Efficient Sonochemical Degradation of 4-Chlorophenol Catalyzed by Titanium Dioxide Hydrate

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A nanocrystalline anatase hydrate (Titanhydrat-0, TH) is a highly efficient catalyst for low intensity sonochemical degradation of 4-chlorophenol (4-CP). The initial disappearance rate of 4-CP increases by a factor of 95 under the TH dosage of 0.5 $g\,dm^{-3}$. After 120 min of ultrasonic irradiation 63% of 4-CP is completely mineralized under the TH dosage of 0.5 $g\,dm^{-3}$. However, in homogeneous sonochemical degradation, no mineralization at all occurs. Moreover, we deduce that the process of sonochemical mineralization mainly occurs at the interface region of TH. The process of sonocatalytic degradation is simple and inexpensive, and appears to be a potentially powerful method of remediation of contaminants in water.

The application of ultrasonic irradiation for the remediation of contaminants has been used successfully as an advanced oxidation process.[1] Sonochemical degradation of a wide variety of substances such as volatile organic compounds,[2] surfactants,[3] dyes,[4] polymers,[5] and metal-organics[6] in water have been investigated extensively. The chemical effects of ultrasound derive mainly from acoustic cavitation: the formation, growth and implosive collapse of bubbles in a liquid. Bubble collapse produces intense local heating, high pressures.[1] Under these extreme conditions, the substrate molecules can undergo degradation by direct pyrolytic reactions inside the cavitation bubbles or by indirect reactions in the bubble interface or bulk medium via intermediate reactive species such as H atoms, OH radicals, O atoms, HO_2 radicals, and H_2O_2.[1]

Many efforts have been devoted to improve the efficiency of sonochemical degradation and mineralization, especially in the case of hydrophilic compounds. It was found that the sonochemical bleaching and the mineralization process can be accelerated by adding reactive chemicals (such as O_3,[7] Fe^0,[8] Fe^{2+}, and/or H_2O_2[9]), several kinds of particles[10] and salt.[11] Pandit et al.[10b] reported that the rate of the degradation of 2,4,6-trichlorophenol (100 ppm) in the presence of anatase grade TiO_2 (0.5 $g\,L^{-1}$) increased by a factor of 4 by ultrasonic horn (22.7 kHz and applied power of 60 W or 0.6 $W\,mL^{-1}$). Sekiguchi et al.[10d] reported that the rate of the degradation of chlorobenzene increased two times under ultrasonic irradiation (20 kHz and output of 300 W) and in the presence of α-alumina particles of 1 mm diameter. In connection with our recent work on the use of a nanocrystalline anatase hydrate (Titanhydrat-0, TH) modified by metal compounds as photocatalyst for visible light detoxification,[11] we have now found that unmodified titania is a highly efficient catalyst for low intensity sonochemical degradation of some organic compounds. Herein, we report on the sonocatalytic disappearance and mineralization of 4-chlorophenol (4-CP), an ubiquitous water pollutant.

4-Chlorophenol (4-CP, Fluka) was purified by distillation at low pressure. The fraction boiling at 355 K (p = 5 Torr) was collected. Doubly distilled water was used during all manipulations. Titanhydrat-0 (TH, Kerr McGcc) is mainly anatase with specific surface area of 334 $m^2\,g^{-1}$. Crystal modifications were identified by XRD diffractograms recorded on a Philips X'Pert PW 3040/60. Specific surface areas were determined with a Gemini 2370

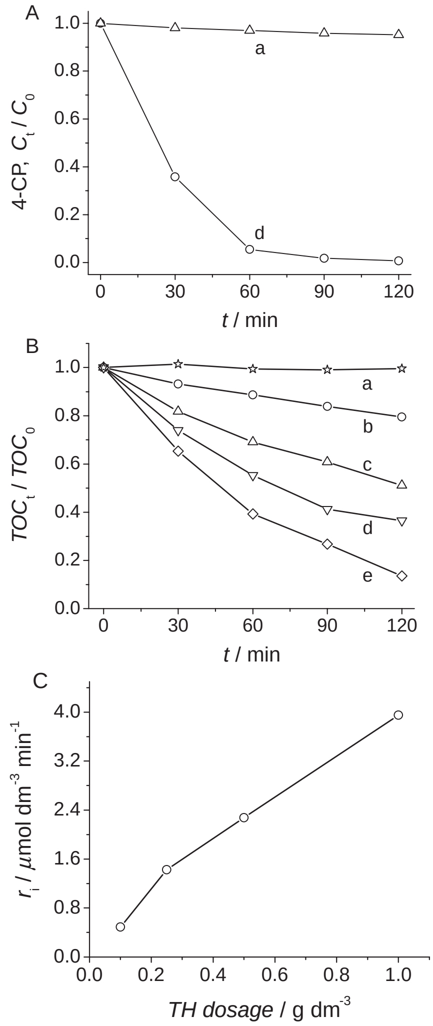

Figure 1. 4-CP sonochemical disappearance (A) and mineralization (B); $c_0 = 2.5 \times 10^{-4}\,mol\,dm^{-3}$; a) without catalyst, b) TH, 0.1 $g\,dm^{-3}$, c) TH, 0.25 $g\,dm^{-3}$, d) TH, 0.5 $g\,dm^{-3}$, e) TH, 1 $g\,dm^{-3}$; C) Dependence of the initial rate (r_i) of 4-CP sonochemical mineralization on the different dosage of TH.

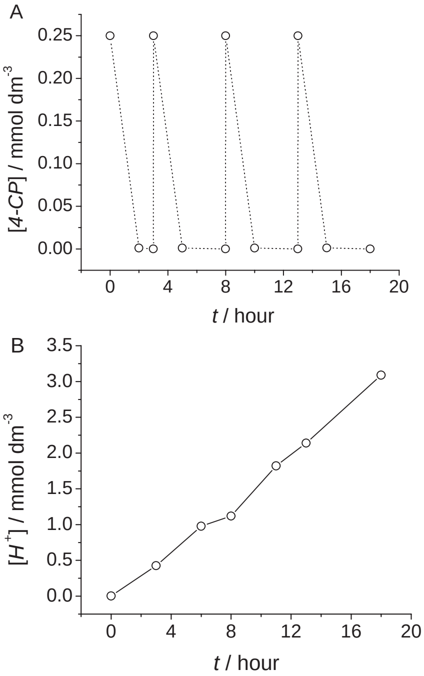

Figure 2. Four cycles of sonochemical disappearance of 4-CP (A) and production of H^+ (B) in the presence of TH (0.5 g dm^{-3}).

instrument according to Brunauer_Emmett_Teller theory. The sonochemical degradation of 4-CP was performed in aqueous solution under air bubbling slowly in a brown glass vessel of 50 cm^3 sonicated by an ultrasonic cleaner of 4 dm^3 volume (Bandelin Sonorex, Super RK 106, 120 W output, 35 kHz, and intensity: 0.29 W cm^{-2}) and temperature was maintained at 20–30 °C. Samples were withdrawn and filtered through a Millipore membrane filter (0.22 µm) and then subjected to HPLC and TOC analysis. An HPLC (Shimadzu SCL-10A VP controller, Shimadzu LC-10AT VP liquid chromatograph with SPD-10A VP UV/Vis detector) was used to determine concentrations of 4-CP. A reverse-phase column (Supelco Discovery C-18) and water–isopropanol eluent (50/50, v/v) were employed. Absorbencies at 225 nm were measured for the detection of 4-CP. TOC measurements were made on a Shimadzu Total Carbon Analyzer TOC-500/5050 with NDIR optical system detector.

Figure 1 displays the disappearance and mineralization of 4-CP under ultrasonic irradiation and air bubbling in the presence or absence of TH. Surprisingly, the effect of TH addition is extremely high and after 120 min of ultrasonic irradiation, 99.3% of 4-CP has disappeared and 63% of 4-CP is completely mineralized under the TH dosage of 0.5 g dm^{-3}. However, in homogeneous sonochemical degradation of 4-CP, only 5% of 4-CP has disappeared and no mineralization at all occurs. In this case, the initial disappearance rate of 4-CP is 95-fold enhanced under the TH dosage of 0.5 g dm^{-3}. To substantiate the role of additional TH, we varied its concentration. The results show that 21, 49, 63, and 86% of 4-CP are completely mineralized after 120 min of ultrasonic irradiation and the initial rate of 4-CP sonochemical mineralization are 0.49, 1.43, 2.28, and 3.95 µmol dm^{-3} min^{-1} in the present of TH catalyst dosage of 0.1, 0.25, 0.5, and 1.0 g dm^{-3}, respectively (Figure 1b and Figure 1c). These results clearly illustrate the process of sonochemical mineralization mainly occurs at the interface region of TH.

To examine the stability of TH catalyst, a relatively long-term ultrasonic irradiation was performed. In this experiment, the concentration of 4-CP was re-adjusted to its initial value after some defined time. The results show that, in four sonodegradation cycles, after 3.0 h of ultrasonic irradiation 4-CP has completely disappeared in every cycle (Figure 2). Moreover, the concentration of hydrogen ions, one of the products for 4-CP sonochemical mineralization, continuously increases as the increase of reaction time.

Sonochemical degradation and mineralization of 4-CP catalyzed by TiO_2 appears to be a potentially powerful method of remediation of contaminants in water, which may compete with or serve as an adjunct to other advanced oxidation processes.

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