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Effect of TiO_2–Pd and TiO_2–Ag on the photocatalytic oxidation of diclofenac, isoproturon and phenol

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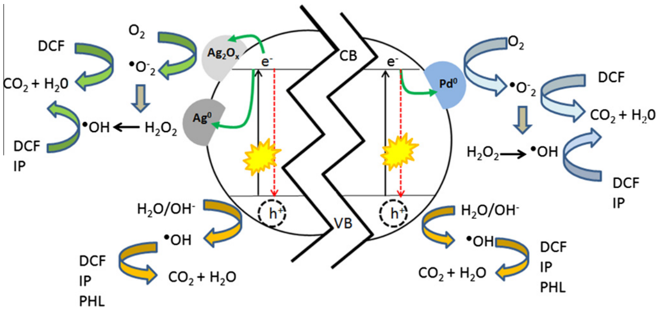
HIGHLIGHTS

- Effects of Ag and Pd on photocatalytic oxidation of pollutants were studied.
- The state of oxidation of metals affect photodegradation of the pollutants.
- The highest degradation rate for isoproturon was obtained with TiO_2–Pd.
- The highest degradation rate for diclofenac and phenol were obtained with TiO_2–Ag.
- The photodegradation of the by-products of all pollutants were identified.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of silver and palladium metals on the photocatalytic degradation of diclofenac sodium salt (DCF), isoproturon (IP) and phenol (PHL) in water over lab-made TiO_2 synthesized following a sol–gel method were investigated. Silver and palladium catalysts were prepared by photodeposition at 1 wt.% of loading metal. The resulting materials were characterized through BET, XRD, TEM, SEM, XPS and DRS-UV–Vis. The photodeposition test conditions of both metals determined their final oxidation state, with reduced particles of palladium and silver as well as silver oxides found on the catalysts. The results showed that the type of metal had different effects on the photodegradation mechanism depending on the nature of the pollutants. Accordingly, the highest degradation rate for IP and DCF was obtained when using the catalyst photodeposited with palladium and for PHL the catalyst photodeposited with silver. The photodegradation intermediates of PHL, DCF and IP were also identified.

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1. Introduction

Concern is growing about the potential effects on health of a group of anthropogenic contaminants known as "emerging contaminants" (ECs) [1] which include, among others, the herbicide isoproturon (IP) [2,3] and diclofenac sodium salt (DCF). IP, which is included on the EU list of priority substances in the field of water policy [4], is one of the most commonly used herbicides in the world, in particular on cereal crops. Its half-life is approximately 40 days in moderate climates and 15 days in tropical climates. DCF is a non-steroidal, anti-inflammatory drug commonly used as an analgesic, antiarthritic and antirheumatic agent. About 15% of the drug is excreted unmodified after human consumption [5].

There are various methods that can be used to eliminate organic pollutants including activated carbon or WWTPs (wastewater treatment plants). However, adsorption on activated carbon results

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in pollutant transfer and not in pollutant elimination and WWTPs are often unable to fully eliminate all pollutant types [6].

Advanced oxidation techniques can also be employed for organic pollutant removal. Among these techniques are AOPs (Advanced Oxidation Processes), which generate hydroxyl radicals that are able to mineralize the organic components to CO_2 and water. TiO_2 photocatalysis is one of the most promising AOPs in the removal of organic pollutants.

The principles of heterogeneous photocatalysis have been extensively discussed in the literature [7,8]. Heterogeneous photocatalytic degradation of organic compounds begins with generation of electron–hole pairs (e^-–h^+) in the semiconductor particles by total or partial absorption of photons of light. If charge separation is maintained the e^-–h^+ pair will migrate to the TiO_2 particle surface. Once on the surface, the e^-– h^+ pair can react with other species at the interface. The e^-–h^+ pairs which do not manage to separate and react with species on the surface recombine. This recombination can take place both on the surface of the particle and in its interior, with the latter situation being one of the problems of heterogeneous photocatalysis.

One way of improving efficiency by favoring separation of the e^-–h^+ pair comprises the deposition of metals on the titanium dioxide surface. This procedure is commonly used as a technique to enhance photocatalytic activity and impede e^-–h^+ recombination. As their Fermi level is lower than that of the TiO_2, the metal deposits on the catalyst surface act as traps for the photogenerated electrons, providing sites for their accumulation. This enhances separation of the photogenerated e^-–h^+ pairs, as well as the separation of sites where reduction occurs (metal deposits) and the oxidation that takes place on the photocatalyst surface [9,10]. In addition, the photoelectrons can enhance the rate of oxygen photoreduction and favor the generation of hydroxyl radicals [11], thereby contributing to more effective organic pollutant photoelimination.

The effects of silver and palladium on photocatalytic removal of organic substrates have previously been described in the literature [12–21]. The activity of metal-modified materials depends on the nature of the organic compound as well as on other factors which include pollutant concentration, pH, metal type and load [10,12].

Silver deposits on TiO_2 have been shown to enhance the mineralization of mono-, di- and poly-carboxylic acids [12] and the removal of 2-propanol [17], chloroform and urea [19]. Meanwhile, palladium deposits have been shown to enhance removal of 2,4-dinitrofenol, formaldehyde and trichloroethylene [13], as well as the colorant methylene blue [20,21].

The present work studies the effect of Ag and Pd deposits on a lab-made TiO_2 (SG) synthesized following a sol–gel method in the photocatalytic removal of PHL, IP and DCF. This lab-made catalyst was chosen as it has been shown in previous studies to have a high degree of efficiency in the elimination of different pollutants from water [22–24].

The metals were photodeposited following a method similar to that described by Maicu et al. [25]. DCF and IP were chosen as they are examples of emerging contaminants [26,27] and PHL was chosen as it is considered the reference molecule for use in photocatalysis studies [11,28–32]. The tests were performed with the photocatalysts in suspension. The photodegradation intermediates of the pollutants were also identified.

2. Experimental

2.1. Materials

Reagents: IP (99%) and methanesulfonic acid (99%) were supplied by Fluka; PHL (99%), DCF (99%), methanol (⩾99.9%), ethanol (⩾99.9%), titanium butoxide (97%), phosphoric acid (⩽85%), palladium (II) nitrate dihydrate (99%) and nitrate silver (99%) were supplied by Sigma–Aldrich; citric acid (99.5%), ammonium formate (⩾99%), sodium hydroxide (98%), and isopropanol (98.5%) were supplied by Panreac and acetonitrile (⩾99.8%) was used with an HPLC grade (Chromanorm).

2.2. Synthesis of the catalysts

The photocatalysts used in these experiments and their properties are listed in Table 1. The lab-made catalyst (SG) was synthesized following a sol–gel procedure described in [33]. Two solutions were used: solution A, comprising a mixture of ethanol–titanium butoxide in a molar ratio of 50:3.5, and solution B, comprising a mixture of water–ethanol-citric acid in a molar ratio of 50:60.8:0.36. Solution A was added drop by drop to solution B and the mixture stirred continuously for 3 h. After 48 h of aging the precipitate was dried at 373 K for 24 h and finally calcined following a controlled temperature program of 302 $K \cdot h^{-1}$ to 1023 K, with the final temperature held for 3 h.

SG-metal samples were prepared by photodeposition following a method previously described [25]. Palladium (II) nitrate dihydrate and nitrate silver were used in the photodeposition method. A solution of palladium (II) nitrate dihydrate (corresponding to 1 wt.% of the metal load) was added to a 0.3 M solution comprised of 5 $g \cdot L^{-1}$ of TiO_2 in a water–isopropanol mixture in 400 mL solution. This alcohol was used as sacrificial agent in the photodeposition process under anoxic conditions via a continuous flow of nitrogen gas to the mixture. A 400 W mercury lamp with photon flow of $2.6 \cdot 10^{-7}$ Einstein s^{-1} L^{-1} (emission < 400 nm) was used in the photodeposition. The product was then recovered by centrifugation and dried at 383 K overnight. A similar procedure was followed for catalyst photodeposition with silver, using silver nitrate as metal precursor.

2.3. Photocatalytic experiments

Catalyst load was fixed at 1 g L^{-1} of catalyst with a contaminant volume of 0.20 L at pH 5. All tests were performed in ultrapure water with 50 mg L^{-1} of PHL, DCF or IP. A statistical treatment was performed on the data presented in this work. Two sets of Solarium Philips HB175 lamps equipped with four 15 W Philips CLEO fluorescent tubes with emission spectrum from 300 to 400 nm (maximum around 365 nm) (9 mW) were employed as UV light source. The standard errors were calculated using 95% confidence limits.

Table 1
Characteristics of the photo-catalysts used in this work.

Sample	Anatase crystallite size (nm)	BET area (m^2 g^{-1})	Band Gap (eV)	Percentage of metal atoms (atomic%)		pH_{PZC}
				XRF	EDX	
SG	56.8 ± 1.6	14	2.98	–	–	6.20
SG-1%Ag	55.6 ± 3.0	13	2.84	0.46	0.46 ± 0.05	6.20
SG-1%Pd	55.3 ± 2.7	13	2.78	0.46	0.44 ± 0.6	4.60

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