

# Photodegradation study of salicylic acid by TiO<sub>2</sub> and synthesized TiO<sub>2</sub>-Cu.

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## Abstract

*Water pollution from emerging contaminants (ECs) or emerging pollutants is an important environmental problem. An heterogeneous photocatalytic treatment, as advanced oxidation treatment of wastewater effluents, has been proposed to solve this problem. In the present study, it was considered for emergent contaminants removal using salicylic acid as a model contaminant molecule. TiO<sub>2</sub> photocatalytic activity was evaluated using photocatalytic reactor configuration: Photocatalyst solid suspension in wastewater in a stirred photoreactor. The used catalyst was characterized by various analysis techniques namely (SEM, XRD, DTA-TGA and FTIR), monitoring the photodegradation of salicylic acid by exposure to UV-rays (250 nm-265 nm) using UV spectroscopy. The effects of catalyst mass, photodegradation time, salicylic acid concentration, pH, CuO content in TiO<sub>2</sub> and ionic strength were investigated.*

**Keywords:** TiO<sub>2</sub>, CuO content in TiO<sub>2</sub>, Pharmaceutical waste, salicylic acid, photodegradation, environment.

## I. Introduction

The waste waters from the pharmaceutical industry are regularly released into the environment without more severe control. Under preliminary treatment, these waters remain loaded with medicinal substances that are considered as a threat to the ecosystem [1-3]. Several chemical types are very toxic and hardly biodegradable. Their removal represents one of the main problems in the treatment process of liquid discharges.

The chemical complexity and the diversity of pharmaceutical rejections make the traditional treatments non effective. However advanced oxidation processes are actually in full development for the degradation of non-biodegradable organic molecules [4-6]. Heterogeneous photocatalysis in the presence of semiconductor powders is gradually becoming a promising alternative for the removal of these soluble organic compounds [7-11]. The use of this technique leads to the complete mineralization of these pollutants in carbon dioxide, water and mineral acids at room temperature and at atmospheric pressure [7, 12].

In the present study, the Salicylic acid (SA) was treated by photodegradation using TiO<sub>2</sub> as a catalyst. This advanced oxidation process is more advantageous than others processes because of the use of TiO<sub>2</sub> as it is non-toxic, photochemically stable, inexpensive and available in different forms. [4, 7, 9, 13]

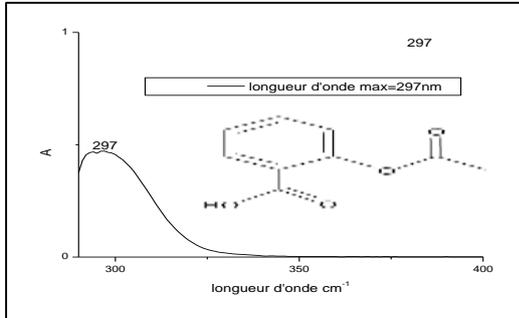
The Salicylic acid, a nonsteroidal anti-inflammatory drug, is one of the reagents used to manufacture aspirin (2-acetyl benzoic acid). It is also the active substance of many drugs with analgesic and antipyretic properties. The continuous release of this reagent's waste water into the environment increases its negative effects on the media even at low concentrations. [14, 15]

The aim of this work is to investigate if the changes in the initial pH, initial salicylic acid concentration, water hardness, TiO<sub>2</sub> initial loading, and NaCl ions influence on the degradation of the chosen pharmaceutical rejection (SA) in presence of the TiO<sub>2</sub> catalyst.

## II. Materials And Methods

### II.1. Presentation of the materials

Salicylic acid ( $C_9H_8O_4$ ) also known as 2-hydroxybenzoic acid is a white crystalline powder whose structure and absorbance spectrum are shown in Fig. 1, was purchased from BIOCHEM and used as received. The experiments were carried out in distilled water recovered using distilling apparatus (GEF 2002).



**Fig.1,** Absorbance spectrum and molecular structure of SA.

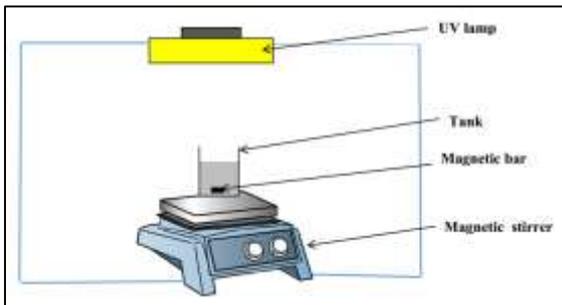
TiO<sub>2</sub> samples, purchased from BIOCHEM whose main properties are summarized in Tab.1, were employed for salicylic acid photocatalytic.

**Tab.1,** Properties of TiO<sub>2</sub> catalyst used in this study.

Chemical formula	TiO <sub>2</sub>
Color	White
Molar weight	79.866g/mol
Density	4.23

## II.2. Reactor

Photocatalytic reactor was constructed with parallelepiped room in which a tank was placed on a magnetic stirrer. The U.V lamp was fixed in parallel to the catalyst plan, 12 cm above the reactor (Fig. 2).



**Fig.2,** Experimental installation

## II.3. Characterization

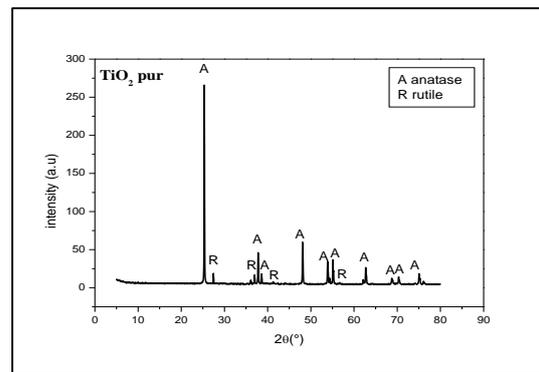
The pH of the solutions was measured by conventional method using a pH meter (pH 211

HANNA). The microstructures of the samples were observed by scanning electron microscope (Quanta 250 with tungsten filament by the company FEI). The observation of each sample was made at different magnifications. The phase compositions and their relative amounts were characterized by X-ray diffractometer (new range D8 Advance A 25 the brand BRUKER), the spectra FTIR was obtained by using (Shimadzu infinity-1).

## III. Results and discussion

### III.1. Characterization of the catalyst

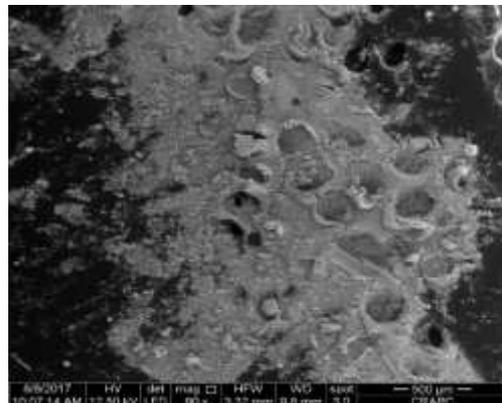
#### A. Analysis by XRD

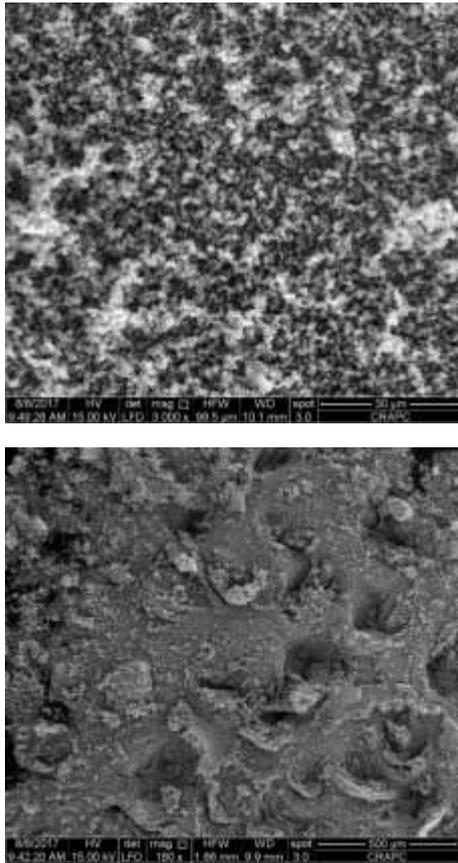


**Fig.3,** XRD patterns of TiO<sub>2</sub> powders

Fig.3 shows XRD patterns of TiO<sub>2</sub> powders calcinated at 850°C. The TiO<sub>2</sub> particles show a mixture of anatase and rutile structures with dominance of anatase. The appearance of rutile peaks is due to high temperatures that promote the transformation of anatase into rutile. The intense reflection at  $2\theta = 25.34^\circ$  and at  $2\theta = 48^\circ$  are assigned to anatase [16-18].

#### B. Microscopy (SEM)



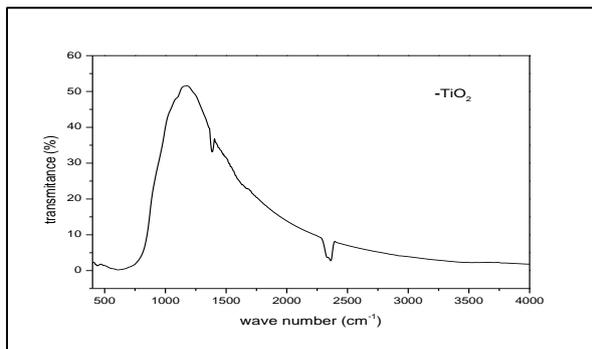


**Fig.4.** SEM images of calcined TiO<sub>2</sub>

The SEM micrograph (Fig.4), at 90x, 180x and 3000x magnifications, shows that the morphology of the calcinated TiO<sub>2</sub> is porous spherical. In a previous study, it's proved that the particle of TiO<sub>2</sub> in anatase phase has mostly spherical morphology[19, 20], this fits well with the XRD results.

### C. Analysis by FTIR

FTIR spectra of the calcined samples are shown in Fig. 3. An absorption peak appearing at 1382 cm<sup>-1</sup> is observed, it refers to the vibration of Ti-O-Ti. It is also noticed that the strong band in the range of 900–500 cm<sup>-1</sup> is assigned with the characteristic vibrational modes of TiO<sub>2</sub> [21,22].

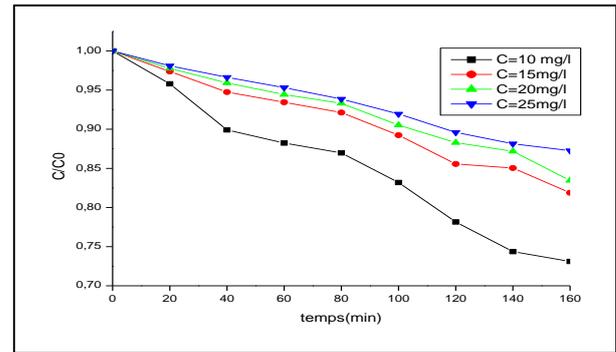


**Fig.5.** FT-IR spectra of calcined

## III.2 Photocatalytic degradation of a Salicylic acid

### III.2.1 Effect of initial salicylic acid concentration

The effect of salicylic acid concentration was studied in a range between 10mg/L to 25 mg/L at 500 mg/L TiO<sub>2</sub>; Irradiation of solution with UV lamp power 265-300 Watts. The results are shown in Fig.6



**Fig.6.** Evolution of reduced concentration of salicylic acid versus time for different initial concentrations.

### III.2.2. Effect of TiO<sub>2</sub> catalyst loading

Selection of optimum catalyst loading is important in order to minimize excess of catalyst. The catalyst concentration is critical especially for suspension catalyst systems. In this case, it must be sufficient to adsorb a maximum of pollutants, but should not be in excess to reduce the opacity of the solution to radiation. Fig5 shows the effect of catalyst loading on 15 mg/L SA conversion.

Basing on the results, the elimination rate of salicylic acid increases with catalyst loading up to 1g /L. Beyond this value the photodegradation decreases. This allows us to conclude that we were operating in a heterogeneous catalytic regime.

The oxidation rate limits correspond to the maximum amount of TiO<sub>2</sub> for which the maximum of the salicylic acid molecules are practically eliminated. For higher amounts of the catalyst, the reaction rate decreases due to the saturation of the photon absorption or screen effect which prevents the penetration of light onto the surface of the catalyst grains.

### III.2.3. Effect of initial pH

PH is an essential parameter to take into account in adsorption processes. The study was carried out by

putting in contact 3 mL of the stock solution (salicylic acid, 1000 mg/L) and 0.1 g of calcined TiO<sub>2</sub> at different pHs (2, 4, 6, 8 and 10). The solution is adjusted by addition of the solution of HCl (0.1N) or NaOH (0.1N). Fig. 4 shows the influence of pH on photodegradation of salicylic acid.

According to these results, the elimination of acid increases when pH increases. This is probably due to the excess of hydroxide ions generated by a large production of hydroxide radicals.

Moreover, in acid medium, the salicylic acid molecule is neutral and the TiO<sub>2</sub> surface is positively charged, therefore, there will be no attraction between the surface and the molecule.

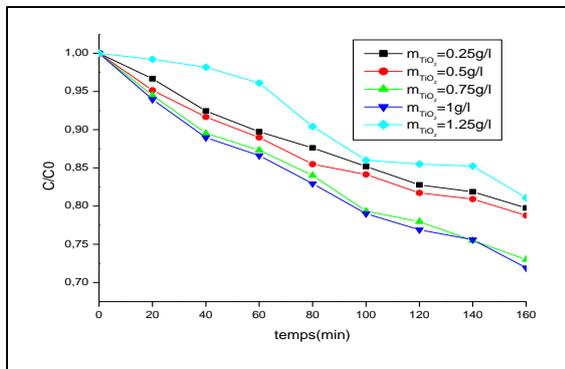


Fig.7, Effect of the pH on photodegradation of salicylic acid

### 3-2-4 Effect of NaCl Ions

Fig.8 shows the influence of ionic strength on photodegradation of salicylic acid (15mg/L SA; pH=8; 0.2g TiO<sub>2</sub>).

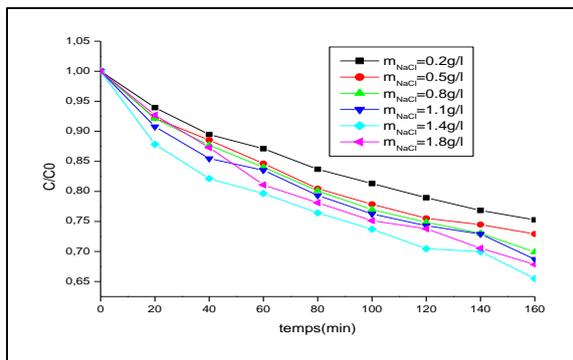


Fig.8, Influence of ionic strength on photodegradation of SA.

According to the results, the increase in NaCl concentration promotes the degradation of salicylic acid by photocatalysis.

The photocatalytic activation is delayed up to 1.8 g/L of NaCl. This is due to the congestion caused by the ions, thus preventing OH radicals from reaching the sites of degradation (catalyst surface): the OH radical formation is decreased and the degradation process is stopped.[6]

### III.2.5. Influence of CuO content

Figure 9 shows the influence of the hardness of water on photodegradation of salicylic acid.

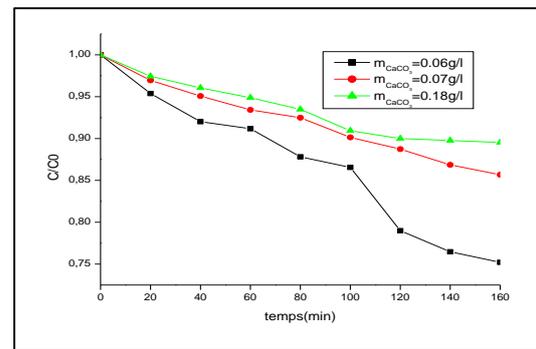


Fig.9, Effect of CuO content on photodegradation of SA.

According to these results, the increase in CuO content loading decreases the degradation of salicylic acid by photocatalysis. This result indicates that the presence of a greater amount of Cu affects negatively on photocatalysis ability.

## IV. Conclusion

This study, which takes part of the general context of environmental depollution, was intended to study the impact of different parameters on the elimination of salicylic acid by photocatalysis in heterogeneous media.

In this medium, we were interested in the photodegradation of the pollutant by TiO<sub>2</sub> catalyst. The influence of the initial salicylic acid concentration, catalyst loading, pH, CuO content in TiO<sub>2</sub> and NaCl ions were studied.

The results show that the best degradation percentage is obtained with low concentrations of salicylic acid (10mg.L<sup>-1</sup>). The basic medium (pH=8) promotes the elimination of the pollutant. The optimal loading of TiO<sub>2</sub> catalyst is 1g.L<sup>-1</sup>. NaCl ions

and CuO content in TiO<sub>2</sub> negatively affect the degradation of salicylic acid.

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