

# PHOTOCATALYTIC DEGRADATION OF BISPHENOL A IN AN AQUEOUS SUSPENSION OF TITANIUM DIOXIDE.

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## Introduction:

Bisphenol A (BPA) is a monomer used in the epoxy resin and polycarbonate manufacture. This compound is catalogued like an endocrine disruptor that causes several diseases and syndromes. This is distributed as a result of its multiple use, to its low degradability, to that it can be transported by air, ground and water, to its bioaccumulation in the trophic chain because is accumulated in the fat of the organisms and, to that are transmitted to the descendants through the mother during the gestation. Human exposition to this non biodegradable substance is increasing in the time, particularly through contaminated water by industrial remainders. Considering that the water is one of main means where it is deposited as remainder of industrial processes is tried to create systems for water treatments and purification of the same. Nevertheless, the traditional technologies that are used for the separation of organic substances of the treated water are based on processes of adsorption with activated coal or by drag with air. This implies that these processes only transfer the polluting agents of their watery phase to other that is also contaminated, therefore the problem persists. This problem has generated the necessity to implement new processes to treat non biodegradable compounds [1-4].

At the moment, exists a group of technologies based on processes of destruction of the polluting agents by means of hidroxyl radicals ( $\cdot\text{OH}$ ) which have a high potential of oxidation and attribute the capacity to oxidize or to degrade almost the totality of the polluting agent transforming it into inoffensive compounds to the environment and even can arrive until the mineralization or  $\text{CO}_2$  formation. These technologies are called "advanced processes of oxidation" (APO's), which are beginning to be implemented in North America, Europe and Japan [5-7].

In this work, oxidation process is studied; particularly the photo heterogeneous degradation with titanium dioxide in water is evaluated like alternative for the BPA degradation. Use a photo catalytic reactor with illumination UV and the quantification of the removal of the polluting agent was carried out using liquid chromatography (HPLC). The influence of titanium dioxide amount, BPA concentration, reaction temperature and the catalyst state like suspension and immobilized were also determinate.

## Materials and methods:

Bisphenol A Aldrich in solid state; Titanium dioxide ( $\text{TiO}_2$ ) Degussa P25 with a density of  $3.8 \text{ gr/cm}^3$  were used. Use a photo catalytic reactor made up of a UV radiation lamp (Lexmana) of 40W of power and emission of 360nm (length 124cm. and diameter 2cm) and a Pirex tube that surrounds the radiation source (diameter 4 cm and length 110cm). Drained space between the lamp and the pirex tube corresponds to the area by where the solution flows. The recirculation of this solution is carried out by means of hoses of silicone rubber (0.5 cm of diameter), which connected to a pump to generate a flow of 400 mL/min.

### *Experimental procedure of the $\text{TiO}_2$ in suspension.*

Four different concentrations from Bisphenol A were prepared: 0; 0.01; 0.05; 0.1 mM in a liter of water. Four different amounts from titanium dioxide were used 0; 100; 250; 500 mg/L of  $\text{TiO}_2$ . The solution of water, dioxide titanium and Bisphenol A was shaken during approximately 10 minutes with a magnetic agitator and an agitation plate, before being recirculated by the photo catalytic reactor. Each test was of 4 hours and samples were taken hourly. After, the solution was filtered with plastic filter with Pall ring of  $0.2 \mu\text{m}$  nylon acrodisc, and later to be analyzed in HPLC equipment. In the figures 1 and 2 are shown a schema and a picture of the photo reactor

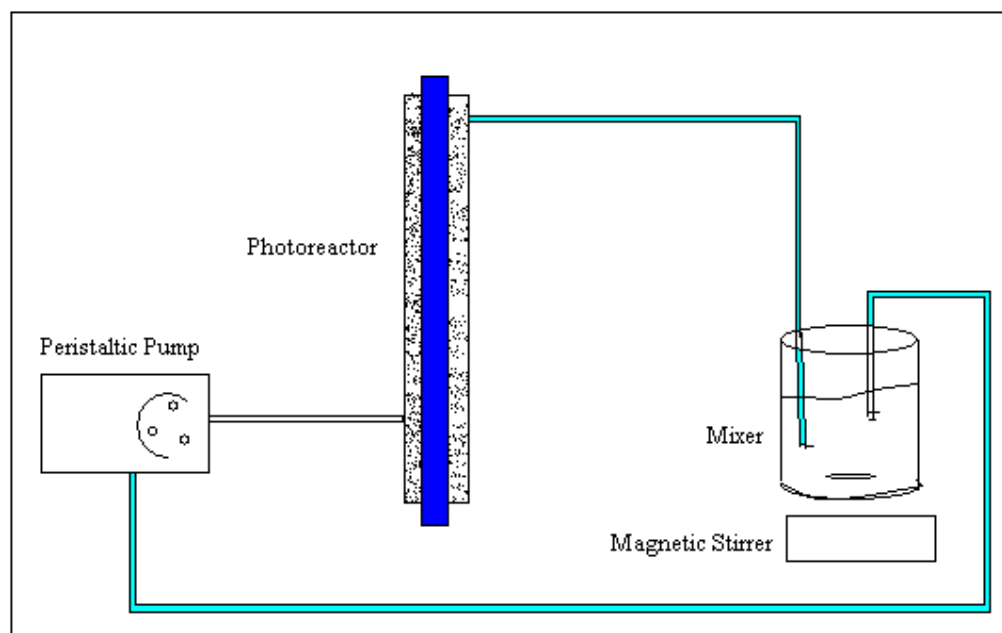


Fig. 1 Schema of photoreactor for photocatalytic decomposition of Bisphenol A

### **Experimental procedure of the TiO<sub>2</sub> immobilized**

Films of three materials were developed; acrylic, acetate and glass, with the purpose of to find the best alternative to fix TiO<sub>2</sub>.

A solution concentrated of 5g/L of TiO<sub>2</sub> in water was prepared, which was deposited on each surface. As far as the acrylic and to acetate, it was let dry the solution to room temperature, with the purpose of to evaporate the water of the solution. Whereas the glass was activated with increases of 50°C of temperature until arriving at 400°C during one hour, using a muffle 47900 Barnstead [8]. These films were located inside the photo reactor. The quantification of the BPA concentration was realized with HPLC equipment as with the catalyst in suspension. The TiO<sub>2</sub>, was proved by XRD analysis as shown in fig 2.

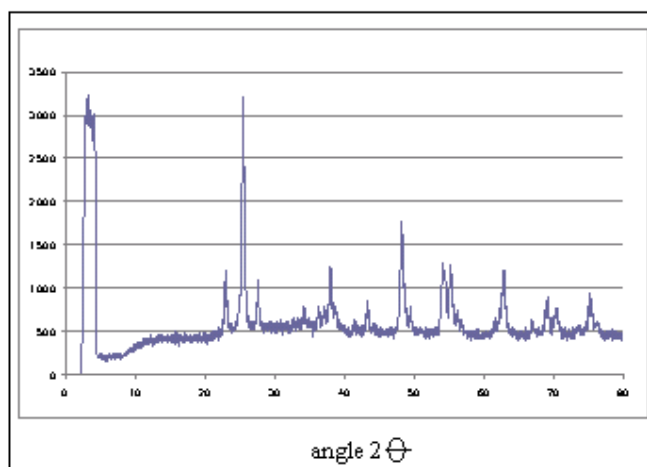


Fig. 2. XRD Analysis for the catalyst TiO<sub>2</sub>

### **Analysis HPLC**

High Performance Liquid Chromatography (HPLC) was used to quantify the concentration of Bisphenol A. The conditions used in this quantitative analysis of BPA were: A movable phase of 20mM of sodium phosphate like solution buffer (pH 7) and acetonitrile in proportion 65%:35% and a volumetric flow of 1 mL/min. An analytical column of adjustment of diodes with a length of 250mm with +0.35/0.55 V and temperature of 20 ± 3°C was used (Allsphere ODS 2-5μ). The used method was isocratic, injecting 10μL and the time of analysis by each sample was of 30 minutes.

### **Results and Discussion:**

The concentration of BPA with respect to the time was correlated by means of the equation of reaction rate of first order, since report a good adjustment of the data obtaining coefficients of correlation between 0.8-0.9. This linearization allowed to find the reaction constant apparent ( $K_{ap}$ ).

### **Catalytic Photodegradation of BPA using $\text{TiO}_2$ in suspension:**

The different experiments show to the behavior of the apparent constant of reaction ( $K_{ap}$ ) with respect to the concentration of catalyst in suspension  $22.54 \pm 2.61^\circ\text{C}$ . It is observed that for a low concentration of Bisphenol A owns high values of  $K_{ap}$ . This indicates that the photo degradation reaction happens faster for low concentrations because exists less competition by the actives sites assets in a certain amount of catalyst [9]. It is observed, in the figure 2, that the tendency of  $K_{ap}$  with respect to the amount of  $\text{TiO}_2$  is similar for the three concentrations of BPA. Initially the apparent constant owns an ascending behavior when amounts of titanium dioxide are smaller or equal to 100 mg/L and descendant for higher amounts. The highest  $K_{ap}$  ( $0.0154 \text{ min}^{-1}$ ) is obtained when the initial concentration of BPA is 0.01mM and the amount of  $\text{TiO}_2$  is 100 mg/L.

The diminution of the apparent constant of reaction when increasing the amount of  $\text{TiO}_2$  to an amount superior to 100 mg/L, can be explained from the following three phenomena, which can limit or inhibit the photo reaction catalysis falling  $K_{ap}$

- Intermediary formation in the photo catalytic process

The photo catalysis heterogeneous with  $\text{TiO}_2$  can disturb to the BPA molecule generating intermediary products of degradation which can generate competition to occupy the active sites of the catalyst [10-11].

- Effect Screening

A high amount of  $\text{TiO}_2$  particles in suspension contributes to the formation of a screen that it prevents that the light photons activate to the catalyst [12].

- Adsorption of BPA in the surface of the catalyst ( $\text{TiO}_2$ )

Considering the expression of Langmuir- Hinshelwood and that the reaction is of first order, one correlates the constants of surface  $k$ , adsorption  $K_c$  and the apparent constant reaction  $K_{ap}$ . This analysis showed that the rank of  $K_c$  is between 0.05-0.41  $\text{min}^{-1}$ , whereas the rank of  $k$  is between 0.0003-0.0012  $\text{min}^{-1}$ . These results indicate that the adsorption reaction is faster than the reaction in the surface, allowing to predict that the limit stage of the degradation of BPA is the surface reaction. For 100 mg/L of  $\text{TiO}_2$ , the constant of the reaction in surface  $k$  tends to increase and the equilibrium constant of  $K_c$  adsorption tends to fall down, whereas for high concentrations happens inverse, this indicates that the reaction in the surface becomes slower when increasing the catalyst concentration [13-15].

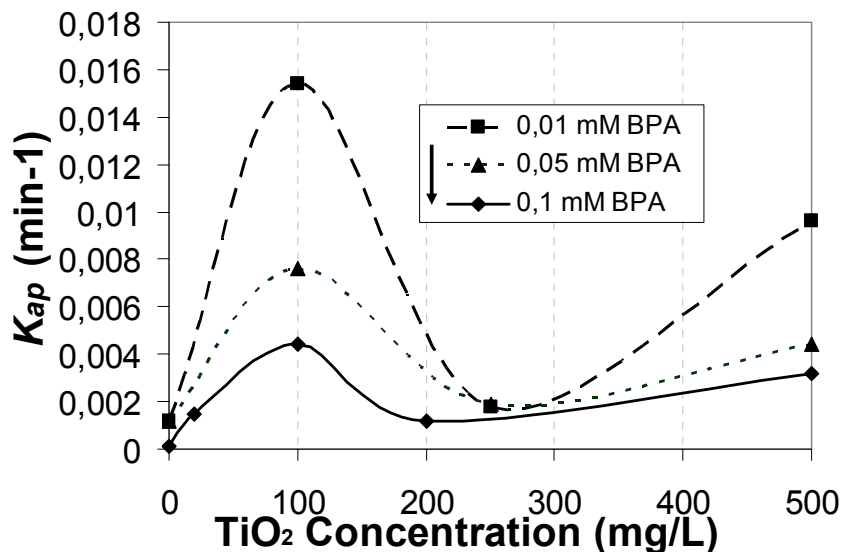


Fig 3. . Apparent constant Rate vs. TiO<sub>2</sub> amount

The photo catalysis reaction was evaluated with 4 different temperatures ( $22,54 \pm 2,61^{\circ}\text{C}$ ,  $35,17 \pm 2,71$ ,  $46,82 \pm 3,45$  and  $58,51 \pm 4,06^{\circ}\text{C}$ ). These values allowed to predict the experimental activation energy for a rank of temperature between  $20^{\circ}\text{C}$ - $60^{\circ}\text{C}$  from the Arrhenius equation, the value found was  $14,54$  is of is of  $\text{KJ/mol}$  and the form factor (A) was equal to  $1.47$  [8, 12, 13, 16].

### **Photo catalytic degradation of BPA using immobilized TiO<sub>2</sub>**

The support of titanium dioxide used were; acetate, acrylic and glass. The TiO<sub>2</sub> supported in acetate generated a loosening of catalyst of 95% at the end of the test. The acrylic used like TiO<sub>2</sub> support generated adsorption of the solution, reflected in the increase in the film weight. Whereas catalyst support in glass obtained better results removing 47.65% of BPA and coming off 52% of TiO<sub>2</sub> at the end of four hours of process. In order to improve the fixation efficiency the use of a binder must consider or to realize a pre treatment to the film surface using a diluted solution of HF and a washing with NaOH to increase the number of radicals \*OH and to improve the contact with titanium dioxide and the glass supports [17].

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