Treatment of aqueous bisphenol A using nano-sized zero-valent iron in the presence of hydrogen peroxide and persulfate oxidants

B. Girit, D. Dursun, T. Olmez-Hanci and I. Arslan-Alaton

ABSTRACT

Bisphenol A (BPA) is an industrial pollutant considered as one of the major endocrine-disrupting chemicals found in natural waters. In the present study, the use of a commercial, air-stable, zero-valent iron (ZVI) powder, consisting of Fe⁰ surface stabilized nanoparticles was examined for the treatment of 20 mg/L, aqueous BPA solutions. The influence of pH (3, 5, 7), addition of hydrogen peroxide (HP) and persulfate (PS) oxidants (0.0, 1.25 and 2.5 mM) as well as temperature (25 and 50°C) was studied for BPA treatment with 1 g/L ZVI. ZVI coupled with HP or PS provided an effective treatment system, which was based on rapid ZVI-mediated decomposition of the above-mentioned oxidants, resulting in complete BPA as well as significant total organic carbon (TOC) (88%) removals, in particular when PS was employed as the oxidant. Increasing the PS concentration and reaction temperature dramatically enhanced PS decomposition and BPA removal rates, whereas HP was not very effective in TOC removals and at elevated temperatures. According to the bioassays conducted with Vibrio fischeri and Pseudokirchneriella subcapitata, the acute toxicity of aqueous BPA fluctuated at first but decreased appreciably at the end of ZVI/PS treatment.

Key words | bisphenol A, hydrogen peroxide and persulfate, hydroxyl and sulfate radicals, Pseudokirchneriella subcapitata, Vibrio fischeri, zero-valent iron nanoparticles

INTRODUCTION

In the past decades, the presence of endocrine-disrupting chemicals in drinking water sources has attracted scientific as well as public interest due to their potential harmful environmental and health impacts. Endocrine disruptors are linked to increasing cases of breast cancer, infertility, low sperm counts, genital deformities, obesity, early puberty and diabetes, as well as alarming mutations in wildlife (O’Connor & Chapin 2003; Flint et al. 2012). They are also suspected of causing behavioral and learning problems in children, which coincides with their intensive, global consumption (Rezg et al. 2014; Selvara et al. 2014). Among them, bisphenol A (2,2-bis(4-hydroxyphenyl)propane; BPA) is a synthetic estrogen used to harden polycarbonate plastics and epoxy resins (O’Connor & Chapin 2003). BPA is fabricated into thousands of products made of hard, clear polycarbonate plastics and tough epoxy resins; including safety equipment, eyeglasses, computer and cell phone casings, water and beverage bottles. BPA is also consumed as a resin in dental fillings, coatings on cans, powder paints and additives in thermal paper (Flint et al. 2012). Primary sources of its environmental release are effluents and emissions from its manufacturing facilities. In addition, BPA residues in polycarbonate products and epoxy resins may leach out into the aquatic and terrestrial environment (Yamamoto & Yasuhara 1999). BPA concentrations reported in surface water range between 0.016 and 0.5 mg/L; however, levels >10 mg/L BPA have also been detected in old landfill leachate (Yamamoto et al. 2001). Studies have demonstrated that BPA can affect growth, reproduction and development in aquatic organisms (O’Connor & Chapin 2003). Also, evidence of endocrine-related effects in fish, aquatic invertebrates, amphibians and reptiles has been reported at relevant exposure levels, which are much lower than those required for acute toxicity (Selvara et al. 2014). These low concentrations render their effective removal by conventional biological, physical and chemical methods difficult and costly. Biologi-
hand, advanced, tertiary treatment methods including activated carbon adsorption and membrane technologies are ‘concentration’ processes with serious limitations in removing toxic or recalcitrant chemicals.

Alternative tools and methods for treating waters contaminated with micropollutants are advanced oxidation processes (AOPs) using chemical oxidants (hydrogen peroxide (HP), persulfate (PS), ozone) in combination with ultraviolet (UV) light to generate reactive species, i.e. hydroxyl (HO\(^-\)) and sulfate radicals (SO\(_4^{2-}\)), both known as the most powerful oxidizing agents after fluorine. Compared with HP, PS is a strong oxidizing agent with a redox potential of 2.01 eV (Criquet & Leitner 2013). PSerial pollutants can be effectively reduced and in some cases completely eliminated during the application of AOPs (Chen et al. 2007; Molkenthin et al. 2015). In particular, Fenton, Fenton-like and photo-Fenton treatments are known for their superiority in terms of efficient pollutant removal and detoxification (Fernandez-Alba et al. 2002; Arslan-Alaton & Teksoy 2007). Conversely, in some cases the application of AOPs may increase the toxicity to levels higher than that of the original pollutant (Sirtori et al. 2012).

In the present study, commercial nano-scale ZVI particles were employed to degrade the surrogate endocrine-disrupting chemical BPA from aqueous solution. For this purpose, air-stable nano-ZVI was used in combination with two common oxidants, namely HP and PS, forming an advanced oxidative treatment system. In the first part of the study, several baseline and control experiments were conducted under varying pH, ZVI, HP and PS concentrations at temperatures to optimize the removal of BPA and its total organic carbon (TOC) content. In addition, two sets of toxicity bioassays were carried out using test organisms from two different trophic levels, namely the photobacterium Vibrio fischeri (V. fischeri), being most extensively used in related work (Zazo et al. 2007), and the freshwater microalga Pseudokirchneriella subcapitata (P. subcapitata), selected as one of the most sensitive species to follow ecotoxicological behavior of industrial pollutants (Andreozzi et al. 2006), in order to validate possible ecotoxicological risks during their real-world application.

MATERIALS AND METHODS

Materials

Nano-scale ZVI particles (NANOFER 25S) were purchased from NANO IRON (Czech Republic). The organic coating...
of NANOFER 25S is polyacrylic acid (PAA), which has been proven to stabilize the nano-scale ZVI particles (Klimkova et al. 2011). The weight ratio of PAA/ZVI was 1/10 and the average particle size was 50 ± 10 nm. BPA (228 g/mol; C12H16O2; CAS Nr: 80-05-7; purity: 99.9%) and potassium persulfate (K2S2O8; CAS Nr: 7727-21-1; purity: 99.5%) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Analytical grade HP (H2O2; CAS Nr: 7782-84-1; 35% w/w) and chromatographic grade acetonitrile (CH3CN; CAS Nr: 75-05-8) were all obtained from Merck (Darmstadt, Germany). BPA solutions were prepared with distilled water, whereas ultrapure water for the chromatographic measurements was prepared with an Arium 611UV water purification system (Sartorius AG, Göttingen, Germany).

**Experimental procedures**

All BPA treatment and control experiments were carried out for 120 minutes in 500 mL capacity glass beakers under continuous stirring at 150 rpm to ensure uniform ZVI dispersion, mixing and oxygen saturation. Additional aeration or oxygen sparging was not provided. The experimental procedure was as follows; firstly, an aqueous BPA solution was prepared in distilled water and thereafter its pH was adjusted to the desired value with 1 N H2SO4 or NaOH solution. Thereafter, the desired amount of ZVI powder was added into the reaction solution. Finally, HP or PS oxidant was introduced to start the heterogeneous Fenton-like reaction. Several control (HP or PS only, ZVI only) and treatability (presence of oxidants, varying pH and temperature (T)) experiments were conducted. Twenty to 25 mL sample aliquots were taken at regular time intervals, quenched immediately by filtration through 0.22 micron Millipore membranes (Millipore Corp., Billerica, MA, USA) to separate the Fe0 nanoparticles from the reaction solution. The acute toxicity toward the photobacterium *V. fischeri* was measured before and during treatment of BPA using a commercial assay kit (BioToxTM, Aboatox Oy, Turku, Finland) according to the ISO 11348-3 (2008) test protocol. Prior to this test, the pH and salinity of all samples were adjusted to 7.0 ± 0.2 and 2% (w/v), respectively. After mixing 500 μL of untreated or treated BPA solutions with 500 μL of luminescent bacterial suspensions, the light emission after 15 minutes contact time was measured at a temperature of 15 °C. Percent relative inhibition rates were calculated on the basis of a toxicant-free control. The freshwater microalga *P. subcapitata* acute toxicity test was determined using Algaltoxkit F™ (MicroBioTests, Inc., Ghent, Belgium) microbiotests according to ISO 8692 (2012) and OECD Test No. 201 (OECD 2011). In this test, a synthetic freshwater medium was used as the dilution water, which was prepared in accordance with the test protocol. The pre-culture was set up 3 days before the start of the bioassay to secure exponential growth in the inoculum culture. The flasks used in the measurements contained originally 10^4 cells/mL (average value), with 25 mL of original and treated BPA samples. Three replicates were prepared and placed in an algal growth chamber under continuous fluorescent illumination and incubated at 22 ± 1 °C and pH 8.0 ± 0.2. At the start and after 24 and 48 hours, the cell density in the acetone-extracted blind sample and test replicates was measured on 10 cm path-length cuvettes at 670 nm, using a Jenway 6300 model spectrophotometer.

**Bioassays**

The acute toxicity toward the photobacterium *V. fischeri* was measured before and during treatment of BPA using a commercial assay kit (BioToxTM, Aboatox Oy, Turku, Finland) according to the ISO 11348-3 (2008) test protocol. Prior to this test, the pH and salinity of all samples were adjusted to 7.0 ± 0.2 and 2% (w/v), respectively. After mixing 500 μL of untreated or treated BPA solutions with 500 μL of luminescent bacterial suspensions, the light emission after 15 minutes contact time was measured at a temperature of 15 °C. Percent relative inhibition rates were calculated on the basis of a toxicant-free control. The freshwater microalga *P. subcapitata* acute toxicity test was determined using Algaltoxkit F™ (MicroBioTests, Inc., Ghent, Belgium) microbiotests according to ISO 8692 (2012) and OECD Test No. 201 (OECD 2011). In this test, a synthetic freshwater medium was used as the dilution water, which was prepared in accordance with the test protocol. The pre-culture was set up 3 days before the start of the bioassay to secure exponential growth in the inoculum culture. The flasks used in the measurements contained originally 10^4 cells/mL (average value), with 25 mL of original and treated BPA samples. Three replicates were prepared and placed in an algal growth chamber under continuous fluorescent illumination and incubated at 22 ± 1 °C and pH 8.0 ± 0.2. At the start and after 24 and 48 hours, the cell density in the acetone-extracted blind sample and test replicates was measured on 10 cm path-length cuvettes at 670 nm, using a Jenway 6300 model spectrophotometer.
(Bibby Scientific, Radnor, PA, USA). The measured fluorescence (relative units) was used directly as the biomass parameter to calculate growth rates (in d⁻¹) and relative growth inhibitions. A positive control with potassium dichromate solution was also included for each test and all bioassays were run in triplicate. To eliminate their effect on toxicity measurements, residual/unreacted HP and PS were removed with sodium thiosulfate (Merck, Darmstadt, Germany) and manganese dioxide, respectively, which were found to be the most suitable quenching agents to eliminate the interference of oxidants in the *V. fischeri* and *P. subcapitata* bioassays (Olmez-Hanci et al. 2014b).

**RESULTS AND DISCUSSION**

**BPA and TOC removals with nano-ZVI: effect of oxidants**

Control experiments performed in the absence of oxidants (nano-ZVI only) at pH 3.0, 5.0 and 7.0 indicated that 38% and 40%, 28% and 31%, as well as 26% and 28% BPA removals were achieved in 2 and 24 hours, respectively. In these experiments, low but still significant BPA abatements were evident due to BPA adsorption onto Fe⁰ nanoparticles accompanied with a slow oxidation reaction occurring under oxygen-saturated, acidic conditions (Fu et al. 2014).

Fe⁰ surface reaction I

\[
\text{Fe}^0 + \text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2
\]  

(4)

Fe⁰ surface reaction II

\[
\text{Fe}^0 + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}
\]  

(5)

Overall Fe⁰ surface reaction (I + II)

\[
2\text{Fe}^0 + \text{O}_2 + 4\text{H}^+ \rightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O}
\]  

(6)

The above reactions explain why higher BPA removals were observed at pH 3.0 (38–40%) than at pH 5.0 (28–31%) or pH 7.0 (26–28%) in the absence of HP. Owing to the intermittent formation of HP and Fe²⁺, it is expected that even in the absence of HP the Fenton reaction occurs at least to some extent and contributes to BPA removal.

Fenton reaction

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^\cdot + \text{OH}^- \quad k = 53–76 \text{ M/s}
\]  

(7)

In the next step, in order to enhance BPA removal, HP and PS were added into the nano-ZVI treatment system. Figure 1 presents changes in BPA (Figure 1(a)) and TOC (Figure 1(b)) abatements obtained with nano-ZVI (1 g/L) in the presence of HP (2.5 mM) at pH 5.0 and 25 °C. The HP:BPA molar ratio corresponded to 28.4 in these experiments. Figure 1 also features two control experiments, namely treatment of 20 mg/L BPA solution with nano-ZVI only and HP only under otherwise identical conditions. From Figure 1, it is evident that in the absence of nano-ZVI (HP only), no BPA abatement was observed during HP treatment, whereas 28% BPA removal occurred for the control experiment nano-ZVI only. However, for the combined catalytic treatment system, rapid BPA degradation was observed; BPA removal was prompt and complete after 40 minutes. This observation speaks for the initiation of immediate Fenton reactions upon Fe⁰ activation with HP to form HO⁻. The Fe⁰ surface reactions shown in Equations (4)–(6) are the rate-limiting steps of the
nano-ZVI/oxidant treatment system, since they release Fe\(^{2+}\) to form the Fenton’s reagent with HP. It should also be noted here that the following reactions may limit or hinder effective oxidation of BPA by HO\(^*\) (Zha et al. 2014):

$$\begin{align*}
\text{HO}^* \text{ scavenging by H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \text{HO}^* &\rightarrow \text{HO}_2^* + \text{H}_2\text{O} \quad k = 2.7 \times 10^7 \text{ M/s} \quad (8) \\
\text{HO}^* \text{ scavenging by Fe}^{2+} \\
\text{Fe}^{2+} + \text{HO}^* &\rightarrow \text{Fe}^{3+} + \text{OH}^- \quad k = 4 \times 10^8 \text{ M/s} \quad (9) \\
\text{Reduction of H}_2\text{O}_2 to H_2O by Fe}^0 \\
\text{Fe}^0 + \text{H}_2\text{O}_2 + 2\text{H}^+ &\rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O} \quad (10) \\
\text{Thermal H}_2\text{O}_2 decomposition (at >40 \text{ °C}) \\
\text{H}_2\text{O}_2 &\rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \quad (11)
\end{align*}$$

The above Equations (8)–(11) might explain the poor TOC removal rates being observed during nano-ZVI/HP treatment as depicted in Figure 1(b); TOC removal was only 5% after 40 minutes treatment, when BPA was completely degraded, and did not exceed 10% at the end of the 120 minutes reaction. Similarly to BPA, no TOC removal occurred in the absence of nano-ZVI (HP only) whereas 12% TOC removal occurred for nano-ZVI only. HP abatements were also followed during these experiments; HP remained unchanged in the reaction solution in the absence of nano-ZVI, whereas rapid HP decomposition occurred during nano-ZVI only treatment. HP and PS consumption rates will be shown in the forthcoming section of this paper.

Figure 2 refers to BPA (Figure 2(a)) and TOC (Figure 2(b)) removals obtained with the nano-ZVI (1 g/L)/PS (2.5 mM) system at pH 5.0 and 25 °C, together with two complementary control experiments (ZVI only and PS only under otherwise identical conditions). Only 10% BPA degradation was achieved after 120 minutes treatment without nano-ZVI. This could be attributable to the higher redox potential of PS (2.01 eV) as compared with HP (0.77 eV), causing some minor BPA removal by PS only. The combined treatment system effectively degraded BPA in 60 minutes as a consequence of rapid SO\(_4^{2-}\) formation (redox potential: 2.5–3.0 eV) by a Fenton-like reaction between the released Fe\(^{2+}\) and PS (Zhao et al. 2010; Xiong et al. 2014):

$$\begin{align*}
\text{Fe}^0 \text{ surface reaction} \\
\text{Fe}^0 + \text{S}_2\text{O}_8^{2-} &\rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-} \quad (12) \\
\text{Fenton-like reaction forming SO}_4^{2-} \\
\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} &\rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad k = 27 \text{ M/s} \quad (13) \\
\text{Parallel to the above given reactions, SO}_4^{2-} \text{ scavenging is also expected. Again, SO}_4^{2-} \text{ can be simultaneously consumed by Fe}^{2+} \text{ and S}_2\text{O}_8^{2-} : \\
\text{SO}_4^{2-} \text{ scavenging by Fe}^{2+} \\
\text{Fe}^{2+} + \text{SO}_4^{2-} &\rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} \quad k = 3 \times 10^8 \text{ M/s} \quad (14)
\end{align*}$$
SO$_4^{2-}$ scavenging by S$_2$O$_8^{2-}$

S$_2$O$_8^{2-}$ + SO$_4^{2-}$ → S$_2$O$_8$ + SO$_4^{2-}$  \( k = 6.1 \times 10^5 \text{ M/s} \)  (15)

The higher oxidation efficiency of the heterogeneous treatment system can be explained by the fact that during the heterogeneous Fenton-like reaction, Fe$^{2+}$ is not added initially, but gradually released from Fe$^{0}$ into the reaction solution, thus minimizing the scavenging effect of free radicals by Fe$^{2+}$ (Rodriguez et al. 2014) as shown in Equation (14).

However, different from the nano-ZVI/HP process, high TOC removal rates and efficiencies were obtained by the nano-ZVI/PS treatment system. In fact, previous studies comparing the efficiency and kinetics of AOPs driven by HO$^\cdot$ and SO$_4^{2-}$ indicated that the reactivity and selectivity of SO$_4^{2-}$ may appreciably differ from that of HO$^\cdot$ for some specific pollutants and eventually their degradation products (Torres-Luna et al. 2013; Orellana-García et al. 2015). In former work we could demonstrate that SO$_4^{2-}$ exhibited a higher selectivity for the degradation of phenol over phenolic derivatives including alkyl phenol polyethoxylates as compared to HO$^\cdot$ (Arslan-Alaton et al. 2013). As is also evident in Figure 2(b), 80% TOC removal was achieved when BPA was completely degraded after 60 minutes treatment, speaking for the superiority of using PS instead of HP as the oxidant for both efficient BPA degradation and mineralization under the studied reaction conditions.

**Effect of temperature**

The effect of increasing temperature on Fenton’s reagent applied for the treatment of industrial pollutants has been investigated in the past (Arslan-Alaton & Teksoy 2007; Olmez-Hanci et al. 2015). Apparently, temperature has to be optimized to maximize Fenton and Fenton-like treatment systems. In the present work, ZVI/HP, ZVI/PS, HP only and PS only experiments where repeated at 50°C to examine the effect of reaction temperature on BPA and TOC removal rates. For that purpose, two parallel sets of experiments were conducted in the presence of 1.25 and 2.5 mM oxidant (HP, PS) concentrations, considering that increasing the reaction temperature would accelerate thermal decomposition of the oxidant so that it might not be fully used for oxidation of BPA and intermediates. Figure 3 comparatively displays BPA (Figure 3(a)) and TOC (Figure 5(b)) abatements at 25 and 50°C for ZVI (1 g/L)/HP (1.25 mM) and 50°C for HP only (1.25 mM) treatments of 20 mg/L BPA at pH 5.0. As is obvious from Figure 3(a), raising the reaction temperature to 50°C did not improve BPA degradation, which was thought to be a direct consequence of accelerated, thermal HP decomposition becoming more effective at 50°C (see Equation (8)) and thus inhibiting its function as a free radical initiator and ZVI activator. Similar abatement profiles were observed for the TOC parameter; ZVI/HP treatment rates decreased when the reaction temperature was increased to 50°C due to inefficient HP consumption. In other words, increasing the temperature to 50°C did not improve the TOC removals when HP was used as the oxidant. BPA removal was also minor (3% after 120 minutes) for the HP only experiment conducted at 50°C. BPA removal was in the range of 15% (40 minutes) to 20% (120 minutes), and TOC removal was in the range of 2% (40 minutes) to 18% (120 minutes) at 50°C in the presence of 1.25 mM HP. From the experimental findings it could be inferred that for efficient BPA degradation with the ZVI/HP treatment system, ambient
temperature conditions should be preferred and increasing the reaction temperature had a negative influence on treatment performance. Conclusively, increasing either the temperature or oxidant concentration did not exert a noticeable positive effect on TOC abatements for BPA removal with the ZVI/HP process.

Conversely, during ZVI/PS treatment, increasing the temperature from 25 to 50 °C in the presence of 1.25 mM PS exhibited a very positive effect on BPA (Figure 4(a)) and TOC (Figure 4(b)) abatement rates. BPA removal was complete in only 5 minutes at 50 °C, whereas not more than 67% BPA degradation could be reached at 25 °C with 1.25 mM PS (Figure 4(a)). TOC removals were also improved from 43% (120 minutes) to 88% (120 minutes) at 50 °C, with 80% TOC being already removed after 5 minutes treatment with the ZVI/PS (1.25 mM) treatment process. From these data it could be concluded that increasing the reaction temperature from 25 to 50 °C exhibited a positive effect on BPA and TOC removals when PS was employed as the oxidant of the nano-ZVI treatment system. It should also be pointed out that elevating the temperature from 25 to 50 °C was more effective on TOC removals than doubling the PS concentration from 1.25 to 2.5 mM for the treatment combination. However, considering economic and technical aspects as well as operation costs of real-scale water treatment plants, it was decided to select the ZVI/PS (2.5 mM instead of 1.25 mM) process working at pH 5 and 25 °C as the more realistic and appropriate treatment system for full-scale process integration.

Changes in oxidant consumption rates

Obviously, the treatment performance of heterogeneous and homogeneous oxidation systems directly depends on the effective use of oxidant (Arslan-Alaton & Teksoy 2007). During BPA treatment, HP and PS are thought to be consumed by different mechanisms; they undergo several adsorption, redox, thermal and catalytic decomposition reactions, all of which more or less contribute to BPA removal via indirect free radical oxidation. Changes in HP and PS consumptions during BPA treatment in the presence of oxidant only (HP, PS) as well as the nano-ZVI/oxidant treatment combination was followed at 25 and 50 °C. From Figure 5, it can be seen that HP consumption is generally speaking appreciably faster than PS decomposition. This is not surprising, since HP consumption is already high at room temperature and thus could only increase from 93% to 100% after 120 minutes BPA treatment when the temperature was elevated from 25 °C to 50 °C, respectively. PS decomposition conversely increased considerably upon temperature rise from 32% at 25 °C to 100% at 50 °C.
after 120 minutes treatment. However, in the absence of nano-ZVI, the oxidant consumption rates were slow and rather inefficient; namely 14% and 20% for PS and HP, respectively, even at 50 °C. It should be emphasized here that the slowest decomposition rates were observed in the absence of nano-ZVI in the case of both oxidants. These poor oxidant consumption rates being observed particularly in the absence of nano-ZVI catalyst revealed that oxidant decomposition was mainly of a catalytic rather than thermal nature, as has been suggested in previous work (Xiong et al. 2014). This was evident upon comparative assessment of the obtained oxidant exhaustion profiles, which became very pronounced for the nano-ZVI/oxidant treatment systems. Parallel to PS consumption, BPA and TOC removals increased appreciably, whereas HP decomposition proceeded much faster than the BPA and TOC removals.

Changes in acute toxicity

It has already been documented that advanced oxidation may result in the formation of some degradation intermediates being more inhibitory/toxic than the original pollutant. Hence, toxicity testing is crucial to ensure ecotoxicologically safe real-scale applications (Andreozzi et al. 2006). Figure 6 depicts percent relative V. fischeri and P. subcapitata inhibition rates versus treatment time for 20 mg/L aqueous BPA oxidation in the presence of 1 g/L ZVI and 2.5 mM PS at pH 5.0 and 25 °C. It has already been documented that advanced oxidation creates being more inhibitory/toxic than the original pollutant. Hence, toxicity testing is crucial to ensure ecotoxicologically safe real-scale applications (Andreozzi et al. 2006). Figure 6 depicts percent relative V. fischeri and P. subcapitata inhibition rates versus treatment time for 20 mg/L aqueous BPA oxidation in the presence of 1 g/L ZVI and 2.5 mM PS at pH 5.0 and 25 °C, being selected as the most appropriate treatment conditions to obtain relatively high BPA and TOC removals. The inhibitory effect of aqueous BPA solution, originally being in the range of 65% (P. subcapitata) to 72% (V. fischeri), fluctuated through the reaction most probably due to the formation and subsequent oxidation of transformation products, and ultimately decreased to 20% (P. subcapitata) to 24% (V. fischeri), revealing that relatively less harmful, low toxicity degradation products were formed during ZVI/PS treatment. The fluctuation was more pronounced for P. subcapitata which appeared to be more sensitive to toxicity changes during nano-ZVI/PS treatment. Considering the treatability results and incomplete mineralization, complete detoxification was in fact not expected. Similarly, during hot PS treatment of aqueous 20 mg/L BPA solution, acute toxicity tests conducted with V. fischeri indicated that the inhibitory effect first increased, but decreased thereafter, which could be attributed to the transformation and subsequent disappearance of different types of degradation products. These were identified as benzaldehyde, p-isopropenyl phenol, 2,3-dimethyl benzoic acid, 3-hydroxy-4-methyl-benzoic acid, ethylene glycol monoformate and sucinic acid. Moreover, some degradation intermediates, having molecular sizes greater than that of BPA, were qualified revealing that preliminary dimerization reactions may become important during the initial stages of BPA transformation and are usually more toxic than BPA itself (Olmez-Hanci et al. 2013). According to Zazo et al. (2007) and Sanchez-Polo et al. (2013), the initial increase and subsequent reduction in acute toxicity during application of AOPs based on HO· and SO₄²⁻ corresponds to the formation and disappearance of aromatic hydroxylated intermediates, giving rise to relatively low molecular weight carboxylic acids of rather low toxicity. Currently, the identification of degradation products is in progress and will be reported in future work.

CONCLUSIONS AND RECOMMENDATIONS

Air-stable, zero-valent-iron nanoparticles were employed as heterogeneous catalysts for the treatment of aqueous BPA solutions. The common oxidants H₂O₂ (HP) and S₂O₅²⁻ (PS) were applied to enhance BPA and TOC removals. The effect of reaction temperature was also investigated. The following conclusions could be derived from this work:

- BPA degradation with ZVI/PS was faster than ZVI/HP treatment.
- Poor TOC removals were observed during ZVI/HP treatment (≈10%).
Complete BPA degradation accompanied with significant TOC removals (>80%) was achieved with ZVI/PS treatment, in particular at 50 °C.

Treatment performance depended upon the type of oxidant (HP, PS) applied as well as oxidant concentration and reaction temperature.

Oxidants (HP, PS) were totally consumed in 30–40 minutes during ZVI/PS and 50–60 minutes during ZVI/HP treatment.

The toxic effect of BPA increased during the initial stages of oxidation most probably due to the formation of relatively toxic intermediates, but gradually decreased as the treatment progressed, showing an overall fluctuating behavior.

The sensitivity of the selected test organisms (V. fischeri; P. subcapitata) varied appreciably. Hence, it is advisable to use more than one organism to follow changes in toxicity profiles during treatment.

REFERENCES

Acknowledgements

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B. Girit et al. | Bisphenol A treatment with nano-ZVI in the presence of oxidants


O’Connor, J. C. & Chapin, R. E. 2005 Critical evaluation of observed adverse effects of endocrine active substances on reproduction and development, the immune system, and the nervous system. Pure Appl. Chem. 75, 2099–2123.


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