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Enhanced sonocatalytic treatment of ibuprofen by mechanical mixing and reusable magnetic core titanium dioxide

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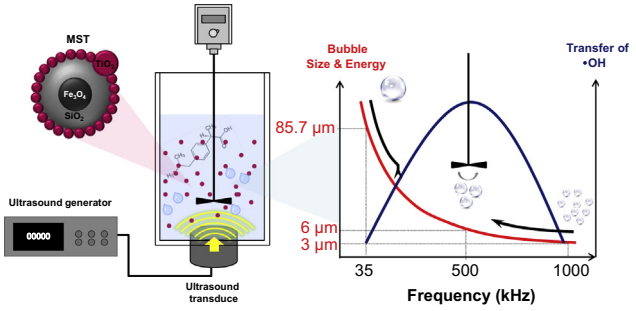
HIGHLIGHTS

- MST was synthesized and evaluated as a recyclable sonocatalyst for IBP removal.
- MST coupled sonocatalysis for IBP removal was studied with various parameters.
- Mechanical mixing makes to reverse the US frequency effect on IBP removal.
- MST was almost as effective as commercial TiO_2 and showed a high reusability.

GRAPHICAL ABSTRACT



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ABSTRACT

As a reusable sonocatalyst, magnetically separable titanium dioxide (MST) was synthesized by a sol–gel method and was evaluated in the removal of ibuprofen (IBP). MST was carefully characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), N_2 gas isotherms, band-gap energy, magnetization, zeta potential, and particle size distribution. The kinetics of IBP removal by sonolysis or MST-assisted sonocatalysis was systematically evaluated with various operational parameters such as pH, temperature, ultrasound (US) frequency, and mechanical mixing intensity. For the first time, authors found that mechanical mixing had an opposite effect on the oxidation rate constants of IBP removal by sonolysis or sonocatalysis according to US frequency. Specifically, the magnitude orders of oxidation rate constants in sonolysis and sonocatalysis with mixing (350 rpm) were the same (35 > 1000 > 300 > 500 > 700 kHz), but sonolysis without mixing showed the following order: 500 > 1000 > 35 kHz. In addition, the removal rate constant of IBP by sonocatalysis at the lowest US frequency (35 kHz) increased exponentially as the mechanical mixing speed increased. MSM exhibited a high reusability because it has similar rate constants with an average value of $17 \pm 0.3 \times 10^{-3}$ min^{-1} five repetitive kinetic tests.

1. Introduction

Ibuprofen (IBP) is ubiquitous in the environment and has been detected in many water sources and in wastewater [1,2]. An assessment by the World Health Organization (WHO) indicated

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that IBP is the leading endocrine disrupting compound (EDC). For example, the detected concentrations of IBP have been higher than those of erythromycin, bleomycin and others. IBP exposure is associated with various health and ecotoxicological risks to the human and aquatic wild life; even very low concentrations have resulted in harmful effects on the human endocrine system and aquatic wild life reproduction [1–4]. Thus, the removal of IBP from water represents an emerging environmental concern.

Recently, energy-based heterogeneous catalysis has received significant attention in the treatment of various organic pollutants. Specifically, because of their high catalytic performance, heterogeneous catalysts have been studied in the removal of EDCs by environmentally friendly wave-energy oxidations such as ultrasound (US) or ultraviolet (UV) irradiation [5,6]. As a representative photocatalyst, TiO_2 is highly stable, resistant to acidic or alkaline conditions, nontoxic, safe, inexpensive, and has a strong redox reaction. Thus, TiO_2 is known as the best material for oxidizing organic pollutants [7,8]. When TiO_2 is applied in UV-based oxidation, various organic pollutants can be degraded or even mineralized into CO_2 and H_2O because of the production of hydroxyl radicals (·OH), which have a strong oxidation potential (2.8 V) [9]. However, the use of TiO_2/UV is difficult with nontransparent and highly turbid wastewater [10]. On the other hand, US can decompose organic pollutants by cavitation and photocatalysis and can penetrate turbid aqueous media. The penetration depth of UV is a few millimeters, while that of US is 15–20 cm [11]. Furthermore, ·OH generation increases when TiO_2 is combined with US. For example, TiO_2-assisted US exhibited a 2–4 times higher decomposition efficiency of methyl orange than US alone [12,13]. The pore volume of TiO_2 supplies additional nuclei to increase the number of cavitation bubbles, eventually increasing the ·OH generation when the bubbles burst [14]. In addition to the cavitation effect, UV emission by the sonoluminescence of US excites TiO_2 to produce additional ·OH through the decomposition of water molecules by holes (h^+) [15].

Until now, various TiO_2-based sonocatalysts have been synthesized and applied in conjunction with US, and various operational parameters have been studied [16–19]. Although these studies focused on different sonocatalysts based on TiO_2, there is no study on reusable sonocatalysts or how to enhance the oxidation efficiency of sonolysis or sonocatalysis by mechanical mixing. In fact, the recovery and reusability of sonocatalysts are the key issues in resolving the applicability for the industrial-scale treatment processes [20]. Several techniques are available for the recovery and reuse of catalysts, including coagulation by using aluminum chloride [21], separation using ultrafiltration (UF) membranes [8], film-type catalysts [22], and magnetic catalysts. Among these techniques, the most effective and simplest method involves the recovery and reuse of magnetically active catalysts. Although some studies on magnetic TiO_2 prepared by coating TiO_2 on the magnetic core of Fe_3O_4 or Fe_2O_3 were reported, they were limited to UV oxidation processes [20,23–28].

The objectives of this study were to synthesize magnetically separable titanium dioxide (MST), and apply it in a US oxidation system for the removal of IBP in aqueous media. Several batch tests were conducted to investigate the effect of important operational parameters such as US frequency, mechanical stirring, pH and temperature, as well as the degree of recovery and reusability of MST.

2. Materials and methods

2.1. Materials

Magnetite nanopowder (Fe_3O_4, ~50 nm, Aldrich), tetraethyl orthosilicate (TEOS, grade 99%, Aldrich), titanium butoxide purum (TBT, grade ⩾97%, Fluka), aqueous ammonia solution (30%, Duksan, Korea), and ethanol (grade 99.9%, Duksan, Korea) were obtained and utilized to synthesize MST. Ibuprofen (IBP, grade 98%) was purchased from Aldrich (USA). In order to compare the performance of synthesized MST, nanosized TiO_2 (Degussa, P25, anatase/rutile = 75/25%) was obtained and used for IBP oxidation.

2.2. Sonocatalysis experiment

2.2.1. MST preparation and sonocatalysis reactor setup

As a sonocatalyst, MST was prepared and used for sonocatalysis reactor. The preparation method of SiO_2 coated nano-magnetite and MST were described in Supporting information (SI). The setup of the sonocatalytic reactor is shown in Fig. 1. A glass, horn-type sonoreactor (Φ 100 × H 115 mm, total volume: 0.8 L, effective volume: 0.5 L) made of Pyrex with a single piezoelectric transducer module (PZT, Tamura, Japan) was used for the kinetic evaluation of the sonocatalytic removal of IBP. The transducer was coupled with an ultrasonic generator (Mirae Ultrasonic MEGA-100, Korea). A stirrer (MS 3060D) was used for the mechanical mixing. The temperature in the solution was maintained with a temperature controller (RC-10V, Immersion circulator).

2.2.2. Sonolysis and sonocatalysis for IBP oxidation

The IBP stock solution (1000 mg L^{-1}) was made by dissolving 0.1 g of IBP powder in 100 mL of methanol. Then, IBP containing water (1 mg L^{-1}) was prepared by adding 5 mL of IBP stock solution into 5 L of deionized water. After adding 1.5 g of MST into 500 mL of the IBP solution (1 mg L^{-1}) [29], the suspension was homogenously mixed using a stirrer at a constant speed, temperature (24 ± 1 °C), and calorimetric power density (41 W L^{-1}).

Batch tests were conducted based on the aforementioned conditions to investigate the effect of the US frequency at 35, 300, 500, 700, and 1000 kHz on the oxidative removal of IBP and I_3^- production. For these tests, the pH and mechanical mixing speeds were fixed at 6.6 ± 0.5 and 350 rpm, respectively. At either 35 or 500 kHz, the effect of mechanical stirring (0, 150, 250, 350 rpm) on the removal of IBP was also determined at pH 6.6 ± 0.5. To determine the effect of pH, batch tests were conducted by adjusting the initial pH of the suspension to 3, 4, 4.9, 5.5, or 6.6 using 1 mol L^{-1} of HCl at a fixed frequency of 35 kHz. The effect of temperature on the IBP removal was also investigated at 25, 40, or 55 ± 1 °C using a temperature controller with a water jacket. For these tests, the US frequency, pH, and mechanical mixing speed were fixed at 35 kHz, 6.6 ± 0.5, and 350 rpm, respectively. Under the same conditions described above, P25 was applied to the sonocatalytic degradation of IBP and its performance was compared to that of MST.

2.2.3. Reusability tests of MST

Following the sonocatalytic oxidation reaction, MST was recollected by centrifuging the suspension. Then, the separated MST was washed at least three times with distilled water and subsequently dried at room temperature. The dried MST was reused for the subsequent sonocatalytic oxidation process conducted under the same conditions: 500 mL of IBP solution (1 mg L^{-1}) and reclaimed MST (3 g L^{-1}). With five cycles of MST reusability, the sonocatalytic oxidation efficiencies of IBP were investigated in triplicate tests for 1 h.

2.3. Analysis

2.3.1. Characterization

To ascertain the physicochemical properties of MST, several analyses such as BET surface area, XRD, FT-IR, band-gap energy, magnetization, particle distribution were conducted. All information of analytical methods was in SI.