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Photocatalytic decomposition of selected biologically active compounds in environmental waters using TiO_2/polyaniline nanocomposites: Kinetics, toxicity and intermediates assessment[☆]

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A B S T R A C T

A comprehensive study of the removal of selected biologically active compounds (pharmaceuticals and pesticides) from different water types was conducted using bare TiO_2 nanoparticles and TiO_2/polyaniline (TP-50, TP-100, and TP-150) nanocomposite powders. In order to investigate how molecular structure of the substrate influences the rate of its removal, we compared degradation efficiency of the initial substrates and degree of mineralization for the active components of pharmaceuticals (propranolol, and amitriptyline) and pesticides (sulcotrione, and clomazone) in double distilled (DDW) and environmental waters. The results indicate that the efficiency of photocatalytic degradation of propranolol and amitriptyline was higher in environmental waters: rivers (Danube, Tisa, and Begej) and lakes (Moharač, and Sot) in comparison with DDW. On the contrary, degradation efficacy of sulcotrione and clomazone was lower in environmental waters. Further, of the all catalysts applied, bare TiO_2 and TP-100 were found to be most effective in the mineralization of propranolol and amitriptyline, respectively, while TP-150 appeared to be the most efficient in terms of sulcotrione and clomazone mineralization. Also, there was no significant toxicity observed after the irradiation of pharmaceuticals or pesticides solutions using appropriate catalysts on rat hepatoma (H-4-II-E), mouse neuroblastoma (Neuro-2a), human colon adenocarcinoma (HT-29), and human fetal lung (MRC-5) cell lines. Subsequently, detection and identification of the formed intermediates in the case of sulcotrione photocatalytic degradation using bare TiO_2 and TP-150 showed slightly different pathways of degradation. Furthermore, tentative pathways of sulcotrione photocatalytic degradation were proposed and discussed.

1. Introduction

Pharmaceuticals and pesticides are being subject to high concern among the scientific community due to their persistence in the environment (Edwards and Kjellerup, 2013). Certain pharmaceuticals, as well as pesticides may be detected up to concentrations of $\mu g\ L^{-1}$ in the freshwater environment (Murray et al., 2010). Active pharmaceutical ingredients belong to a diverse group of bioactive chemicals that are metabolized in human bodies. Propranolol is the first generation of nonselective β-blockers of adrenergic receptors in heart. Although <1% of the applied

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propranolol is excreted unchanged, its concentration in sewage water treatment plant was found up to 0.59 $\mu g\,L^{-1}$ (Ternes, 1998). Amitriptyline belongs to a class of dibenzocycloheptadiene derivatives. It is a tricyclic antidepressant pharmaceutical which is prescribed in the treatment of mental illness such as depression including clinical/endogenous depression (Abbar et al., 2011). The mechanism of action of the amitriptyline is reflected in the blockage of serotonin reuptake in the central nervous system (Bendtsen et al., 1996). People can be exposed to pharmaceuticals that pollute the water environment through drinking water or consumption of aquatic organisms (Bottoni et al., 2010). Namely, amitriptyline was found in drinking water in France in low concentration (Togola and Budzinski, 2008), as well as in surface waters in the UK (Kasprzyk-Hordern et al., 2008). Also, after the treatment of wastewater in Canada amitriptyline was detected in the solid residue (Sabourin et al., 2012). Besides, contamination of soil and water resources was a consequence of the significant use of pesticides in agricultural practices (Ahmed et al., 2011). Sulcotrione belongs to the relatively new class of triketone herbicides and is used to weed control of grasses and broadleaf in corn crop yields (Chaabane et al., 2007). Because of its solubility in water after sulcotrione application the pollution of surface and groundwater was observed. Also, in the presence/absence of sunlight sulcotrione shows high stability in water (Tomlin, 2009). Due to clomazone high water solubility (1.100 $mg\,L^{-1}$) and long half-life dissipation, averaging from 28 to 84 days, it can cause groundwater contamination (Mervosh et al., 1995). Great attention is paid to the methods for pharmaceuticals and pesticides removal since their concentration in the environment increase every year (Gadipelly et al., 2014; Reddy and Kim, 2015).

Removal of organic pollutants from environmental waters among other Advanced Oxidation Processes was based on TiO_2 photocatalytic process because of its relatively low-cost, environmentally friendly, sustainable treatment technology, and overcoming of the conventional technologies shortcomings. In the past decades, organic chelating ligands have been a key research topic in the sense of the modification of TiO_2 nanoparticles. Also, this type of modification results in the occurrence of other desirable properties besides inducing of dramatic changes in the electrical and optical properties of the nanoparticles (Dong et al., 2015). Moreover, for TiO_2 sensitization many conductive polymers were used (Li et al., 2008). Recently, several studies were based on the combination of TiO_2 nanoparticles with polyaniline (PANI) with the aim of improving their performance in relation to UV light or sunlight activity (Xiong et al., 2004; Li et al., 2006; Zhang et al., 2006; Wang et al., 2010; Radoičić et al., 2013).

The aim of this work was to investigate the photodegradation kinetics of pharmaceuticals (propranolol, and amitriptyline) and pesticides (sulcotrione, and clomazone) using UV irradiation in the presence of bare TiO_2 nanoparticles, as well as TiO_2/PANI (TP) nanocomposites, synthesized with different molar TiO_2: PANI ratios (TP-50, TP-100, and TP-150). The kinetics of the photodegradation was monitored by ultrafast liquid chromatography with diode array detector (UFLC–DAD). The process of mineralization was accompanied by determination of total organic carbon (TOC). For the most effective catalyst cytotoxicity of starting compound and its intermediate species formed during decomposition by determining the cell growth effects in rat hepatoma (H-4-II-E), mouse neuroblastoma (Neuro-2a), human colon adenocarcinoma (HT-29), and human fetal lung (MRC-5) cell lines was evaluated. In addition, the influence of matrix effect on the efficiency of the mentioned organics removal from various environmental waters was studied. Finally, due to the highest percentage of photocatalytic degradation and mineralization of sulcotrione using bare TiO_2 and TP-150, formed intermediates were identified and tentative photodegradation pathways have been proposed.

2. Experimental

2.1. Chemicals, solutions, water samples and catalysts

All chemicals, the environmental water samples collection and the physicochemical characteristics of water samples were given in Supplementary Material.

TiO_2 catalysts, bare and modified with polyaniline in different TiO_2: PANI molar ratios (TP-50, TP-100, and TP-150), were prepared as previously described (Radoičić et al., 2013). Details are given in the Supplementary Material. The formation of nanocomposite was proved using Raman spectroscopy and TEM measurements (Radoičić et al., 2013).

2.2. Photodegradation procedure

The photocatalytic degradation was carried out in a cell under UV irradiation described previously (Šojić et al., 2014). The UV radiation intensity for mercury lamp was 5.30 $mW\,cm^{-2}$. The radiation energy fluxes were measured using a Delta Ohm HD 2102.2 (Padova, Italy) radiometer which was fitted with the LP 471 UV (spectral range 315–400 nm) sensor. Also, the lamp output was calculated to be ca. 8.8×10^{-9} Einstein $mL^{-1}\,min^{-1}$ using potassium ferrioxalate actinometry (Šojić et al., 2009).

Experiments were performed using 20 mL of 50 $\mu mol\,L^{-1}$ pharmaceutical (propranolol, and amitriptyline), or pesticide (sulcotrione, and clomazone) suspension containing 0.5 $mg\,mL^{-1}$ of catalyst (bare TiO_2 or TP). The aqueous suspension of catalyst was sonicated (50 Hz) in the dark for 15 min before irradiation, in order to uniformly disperse the photocatalyst particles and to attain adsorption equilibrium. Before irradiation, the suspension thus obtained was set at 25 ± 0.2 °C in a stream of O_2 (3.0 $mL\,min^{-1}$). During irradiation, the mixture was stirred at a constant rate under continuous gas flow. All experiments were performed at the natural pH.

2.3. Analytical procedures

Experimental conditions for the LC–DAD, inductively coupled atomic emission spectrometry (ICP–OES), ion chromatography (IC), LC–ESI–MS/MS (detailed information about retention times, precursor and product ions, as well as positive and negative mode MS^2 spectra of sulcotrione and intermediates were given in Table S12, Figs. S9–S13), electrical conductivity, total organic carbon (TOC), and pH measurements can be found in the Supplementary Material.

2.4. Toxicity tests

Examination of the cytotoxic effect on the growth of cell lines was described in the Supplementary Material. The cell growth was evaluated by the colorimetric SRB assay of Skehan et al. (1990) modified by Četojević-Simin et al. (2012).

3. Results and discussion

3.1. Efficiency of photolytic and photocatalytic degradation of selected pharmaceuticals and pesticides

There are several indications that photochemical degradation is one of the most important processes with regard to the determination of the environmental fate of organics in the environment. Many of these compounds have aromatic rings, heteroatoms, and