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Catalytic degradation of brominated flame retardants by copper oxide nanoparticles

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HIGHLIGHTS

- CuO nanoparticles efficiently catalyze degradation of brominated flame retardants.
- The catalytic mechanism involves generation of hydroxyl and superoxide radicals.
- Hydrogen peroxide is essential as an oxidation agent and catalyst activator.
- The reaction is compared to Fenton reactions and to nZVI reductive dehalogenation.

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ABSTRACT

The catalytic degradation of two brominated flame retardants (BFRs), tribromoneopentyl alcohol (TBNPA) and 2,4 dibromophenol (2,4-DBP) by copper oxide nanoparticles (nCuO) was investigated. The degradation kinetics, the debromination, and the formation of intermediates by nCuO catalysis were also compared to Fenton oxidation and nano zero-valent iron (nZVI) reduction methods. BFRs have been added to various products like plastic, textile, electronics and synthetic polymers at growing rates. In spite of the clear advantages of reducing fire damages, many of these BFRs may be released to the environment after their beneficial use and become contaminants. The two studied BFRs were fully degraded with sufficient time (hours to days) and oxidation agent (H_2O_2). Shorter reaction times showed differences in reaction pathway and kinetics. The 2,4-DBP showed faster degradation than TBNPA, by nCuO catalysis. Relatively high resistance to degradation was recorded for 2,4-DBP with nZVI, yielding 20% degradation after 24 h, while the TBNPA was degraded by 85% within 12 h. Electron Spin Resonance (ESR) measurements show generation of both hydroxyl and superoxide radicals. In addition, inhibition of 2,4-DBP degradation in the presence of spin traps implies a radical degradation mechanism. A catalytic mechanism for radical generation and BFR degradation by nCuO is proposed. It is further suggested that H_2O_2 plays an essential role in the activation of the catalyst.

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1. Introduction

Flame retardants are chemicals used to reduce the flammability of combustible materials such as plastic, textile, electronics and synthetic polymers (De Wit, 2002; Watanabe and Sakai, 2003). The requirements to add flame retardants to industrial products have contributed to a significant decrease in fire incidents over the past three decades (Birnbaum and Staskal, 2004). However, while there are clear advantages to reducing fire damages, flame retardants may also act as a source of contamination; harmful compounds are often released into the environment from products containing such compounds. Brominated flame retardants (BFRs) are the most frequently used – and the largest – group of commercial flame retardants, due to their low cost, high performance and efficiency (Birnbaum and Staskal, 2004). BFRs act primarily by chemical interference with the radical-chain reaction mechanism taking place in the gas phase during combustion (Rahman et al., 2001). BFRs are often toxic and persistent, and can bioaccumulate in the environment. Polybrominated biphenyls, a group of BFRs, were removed from the market due to their toxicity (Birnbaum and Staskal, 2004); in other cases, toxic BFRs have remained in use because of an absence of reasonable alternatives.

In the current study we examine the catalytic degradation of two brominated flame retardants: (i) tribromoneopentyl alcohol (TBNPA) (3-bromo-2,2-bis(bromomethyl) propanol), a tri-brominated aliphatic alcohol, and (ii) 2,4 dibromophenol (2,4-DBP), a di-brominated aromatic alcohol. The 3D molecular structure of these BFRs is shown in Fig. S2. These compounds were selected as representative BFRs that may pollute aqueous environments, related to general environmental contamination caused by BFR release.

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TBNPA has high water solubility, 1930 mg L^{-1} (20 °C) (EPA, 2005). Due to steric effects, the three bromine atoms are held very close to each other, which lead to a relatively high resistance to biodegradation. Its half-life is estimated to be about 100 years. TBNPA migrates relatively rapidly with minimal retardation in the soil-aquifer zone, and consequently may cause aquifer contamination (Ezra et al., 2005; 2006). A summary of available TBNPA toxicity data (EPA, 2005) concluded that adequate information exists to support the evaluation of acute oral toxicity, acute eye irritation and a moderate dermal irritation, as well as acute toxicity for aquatic organisms such as fish, algae and freshwater invertebrates. Halogenated phenols are xenobiotic and pose serious hazards to water bodies and soils, being considered toxic, bioaccumulative, poorly biodegradable and treatment-resistant (Cravotto et al., 2005). Bromophenols, especially 2,4-DBP and 2,4,6 tribromophenols (2,4,6-TBP), are used as flame retardants and in the industrial synthesis of flame retardants. Although bromophenols are also produced naturally by marine organisms (Hassenklöver et al., 2006), anthropogenic manufacturing and the combustion of municipal waste are major sources of terrestrial contamination.

To degrade many persistent organic pollutants, advanced oxidation processes (AOPs) often prove to be efficient, low-cost, robust, and rapid. AOPs are a family of reactions based on generation of the powerful hydroxyl radical. This non-selective chemical oxidant has an oxidation potential of 2.8 V (Ikehata et al., 2006), and it can therefore attack almost every organic compound (Vogelpohl and Kim, 2004; Poyatos et al., 2010). Nanoparticles, which can be used in some AOPs, exhibit enhanced catalytic activity compared to their bulk material analogs, because of unique properties that are derived from their size, including enhanced surface area and increase in surface reactivity. Because catalytic processes occur on the interfacial surface, smaller particles are expected to offer higher activity (Hariharan, 2006; Pouretedal et al., 2009; Khin et al., 2012).

Here, we investigate the catalytic activity of copper oxide nanoparticles (nCuO), under oxidative conditions, for the degradation of TBNPA and 2,4-DBP. To date, copper oxide at different sizes and in combinations with other materials has been investigated as a catalyst for the elimination of contaminants in the gas phase (Tzortzatou and Grigoropoulou, 2010; Rau et al., 2011) and in aqueous solutions (Batista et al., 2010; Massa et al., 2011), and it has been demonstrated that effective nCuO catalytic reaction for degradation of organic water contaminants is independent of light radiation, although the catalytic mechanism is not fully understood (Ben-Moshe et al., 2009). In this study, we also compare the catalytic degradation of TBNPA and 2,4-DBP to known treatment methods – Fenton oxidation and nZVI reductive dehalogenation – and provide an insight into the catalytic mechanism. Finally, we use electron spin resonance (ESR) spectroscopy to measure both radical species in the reaction and the change in copper properties before and after the reaction.

2. Materials and methods

2.1. Materials

Copper (II) oxide (CuO) nanoparticles with average size 29 nm, iron (II) chloride tetrahydrate ($Cl_2Fe{\cdot}4H_2O > 99\%$), iron (III) chloride hexahydrate ($Cl_3Fe{\cdot}6H_2O > 98\%$), sodium bromide ($NaBr > 99.5\%$), 4-hydroxybenzoic acid > 99%, lithium hydroxide monohydrate ($LiOH{\cdot}H_2O > 99\%$), N-tert-butyl-α-phenylnitrone (PBN) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were purchased from Sigma. Tribromoneopentyl alcohol (TBNPA) was supplied by Dead-Sea-Bromine-Group; 2,4-dibromophenol (Supelco), sodium borohydrate ($NaBH_4$, Nile chemicals), hydrogen peroxide (H_2O_2/H_2O 30% v/v solution, Frutarom), toluene (>99.5%, Frutarom), acetone (>99.5%, Mallinckrodt) and dimethyl sulfoxide (DMSO > 99.9%, Mallinckrodt) were also employed. All the experiments, eluents and standards were conducted using double deionized water (18.2 MΩ cm). Further details on the CuO nanoparticles are given in Ben-Moshe et al. (2009).

2.2. Reaction systems

The catalytic activity of nCuO for the degradation of TBNPA and 2,4-DBP was examined in batch experiments. The nCuO particles (1 g L^{-1}) were suspended in 100 mL aqueous solution spiked with TBNPA or 2,4-DBP to give an initial concentration of 35 or 25 mg L^{-1} (∼0.1 mM), respectively. Subsequently, 5 mL of H_2O_2 (1.5% final concentration) were added to initiate the catalytic reaction. The experiments were conducted at room temperature under ambient fluorescent lighting and stirred (400 RPM) for 12 h for TBNPA or 8 h for 2,4-DBP in open 100 mL flasks. Samples (5 mL) were removed, filtered, and then analyzed at different time intervals. Additional controls included reaction mixtures without (a) nanoparticles, (b) hydrogen peroxide, and (c) both nanoparticles and hydrogen peroxide, were prepared in parallel and analyzed in the same manner as the catalytic reactions. For some experiments, higher initial BFR concentrations were used to follow low concentrations of intermediates or bromide ions. In all cases, the specific experimental conditions are specified when relevant.

Similar systems were prepared for comparison of the CuO system to degradation by Fenton reaction (oxidation) or nZVI (reduction). For degradation by the Fenton oxidation reaction, dissolved $FeCl_2$ (1 mM final concentration) was added to a solution containing TBNPA or 2,4-DBP (final concentrations 35 and 250 mg L^{-1}, respectively). The initial pH of the reaction mixture was 3.8 for TBNPA and 3.7 for 2,4-DBP, without any buffering. Hydrogen peroxide (11 mM final concentration) was then added to initiate the reaction. Samples were removed at different time intervals and prepared for analysis of organic substances. The reactions took place under ambient fluorescent lighting at room temperature, while stirred for 30 min in open flasks.

The nZVI was synthesized using a method described previously in the literature (Wang and Zhang, 1997). A sample of 100 mL of dissolved $NaBH_4$ (3 M) was added drop-wise to 100 mL dissolved $FeCl_3{\cdot}6H_2O$ (1 M) under an argon blanket. The solid precipitate was then filtered out in an anaerobic chamber and washed with 200 mL acetone followed by 1000 mL deionized water. The reduction activity of nZVI was tested under anaerobic conditions by suspending 2 g L^{-1} of the reduced iron in a 100 mL aqueous solution containing 350 mg L^{-1} TBNPA or 250 mg L^{-1} 2,4-DBP in closed glass bottles. Samples were then removed at different time intervals through a septum cap and prepared for analysis of organic content and bromide ions. The reactions took place under ambient fluorescent lighting at room temperature.

2.3. Analysis

Quantification of TBNPA and 2,4-DBP was done using Gas Chromatograph equipped with Electron Capture Detector (GC/ECD) and DB-VRX capillary column (30 m, 0.32 mm, 1.8 μm). Helium was used as a gas carrier at a flow rate of 1 mL min^{-1}; the injector temperature was held at 120 °C for TBNPA and 250 °C for 2,4-DBP. For both analytes the detector temperature was held at 300 °C and the temperature program was as follows: 100 °C for 1 min, temperature ramp of 15 °C min^{-1} to 250 °C, 250 °C for 3 min. All samples were filtered (0.22 μm) immediately after removal from the reaction flask and a liquid–liquid extraction method was performed using toluene as the extraction solvent.

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