Journal of Hazardous Materials 304 (2016) 329–336

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

UV and solar photo-degradation of naproxen: TiO_2 catalyst effect, reaction kinetics, products identification and toxicity assessment

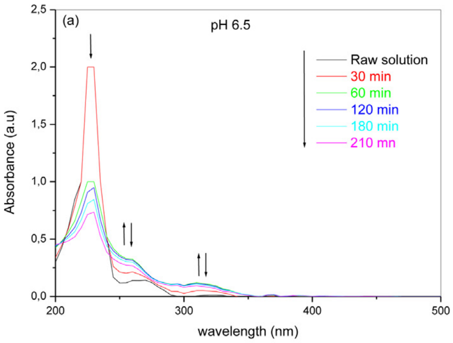
Nabil Jallouli[a], Kais Elghniji[b], Olfa Hentati[a,c], Ana R. Ribeiro[d], Adrián M.T. Silva[d], Mohamed Ksibi[a,c,*]

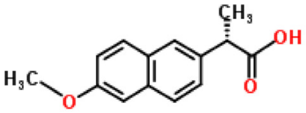
[a] *University of Sfax, Laboratory of Water, Energy and Environment, National School of Engineers of Sfax (ENIS), Route de Soukra Km 3.5, PO Box 1173, 3038 Sfax, Tunisia*
[b] *University of Gafsa, Research Unit of Materials, Environment and Energy, Campus Universitaire Sidi Ahmed Zarroug, 2112 Gafsa, Tunisia*
[c] *Higher Institute of Biotechnology of Sfax (ISBS), Route de Soukra Km 3, 5 PO Box 1175, 3038 Sfax, Tunisia*
[d] *LCM – Laboratory of Catalysis and Materials – Associate Laboratory LSRE-LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

HIGHLIGHTS

- Degradation kinetics and mineralization rate of naproxen (NPX) were studied.
- Direct photolysis and TiO_2/UV approaches were evaluated.
- The formation of by-products was followed by UHPLC-DAD-MS.
- Ecological risk assessment of NPX-treated solutions was assessed using *E. andrei*.

GRAPHICAL ABSTRACT





Variation of the UV-vis spectra of a naproxen-treated solution over the time by photocatalysis under the TiO_2/UV system.

ARTICLE INFO

Article history:
Received 18 July 2015
Received in revised form
18 September 2015
Accepted 22 October 2015
Available online 28 October 2015

Keywords:
Naproxen
Photolysis
Photocatalysis
Chemical oxygen demand (COD)
Acute toxicity

ABSTRACT

Direct photolysis and TiO_2-photocatalytic degradation of naproxen (NPX) in aqueous solution were studied using a UV lamp and solar irradiation. The degradation of NPX was found to be in accordance with pseudo-first order kinetics, the photocatalytic process being more efficient than photolysis. The NPX removal by photolysis ($pH_{initial}$ 6.5) was 83% after 3 h, with 11% of chemical oxygen demand (COD) reduction, whereas the TiO_2-UV process led to higher removals of both NPX (98%) and COD (25%). The apparent pseudo-first-order rate constant (k_{app}) for NPX degradation by photolysis ranged from 0.0050 min^{-1} at pH 3.5 to 0.0095 min^{-1} at pH 6.5, while it was estimated to be 0.0063 min^{-1} under acidic conditions in photocatalysis, increasing by 4-fold at pH 6.5. Ultra High Performance Liquid chromatography (UHPLC) coupled with a triple quadrupole detector and also a hybrid mass spectrometer which combines the linear ion trap triple quadrupole (LTQ) and OrbiTrap mass analyser, were used to identify NPX degradation products. The main intermediates detected were 1-(6-methoxynaphtalene-2-yl) ethylhydroperoxide, 2-ethyl-6-methoxynaphthalene, 1-(6-methoxynaphtalen-2-yl) ethanol, 1-(6-methoxynaphtalen-2-yl) ethanone and malic acid.

---

[*] Corresponding author at: University of Sfax, Laboratory of Water, Energy and Environment, National School of Engineers of Sfax (ENIS), Route de Soukra Km 3.5, PO Box 1173, 3038 Sfax, Tunisia. Fax: +216 74 674 364.
E-mail address: mohamed.ksibi@isbs.rnu.tn (M. Ksibi).

http://dx.doi.org/10.1016/j.jhazmat.2015.10.045
0304-3894/

Solar photocatalysis of NPX showed COD removals of 33% and 65% after 3 and 4 h of treatment, respectively, and some reduction of acute toxicity, evaluated by the exposure of *Eisenia andrei* to OECD soils spiked with NPX-treated solutions.

1. Introduction

Nowadays, huge amounts of pharmaceuticals are consumed. These substances and/or their metabolites are found in the environment due to the improper disposal of unused medicines, their excretion by humans or animals, as well as their low or non-biodegradability at wastewater treatments plants, representing a risk for human health and for other species, even when present at very low concentrations [1–3]. Owing to their characteristics, the toxicity of the pharmaceutical compounds has awakened the interest of several research groups.

In a study carried out in Sweden, between 1995 and 1998, Ericson and Källen [4] observed the occurrence of congenital malformations and cardiovascular diseases in children whose mothers had used Non-Steroidal Anti-Inflammatory Drugs (NSAIDs), including naproxen (NPX), during the first term of their pregnancies. Moreover, many studies [5–11] have referred to the toxicity of other pharmaceuticals to living organisms, showing the effects on the endocrine system of fish even at levels of some ng L^{-1}. For example, clofibric acid, used as a regulator of lipids in the blood, reveals an “estimated persistence in the environment of 21 years and is still detected in lakes and rivers after it was withdrawn from the market” [11].

In recent years, NPX and its intermediates have been detected in surface water, groundwater, wastewater, seawater and even in drinking water, at concentrations ranging from few ng L^{-1} to several $\mu g\,L^{-1}$ [12]. For instance, NPX was recently quantified up to 178 ng L^{-1} in seawater samples from Portugal [13]. Unfortunately, several pharmaceuticals can cause adverse effects on biota, such as impairing the lipid peroxidation system of bivalves [14]. Occurrence of NSAIDs, including NPX, was investigated in wastewaters from two urban areas of India, and the risk quotient of NSAIDs calculated by six different bioassays (bacteria, duckweed, algae, daphnia, rotifers and fish) showed a high risk to all the tested species [15]. Also the environmental hazard quotient of NPX detected in hospital effluents was considered high to algae, which had high sensitivity to this pharmaceutical [16]. NPX contamination is, therefore, becoming a serious problem.

In this context, it is useful to apply efficient technologies to treat urban and industrial wastewaters containing pharmaceutical substances, in order to avoid as far as possible the existence of pharmaceuticals in the aquatic environment. Among them, advanced oxidation processes (AOPs) have recently been a subject of major interest. In the case of NSAIDs, several conventional, advanced and combined oxidative treatments have been studied. For the particular case of NPX, chlorination, biofilm reactors, photolysis and heterogeneous photocatalysis alone or combined with nanofiltration have been applied [17–20]. Some results of the above-mentioned treatments have shown higher toxicity for the treated water than for the untreated effluent, due to the toxic by-products that are generated in these processes. For example, NPX photodegradation results in the formation of smaller and more hydrophobic by-products, such as 1-(6-methoxynaphtalen-2-yl) ethanol and 2-ethyl-6-methoxynaphthalene, which were reported to have high toxicity to a variety of organisms [21]. It was also reported that the photoderivatives of NPX degradation were more toxic than the parent compound, for three organisms tested, the rotifer *Brachionus calyciflorus* and two crustaceans, *Thamnocephalus platyurus* and *Ceriodaphnia dubia* [22].

The present work aims to compare the NPX degradation kinetics and chemical oxygen demand (COD) removals obtained by direct photolysis and TiO_2-photocatalysis (UV and solar). The main reaction by-products were identified by ultra-high performance liquid chromatography with diode array and mass spectrometry detection (UHPLC-DAD-MS), using a triple quadupole mass analyzer, and further confirmed by electrospray ionization (ESI) coupled to a hybrid ion trap-orbitrap mass analyzer. Additionally, considering the potential effect of this compound after its accumulation in sewage sludge, soils and sediments, an acute toxicity test using *Eisenia andrei* was successfully applied in the ecological-risk assessment of NPX photo-treated solutions. Earthworm’s avoidance tests were conducted in the laboratory and field, using OECD soils spiked with raw and photo-treated NPX solutions.

2. Material and methods

2.1. Chemicals and standards

(2S)-2-(6-Methoxynaphthalen-2-yl) propanoic acid (NPX) was supplied from Dr Reddy’s Laboratories VERA Ltd., India (93% purity). Acetonitrile (HPLC grade) and acetic acid (99% purity) were purchased from Sigma–Aldrich (Steinheim, Germany). Ethanol (HPLC grade) was purchased from Fisher Scientific UK Limited (Leicestershire, UK) and the ultrapure water was supplied by a Milli-Q water system.

2.2. Photolysis and photocatalytic reaction experiments

The laboratory-scale artificial light experiments were conducted in a photoreactor (120 mL) coupled with a stirred reservoir tank, operating in a closed recirculating mode by means of a centrifugal pump, equipped with a 11 W low—pressure mercury lamp (Philips, The Netherlands): irradiance of 26 $\mu W\,cm^{-2}$ at 1 m distance and wavelength range of 200–280 nm ($\lambda_{max} = 254$ nm), as described elsewhere [23]. In a typical run, the system was filled with 1 L of a NPX solution (2.6×10^{-4} M) and the reference Evonik Degussa P25 titanium dioxide (TiO_2-P25) photocatalyst was loaded at 0.4 g L^{-1}in the photocatalytic experiments. The pH of the solution was adjusted by addition of HCl (0.1 M) or NaOH (0.1 M). Before turning on the lamp, the suspension was magnetically stirred in the dark (30 min) in order to establish the NPX adsorption/desorption equilibrium, although no evident decrease of the NPX concentration was observed after four hours in darkness. All experiments were conducted at 298 ± 1 K. At given time intervals, 2 mL aliquots were sampled, diluted and immediately filtered with a cellulose acetate membrane filter (0.45 μm pore size, 25 mm diameter) to remove the catalyst. For the degradation experiments of NPX, using sunlight instead of UV light, a photocatalytic reactor described elsewhere [23] was adapted. The polymethylmethacrylate (PMMA) reactor (35 × 24 × 8 cm, L × W × H) was fabricated with an angle of 26.8 degrees. A constant flow rate (0.18 L min^{-1}) of NPX solution (1.91×10^{-3} M) was pumped through the reactor using a peristaltic pump (Masterflex L/S) and irradiated by sunlight. The experiments were performed from 11 a.m. to 2:30 p.m. (between April and May),