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## Solar photocatalytic oxidation of hydroxy phenols in a CPC reactor with thick TiO<sub>2</sub> films

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### Abstract

Solar Photocatalysis is an advanced oxidation process that is involved on water detoxification as a very promising technology. This process has been used for polishing industrial and municipal wastewaters, mainly with titanium dioxide (TiO<sub>2</sub>) as a catalyst. Most of the reactors use TiO<sub>2</sub> as a powder and need a pump in order to have the water moving through the system. A novel photocatalytic reactor, based on Compound Parabolic Collectors (CPC), was developed. The reactor has TiO<sub>2</sub> fixed as a thick film in the CPC tubes and water flows inside by density differences exclusively. This reactor is designed to avoid catalyst separation and water pumping, steps that are energy – demanding and expensive. The films were prepared by conventional sol – gel method on 13 mm diameter Pyrex tubes. The films were firmly bounded to tubes and used for several test with good efficiencies. Films had a mix of anatase and rutile crystalline phases and its particles are nanoscopic. A CPC reactor with 20 tubes connected to the tank by its upper side only was developed and used. Resorcinol was effectively removed from water, either with or without persulfate as electron acceptor, at laboratory bench (one CPC tube experiments) and at pilot scale (20 tubes in the reactor). Main reaction sub-products (tri – hydroxy benzenes) were also oxidized in reasonable solar irradiation times.

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*Keywords:* TiO<sub>2</sub>; CPC reactor; photocatalysis; resorcinol; thick film; thermosyphon.

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## 1. Introduction

It is worldwide known water is a very valuable liquid for life. In fact, life cannot be the way it is without it. However, water quality is threatened by domestic, industrial, agriculture runoffs, and natural wastes that are introduced to water courses and water bodies. Among these substances, phenolic compounds are widely used and eliminated into wastewaters worldwide. From homes, the domestic wastewater receive several personal care and hygiene products (PCHP) that contain phenolic molecules, in addition to industrial wastewater [1 – 5] from such processes like olive washing, foundry, oil refining and processing, cooking, coal gasification, pesticide production, pharmaceutical production, dyestuff elaboration, etc., that might have high loadings of these compounds. Even more, most of municipal and industrial wastewater all around the world is not treated, and the scenario is worst when considering 1,500 km<sup>3</sup> of wastewaters that pollute 12,000 km<sup>3</sup> of freshwater, and that 70 % of industrial wastewater and 80 – 90 % of all wastewater are disposed without any treatment in developing countries [6, 7]. Mexico generates 7.49 km<sup>3</sup> of municipal and 6.01 km<sup>3</sup> of industrial wastewater; treatment is given to 2.78 km<sup>3</sup> of the former waters and to 1.16 km<sup>3</sup> of the later ones [8].

Resorcinol is a phenolic molecule that is used in pharmaceutical industry against acne, and as a raw material in chemical industry in the manufacture of pesticides, dyes, plasticizers, etc. [9]. This molecule has only one aromatic ring (Fig. 1) and 2 hydroxy groups. It's slowly biodegradable at wastewater treatment plants (WWTP) under acclimated sludge, anaerobic mainly, and into batch reactors, [9 – 12]. Resorcinol, like several aromatic molecules, is quite dangerous (HMIS, Health hazard: 2; NFPA, Health hazard: 2), then its removal from wastewater is mandatory [13].

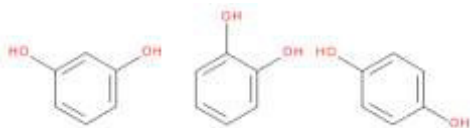
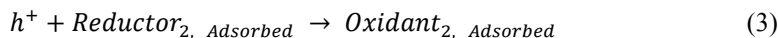
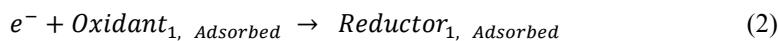
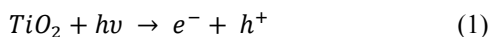


Fig. 1. Di-hydroxy benzenes (From left to right: Resorcinol, Catechol and Hydroquinone).

Photocatalysis is a very promising process that has proved to be effective on removal of organic molecules and some heavy metals from water. The catalyst most used all around the world has been Titanium Dioxide (TiO<sub>2</sub>), which has been very safe and effective. Photocatalytic oxidation (PCO) is based on the interaction of high energy photons with a catalyst: each photon must have more energy ( $h\nu$ ) than the Bandgap Energy ( $E_{\text{gap}}$ , the energy an electron needs to jump from valence to conduction layer) of the catalyst, then the photon can promote the migration of one electron ( $e^-$ ) from valence to conduction layer on the molecule. The electron on conduction layer and the hole it left on valence layer ( $h^+$ ) can either recombine or interact with adsorbed particles. When the electron interacts with an oxidant (electron-acceptor) and the hole with a reducer species (in this case, adsorbed water or hydroxy ions), the hole is able to generate a hydroxyl radical, the second most reactive chemical species (Equations 1 to 3).

To perform photocatalytic oxidations, it is needed a source of radiation in order to have activated the catalyst particles with the required energy. The energy per photon required to promote photocatalysis depends on factors such as the catalyst molecule, crystal phase and impurities added to the catalyst. For TiO<sub>2</sub> photocatalysis, UVA radiation (wavelength between 300 and 400 nm) is enough to start the process. Either Sun, UVA lamps and/or solar simulators can provide this radiation. Solar energy is free and has an important UVA component of around 3.5 % of total irradiance [14], then, its usage must be promoted for photochemical processes. Mexico has UVA irradiances that can be 30 W/m<sup>2</sup> or higher on sunny days; even more, it has been recorded [15] 10 W/m<sup>2</sup> on cloudy days (with instantaneous maximum of 30 W/m<sup>2</sup>) what are competitive with the radiations from lamps on photocatalysis.



Depending on the path that solar radiation follows on the atmosphere, the radiation received on a place can be classified as Direct, Diffuse, Global and Albedo. PCO process can be performed on several kinds of photo-reactors, with or without any sun concentrating systems. The presence of concentrating devices gives several times the energy per area unit that naturally Sun does, but they do not allow the reactor to use diffuse radiation (visible and UV). As it is widely known, diffuse radiation is a low percentage of global visible radiation; however, UV diffuse radiation can reach up to 50 % of global UV irradiance on sunny days, and almost 100 % on cloudy days. Then, non – concentrating devices are a good option for PCO, what simplifies reactor design and operation since mobile parts and concentrating optics are absent. An intermediate option, which concentrates the advantages of concentrating and non – concentrating devices are the Compound Parabolic Collectors (CPC) [16], that consist, for a cylindrical absorber, on a combined reflecting profile whose geometry mixes 2 parabolas and one involute, curves related to the diameter of the circle and to the concentration ratio [16, 17].

Titanium dioxide can be used as slurry or fixed inside the photocatalytic reactors. In the former case, quantum yields are higher than with the second, but it is mandatory to recover catalyst from treated water, involving extra energy and equipment. It is not recommended to leave nanosized TiO<sub>2</sub> on treated water because there are suspects that it can damage liver and heart on mice and, potentially, it can affect to human beings [18]. Then, immobilizing the catalysts, what eliminates the recovery stage, is a good alternative, despite the disadvantage of lowering efficiencies and having mass transfer limitations.

Despite it has been a common practice to link PCO kinetics parameters with reaction time, it is just valid when UV Irradiance ( $G_{UV}$ ) is constant over time; for instance, when UV lamps are used as energy sources. According to Langmuir – Hinshelwood (L-H) kinetics model [16, 24], what is widely used and accepted as a simple and representative, time is the independent variable. If the catalyst particles are activated by photons whose energy is equal to or greater than its  $E_{\text{gap}}$ , the photons flow ( $G_{UV}$ ) determines the rate of generation of active centers at catalyst surface. If  $G_{UV}$  is constant over time, then the amount of photons per time is also constant and L-H model can be expressed either as a function of UV energy dose [16] ( $E_{UV}$ , UV energy accumulated over reaction time) or time (t):

$$r = -\frac{dC}{dt} = \frac{kKC}{1+KC} = -\frac{dC}{dE_{UV}} \quad (4)$$

Here k, K and C represent, respectively, the kinetics constant, the adsorption constant and the pollutant concentration. When  $G_{UV}$  changes over time, the use of equation (4) will give a different behavior with time and  $E_{UV}$  as independent variables. The UV Irradiance data from Estacion Radiometrica were then used to describe PCO kinetics instead of reaction time and Irradiance during the reaction period has to be converted to the accumulated energy received by reactor ( $E_{UV}$ ). One option is to manage Irradiance data as described by Blanco, Malato and Maldonado [14], who present a set of equations that they used to describe kinetics as a function of UVA energy dose per total volume V that is received by a collector area A and for a n sampling period of time  $\Delta t$ , with an Irradiance averaged for  $\Delta t$ :

$$Q_{UV,n} = E_{UV,n}/V = Q_{UV,n-1} + \Delta t \cdot G_{UV,average} \cdot \frac{A}{V} \quad (5)$$

Another option is the analysis presented here by authors. UV irradiance is recorded over the day (or reaction time), an arbitrary hour is set as 0 seconds of insolation (in the present work, 7:00 a.m.). From

this point, UVA irradiance is integrated, mathematically or graphically, over insolation time  $t$  (Equation (6)) in order to get accumulated UVA energy received (per total volume unit if needed) and accumulated UVA energy dose is set as 0 when photocatalytic oxidation reactions starts:

$$Q_{UV,n} = \frac{A}{V} \cdot \int_0^t G_{UV} \cdot dt \quad (6)$$

When equation (5) is the basis for the UVA energy calculation, it is possible to average a peak and a valley of local irradiances and to have a wrong determination of the energy. A big advantage of the usage of equation (6) is that it takes the temporary variations of  $G_{UV}$  into account and it transforms peaks and valleys of  $G_{UV}$  into a sigmoidal curve, which allows overcoming big  $G_{UV}$  variations and has to give a more precise result of accumulated UVA energy. The requisite is that the measurement of  $G_{UV}$  be performed continuously (once each 5 minutes as a minimum) over the day or, at least, over PCO reaction time. This analysis gives  $E_{UV}$  values like the ones presented on Fig. 7.

## 2. Materials and methods

In this work a photocatalytic reactor with immobilized  $TiO_2$  thick film is developed and tested for solar detoxification of water. The reflecting surfaces, the Pyrex pipes used for reaction, and the films are characterized, as well as the reactor is operated under solar irradiance, with promising results. Circulation of water throughout the system was performed only by thermosyphon effect; Resorcinol, whose oxidation products are strongly adsorbed on Titanium Dioxide films (they are removed by PCO latter), is oxidized by photocatalytic reactions.

Chemicals. Resorcinol (BioXtra,  $\geq 99\%$ ), 1,3,5-Trihydroxybenzene dehydrate (97%), Pyrogallol (pure), 1,2,4-Benzenetriol (99%), Methylene blue (99%), titanium isopropoxide (97%), tetraethyl orthosilicate (reagent grade, 98%), isopropanol (analytical grade), acetylacetone (ReagentPlus®,  $\geq 99\%$ ), hydrochloric acid (36%), sodium persulfate (analytical grade) and ethanol (absolute grade) were purchased from Sigma-Aldrich (Mexico), Fermont (Mexico) and Reasol (Mexico). They were used without further purification.

Analysis and equipment. The oxidation of resorcinol was measured by spectrophotometrically with an UV 1601 spectrophotometer (Shimadzu). Resorcinol has characteristic maximum absorbance peaks at 225 and 275 nm. The formation of the first photocatalytic oxidation products was tracked with the spectrophotometer. The wavelengths of maximum absorbance are presented in table 1. There is an overlapping of maximum absorbance wavelengths for Resorcinol and the trihydroxybenzenes, what made complicated the individual quantification of each one. It is possible to apply a method based on Lambert – Beer Law, which states that total absorbance, at a fixed wavelength and optical length, is equal to the sum of the individual contributions of the  $n$  chemical species absorbing. [19] This method did not give accurate results with resorcinol and the trihydroxybenzenes because of the very close absorbance peaks. In this work, the results are presented only as direct absorbance at 225, 272, 300, 330 and 500 nm, what implies that the values belong to the contributions of more than one molecule. The water flow through the reactor was analyzed with a video camera that recorded the position of a dye (methylene blue) that was used as a marker. The reactor was exposed to sunlight, then, the plug of the dye traveled inside the reactor lines and the flow was evaluated with basic hydraulic equations. It was done in this way because the flow was lower than the detection limits of the available meters.

The PCO efficiency ( $E$ ) was evaluated as the reduction of the absorbance at the wavelengths indicated as:

$$E = \frac{A_o - A_t}{A_o} \quad (7)$$

$A_0$  is the initial absorbance and  $A_t$  is the absorbance at  $t$  time at the wavelength analyzed. UVA irradiance was measured at Estación Radiométrica (Universidad Nacional Autónoma de México, Planta Solar, Instituto de Ingeniería) with a UV radiometer (Eppley, model TUVR) that measures radiation from 290 to 385 nm).

*Photocatalytic reactor.* The reactor was intended to perform both PCO of Resorcinol and water circulation by density gradients (created by temperature gradients). It is the first approach to this goal, and then the departure point was set here. The small pilot scale reactor consisted on a horizontal Cu head pipe (nominal diameter: 2 inches) with 20 Pyrex pipes (13 mm external diameter, 1.5 mm thick, 310 mm length) covered in its internal wall with 3  $\text{TiO}_2$  layers that were applied by conventional sol – gel process, with Titanium Isopropoxide as Ti source in the precursor [20, 21]. The molar ratio of the components of the  $\text{SiO}_2$  precursor is 50 : 0.5 : 1 (Ethanol: Hydrochloric acid: Tetraethyl ortho silicate) and composition of  $\text{TiO}_2$  precursor is 5 : 5 : 0.05 : 1 (molar ratios, Isopropanol Acetyl Acetone Hydrochloric acid Titanium Isopropoxide).  $\text{TiO}_2$  films were sintered at 575 °C during 2 hours within an air atmosphere. These films were deposited on the glass pipes previously covered with a thin layer of  $\text{SiO}_2$  (400 °C, 4 hours), intended to avoid the migrations of  $\text{Na}^+$  ions from the glass [20] to the catalyst film and to improve the adherence of Titania. The Pyrex pipes were vertically plugged to the head pipe in parallel on its upper side and to a distribution line on its lower side, closing a loop with the main head (Fig. 2). Main head and Pyrex pipes were connected by a flexible polyethylene line (internal diameter: 9.5 mm). Pyrex pipes were tilted 20° from horizontal position, south faced and fixed on the ground. The CPC reflecting surface was 3M high reflectivity aluminum tape on Cu plates curved on 6 mm acrylic frames with de CPC profile ( $A_{\text{collector}} = 0.245 \text{ m}^2$ ). The concentration ratio was fixed at 1.25 in this reactor as a first approach. Several sampling ports were present at the base of Pyrex tubes and at the top of the main head.

*Experiments.* Some preliminary tests were performed to choose a reflecting tape for CPC construction, with individual pipes inside their CPC reflector, in a solar simulator (Atlas Corp, Suntest X++, Fig. 2); different irradiances, reflecting surfaces and initial concentrations of MB solutions were analyzed. Once they were concluded, 3 CPC reactor pipes were first placed individually inside the solar simulator with constant UVA irradiances and, later, under sunlight, to perform PCO of resorcinol solutions. Finally, the CPC reflectors were covered by the reflective film, and then the photocatalytic reactor was assembled and used for detoxification of polluted water. The reactor was operated both with circulation from main head to Pyrex pipes trough a conducting line and without this circulation. The reactor was covered during an adsorption period with a HDPE black cover; later, it was exposed to direct sunlight and PCO was performed during sunny days. Absorbance and temperature at the top of the main head were periodically measured by UV-Vis spectrophotometry and bulb thermometers.



Fig. 2. Solar photocatalytic reactor (left) and solar simulator (right).

### 3. Results

3.1 *Properties of  $\text{TiO}_2$  films.* The  $\text{TiO}_2$  films were thick, porous and composed of a mix of anatase and rutile nanosized crystalline structures (Fig. 3 and 4). XRD data were processed with Match! Software

to determine the crystalline phase content and SEM image was analyzed with ImageJ software to calculate the average size of the particles.

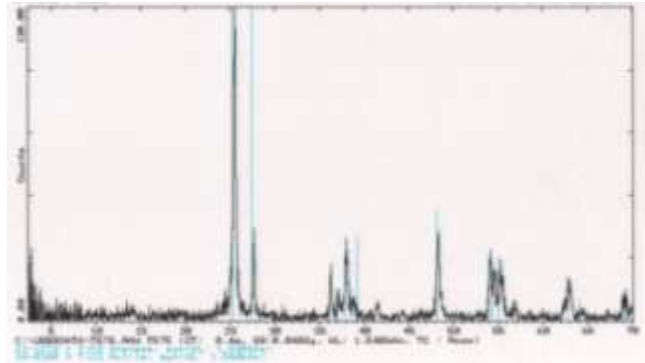


Fig. 3. X Ray Diffraction graph of the catalyst.

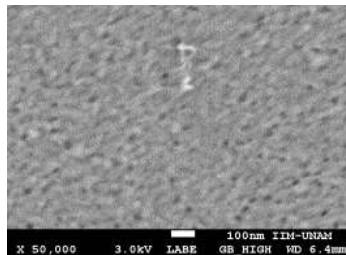


Figure 4. SEM images of the TiO<sub>2</sub> films

The films have an average particle size of 28 nm and 51.3 % of anatase crystals, with Diffraction peaks only for rutile and anatase. Films were either porous (Fig. 4) and presented a cracked surface (not shown). These ruptures at surface might be considered an imperfection, but they could be helpful to mass transfer and water flow nearby the film. Experimental thickness of TiO<sub>2</sub> films, determined by direct SEM analysis, is 13.4 μm.

**3.2 Performance of mirrors and Pyrex pipes.** Three different reflecting self-adhesive aluminum foils were evaluated for the elaboration of the CPC concentrator: Two are produced by 3M (3 M and 3 M+) and the third, whose usage is as automotive decoration, by Chroma (Chroma, Guardian Stripez, self-adhesive decal strips). Evaluation was performed by comparing photolysis of Methylene Blue (MB) activated with solar simulator (70 W<sub>UVA</sub>/m<sup>2</sup>) and with solar radiation. Results indicate that the 3 films are very competitive, with very similar efficiencies (Fig. 5); however, 3 M+ presented the best discoloration values and higher reflectance for wavelengths below 400 nm, then this reflecting film was selected for CPC mirrors. Fig. 5 (A, B, C) indicates that radiation source, energy dose and initial concentration did not make an important difference on MB photolysis efficiency for the 3 reflecting materials. Reflectance of Aluminum films has a small effect on efficiencies (Fig. 5 D). Solar radiation intensity is low on UVB range, but it is important in UVA spectrum [22]. The results with MB photolysis efficiencies are quite close for the 3 reflecting materials, and then the selection was done considering the tests based on solar radiation because of the intended use of Sun energy. Pyrex pipes used in this work presented transmittances from 40 % to 80 % for UVA radiation (Fig. 5, D), and then it is experimentally showed that is a suitable material to perform Solar PCO.

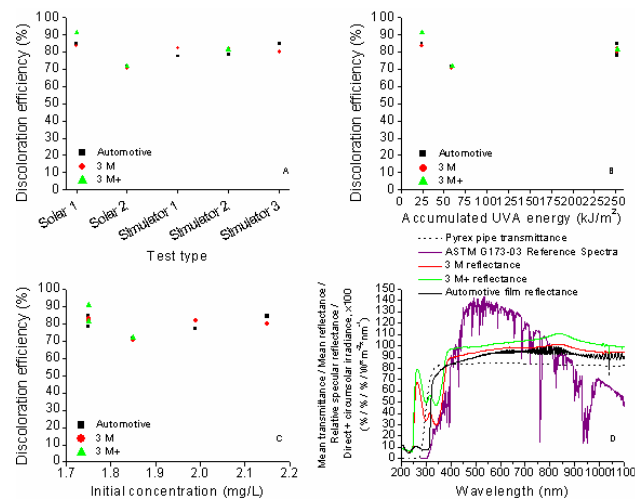


Fig. 5. Reflective aluminum film selection and Pyrex pipes properties. Based on PCO of MB.

**3.3 Photocatalytic Oxidation of Resorcinol.** Resorcinol was removed by PCO in the Solar Simulator ( $70 \text{ W/m}^2$ , 1 hour) and with Sun Irradiance (3 hours). Results (Fig. 6) indicate that the reflective films play a major role for Resorcinol removal at basic pH and persulfate ion presence decreased the removal efficiency. The effect of the reflective films is like expected on the basis of their reflectance; however, it has been reported [14, 16] that persulfate increases oxidation rate and efficiency. Then, some results are in opposition of these works. One possible explanation is the chemisorption of trihydroxybenzenes and/or other initial products of oxidation to the catalyst, what can stop the adsorption of new Resorcinol molecules and poison the catalyst. This competitive inhibition can be increased due to the extremely low turbulence inside the reactor pipes. The figure also presents the effect of initial pH and the absence of either catalyst or persulfate, for different sources and intensities of radiation. These results indicate that the higher discoloration efficiencies were obtained at basic pH values (no persulfate added) and at neutral pH values (persulfate added). Even more, the best performance of the reactors is with solar radiation, what is lower than the UVA energy delivered by the simulator. These outcomes might be related, then, with the spectral distribution of their irradiances. The spectral standard distribution of solar irradiance is presented in Fig. 6 (D), and it starts on 300 nm (almost  $0 \text{ W/m}^2/\text{nm}$ ), increasing almost linearly up to 400 nm (around  $1.0 \text{ W/m}^2/\text{nm}$ ) [22]. On the other hand, the solar simulator presents a similar behavior, with  $0 \text{ W/m}^2/\text{nm}$  at 300 nm and  $0.75 \text{ W/m}^2/\text{nm}$  from 375 to 400 nm. In Mexico City, spectral distribution of solar irradiance (Fig. 7) is similar to standard spectral distribution [22]. Irradiances higher than  $1 \text{ W/m}^2/\text{nm}$  are present from 390 to 400 nm, even in a cloudy day (irradiations from 300 to 350 nm were estimated as a straight line, based on the data presented in references [22, 23]).

PCO tests on CPC reactor were done with the use of solar UV irradiance during March and April, 2013. On Fig. 8 the absorbance of solutions during PCO tests is presented for the test where recirculation is allowed from the main head to the pipes and vice versa. Resorcinol is fast converted into tri-hydroxy benzenes at neutral pH, but it happens faster at basic pH (10.4) and the accumulation of these species is higher. Despite this difference, important removals of absorbing species are performed in all experiments. An important aspect to be considered is that, at the initial moments of PCO reaction, films became red-colored. As reaction continued, the color was eliminated.

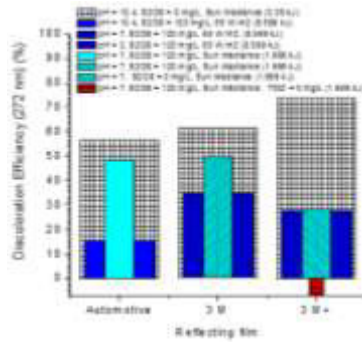


Fig. 6. Solar Simulator and solar Resorcinol PCO. 1-pipe CPC reactor, solar simulator.

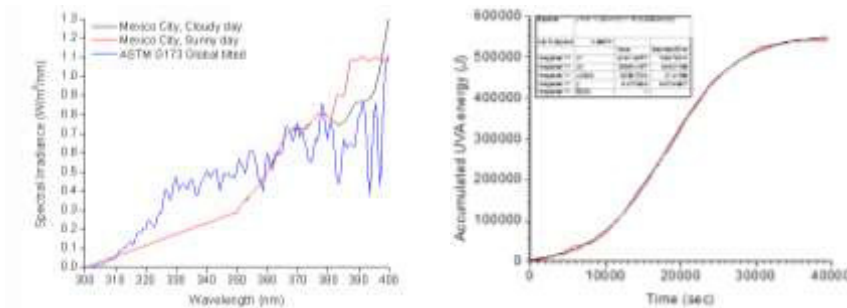


Fig. 7. Spectral UVA irradiance in Coyoacán, Mexico City and typical accumulated UVA energy (Irradiance data as a courtesy of Lourdes A. Quiñonez at Estacion Radiometrica, UNAM).

The effect of the recirculation of water is not very important. Similar reductions of absorbance during PCO are observed without recirculation (Fig. 9) than with recirculation (Fig. 8). It indicates that water can flow by differences of density (thermosyphon circulation) on each pipe individually. When recirculation was allowed, the same difference of densities caused the flow from pipes to main head. In both cases, the PCO performance was effective.

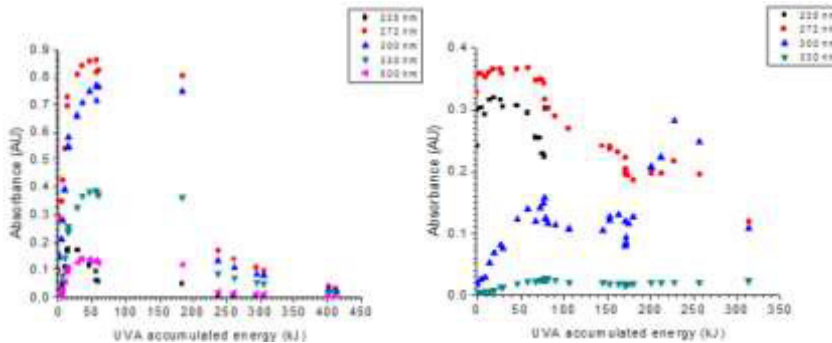


Fig. 8. Solar PCO of resorcinol with recirculation between main head and pipes allowed. Dates: March 30<sup>th</sup> to April 2<sup>nd</sup> (initial pH = 10.4), and April 12<sup>th</sup> to 15<sup>th</sup> (initial pH = 7), 2013.

The flow, when recirculation was allowed, was measured during a sunny day. MB concentrated solution was injected to the HDPE line and the plug movement was tracked (April 2<sup>nd</sup>, 2013, 15:00



p.m.)). It resulted on an average flow of 1 mL/min. When this flow was diverted on the 20 Pyrex pipes, the resulting condition was that water flowed through the first 3 pipes mainly (the first pipe is the one closer to the HDPE ending) during the starting 10 minutes. After 20 minutes, water ascended on next 4 pipes, and after 50 minutes, water has ascended on all of the pipes. The turbulence on HDPE was very low ( $Re = 1.6 \times 10^{-3}$ ) and, as a consequence, it is lower on each of the Pyrex pipes.

The catalyst was regenerated, after each reaction, by rinsing with distilled water, filling with a solution of sodium persulfate (0.01 M) and placing the reactor under Sun radiation. This cleaned up the catalyst from tests to test, and the photocatalytic oxidation capability was kept. This is verified on Figures 8 and 9, whose experimental data belong to tests performed with the same  $TiO_2$  film treated on this way.

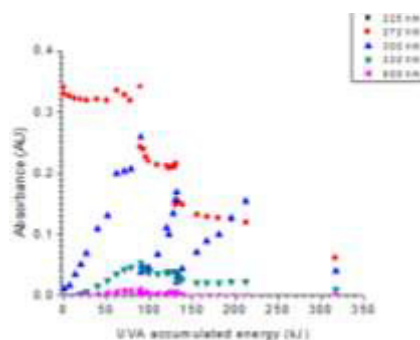


Figure 9. Solar PCO of resorcinol at neutral pH with recirculation between main head and pipes blocked. Date: April 22<sup>nd</sup>, 24<sup>th</sup>, 26<sup>th</sup>, 2013.

#### 4. Conclusions

- High reflectance aluminum films are effective to perform PCO in CPC solar reactors
- Automotive aluminum films are competitive against 3M films on UV reflectance
- Thick  $TiO_2$  were composed of a mix of anatase and rutile crystalline phases.
- $TiO_2$  particles on the film were nanosized all over the surface.
- Changes in initial pH values affected the formation of initial oxidation products, but the removal of absorbing species has not presented a clear dependence on initial pH.
- Thermosyphon circulation of water inside the reactor was enough to have the water treated on the photocatalytic reactor. Water flow has to be increased in order to reduce treatment time and byproduct adsorption on catalyst surface.
- Despite chromatographic techniques were not available for this works, spectral absorbance curves allow to establish that main byproducts are produced at the beginnings of PCO reactions and, after some energy consumption, they are oxidized into smaller molecules.
- Resorcinol removal efficiency was 75 % or higher, what might be acceptable if a biological treatment were proposed after PCO.

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