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Solar-induced heterogeneous photocatalytic degradation of methyl-paraben

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ABSTRACT

A solar-induced heterogeneous photocatalytic study on the treatment of methyl-paraben in water has been performed. A solar simulator equipped with a 150 W xenon ozone-free lamp was employed for the experimental runs. Various commercial TiO_2 catalysts have been assessed and the effect of catalyst loading has been extensively studied. Titanium dioxide Aeroxide P-25 was determined as the optimum catalytic material, even at low catalyst loadings. MeP abatement increased with increasing P-25 loading up to $0.5\ g\ L^{-1}$, above which further increase brings no actual improvement on the initial rate of the reaction. The addition of an electron acceptor (i.e. hydrogen peroxide) inhibited the degradation rate of MeP, whereas superoxide radicals were found to be the dominant reactive species in the heterogeneous solar-induced photocatalytic degradation of MeP. Experimental design methodology was applied to assess the significance of variables such as initial pH_0, MeP concentration and catalyst dosage and to evaluate their effect on the pseudo-first order reaction rate constant (k_{app}) of the photocatalytic reaction. Complete elimination of $1\ mg\ L^{-1}$ MeP was achieved after 35 min at inherent pH 5.2 and $0.5\ g\ L^{-1}$ Aeroxide P-25, whereas for the respective run with $10\ mg\ L^{-1}$ MeP 240 min reaction time was required. Under the latter conditions, 42% of mineralization was obtained and six intermediates were identified by GC–MS, namely propyl acetate, 2-(2-butoxyethoxy) ethanol, 2,5-dihydroxy-methyl benzoate, hydroquinone, diethyl phthalate and 1,2-benzenedicarboxylic acid bis-(2-methylpropyl) ester.

1. Introduction

Ever since the first use of parabens as preservatives in drugs around 1920 [1], they are now considered as the most abundant organic substance present in various formulations of Personal Care Products (PCPs) (i.e. facial and body cosmetics, skin and hair care products), where they act as broad-spectrum antimicrobials and anti-fungals to avoid spoilage and thus increase the shelf life [2–4].

Parabens are synthetic esters of *p*-hydroxybenzoic acid, with alkyl substituents ranging from methyl to butyl or benzyl groups [5]. Methyl paraben (MeP) is considered the most utilized antimicrobial amongst a homologous series of parabens (e.g. methyl, ethyl, propyl, butyl, heptyl and benzyl paraben), used either on its own or as a mixture with propyl paraben in order to enhance the antimicrobial performance (i.e. synergistic effect) [6].

More than a decade ago, a number of studies reported potential paraben estrogenicity and provided evidence of intact parabens being present in human breast cancer tissue, thus raising serious concerns in regard to human health and environmental safety [7–9]; to appease public concern numerous cosmetics industries decided to voluntarily exclude the use of parabens from their products, thus introducing to the market the so called 'paraben free' formulae. To this point, the use of parabens remains a controversial issue and actual connection between the use of paraben-containing underarm cosmetics and breast cancer has not been verified [10].

Notwithstanding the alleged exclusion of parabens from PCPs, recent reports from the Cosmetic Ingredient Review Expert Panel revealed that the number of cosmetics containing parabens was increased by 1.7 times in 2006 compared to 1981 [11]. However, there seems to be a slightly decreasing trend in the paraben content of PCPs; in early 1980s, most formulations contained parabens in concentrations up to 1% or more [1], whereas, a decade later, another study reported that the content of parabens in 215 tested products from the Danish market ranged from 0.01% to 0.87% [3].

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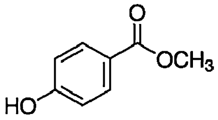

Fig. 1. Physicochemical properties of methyl-paraben.

The widespread use of parabens in PCPs, pharmaceuticals and food products ultimately leads to high levels of human exposure [12,13]; at the same time, studies regarding the activity of parabens as xeno-estrogens continue to emerge [14–18] causing escalating concerns. In European Union (EU) countries, the allowable content of parabens in cosmetic products is 0.4% for single ester and 0.8% for mixtures of all parabens [19]. The same threshold limits have been adopted by the United States (Food and Drug Administration, FDA) and Canada (Health Canada). So far, no legislation exists in country level [20], with the exception of Denmark which in 2011 decided to introduce additional restrictions, banning the use of some parabens (propyl, isopropyl, butyl- and isobutyl-parabens) in personal care products intended for children younger than 3 years [21].

The presence of parabens in wastewater treatment plants (WWTPs) has been confirmed through measurements of intact esters of parabens in raw sewage at levels as high as 2.92 mg L^{-1} and 2.43 mg L^{-1} for methyl and propyl paraben, respectively (i.e. the parabens detected at the highest levels) [22,23]; even though a major source of parabens entering the WWTPs is the washing-off of PCPs prior to skin absorption, however, the presence of intact paraben esters in human urine verifies that these compounds may escape metabolism by either skin esterase if exposure is dermal, or by intestinal and liver metabolic systems if exposure is oral [24].

Despite the considerable removal during conventional sewage treatments that may reach up to 99.9%, parabens have been still detected in ground and/or surface water [25–28].

Up to now, there are some studies that have investigated the elimination of parabens from aqueous matrices with varying process efficacies; photolysis reactions induced by both solar and UVC irradiation resulted in low removal efficiencies [29–31]. Higher removal efficiencies were achieved by coupling UV irradiation with H_2O_2 [32,33] or by applying advanced oxidation processes such as ozonation [34], UV-induced photocatalysis [35,36] and electrochemical oxidation on BDD anode [37].

The present study aims to investigate the TiO_2-mediated photocatalytic degradation of methyl-paraben (MeP) under the influence of simulated solar light. To the best of our knowledge, this is the first study reporting solar-induced photocatalytic degradation of MeP employng titania catalysts. The influence of various commercial TiO_2-type catalysts, the catalyst loading, the effect of the water matrix and addition of oxidant (e.g. hydrogen peroxide) on the efficiency of the process was evaluated. Experimental design methodology was applied to assess significant variables and investigate their effect on MeP degradation. The presence of radical scavengers was employed to provide insight on the photo degradation mechanism through different active species. Transformation products of MeP were identified and a degradation pathway was proposed.

2. Materials and methods

2.1. Materials

Methyl-paraben (>99%) was supplied by Fluka and was used as received, protected from any source of light and air and stored at room temperature. The chemical structure and main properties of MeP are shown in Fig. 1.

The photocatalysts used were commercial TiO_2 powders, i.e. the benchmark catalyst Aeroxide P-25 (Evonik Industries, Germany), Kronos Vlp 7000 and Kronos Vlp 7001 (both from Kronos Titan GmbH, Germany) (Table 1). NaOH and H_2SO_4 were used to adjust the pH when necessary. Hydrogen peroxide (H_2O_2, 30% w/v) was supplied by Merck and used without further purification. Double distilled water (Millipore Waters Milli-Q) was used for the preparation of all aqueous solutions employed in the present study. HPLC grade acetonitrile was purchased from Merck (Peypin, France), ammonium acetate was supplied by Panreac and MeOH from ChemLab. The wastewater was collected from a municipal wastewater treatment plant (WWTP) downstream of the disinfection unit currently employing chlorination and was characterized as follows: pH 7.5, electrical conductivity 982 $\mu S\,cm^{-1}$, COD = 6 mg O_2 L^{-1}, TSS = 3 mg L^{-1}.

2.2. Experimental setup and procedure

Photocatalytic experiments were carried out in a bench-scale open Pyrex glass reactor (0.3 L capacity) located directly below the beam output of a solar simulator a solar simulator (Newport, model 96000) equipped with a 150 W xenon ozone-free lamp and an Air Mass 1.5 Global Filter (Newport, model 81094) which simulates solar irradiation reaching the surface of the earth at a zenith angle of 48.2°. The output irradiance was measured actinometrically using 2-nitrobenzaldehyde as chemical actinometer and was calculated at 7.5 W m^{-2} [38,39].

All experiments were conducted in a photochemical batch reactor made of borosilicate glass. In a typical experimental run 0.3 L of known concentration of MeP aqueous solution were loaded in the reaction vessel along with an appropriate amount of catalyst. The suspension was left in the dark under continuous magnetic stirring for 30 min to reach equilibrium state. Samples were withdrawn right after equilibrium state between catalyst and substrate had been reached and prior to irradiation. This was considered the time zero of the reaction. Samples were withdrawn at frequent time intervals and were centrifuged at 13,000 rpm for 6 min to remove the catalyst particles. For experimental runs necessitating the use of H_2O_2 as oxidant, a predetermined volume of 30% H_2O_2 was inserted in the reaction medium before turning on the lamp. In order to eliminate any residual hydrogen peroxide remaining in the sample aliquots a small amount of Na_2SO_3 solution was added and the oxidant elimination was verified with Merckquant® test strips.

2.3. Methodology

2.3.1. Analytical determinations

The decay of MeP concentration during the reaction was monitored through a high performance liquid chromatography and mass spectrometry (HPLC–MS) system in negative ionization mode. Analysis was carried out using a Waters Alliance 2695 HPLC system coupled to a benchtop triple quadrupole Quattro micro MS from Waters – Micromass (Manchester, UK) equipped with an electrospray probe and a Z-spray interface. Chromatographic separation was achieved on a Luna C-18 column (5 μm, 250 mm × 4.6 mm) and a security guard column (4 mm × 3 mm), both from Phenomenex. The mobile phase eluted isocratically for 7 min with acetonitrile (50%) – ammonium acetate 5 mM (50%) at 30 °C, while the injection volume was 50 μL. The flow rate was 1 mL min^{-1}; however, the flow was split and reduced to 0.4 mL min^{-1} before entering the mass spectrometer. MS detection was achieved in SIR (Selected Ion Recording) mode (*m*/*z* 151).

Mineralization was followed by measuring the dissolved organic carbon (DOC) by direct injection of filtered samples into a Shimadzu V_{CSH} Total Organic Carbon Analyzer and pH was determined with a Crison GLP 21 pH meter. Residual hydrogen peroxide was measured