



Photocatalytic transformation of the antipsychotic drug risperidone in aqueous media on reduced graphene oxide–TiO₂ composites



P. Calza^a, C. Hadjicostas^b, V.A. Sakkas^{b,*}, M. Sarro^a, C. Minero^a, C. Medana^c, T.A. Albanis^b

^a Department of Chemistry and NIS centre, University of Torino, via P. Giuria 7, 10125 Torino, Italy

^b Department of Chemistry, University of Ioannina, Ioannina 45110, Greece

^c Department of Molecular Biotechnology and Health Sciences, University of Torino, via P. Giuria 5, 10125 Torino, Italy

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ABSTRACT

In the present study reduced graphene oxide–TiO₂ composites were synthesized at two different ratios (1:10 and 1:5) through a hydrothermal method using graphene oxide and commercial P25 as starting materials. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), BET surface area and ultraviolet–visible (UV–vis) absorption spectroscopy were employed to investigate the morphology and properties of the produced composites. The photocatalytic performance of TiO₂–rGO catalysts was evaluated under artificial solar light and visible light in distilled water, as well as, different surface waters (at natural pH) with respect to risperidone (antipsychotic drug) degradation. Irrespectively of the irradiated aqueous matrix, the photocatalytic efficiency of the tested composite materials under simulated solar light and visible light irradiation was higher compared to bare TiO₂–P25 (reference catalyst).

The identification of intermediate compounds, the assessment of mineralization and the evaluation of toxicity were performed as well. LC/HRMS was brought to bear in assessing the temporal course of the photocatalyzed process. Along with risperidone decomposition, the formation of twenty intermediate compounds (TPs) occurred in the presence of TiO₂. Irradiation of risperidone in the presence of the hybrid material resulted in the identification of thirty-four TPs. The transformation of risperidone progressed through the formation of compounds more harmful than the drug itself, as assessed by the measurement of acute toxicity, evaluated using the *Vibrio fischeri* bacteria test. When employing TiO₂–rGO, all the identified transformation products were quicker degraded compared to TiO₂–P25. At the same time both the reduction of toxicity and mineralization were faster achieved than with bare TiO₂–P25.

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1. Introduction

Risperidone (4-[2-[4-(6-fluorobenzo[d]oxazol-3-yl)-1-piperidyl]ethyl]-3-methyl-2,6-diazabicyclo[4.4.0]deca-1,3-dien-5-one) is a benzisoxazole antipsychotic drug, mainly used to treat schizophrenia and other psychiatric illnesses.

Risperidone (RS) is easily and well absorbed by the human body while it is metabolized to 9-hydroxy-risperidone that has a similar pharmacological activity as RS [1]. One week after oral administration, RS and its major metabolite are excreted 70% in the urine and, to a much lesser extent, in the faeces (14%) [2]. Both chemicals that form the active antipsychotic fraction have been detected in human breast milk [3].

Risperidone's production and use as an antipsychotic drug may result in its release to the environment [1]. However, information concerning the fate and environmental behavior of RS (partitioning, transport, degradation, interaction with other environmental media) is still scarce. As regards the aquatic environment, RS does not contain chromophores that absorb at wavelengths >290 nm and, therefore, is not expected to be susceptible to direct photolysis by sunlight [1]. In addition, volatilization from water surfaces is not expected to be an important fate process [1]. At the same time, hydrolysis is not expected to be an important environmental fate process since this compound lacks functional groups that hydrolyze under environmental conditions [1].

Currently, studies on the environmental transformation of RS are scarce. A recent study carried out in the Santorini Island (Aegean Sea, Greece), reported the occurrence of RS as well as its metabolite (9-hydroxy-risperidone) in influent and effluent wastewaters up to concentration levels of 3.2 and 11.8 ng L⁻¹, respectively [4]. Although the concentration in the aquatic environment is too low

* Corresponding author. Fax: +3026510 08795.
E-mail address: vsakkas@cc.uoi.gr (V.A. Sakkas).

to pose a very acute risk according to RS Safety Data Sheet (in accordance with Regulation (EC) No. 1907/2006), RS is hazardous to the aquatic environment (Aquatic Chronic 2, H411, R51/53, N, T) [5]. Therefore, a crucial need for more enhanced technologies that can reduce its presence in the environment has become evident.

HPLC/MS technique is the more suitable technique to analyze RS in different matrices [6–8].

Advanced oxidation processes, above all photocatalytic processes, are frequently used to treat emerging pollutants, and achieve their complete mineralization [9–13]. The degradation of pollutants by means of TiO_2 is well documented in the literature [14–15]. However, conventional TiO_2 photocatalysis has barriers in practical remediation of organic pollutants due to the low efficiency in sunlight absorption [16].

In exploring approaches to increase the efficiency of TiO_2 photocatalyst, graphene based nanocomposite systems have been utilized [17–24]. The great interest on the employment of graphene/graphene derivatives based TiO_2 both in terms of energy production as well as environmental remediation is attributed to the higher light absorption ability of the composites, as well as, the reduced recombination rates of electron-hole pairs, further improving the photocatalytic efficiency [25,26].

In the present work reduced graphene oxide– TiO_2 photocatalysts were synthesized at two different ratios (1:5 and 1:10, named, TiO_2 -rGO₂₀, TiO_2 -rGO₁₀) through a hydrothermal method using graphene oxide and commercial P25 as starting materials. After characterization of the synthesized composites (morphological and textural characteristics, crystal structure and optical properties), their photocatalytic activities were assessed through the photodegradation of RS under a variety of experimental conditions, such as, different aqueous matrices (distilled, tap, river and lake water) under artificial solar light and visible light. According to our knowledge this is the first time that the photocatalyzed transformation of RS is examined. Moreover, we explore here the transformation of an RS using heterogeneous photocatalysis by assessing the mechanism of transformation and the toxicity related to the drug and to its transformation products.

2. Experimental

2.1. Material and reagents

Sulfuric acid (>95%), potassium permanganate (99%), hydrogen peroxide (30%), hydrochloric acid (37%), ethanol (99%), sodium nitrate (99%), commercial Evonik P25- TiO_2 powder, and risperidone (98%) were provided from Sigma–Aldrich Chemie (Steinheim, Germany). Natural graphite (99.99% purity, 20 μm , from Sigma–Aldrich Chemie) was used as precursor of graphene oxide (GO). Acetonitrile, LC/MS water and formic acid were obtained from Merck (Darmstadt, Germany). HPLC grade water was from MilliQ System Academic (Waters, Millipore). HPLC grade methanol (BDH) and acetonitrile (Aldrich) were filtered through a 0.45 μm filter before use. Reagent grade formic acid was from Fluka Chemie (Sigma).

2.2. Synthesis of graphene oxide

GO was prepared from graphite powder according to the modified method reported by Hummers and Offeman [27,28]. Briefly, 1.0 g of graphite and 0.5 g NaNO_3 were added into 23 mL of 273 K concentrated H_2SO_4 . Next, 3 g of KMnO_4 was added gradually with continuous stirring and cooling, while at the same time the temperature of the mixture was maintained below 293 K. Then, the ice-bath was removed and the obtained mixture was stirred at 308 K for 30 min. After that time, 46 mL of distilled water was added

slowly in order to reach temperature of 371 K, and at that temperature the mixture was maintained for 15 min. The resultant reaction was terminated by addition of 140 mL of distilled water followed by 10 mL of 30% H_2O_2 aqueous solution. The GO was collected by centrifugation. The solid materials were washed repeatedly with water and ethanol. The resultant materials were dried under vacuum overnight at 323 K to obtain GO.

2.3. Preparation of reduced graphene oxide– TiO_2 composites (hydrothermal method)

GO was first dissolved in H_2O by ultrasonic treatment for 1 h to yield a yellow-brown solution. TiO_2 -P25 was added into the GO colloidal solution and the mixture was stirred for another 1 h. The homogeneous suspension was transferred to a Teflon-lined autoclave and was subjected to hydrothermal treatment at 453 K for 6 h [27,29,30]. It has been reported [29,30] that besides temperature the autogenous pressure developed inside the sealed autoclave also contributes to the reduction of GO. TiO_2 -rGO nanocomposites were synthesized with a weight ratio between rGO and TiO_2 -P25 at 1:5 (denoted as TiO_2 -rGO₂₀) and 1:10 (denoted as TiO_2 -rGO₁₀). The obtained composites was collected by centrifugation, washed repeatedly with water, and dried under vacuum at 333 K.

2.4. Materials characterization

Characterizations of the synthesized TiO_2 -rGO materials were performed, including SEM, TEM, XRD, FT-IR, UV–vis spectroscopy and calculation of the surface area.

The morphology of the materials was studied by scanning electron microscopy (SEM) using a JOEL microscope (JSM-5600, JEOL, Tokyo, Japan) while transmission electron micrographs were obtained using a JEOL JEM-2010F microscope (TEM).

In addition, the crystal structures of materials were investigated by X-ray diffraction (XRD), using a D8 Advance Brüker diffractometer operating with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) and a secondary beam graphite monochromator. Powder samples were scanned over an angular 2θ range from 5 to 90°.

Fourier Transform Infrared spectra (FTIR) were acquired using a Perkin Elmer (spectrum 100, Waltham, MA, USA) Infrared spectrophotometer.

UV–vis absorption spectra were obtained using a Jasco V-570 UV–vis spectrophotometer (Hachioji, Japan).

The specific surface area, of the synthesized photocatalysts was calculated from N_2 adsorption–desorption isotherms obtained with a Quandachrome gas adsorption instrument (QUAN-DACHROM, Bounton Beach, FL, USA).

2.5. Irradiation experiments

Photocatalytic activities of the catalysts (TiO_2 -P25, TiO_2 -rGO₂₀, TiO_2 -rGO₁₀) were assessed through the photodegradation of risperidone (RS) under a variety of experimental conditions, such as, different aqueous matrices (distilled, tap, river and lake water) under artificial solar light and visible light. The catalysts (5 mg) were suspended in an aqueous solution of RS (2 mg L^{-1} , 50 mL) with a magnetic stirring bar in a cylindrical quartz glass reactor that was positioned at 18 cm distance from light source. Catalyst loadings were relatively low (100 mg L^{-1}) in order to obtain slower kinetics and compare the performance of the respectively materials, as well as to avoid dark zones in the illuminated slurry. Irradiation was carried out using a Suntest CPS+ apparatus from Heraeus (Hanau, Germany) equipped with a Xenon arc lamp (1500 W) and glass filters restricting the transmission of wavelengths below 290 nm (simulated solar light). For visible light experiments a cut-off long pass filter was used ($\lambda > 430 \text{ nm}$). Chamber temperature

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