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Environmental remediation by an integrated microwave/UV illumination technique
IX. Peculiar hydrolytic and co-catalytic effects of platinum on the TiO_2 photocatalyzed degradation of the 4-chlorophenol toxin in a microwave radiation field

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Abstract

The photocatalyzed degradation of the 4-chlorophenol toxin (4-CP) in aqueous naked TiO_2 and platinized TiO_2 suspensions simultaneously subjected to UV light and microwave radiation was revisited to examine the fate of this toxin in the microwave-assisted photocatalytic process by monitoring loss of total organic carbon (TOC; mineralization), formation of chloride ions (dechlorination of 4-CP), and identification of intermediates using HPLC and electrospray mass spectral (LC–MSD) techniques. Attempts are made to delineate microwave thermal and nonthermal factors that impinge on the degradation by comparing experimental results from microwave-generated heat versus results from a conventional (externally heated) thermally-assisted process, and from results in which the thermal factors were minimized by examining the degradative process at constant ambient temperature (25 °C). Possible microwave radiation effects on the Pt co-catalyst supported on TiO_2 were also probed through comparison of the degradation of 4-CP occurring on Pt/TiO_2 and on naked TiO_2 photocatalysts. Results suggest that, in a microwave radiation field, naked TiO_2 and Pt/TiO_2 particle surfaces interact with the microwaves. The degradation pathway exhibited characteristics of hydrolysis of reactants and intermediates. Nonthermal microwave effects play a role in the overall degradative process occurring in platinized TiO_2 dispersions. The possible nature of these unusual microwave effects is briefly discussed.

Keywords: Microwave-assisted photocatalysis; Soil contaminants; Microwave thermal effects; Microwave nonthermal effects; Environmental protection; Titanium dioxide; 4-Chlorophenol

1. Introduction

Chlorophenols constitute an important class of soil and water pollutants arising from their wide use as pesticides, herbicides, and as wood preservatives. In particular, 4-chlorophenol (4-CP), a representative of this class, is generated as a by-product of waste incineration. Accordingly, novel methodologies must be found or existing technologies must be improved to achieve efficient and total decomposition of such chlorinated phenols. Past investigations into the photocatalytic degradation of 4-CP and related derivatives in TiO_2 aqueous dispersions have emphasized (i) degradative pathways [1–11]; (ii) TiO_2-assisted electrochemistry [12,13]; (iii) degradative processes occurring on coupled TiO_2/CdS

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systems [14], on incorporated co-catalysts as embodied by platinized titania (Pt/TiO_2) [15], and on polyoxometalates [16], together with; (iv) exploring laboratory-scale and large-scale applications of TiO_2 photocatalysis [17]. Studies have also been reported on reactors that saw TiO_2 particles supported on optical fibers [18,19].

In earlier reports, some characteristic features of microwave-assisted degradation reactions occurring on TiO_2 and some details of photooxidations and photoreductions were described for such systems as dyes (e.g. rhodamine-B), polymers, and surfactants [20,21], herbicides such as 2,4-dichlorophenoxyacetic acid [22], and endocrine disruptors such as bisphenol-A [23]. These reactions occurred at the TiO_2/water interface subjected to integrated UV light and microwave radiation. Several features of the microwave equipment were also tested. For instance, microwave radiation was used to power a microwave plasma electrodeless UV lamp [24–26].

Microwave radiation has found a niche in several synthetic chemical applications [27,28] and in the detoxification of an increasing number of chlorinated products [29–32]. Reports indicate that the decomposition dynamics are mostly governed by conventional microwave-generated heating (thermal) effects.

A characteristic feature of reactions that take place on TiO_2 originating from absorption of microwave radiation by the components of the reaction system involves microwave-generated thermal effects (i.e. caloric effects) and non-thermal (i.e. non-caloric) microwave effects [21–23,33]. In this regard, electron paramagnetic resonance (EPR) spectroscopic evidence showed that a greater number of $^{\bullet}OH$ radicals are produced in the microwave-assisted photocatalytic process (PD/MW) in aqueous TiO_2 dispersions [34]. The dynamics of the decomposition of organic pollutants by conventional TiO_2 photocatalysis were significant enhanced under microwave irradiation. It is worth pointing out that microwave radiation is not simply a source of heat that accelerates the degradation reactions. Other factors that we refer to as nonthermal factors are also at play.

The present study focused on three fundamental issues that were examined using the decomposition of a model compound of chlorine-containing toxins and dioxins, namely 4-chlorophenol, in naked TiO_2 and platinized titania (Pt/TiO_2) dispersions subjected to simultaneous irradiation by UV light and microwaves; 4-CP contains a phenolic OH group, a chlorine substituent and an aromatic ring. First we examined the microwave effects that might impact on the TiO_2 photocatalytic degradation process to provide further details on the mechanism of microwave-assisted decomposition. Next we probed the influence of Pt co-catalyst deposits supported on TiO_2 on the formation of intermediates, on the nature of the intermediates, on the dechlorination process, and on the formation of $^{\bullet}OH$ and $^{\bullet}OOH$ radicals when microwave radiation is also involved in Pt/TiO_2 photocatalysis. Finally, attempts were made to unravel the role of microwaves by a further examination of the possible implication of thermal (caloric) and nonthermal (non-caloric) microwave factors in the photocatalytic degradation of 4-CP.

2. Experimental

2.1. Chemicals and materials

Titanium dioxide was Degussa P-25 grade. High-purity grade 4-chlorophenol was purchased from Tokyo Kasei Kogyo Co. Ltd.

Platinized titanium dioxide particulates (Pt/TiO_2) were prepared by the photocatalytic deposition method [35] as modified by Harada et al. [36] and reported recently also by Radoiu et al. [32]. Thus, TiO_2 particles (P-25; 2 g loading) and 2-propanol (0.5 mL) were added to a 100 mL aqueous solution containing $H_2PtCl_6{\cdot}6H_2O$ (0.5 vol%; 0.02 mM); the pH of the dispersion was adjusted to pH 4.0 by addition of sodium acetate. The suspension was pre-purged with pure nitrogen gas and then irradiated with a 75 W low-pressure mercury lamp for 3 h at ambient temperature. The platinized TiO_2 particulates were separated by filtration, added to a dilute HCl solution (1 M, 200 mL), stirred for 1 h, re-filtered and repeatedly washed with deionized water until no more Cl^- ions were detected in the supernatant liquid. The sample was subsequently dried for ca. 2 days in a vacuum oven at 120 °C.

2.2. Characterization of the photocatalyst specimen

The amount of Pt loaded onto TiO_2 particles (ca. 0.29 wt.%) was determined with a Hitachi 4700 FE-SEM electron microscope using energy dispersive spectroscopy (EDS) for an average set of seven EDS data points employing an appropriate calibration method. The BET specific surface areas of P-25 TiO_2 and Pt/TiO_2 specimens were, respectively, 51.8 and 47.6 $m^2\,g^{-1}$. The bandgap energies were ascertained to be 3.10 eV for P-25 TiO_2 and 3.11 eV for Pt/TiO_2. Note that the anatase content remained at 83% (by X-ray diffraction methods) in these two specimens.

2.3. Experimental devices and procedures

Continuous microwave irradiation of the dispersions was achieved using a Shikoku Keisoku ZMW-003 apparatus consisting of a 2.45 GHz microwave generator (maximal power, 1.5 kW) fabricated by Shibaura Mechatronics Co., Ltd. (see microwave cavity A in Fig. 1 of [33]). Some details of the microwave system were reported previously [20–26,33,34]. The microwave power radiated from the magnetron was ca. 220 W measured using a power monitor.

A 30 mL air-equilibrated aqueous 4-CP solution (0.1 mM, initial pH 6.0) containing the photocatalyst particles (loading, 60 mg) was introduced into the reactor through a waveguide. Optimal low reflection of the MW radiation was