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An innovative ultrasound, Fe^{2+} and TiO_2 photoassisted process for bisphenol a mineralization

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ABSTRACT

This paper explores the degradation of a model pollutant, bisphenol A, by an advanced oxidation process that combines sonolysis, Fe^{2+}, and TiO_2 in a photoassisted process. Experiments were done under saturated oxygen conditions. The effect of different Fe^{2+} (0.56 and 5.6 mg/L) and TiO_2 (10 and 50 mg/L) concentrations was investigated on both the elimination and mineralization of the pollutant. A pronounced synergistic effect that led to the complete and rapid elimination of dissolved organic carbon (DOC) was observed even at low catalyst loadings. In this system, almost a complete removal of DOC (93%) was observed after 4 h using 10 and 5.6 mg/L of TiO_2 and Fe^{2+}, respectively, whereas at the same time, only 5, 6, and 22% of DOC was removed by an individual process alone (TiO_2 photocatalysis, ultrasound, and photo-Fenton, respectively). In this system, ultrasound has the principal role of eliminating the initial substrate and providing hydrogen peroxide for the photocatalytic systems, while photo-Fenton and TiO_2 photocatalysis are mainly responsible for the transformation of the intermediates in CO_2 and H_2O. The role of H_2O_2 generated from the sonochemical process is also discussed.

1. Introduction

Because of continuous growth of the chemical industry, the quantity and variety of non-biodegradable organic substances commercialized in the world has increased in the last two decades. If not treated, these compounds sooner or later appear in the environment. Thus, research is needed into new and effective technologies to remove these compounds from water sources.

Recent results have shown that advanced oxidation processes (AOPs), which are based on the formation and use of the extremely oxidant hydroxyl radical, offer promising alternatives for removal of chemical contamination in water (Pulgarin and Kiwi, 1996; Ribordy et al., 1997; Herrera et al., 1998; Parsons and Byrne, 2004). Different AOPs, each with unique characteristics and advantages, offer different ways for generating •OH radicals, and a high variety of organic compounds can be removed from water sources using AOPs.

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Photoassisted systems such as photo-Fenton (Neyens, and Baeyens, 2003; Chiou et al., 2006) and TiO_2 photocatalysis (Kiwi et al., 1993; Devipriya and Yesodharan, 2005; Malato et al., 2007), and more recently sonochemical processes (Pétrier and Casadonte, 2001; Mason and Pétrier, 2004) appear to be the most attractive AOPs for water treatment applications.

Because of its simplicity and high oxidizing power, the photo-Fenton process is an AOP frequently used for oxidation and degradation of organic substances (Neyens and Baeyens, 2003; Chiou et al., 2006). In this case, a hydroxyl radical is formed through UV light, hydrogen peroxide, and Fe^{2+} or Fe^{3+} reactions.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (1)$$

$$Fe^{3+} + OH^- \rightarrow Fe(OH)^{2+} \quad (2)$$

$$Fe(OH)^{2+} + h\nu \rightarrow {}^{\bullet}OH + Fe^{2+} \quad (3)$$

TiO_2 photocatalysis is another interesting AOP that has gained considerable attention as a means of water remediation (Devipriya and Yesodharan, 2005; Malato et al., 2007). In this process, UV light ($\lambda \leq 387$ nm) is used to excite an electron from TiO_2 to produce an electron-hole pair,

$$TiO_2 + h\nu \rightarrow TiO_2\,(e^- + h^+). \quad (4)$$

Oxygen and hydrogen peroxide dissolved in solution can scavenge excited electrons, limiting the electron-hole recombination,

$$TiO_2\,(e^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet -} \quad (5)$$

$$TiO_2\,(e^-) + H_2O_2 \rightarrow TiO_2 + {}^{\bullet}OH + OH^-. \quad (6)$$

Organic compounds may undergo oxidation directly at the hole. The hole can also undergo charge transfer with adsorbed water molecules or with hydroxide surface-bound species, forming •OH radicals,

$$TiO_2\,(h^+) \text{ or } {}^{\bullet}OH + R \rightarrow \text{oxidation products} \quad (7)$$

$$TiO_2\,(h^+) + H_2O \rightarrow TiO_2 + {}^{\bullet}OH + H^+ \quad (8)$$

$$TiO_2\,(h^+) + OH^- \rightarrow TiO_2 + {}^{\bullet}OH. \quad (9)$$

On the other hand, sonochemical processes are based on the cyclical formation, growth, and adiabatic implosion of microbubbles. During the implosion of cavities, occurring in extremely small intervals of time, a high quantity of energy is released in a very small volume. Under these conditions, organic substances with an elevated fugacity character are pyrolized (Okuno et al., 2000; Jiang et al., 2002) while non-volatile compounds are degraded by hydroxyl radicals coming from water and oxygen dissociation (Torres et al., 2007a),

$$H_2O \rightarrow H + {}^{\bullet}OH \quad (10)$$

$$O_2 \rightarrow 2O \quad (11)$$

$$O + H_2O \rightarrow 2{}^{\bullet}OH \quad (12)$$

$$H + O_2 \rightarrow {}^{\bullet}OH + O. \quad (13)$$

Hydrophobic and hydrophilic compounds mainly degrade at the interface of the bubble and in the solution bulk, respectively. Because of the short lifetime of •OH radicals, a high fraction of these recombine at the interface, before reacting with hydrophilic substances.

$$2{}^{\bullet}OH \rightarrow H_2O_2 \quad (14)$$

Thus, because of the formation of highly hydrophilic intermediates via •OH attack, complete mineralization is rarely achieved even under long sonication periods (Peller et al., 2001; Torres et al., 2007a).

On the other hand, organic contaminants are mineralized by the photo-Fenton process or TiO_2 photocatalysis (Devipriya and Yesodharan, 2005; Chiou et al., 2006). However, a large quantity of oxidants and catalyst are often required for these processes, and compliance with environmental and economic requirements for water treatment is thus not always attained. Hence, the combination of several oxidation processes to overcome this weakness has become one of the most promising approaches and most active research fields in recent years (Bandara et al., 1997; Adewuyi, 2005; Lesko et al., 2006; Torres et al., 2007a; Méndez-Arriaga et al., 2009).

Previous results have indicated that ultrasound/photocatalysis coupling is a process of interest for mineralization of organic contaminants (Stock et al., 2000; Berberidou et al., 2007; Torres et al., 2008a). However, high TiO_2 loading has a detrimental effect on cavitation, and the best synergistic effects are therefore found at low quantities of TiO_2. Control experiments indicated that under these conditions, relatively high concentrations of H_2O_2 resulting from ultrasound remain in solution (Torres et al., 2008a). Thus, the addition of low quantities of iron ions to produce the Fenton and photo-Fenton processes (Eqs. (1)–(3)) could enhance the efficiency of organic pollutant removal. For studying this effect, two catalytic Fe^{2+} concentrations (0.56 and 5.6 mg/L) were tested, for BPA elimination and mineralization, in an innovative ultrasound/Fe^{2+}/TiO_2 photoassisted process. This work reports the use of ultrasound combined with TiO_2 and Fe^{2+} photocatalysis for the complete mineralization of a known endocrine-disrupting compound, bisphenol A (BPA). Experiments were done under saturated oxygen solutions, with oxygen selected instead of air to avoid nitrite and nitrate ion formation during sonication of aqueous solutions (Torres et al., 2007a) and because of its excellent performance in photocatalysis (Ochuma et al., 2007) and ultrasound (Torres et al., 2007b;