Implementation of a Photocatalytic / Adsorption hybrid reactor: Application to the elimination of recalcitrant pollutants.

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Abstract

This research proposal will be part of the implementation of a new hybrid process based on the coupling of both photodegradation and adsorption of Green Malachite (GM) and/or Red Congo (RC); two emerging and priority pollutants considered as recalcitrant and likely to pollute surface waters and /or groundwater.

The method consisted in irradiating a more or less uniform film based on titanium dioxide spread on the surface of a lamellar glass reactor by ultraviolet radiations in order to eliminate the two used targeted micro pollutants by both photodegradation and/or adsorption.

The lamellar reactor designed and constructed was a borosilicate glass device constituted by a dark chamber in which the UV rays are emitted by a UV lamp of type A (T5-8W). The system power was supplied by a crushing peristaltic pump and operating at a flow rate of 5mL.min^{-1}.

The deposition of titanium dioxide (TiO_2) on the reactor surface was carried out by the sol-gel method (Deep-Coating).

The photodegradation of the molecule GM or RC was monitored by analyses of the samples taken every 30 minutes for a residence time of up to 800 min.

During the whole operation, the pH and maximum absorption wavelength λ_{max} were monitored.

Quantification of the GM and / or RC solutes is carried out using a UV-Visible spectrophotometer (6800 UV / VIS Jenway) at appropriate wavelengths (618nm for VM and 500nm for RC).

The photocatalytic deposition characterization was carried out using X-ray Diffraction (DRX) and spectroscopic (Fourier Transform Infrared (IFTR))methods. The approach adopted in this continuous process was to be able to remove organic compounds without deteriorating the photocatalytic support which must remain adhered to the reactor surface.

Keywords: *Photodegradation; Adsorption; Titanium Dioxide; Lamellar reactor.*

I. Introduction

Pollution from pharmaceuticals and personal care products (PPCPs), emerging contaminants in surface and ground waters, is becoming recognized as an environmental concern in many countries. **[1]**

Various chemical and physical processes, such as chemical precipitation and separation of pollutants, electrocoagulation, elimination by adsorption on activated carbon …etc., are currently used. One difficulty with these methods is that they are not destructive but only transfer the contamination from

one phase to another. Therefore, a new and different kind of pollution is faced and further treatments are deemed necessary.

In recent years as an alternative to conventional methods, "advanced oxidation processes" (AOPs), based on the generation of very reactive species such as hydroxyl radicals that have been proposed to oxidize quickly and non-selectively a broad range of organic pollutants. **[2]**

The use of TiO_2 suspended in water causes two major problems: the separation of the catalyst from the treated water and the recycling of TiO_2. Since the Ti O_2 particles size is of the order of 50 nm, the price required for separation makes the process difficult to achieve on a large scale.

II. Materials and methods

A. . Chemical and reagents

The MG (Chemical formula: $C_{23}H_{25}$ N_2CI; Molecular weight = 420 g mol-1; λ_{max} = 618 nm; pKa = 10) used in the present study is a monovalent cationic dye and is classified as C.I. Basic green 4. It was purchased from Fluka AG and was used without any further purification. The chemical structure of MG is shown in Fig. 1.

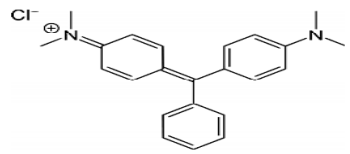

Figure1. Chemical structure of Malachite Green.

The Red Congo (RC) (Chemical formula: $C_{32}H_{22}N_6O_6S_2Na_2$; Molecular weight = 696.7g $mol^{-1;}$ λ_{max} = 500 nm; pKa = 4) used in the present study is a Azo dye.It was purchased from Fluka AG and was used without any further purification. The chemical structure of RC is shown in Fig. 2. **[3]**

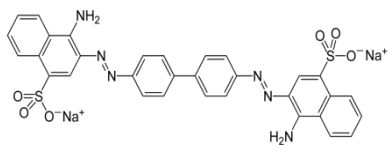

Figure2. Chemical structure of Red Congo.

B. Photocatalyst

The investigated titanium dioxide was (Titanium (IV) oxide) (anatase > 97%). According to the manufacturer's specifications, the crystallites mean size was <100 nm and the specific surface area was >14.0 $m^2 g^{-1}$.

The photocatalyst particles were deposited on 5 cm $\times$7cm glass plates from a suspension of TiO_2 (4g.L^{-1}).

C. Photocatalytic reactor

The photocatalytic experiments were carried out in a lamellar reactor. The polluted solutions (1.25.mg.L^{-1}) were re-circulated at the flow rate of 5 mL.min^{-1} using a peristaltic pump through the photoreactor for during 300 min.

All experiments were carried under a U.V. lamp radiation (Phillips P 8 W) with λ_{max} = 365 nm).

All samplings (15mL) were taken each 30 min using a plastic syringe and then filtered in Millipore disk of 0.45mm.

MG or RC degradations were evaluated by measuring the absorbance with UV-Vis spectrophotometer at the appropriate wavelengths (6800 UV/VIS, Jenway).

III. Results and Discussions

III.1. Immobilization of TiO_2 on glass plates:

TiO_2 nanoparticles were fixed on glass plates by using a Sol-Gel method (Deep-Coating).

An organic suspension of (4 g of Titanium Dioxide in 1 liter of ethanol) was prepared and was sonicated for 15 min.

Before deposition, the glass surface was washed in a basic solution of NaOH in order to increase the number of OH groups.

Then, this suspension was carefully deposited on the glass plates and allowed to dry out at room temperature (20 °C) for a time of 12 h.

The glass plate was subject to a heat treatment according to the following steps:

- drying at 100 ◦C for an hour
- calcination at 475 ◦C for 4 hour . **[2]**

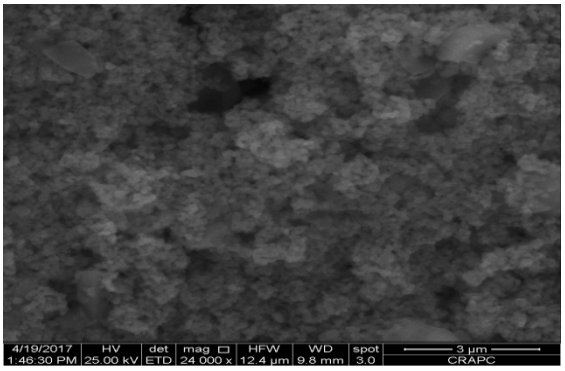

Figure3. Scanning electron microscopy images of TiO2 nanoparticles deposited on glass plates.

As shown in Fig. 1, the first coat was covering the entire surface.

The plates were thoroughly washed with deionised water for the removal of free TiO_2 particles.
The photocatalysis of the dyes was tested with these plates [4].

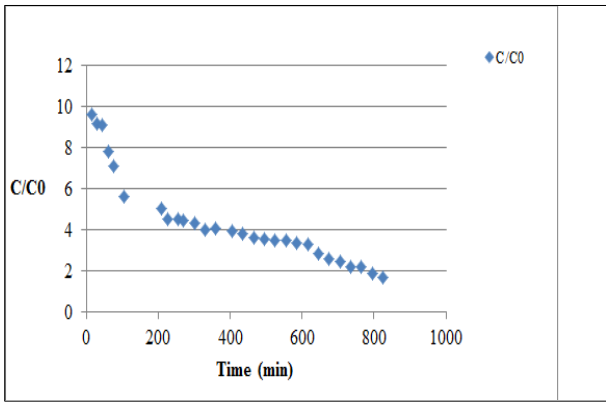

Figure 4. Kinetics of degradation of Malachite green by photocatalysis (TiO2 / UV).

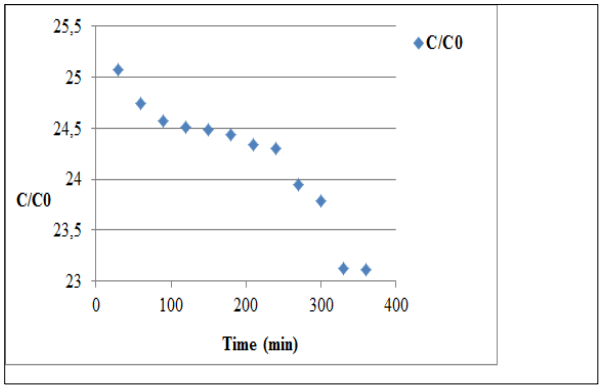

Figure5. Kinetics of degradation of Red Congo by photocatalysis (TiO2 / UV).

The two figures show clearly that the ratio of the concentrations decreased with time: disappearances of 20% and 12% were noted after 60 minutes of irradiation for the GM and for the RC, respectively. This made it possible to confirm the photocatalytic nature of the reaction. The particles of TiO_2 are at the origin of this activation. They absorb UV radiations to give rise to very reactive species which would lead to the degradation of the substance in solution.

IV. Conclusion

The principal objective of this work was the study of the photocatalytic degradation of two dyes, Green Malachite and Red Congo. The photocatalytic experiments were carried out in a lamellar reactor under ultraviolet radiations (UV).

The experimental results obtained showed that the degradation of the two dyes gave disappearances of 20% of GM and RC after 60 minutes of irradiation, respectively.

However, the photocatalytic reactor was effective for the degradation of the organic pollutants.

List of symbols:
AOP: Advanced Oxidation Processes
DRX: X-ray Diffraction
GM: Green Malachite
IFTR: Fourier Transform Infrared
pH: Hydrogen potential.
PPCP pharmaceuticals and personal care products
RC: Red Congo
UV: Ultra Violet

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