

## Methylene Blue and 4-Chlorophenol Photodegradation Using Gamma-Irradiated Titanium Oxide

<sup>1</sup>JAIME JIMÉNEZ-BECERRIL\*, <sup>1,2</sup>ALMA MARTÍNEZ-HERNÁNDEZ,

<sup>1</sup>FRANCISCO GRANADOS-CORREA AND <sup>2</sup>ROSA E. ZAVALA ARCE

<sup>1</sup>Departamento de Química, Instituto Nacional de Investigaciones Nucleares, Apartado México.

<sup>2</sup>Instituto Tecnológico de Toluca, Av. Instituto Tecnológico S/N, Metepec, Estado de México, México.  
jaime.jimenez@inin.gob.mx\*

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**Summary:** This paper presents experiments of heterogeneous photocatalysis of methylene blue and 4-chlorophenol using gamma-irradiated TiO<sub>2</sub> with a gamma source of <sup>60</sup>Co at different doses. Methylene blue and 4-chlorophenol concentration after photo degradation were measured by UV spectrophotometry. More organic degradation was found using the irradiated catalyst than the non-irradiated catalyst, but a desorption process was noted in samples irradiated at the lower doses.

### Introduction

Water is an important natural resource in the world, and the availability of safe drinking water is a high priority; unfortunately, water resources are coming under increasing pressure due to population growth, over-use, and wastage [1]. In response, researchers have developed newer eco-friendly water remediation methods centered on Advanced Oxidations Processes (AOP) [2].

Photocatalysis is a promising AOP method for the treatment of contaminated water because it can be applied at ambient temperature and breaks down a wide variety of organic materials, organic acids, estrogens, pesticides, dyes, crude oil, microbes (including viruses and chlorine resistant organisms), and inorganic molecules such as nitrous oxides (NO<sub>x</sub>); furthermore, in combination with precipitation or filtration, photocatalysis can also remove metals such as mercury [3].

Chlorophenols are contaminants that could be introduced to the environment during the production of other chemicals and could also be produced during disinfection by chlorination of water [4]. Chlorophenols constitute a particular group of priority toxic pollutants because most of them are toxic and hardly biodegradable, and they are difficult to remove from the environment. Their half-lives in water can reach 3.5 months in aerobic waters [5]. They can produce disagreeable tastes and odors in drinking water at concentrations below 0.1 µg•L<sup>-1</sup> and adverse effects (toxicity) on the environment [6].

On the other hand, azo-dyes, the largest group of synthetic dyes, constitute up to 70% of all the known commercial dyes produced and are one of the main pollutant groups of water and wastewater

[7]. Highly substituted aromatic rings joined by one or more azo groups characterize their chemical structures. These substituted ring structures make the molecules recalcitrant; the conventional wastewater treatment processes do not degrade [8]. Many dyes and their break-down products may be toxic for living organisms. Therefore, decolonization of dyes is an important aspect of wastewater treatment before discharge. It is difficult to remove the dyes from the effluent because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems [9]. Methylene blue is selected as a model compound for evaluating the potential TiO<sub>2</sub> to remove dyes from wastewater [10].

In experiments of organic compound degradation carried out using gamma radiation to induce reaction, the radiation chemical yield in heterogeneous systems depends on the chemical composition of the catalyst, and when catalysts have the same composition, those yields depend on the particle size. If the amount of the adsorbed substance per gram of catalyst increases, the radiation chemical yield also increases with a redistribution of the adsorbed radiation energy that takes place between the solid and the adsorbed organic compound [11]. However, researchers have postulated that irradiation induces the conversion of surface Ti–O–Ti bonds to more hydrophilic TiOH (titanol) groups in the presence of water. Photochemical changes are also slightly reflected in the TiO<sub>2</sub> hardness [12].

Photoinduced superhydrophilicity (PSH) is accompanied by photocatalytic activity, as both phenomena have a common ground; the surface contaminants will be either photomineralized or washed away by water. A possible application is self-

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\*To whom all correspondence should be addressed.

cleaning windows. PSH involves reduction of Ti(IV) cations to Ti(III) by electrons and simultaneous trapping of holes at lattice sites (usually bridging oxygen) or close to the surface of the semiconductor. Such trapped holes weaken the bond between the associated titanium and lattice oxygen, allowing oxygen atoms to be liberated, thus creating oxygen vacancies. The subsequent dissociative adsorption of water at the site renders it more hydroxylated. An increased amount of chemisorbed  $-OH$  leads to an increase of van der Waals forces and hydrogen bonding interactions between  $H_2O$  and  $-OH$ . Water can easily spread across the surface, and hydrophilic properties will be enhanced. Water adsorption does not occur uniformly, but produces an amphiphilic surface with alternating hydrophilic and oleophilic regions at the scale of several nanometers (usually  $<10$  nm in size) [13].

The aim of this work is to study the effect on organic photodegradation of gamma-irradiated  $TiO_2$ .

## Results and Discussion

Fig. 1 shows photodesorption obtained in the process of the degradation of methylene blue at an initial concentration of  $15\text{ mg}\cdot\text{L}^{-1}$ ; it is important to note the highest concentration found is  $12.013\text{ mg}\cdot\text{L}^{-1}$  after desorption. This fact made it difficult to measure photodegradation: only the non-irradiated sample shows photodegradation.

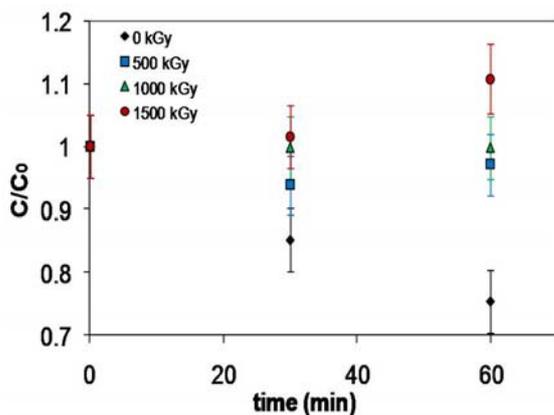


Fig. 1: Methylene blue photodegradation with non-irradiated and irradiated  $TiO_2$ .

To avoid desorption phenomena, in the next experiment, there was a stabilization time of 1 h with constant oxygen bubbling, but no UV irradiation, keeping samples in a dark room. After the stabili-

zation time, photodegradation experiments were carried out. Fig. 2 shows the obtained results.

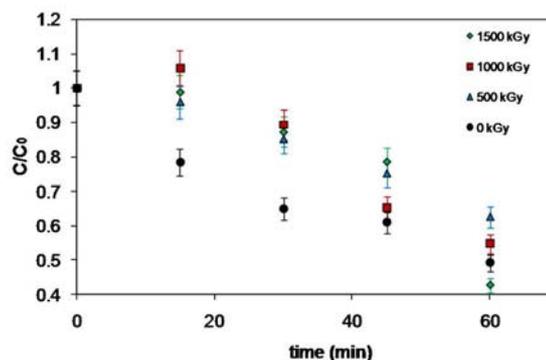


Fig. 2: Methylene blue photodegradation using non-irradiated and irradiated  $TiO_2$ , and 1 h of stabilization.

The stabilization time allows for the observation that gamma-irradiated  $TiO_2$  samples show little desorption at the beginning of experiment, but photodegradation starts at 15 minutes. There was a degradation of methylene blue at similar amounts with irradiated and non-irradiated  $TiO_2$ .

Using 4-chlorophenol, the desorption is lower than methylene blue desorption (Fig. 3). The initial concentration of 4-chlorophenol was  $10\text{ mg}\cdot\text{L}^{-1}$ , and the higher concentration after UV illumination was  $8.384\text{ mg}\cdot\text{L}^{-1}$ . After 1 h of UV illumination, all oxide samples show similar 4-chlorophenol degradation.

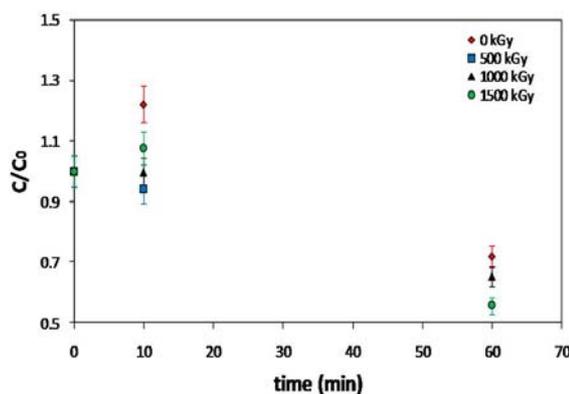


Fig. 3: 4-chlorophenol photodegradation with non-irradiated and irradiated  $TiO_2$ .

Fig. 4 does not show desorption with any  $TiO_2$  sample, using 4-chlorophenol and a stabilization time of 1 h. Thus, it becomes possible to observe

degradation at its initiation and better degradation with gamma-irradiated samples than no-irradiated samples.

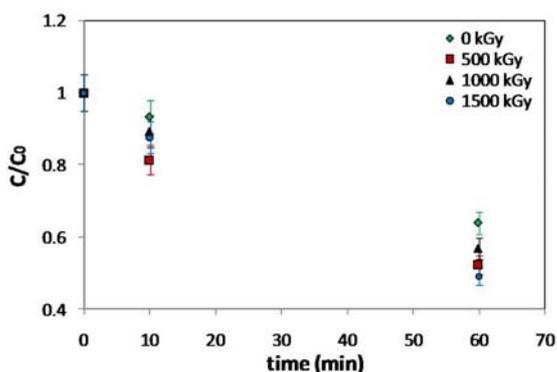


Fig. 4: 4-chlorophenol photodegradation using non-irradiated and irradiated TiO<sub>2</sub>, and 1 h of stabilization.

Photodesorption of small molecules from surfaces has been attributed to various approaches from the lack of sufficiently accurate potential energy surfaces, particularly for electronically excited states involved in the desorption scenario [14]. The desorption could be explained by a thermodesorption, i.e., induced by an increase in surface temperature due to (i) electron-hole recombinations; or (ii) the first oxidative transformation reactions whose enthalpies are very negative. Energy applied by photodesorption should not be excluded [15]. In the case of the O<sub>2</sub> photodesorption kinetics, the rate of the process is proportional to the square root of the UV flux, showing that second-order electron-hole pair recombination is dominant in governing the photodesorption rate [16].

That is, during UV illumination, there are many processes involved that could result in photodesorption of some organic compounds, and most of them are related to electron-hole pair formation-recombination. However, in the case of gamma-irradiated oxides, a modified surface [12] allows adsorbed molecules to stabilize in the dark with surface hydroxyl groups.

## Conclusion

Using TiO<sub>2</sub> irradiated in photocatalysis experiments, degradation of methylene blue and 4-chlorophenol exhibit similar degradation behavior. The stabilization time for TiO<sub>2</sub> and organic compound solutions is necessary to avoid desorption

in the degradation process. Higher doses of TiO<sub>2</sub> show higher degradation, but also high desorption.

## Experimental

TiO<sub>2</sub> was irradiated at doses of 500, 1000, and 1500 kGy, using a <sup>60</sup>Co source of 2.38X10<sup>14</sup> Bq with a dose rate of 12.3 kGy·h<sup>-1</sup>. The samples were put into 20 mL vials, and the samples were hermetically sealed and wrapped in individual and labeled bags; and then, they were placed in the in-camera exposure in the JS-6500 industrial irradiator facility. The radiation was performed from lowest to highest doses. For the measurement and calculation of the absorbed dose in TiO<sub>2</sub>, resulting from the exposure to direct ionizing radiation, red and aniline acrylic dosimeters was used.

The initial concentration was 15 mg·L<sup>-1</sup> of methylene blue, and 50 mL solution samples were put in contact with 50 mg of TiO<sub>2</sub>, non-irradiated and irradiated at different doses. The samples were bubbling with constant oxygen flux. Samples were placed the under UV illumination with an 8-watt UV lamp for 1 h, and 5 mL aliquots were taken every 15 minutes.

After irradiation, samples were filtered with Millipore filters of 0.45µm for later analysis of remaining methylene blue with a UV-Vis Shimadzu model F-2350 spectrophotometer at 664 nm.

For 4-chlorophenol experiments, the initial concentration was 10 mg·L<sup>-1</sup>, and experiments were carried out similar to those with methylene blue; for the development of color, 4-amino-antipyrine method was used, and the samples were analyzed at 510 nm by UV spectrophotometry.

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