtained by EDS. Palladium presence was detected, showed a weight percentage between 0.20 and 0.44, meanwhile for the rest of elements is confirmed that the synthesis process was successful without impurities or traces of precursors reactants.

Table 2. Elemental chemical composition expressed as weight percentage of catalysts evaluated in dyes blue degradation, obtained by EDS.

Catalyst	Al	Ce	Zr	Pd	O	Ti
TiO ₂	0	0	0	0	49	51.01
Pd/Al ₁₀₀	43.91	0	0	0.44	55.7	0
Pd/Al ₈₀ Ce ₂₀	22.58	37.8	0	0.38	39.2	0
Pd/Al ₈₀ Zr ₂₀	33.14	0	13.7	0.29	52.9	0
Pd/Al ₉₀ Ce ₁₀	31.1	23.46	0	0.33	45.1	0
Pd/Al ₉₀ Zr ₁₀	38.56	0.22	6.05	0.24	54.9	0
Pd/Al ₈₀ Ce ₁₀ Zr ₁₀	27.13	20.67	5.5	0.2	46.5	0

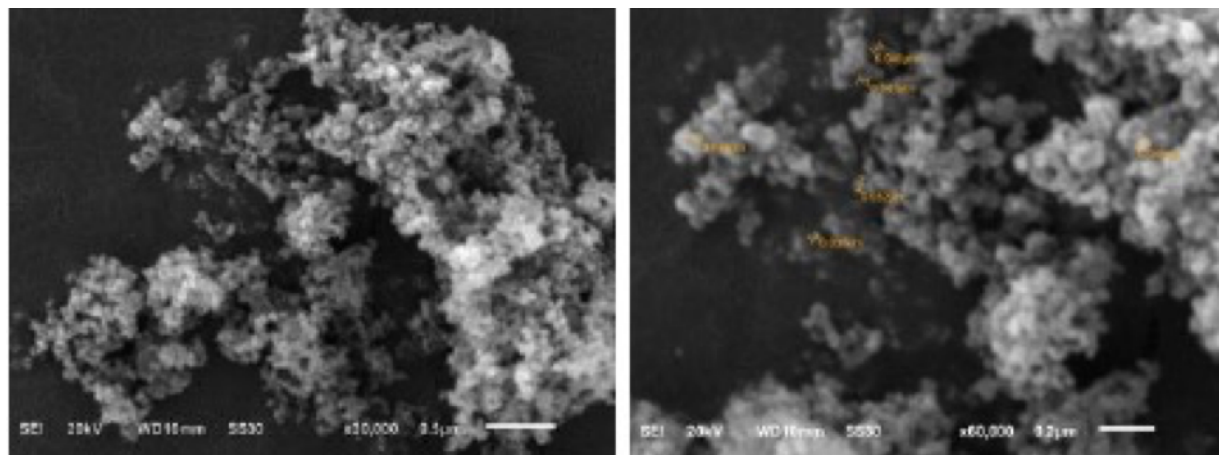


Fig. 5. Images of scanning electron microscope of TiO₂.

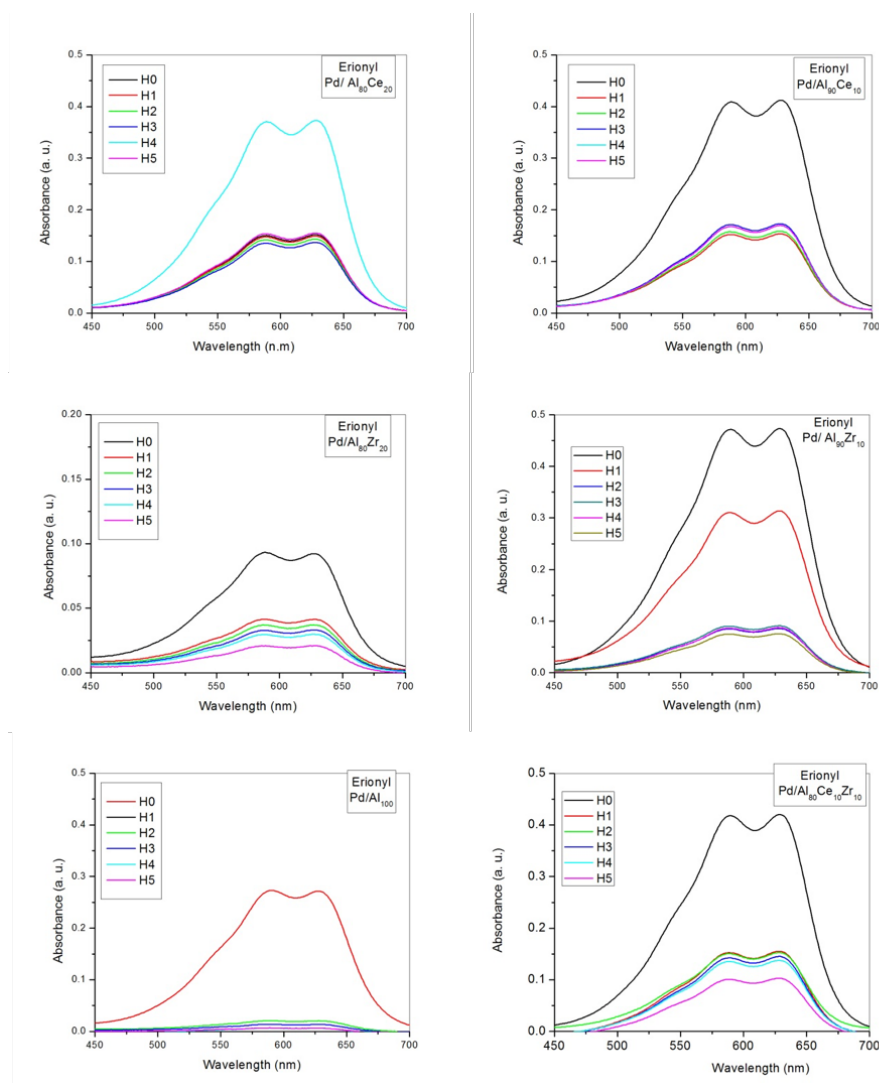


Fig. 6. UV-Vis spectra of erionyl blue dye degradation by palladium catalysts during 5 hours (5H) of photocatalytic process.

3.3 Erionyl blue dye photodegradation

UV-Vis spectra of erionyl blue dye degradation by palladium catalysts are presented in Fig. 6. In all cases erionyl blue dye was degraded, for catalysts containing alumina and ceria supports after one hour (H1) of processes there was not change in the UV-Vis spectra of the dye, meanwhile with catalysts containing alumina zirconia supports degradation was observed after two hours (H2) of processes. Nevertheless, the higher erionyl degradation was reached with Pd/Al₁₀₀ catalyst being better than catalytic performance of TiO₂ showed in Fig. 7. Finally, a comparative graph of degradation percentage of erionyl blue dye by seven catalysts during five hours (H5) of photo catalytic process (Fig. 8) is presented. It was observed that palladium catalyst Pd/Al₁₀₀ have higher catalytic performance (97%) than titanium dioxide (81%) after 4 hours (H4) of the photocatalytic process. The other palladium catalysts achieved percentages of degradation between 60 and 84%. The effect of variations on chemical composition of supports shows an influence over erionyl blue dye degradation. The presence of cerium and zirconium oxide in the support does not seem to have such a favorable effect on degradation. The catalysts containing zirconium oxide show better performance than those containing only cerium oxide. It is important to note that during the first two hours (H2) of photocatalytic process there are remarkable chemical transformations of the dye. In the case of catalysts Pd/Al₁₀₀ and Pd/Al₉₀Zr₁₀ during the first hour (H1) degradation is lower than 50%, but for the rest of catalysts degradation is around 60%. However, upon arriving at the second hour (H2) of the process the behavior is totally reversed.

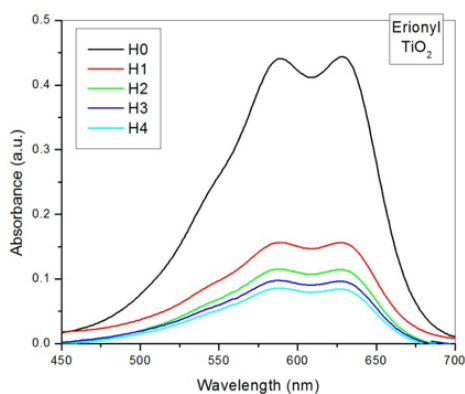


Fig. 7. UV-Vis spectra of erionyl blue dye degradation by TiO₂.

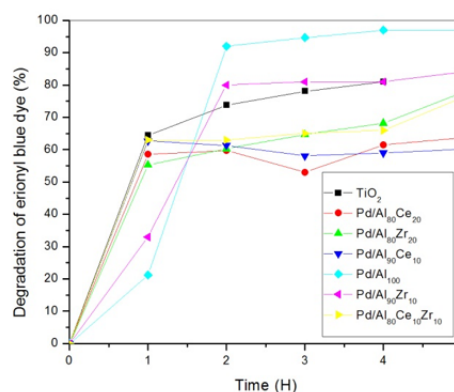


Fig. 8. Comparison of degradation percentages of erionyl blue dye for five hours (H5) of photocatalytic process, with the seven catalysts studied.

After the second hour and up to the fifth hour of processing there are no significant changes in the rate of degradation. The performance of titanium dioxide catalysts in photocatalytic processes is well known for its semiconductor property, whereby they form the hollow-electron pair upon receiving sufficient energy to achieve the jump of an electron from the valence band to the conduction band. This leads to the formation of OH free radicals, responsible for the beginning of the degradation of pollutants in water (Ibrahim and Halim, 2008). The application of this type of catalysts in aqueous media is varied, its efficiency in the degradation of pollutants such as BTEX and colorants (Chen *et al.*, 2010; Barakat *et al.*, 2011). In the case of the palladium catalysts, it is known that these formulations act simultaneously in oxidation-reduction reactions in the catalytic converters of automobiles, for the transformation of hydrocarbons, NO_x and CO. In these reactions there is a synergistic effect between the dispersed metal and the electronic and texture properties of the support. The palladium and the interface between the metal and the support offer the possibility of forming bonds that give way to the oxidation of the contaminating molecules. Research on these materials focuses on the preparation method, it is structural and texture properties, on which its application and catalytic performance depend (van Vegten *et al.*, 2009). Although the palladium catalysts used are not semiconductors, it could be said that they are acting as photosensitizers. That is, its components are excited by light of a specific wavelength such as UV and solar radiation, and subsequently transfer their energy to other reactant molecules, such as dyes.

The main disadvantage of using the anatase phase of TiO_2 in photocatalytic applications lies in their large band gap (3.2 eV), which limits the spectrum of photons that can create electron-hole pairs to participate in oxidation or reduction reactions for the UV region and corresponds to only 4% of incident solar energy (Sugyeong *et al.*, 2014). Therefore, the reduction of the banned TiO_2 band to match the visible spectrum is a very active area of research with strategies based on doping, ion implantation, metal loading, and compound semiconductors. However, in most cases photocatalytic efficacy suffers from induced recombination losses and limited solubility of substitution heteroatoms (Kisch, 2015; Dette *et al.*, 2014).

The electronic behavior of the palladium catalysts is described according to the literature (Pérez Osorio, *et al.*, 2006). The sample $\text{Al}_2\text{O}_3\text{-CeO}_2$ presents a band-gap energy of 3.13 eV, after the addition of zirconia, the band is displaced to 2.96 eV for $\text{Al}_2\text{O}_3\text{-(Ce}_{0.75}\text{Zr}_{0.25})\text{O}_2$ and in addition a gradual change if the zirconia content is increased. The presence of PdO dispersed in this type of supports causes a shift towards the blue band energy forbidden for these combinations of oxides, while maintaining the tendency due to the increased zirconia charge, in fact, the oxide effect of palladium was much more pronounced than the zirconia effect indicating that it can strongly interact with Ce-Zr oxides by changing its electron structure. Finally, with all catalysts, the degradation of the dye is assumed without formation of secondary compounds because the absorption bands decrease in absorbance by keeping the initial form of the colored solution used as reference at time zero.

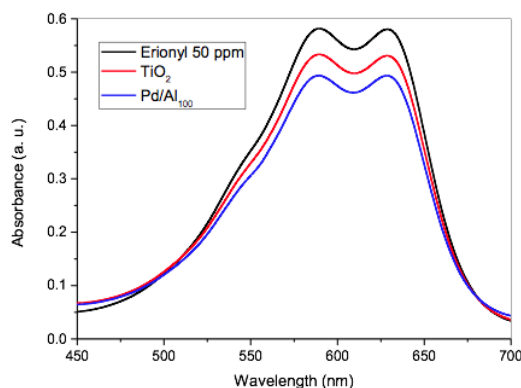


Fig. 9. UV-Vis spectra of erionyl blue dye solution (50 ppm) before and after dark test in contact with TiO_2 and Pd/Al_{100} catalysts for 4 hours in continue agitation.

Figure 9 shows the UV-Vis spectra of the initial solution of the blue erionyl dye (50ppm) and after the dark test was carried out with the TiO_2 and Pd/Al_{100} catalysts without UV light. A greater decrease in the area of the absorption band characteristic of erionyl was observed with Pd/Al_{100} than with TiO_2 . The TiO_2 commonly used in photocatalysis for the degradation of pollutants in aqueous medium, Degusa P-25 with the crystallographic phases of 80% anatase and 20% rutile, has an area of $50 \text{ m}^2/\text{g} \pm 0.15$ (manufacturer's specifications). Due to the above, adsorption is not considered as a determining factor in the photocatalytic performance of TiO_2 and in several investigations it is suggested the use of elements or compounds act as a support to increase its surface area or as dopants to promote greater degradation of contaminants. (Nikazar *et al.*, 2007; Veréb *et al.*, 2012). In the case of the Pd/Al_{100} catalyst, it absorbs 7.5% of the dye, while with TiO_2 it only adsorbs 4%, this behavior can be attributed to the BET surface area of the $213 \text{ m}^2/\text{g}$ catalyst (G. Pérez-Osorio, *et al.*, 2006), this area offers an important adsorption surface for the dye molecule to destabilize and favor its degradation when applying solar radiation. In both cases, it was recover almost 70% of catalysts by filtration after dark test and photocatalytic processes, with a few retention of dye.

Therefore, in Figure 8 when comparing the percentages of degradation of the dye with the catalysts tested it is observed that two linear regions predominate, the first one marked in the first hour (H1) for most of the catalysts, except for the catalysts Pd/Al_{100} and $\text{Pd/Al}_{90}\text{Zr}_{10}$ in which it extends until the second hour (H2) of the photocatalytic process. It can be assumed that in the first stage or region the colorant is adsorbed on the surface of the catalyst to degrade. While in the second occurs the degradation of the dye on the active sites of the catalyst by the incidence of solar radiation. In conclusion it can be said that a synergic effect has been generated between adsorption and photocatalytic activity, which offers a viable alternative for the degradation of organic contaminants such as dyes in water.

Conclusions

Degradation test with solar collector shows favorable results for the case of dye erionyl blue, achieving degradation percentages from 60 to 97 for six palladium catalysts and 84% degradation for TiO_2 .

The catalyst with the best performance was the Pd/Al₁₀₀, since it reaches 97% degradation. The photocatalytic process used in this research is considered a viable alternative in the degradation of erionyl blue dye, due to the use of clean energy and low concentrations of catalyst.

Finally, the proposed catalysts have a good performance in the process of photodegradation, which is comparable to conventionally TiO₂ catalyst used in these processes. It offers the possibility to apply them to reduce the problem of water contaminated with textile dyes. The synthesized catalysts can be classified as sensitizers, i.e. substances that decrease the activation energy in degradation and therefore shift the use of light in the UV region to the region of the visible in the electromagnetic spectrum. However, it is proposed to continue the investigation of additional factors that contribute to the degradation of more stable dyes, using oxidants such as hydrogen peroxide and ozone.

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