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Solar photocatalysis for the abatement of emerging micro-contaminants in wastewater: Synthesis, characterization and testing of various TiO_2 samples

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ABSTRACT

The photocatalytic degradation of a mixture of three compounds spiked in secondary treated wastewater by means of simulated solar radiation over titania suspensions was investigated. Bisphenol-A (BPA) and 17α-ethynylestradiol (EE2) were chosen as representatives of emerging micro-contaminants, while phenol was chosen as a reference contaminant. Ten titania samples were synthesized and employed to evaluate the effect of doping with nitrogen, phosphorous, calcium, silver, sodium and potassium, as well as platinum dispersion on photocatalytic activity. The catalysts were characterized by X-ray diffraction, diffuse reflectance UV–vis spectroscopy, nitrogen physisorption and selective chemisorption of CO or hydrogen.

A 0.5% Pt/TiO_2 catalyst ($38\,m^2/g$ surface area, 72:28 anatase:rutile, 20 and 2 nm crystallite size for TiO_2 and Pt, respectively) was highly active for the degradation of the contaminants, whose reactivity increased in the order: phenol < BPA ≤ EE2; a commercially available Aeroxide P25 TiO_2 exhibited comparable activity.

The effect of various operating conditions, such as 0.5% Pt/TiO_2 concentration (125–1000 mg/L), initial contaminant concentration (100–300 μg/L each), photon flux (17.4×10^{-8}–58×10^{-8} einstein/(L s) provided by a 150 W Xenon lamp) and the water matrix (wastewater and ultrapure water), on degradation was then assessed. Reaction rates increased linearly with catalyst concentration and photon flux, confirming the photo-induced nature of the activation of the catalytic process; likewise, a linear dependence of rate on initial concentration occurred denoting first order kinetics. Degradation in wastewater was slower than in pure water by an order of magnitude, implying the scavenging behavior of effluent's constituents against hydroxyl radicals.

The implications for tertiary wastewater treatment (e.g. mineralization, disinfection and removal of estrogenicity) are also discussed.

1. Introduction

1.1. The broader context

Heterogeneous photocatalysis based on semiconducting materials and driven by ultraviolet and/or visible light has extensively been researched for the development of several environmental applications including water splitting for hydrogen production, self cleaning surfaces, as well as the decontamination and disinfection of water and air [1]. What could ideally make the process attractive and sustainable would be the use of renewable energy to activate an inexpensive, stable, readily available and of high quantum yield semiconductor.

As far as the photocatalyst is concerned, the aforementioned requirements are uniquely fulfilled by titania and the fundamentals of TiO_2 photocatalysis can be summarized as follows [2]: the electronic structure of TiO_2, consisting of an empty conduction band and a filled valence band, facilitates the formation of electron–hole pairs when the semiconductor absorbs photonic energy greater than its band gap energy of about 3.2 eV, i.e. at wavelengths below about 390 nm. Holes are strong oxidizing agents and electrons are good reducing agents, therefore both promote redox reactions. Most organic photodegradation reactions utilize the oxidizing power of holes either directly or indirectly, i.e. through the formation of hydroxyl radicals and other reactive oxygen species.

Unfortunately, the wide band gap energy of TiO_2 overlaps only in the UV region of the electromagnetic spectrum; in this view, the

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process can utilize only about 6% of the solar energy reaching the earth's surface [3]. This limitation can be overcome modifying titania through e.g. doping with metals and non-metals to narrow the band gap energy and, consequently, enhance photoactivity under visible light [2,3].

1.2. The specific problem

In recent years, there have been intensive efforts toward the development of efficient technologies for the removal of persistent micro-contaminants from aqueous matrices. Discharges of conventional wastewater treatment plants (WWTPs) typically contain a wide array of such compounds at the ng/L–μg/L levels that can only partially be removed by biological and/or adsorption processes [4]. Among others, endocrine disrupting compounds (EDCs) constitute an important class of such contaminants, which pose an increasing threat to aquatic organisms, as well as to human health. EDCs include naturally occurring estrogens, synthetic estrogens, phyto-estrogens and xeno-estrogens (i.e. pesticides, plasticizers, persistent organochlorines, organohalogens, alkyl phenols, heavy metals) [5].

In this work, a mixture of bisphenol-A (BPA), 17α-ethynylestradiol (EE2) and phenol was spiked in secondary wastewater and treated by means of solar photocatalysis in titania suspensions. BPA was chosen as a representative xeno-estrogen typically used in the manufacturing of numerous chemical products, while EE2 is a synthetic estrogen used in the oral contraceptive pill. Both are thought to be associated with endocrine disruption, as well as several other adverse effects [6,7]. Phenol was chosen as a reference compound since it is the precursor of numerous xenobiotics in the environment.

1.3. Research aims

The aim of this work was three-fold:

(i) To prepare and characterize various TiO_2 samples that could potentially function as effective photocatalysts. Nitrogen and phosphorous were chosen as examples of non-metallic dopant elements that may be used to expand the spectral response of TiO_2 into the visible region of the electromagnetic spectrum by shifting the valence band edge of the semiconductor upwards to narrow its band gap energy [8,9]. Potassium, sodium and calcium were employed as surface promoters that may result in the creation of oxygen vacancies on the TiO_2 surface [10,11] and, therefore, promote adsorption of O_2 and oxidation of organic compounds [12]. Deposition of Pt crystallites on the photocatalyst surface is known to decrease the rate of electron–hole recombination [13], which is one of the key factors that limit overall photocatalytic efficiency. A similar effect is expected for Ag deposits which, depending on size and shape of Ag nanoclusters, may increase substantially photo-oxidation rates [14].

(ii) To assess the relative activity of the synthesized catalysts for the degradation of the three contaminants under environmentally realistic conditions, i.e. low concentrations and complex water matrices.

(iii) To determine key operating parameters that affect degradation kinetics.

Although the degradation of EDCs by TiO_2 photocatalysis has received substantial attention before (recent literature includes references [15–18]), we propose a systematic approach that would help to develop an effective treatment for the abatement of micro-contaminants in waters.

2. Materials and methods

2.1. Contaminants and the water matrix

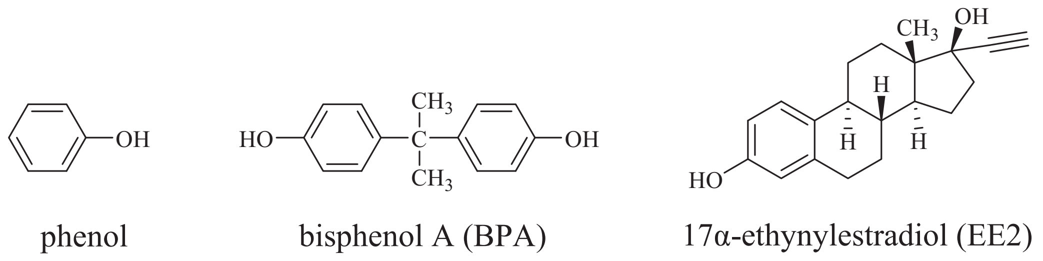
Phenol, BPA and EE2, whose formulae are shown in Scheme 1, were purchased from Sigma–Aldrich and used as received. Stock solutions containing equal concentrations of all three compounds were prepared and the appropriate volume was spiked to the water matrix to achieve the desired concentration in the range 100–300 μg/L for each individual contaminant.

Wastewater (WW) was collected from the outlet of the secondary treatment of the municipal WWTP of Chania, W. Crete, Greece. It was characterized according to standard methods [19] as follows: 24 mg/L chemical oxygen demand, 7.8 mg/L dissolved organic carbon (DOC), 820 μS/cm conductivity and pH 8. Moreover, it contained 220 mg/L chlorides, 188 mg/L bicarbonates, 60 mg/L sulfates, 26 mg/L nitrates and 57 mg/L nitrites, as well as 1200 CFU/mL *Escherichia coli*. Unless otherwise stated, the effluent was first sterilized to inactivate microorganisms and then spiked with the mixture of xenobiotics. This was done to avoid biological degradation of xenobiotics in the stock solutions, as well as for safety reasons.

Some experiments were also performed in ultrapure water (UPW), taken from a water purification system (EASYpureRF – Barnstead/Thermolyne, USA), with 5.5 μS/cm conductivity.

2.2. Synthesis of catalysts

In this work, ten titania catalysts (referred to as samples B–K in Table 1) were synthesized, characterized and tested for the photocatalytic degradation of xenobiotics. Nitrogen-doped TiO_2 was prepared adding slowly 100 mL of aqueous ammonia solution (30%) to 25 mL of $Ti(OPr\text{-}i)_4$ (titanium isopropoxide, TIP) at 0 °C under continuous stirring. A white precipitate was formed, which was then filtered in order to remove the solvent. The sample was dried at 110 °C for 24 h and then calcined at 400 °C for 2 h. After calcination a light-yellow powder was obtained.



Scheme 1. Chemical formulae of the contaminants tested in this work.