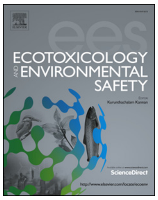
Ecotoxicology and Environmental Safety 159 (2018) 301–309

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



Photocatalytic mineralization and degradation kinetics of sulphamethoxazole and reactive red 194 over silver-zirconium co-doped titanium dioxide: Reaction mechanisms and phytotoxicity assessment

Saraschandra Naraginti[a,c], Yi Li[a,*], Gianluca Li Puma[b,*]

[a] Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Ministry of Education, College of Environment, Hohai University, Nanjing 210098, PR China
[b] Environmental Nanocatalysis & Photoreaction Engineering, Department of Chemical Engineering, Loughborough University, Loughborough LE11 3TU, United Kingdom
[c] Biofuels Institute, School of the Environment, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, PR China

ARTICLE INFO

Keywords:
Photocatalyst
Dyes
Antibiotics
Wastewater
Phytotoxicity

ABSTRACT

The photodegradation and phytotoxicity of the pharmaceutical antibiotic, sulphamethoxazole (SMX) and the azo-dye reactive-red-194 (RR194) under visible-light irradiation of TiO_2 nanoparticles modified by silver and zirconium was investigated. The results indicated that sulphamethoxazole and its toxic degradation by product, 3-amino-5-methylisoxazole and RR-194 could be degraded efficiently by the co-doped Zr/Ag-TiO_2 catalyst. PL studies and ROS generation results suggested that the effective charge separation was carried out while irradiation of the modified TiO_2 nanoparticles. Phytotoxicity tests demonstrated lower percentage of germination in *P. vulgaris* (40%), *V. radiata* (30%) and *P. lunatus* (30%) of the seeds treated with 50 ppm of SMX, compared to the seeds treated with the degradation products (100%). The results with 50 ppm of RR-194 also showed lower percentage of germination in *P. vulgaris* (40%), *V. radiata* (50%) and *P. lunatus* (30%) compared to the degradation products (100%). Furthermore, significant increase in root and shoot development was observed in the seeds treated with the degraded products when compared with SMX and RR-194. Overall, this study contributes to further understanding the photodegradation mechanisms, degradation products and environmental fate of SMX and RR-194 in water which helps in the evaluation and mitigation of the environmental risk of SMX and RR-194 for water reuse and crop irrigation.

1. Introduction

The extensive utilization of antibiotics in aquaculture, stockbreeding and human medicine have raised significant environmental concerns due to the observed increase in antibiotics resistant bacteria and genes [1,2]. In 2013, China consumed approximately 92,700 t of antibiotics, 53,800 t of which have been released into the environment [3]. Often these antibiotics have been detected in lakes, rivers, wastewater effluents [4], estuarine and coastal waters [5,6]. According to USEPA many antibiotics are reported as chemical contaminants of emerging concern, without much regulation and the effect on human health and the environment is inadequately understood [7].

Sulphonamides are belongs to a category of synthetic antibiotics prepared from sulphanilic acid which function as bacteriostatics by suppressing dihydrofolic acid generation. They have prolonged persistence in the environment due to their low degree of biodegradability. The concentration levels of these sulphonamides in water has been reported in the range of 0.13–1.9 $\mu g\,L^{-1}$ [8], and could accumulate in several organisms such as bacteria [9,10]. Sulphamethoxazole belongs to a broad spectrum sulphonamide, and is one of the most extensively prescribed antibiotics worldwide. After administration, the metabolism of the content takes place in the liver, however the unmetabolized [11] and active metabolites [12,13] are then excreted in urine or feces ultimately reaching the gray water sewer systems and/or conventional wastewater treatment plants [14]. SMX is a refractory pollutant and not easily biodegraded by conventional treatments those employed in sewage treatment plants [15]. This necessitates the utilization of high efficiency materials and tertiary oxidative treatment for the effective degradation of SMX. In addition, the degradation products of SMX, such as 3-amino-5-methylisoxazole, could cause a harmful threat to wildlife [16]. Studies have reported the formation of 3-amino-5-methylisoxazole during chemical [17–19] and microbial [20,21] degradation of SMX, and fewer studies have reported its further transformation.

Other common classes of contaminants often found in water and

---

[*] Corresponding authors.
E-mail addresses: envly@hhu.edu.cn (Y. Li), g.lipuma@lboro.ac.uk (G.L. Puma).

https://doi.org/10.1016/j.ecoenv.2018.04.062
Received 5 February 2018; Received in revised form 23 April 2018; Accepted 26 April 2018

wastewater are dyes used in paints manufacturing and textiles. The azo dye RR-194 is a very common in cotton dyeing. Azo dyes are highly carcinogenic, harmful to human health and cause reduced light penetration in aqueous environments adversely affecting photosynthesis [22]. Conventional methods including coagulation, activated-carbon adsorption, biodegradation and membrane filtration have been used for wastewater decolorization. However, these methods cannot completely remove the contaminants and their degradation products and often need further waste disposal after treatment [23]. Thus, the treatment of dyes demands the development of new and effective processes for their removal. Altogether, the untreated release of antibiotics, EDCs and dye effluents would not only induce serious health and environmental hazards but also has a strong impact on the fertility of soil.

Heterogeneous photocatalysis with visible light irradiation of modified titanium dioxide (TiO_2) nanoparticles has emerged one of the effective treatment methods for dyes and pharmaceuticals removal [24–27] and for water reuse in agriculture. Co-doping of TiO_2 with two different atoms has attracted significant interest since the dual effect can synergistically affect the photocatalytic activity of semiconductor materials compared to doping with a single element [28,29]. Addition of Ag and Zr can reduce the recombination of electrons and holes by efficient trapping of electrons. Further, Zr is an isoelectric element exhibiting deep energy level doping properties [30].

In this study Ag and Zr modified TiO_2 nanoparticles have been utilized in the degradation of SMX and RR-194. The possible degradation mechanisms were investigated by HPLC and LC-ESI/MS analysis. Water reuse necessitates the assessment of the phytotoxicity of the SMX, RR-194 and their corresponding degradation products. Therefore the phytotoxicity of the degradation products and parent pollutants was investigated upon three plant seeds *P. vulgaris, V. radiata* and *P. lunatus* to determine the environmental impact of the treated water.

2. Materials and methods

2.1. Materials

Titanium (IV) isopropoxide, terepthalic-acid (TA), nitroblue-tetrazolium-chloride (NBT) and sulphamethoxazole (SMX) from Sigma, reactive red-194 from a local textile industry, hydrazine hydrate, zirconyl nitrate [$ZrO(NO_3)_2$], isopropanol, potassium iodide (KI), EDTA, potassium dichromate ($K_2Cr_2O_7$), ascorbic acid, ethanol and tween-20 are purchased from Alibaba Chemicals.

2.2. Synthesis and characterization of metal modified TiO_2 nanoparticles

Metal modified TiO_2 nanoparticles (Ag/TiO_2 and $Zr/Ag\text{-}TiO_2$) were prepared according to the methodology reported in our previous work [31]. BRUKER D8-Advance X-ray diffractometer was used to obtain XRD data with Cu Kα source ($\lambda = 1.5406$ Å). Imaging of the nanoparticles was carried out using a high resolution transmission electron microscope (JEOL JEM 2100). UV–Vis spectra (DRS mode) were recorded on a JASCO V–670 UV–Vis spectrophotometer. The photoluminescence (PL) spectra were obtained on a HITACHI F-7000 fluorescence spectrophotometer. XPS data was acquired on a Kratos Axis Ultra 165 Spectrometer equipped with a monochromated Al Kα X-ray source ($h\alpha = 1486.6$ eV). A micrometrics ASAP 2020 V4.03 analyzer was used to obtain BET surface area and pores size distributions of the synthesized nanoparticles. The zeta potentials of TiO_2, Ag/TiO_2 and $Zr/Ag\text{-}TiO_2$ nanoparticles were measured at 25 °C by dynamic laser light scattering using Malvern Zetasizer Nano ZS90.

2.3. Degradation experiments and determination of by products

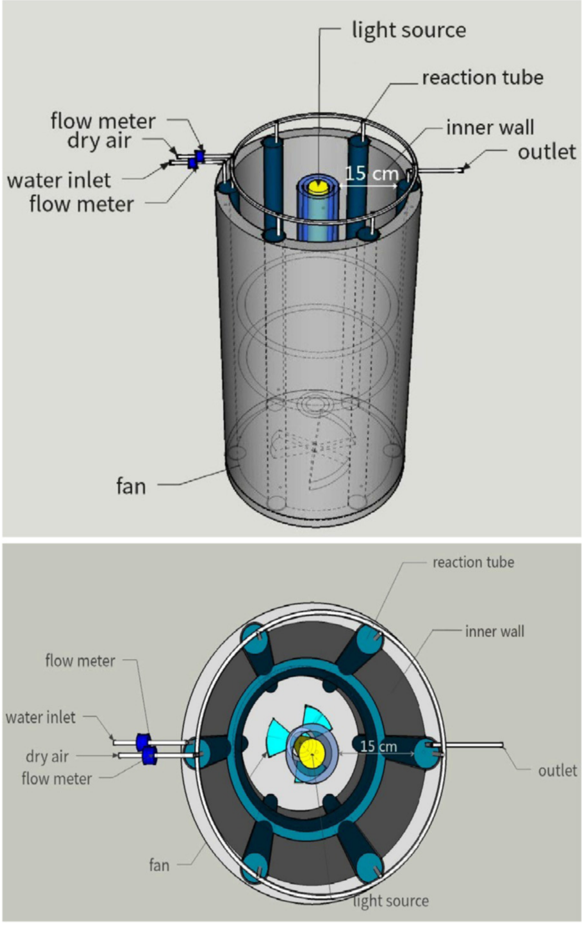


Fig. 1. (a) Multitube reactor set-up for the degradation experiments; (b) top view of the reactor.

A laboratory scale photoreactor (Fig. 1), was designed and utilized for all photocatalytic degradation experiments, which consists of a visible light source (Osram 150 W tungsten halogen lamp with 100 mW/cm^2 intensity, λ: 400–800 nm) positioned at the center of the reactor. Six reaction tubes, 50 mL each, 10 mm internal diameter, were placed at a distance of 15 cm from the light source. Dry air was purged continuously into all the reaction tubes through small pipes at a flow-rate of 2 L min^{-1}, to keep the aqueous solution saturated with oxygen and the catalyst particles in suspension. The inner surface of the photoreactor hood was fitted with a highly polished reflector in order to ensure the maximum reflection and utilization of the light source. The bottom of the reactor was equipped with an electric fan to cool the cabinet during the experiments maintaining a constant temperature (25 ± 2 °C).

The remnant concentration of SMX was determined by a HPLC (Agilent 1260 series) equipped with an Eclipse XDBC18 (4.6 × 150 mm, 5 µm) reverse phase column. Initially 100 mL of SMX solution (20 ppm) and 50 mg of the catalyst were stirred in the dark for 60 min to obtain absorption–desorption equilibrium, [32,33]. The UV detector wavelength was 203 nm, while the mobile phase consisted of water and acetonitrile (70:30 v/v) fed at a flow rate of 1 mL min^{-1} for 60 min [34]. Similar procedure was followed to achieve absorption–desorption equilibrium during degradation of RR-194 (25 ppm), as discussed above. Small sample aliquots (2 mL) were collected at regular time intervals and the solids were separated through centrifugation at 2000 rpm for 5 min. The supernatants were analyzed by a JASCO V–670 UV–Vis spectrophotometer, recording the absorption at 522 nm.

Further, the analysis of SMX and RR-194 degradation products was carried by liquid chromatography tandem mass spectrometer (Agilent 1290 LC system, Agilent 6460 Triple Quadrupole LCMS/MS system with the Zorbax eclipse plus C18 column). Water and acetonitrile (70:30 v/v) as mobile phase at a flow rate of 0.2 mL min^{-1} was used for