

Zero-valent aluminum-mediated degradation of Bisphenol A in the presence of common oxidants

I. Arslan-Alaton, T. Olmez-Hanci, M. Dogan and T. Ozturk

ABSTRACT

The use of a commercial, nano-scale zero-valent aluminum (ZVA) powder was explored for the treatment of aqueous Bisphenol A (BPA). The study focused on the (i) activation of hydrogen peroxide (HP) and persulfate (PS) oxidants with ZVA to accelerate BPA degradation, (ii) comparison of the treatment performance in pure and real surface water (SW) samples, (iii) effects on toxicity and (iv) reuse potential of ZVA nanoparticles after ZVA/HP and ZVA/PS treatments. In pure water, ZVA coupled with HP or PS provided an effective means of BPA treatment particularly when PS was employed as the oxidant. On the other hand, in BPA-spiked SW, the ZVA/HP treatment combination outperformed ZVA/PS oxidation in terms of BPA removal, whereas ZVA/PS oxidation was superior in terms of organic carbon removal. According to the bioassays conducted in pure and real SW samples with the marine photobacteria *Vibrio fischeri* and the freshwater microalgae *Pseudokirchneriella subcapitata*, the toxicity response of BPA and its oxidation products was sensitive to the test organism and water matrix. The inhibitory effect of the reaction solution increased at the early stages of ZVA/PS treatment. The reuse potential of the ZVA/HP treatment system was higher than that of the ZVA/PS treatment system.

Key words | Bisphenol A, nano-scale zero-valent aluminum, oxidants, reuse, surface water, toxicity

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INTRODUCTION

Endocrine disrupting compounds (EDCs) can mimic hormones, bioaccumulate in sewage sludge and soil sediments, may cause reproductive toxicity and cancer besides other harmful effects on human health and the ecological environment (Sharma *et al.* 2016). Among the potential EDCs, Bisphenol A (BPA) is one of the most well-known and studied EDCs. It is an important raw material being widely used as a monomer for the production of polycarbonates, epoxy resins, plasticizers, flame retardants, dental sealants, thermal papers, printing ink, antioxidants, paints and other chemicals (Li *et al.* 2016). It leaches into the environment from utility items such as toys, baby feeding bottles, plastics and tiffin carriers. Considering its estrogenic, mutagenic and teratogenic effects, finding effective and ecotoxicologically safe means of eliminating BPA from the environment has become a priority task. In principle, conventional municipal water and wastewater treatment systems are not designed for the removal of refractory micropollutants such as EDCs (Kasprzyk-Hordern *et al.* 2009; Nie *et al.* 2012; Zhao *et al.* 2016). Previous

studies have demonstrated that BPA was poorly removed in conventional wastewater treatment processes; its half-life in aerobic sludge systems was reported to vary from days to weeks (Hu *et al.* 2007).

Recently, a number of alternative treatment methods, such as biodegradation with algae, fungal treatment, adsorption and advanced oxidation processes (AOPs) including sonolysis, catalytic ozonation, photochemical oxidation, photocatalysis as well as the Fenton's reagent and Photo-Fenton processes have been explored for the degradation of BPA (Li *et al.* 2016; Sharma *et al.* 2016). Among these, the use of zero-valent metals such as zero-valent iron (ZVI; $E^{\circ} = -0.43$ eV) has received major attention recently due to its unique surface properties, high abundance and superior thermodynamic driving force (reactivity). Nano-scale ZVI (n-ZVI) has already been explored for the treatment of endocrine disrupting chemicals, heavy metals, pesticides, halogenated phenol derivatives, azo dyes, bromate, nitrate and perchlorate found in ground- and surface water (SW) (Shi *et al.* 2011; Cheng *et al.* 2015; Girit *et al.*

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2015; Dogan et al. 2016; Lin & Lin 2016). Nevertheless, n-ZVI tends to aggregate due to its high surface energy and intrinsic magnetic interactions (Crane & Scott 2012). An oxide layer often forms on the surface of n-ZVI when exposed to the atmosphere and water (Qiu et al. 2011; Johnson et al. 2013). Aggregation and immediate corrosion are two major drawbacks of ZVI/n-ZVI that limit its applicability and reactivity (Gu et al. 2010; He et al. 2010; Shi et al. 2011; Wang et al. 2015).

Like the relatively well-known and studied ZVI, zero-valent aluminum (zero valent aluminum (ZVA); $E^\circ = -1.66$ eV) may activate molecular oxygen to produce reactive oxygen species (ROS) including hydrogen peroxide (HP), the superoxide (O_2^\bullet) and hydroxyl (HO^\bullet) radical. The so-called 'ZVA/ H^+ / O_2 treatment system' involves two treatment mechanisms, namely the corrosive dissolution of Al^{3+} and simultaneous reduction of O_2 to hydroperoxyl radical (HO_2^\bullet), leading to the formation of HP and generation of HO^\bullet by a consecutive electron transfer mechanism from ZVA to O_2 producing HP as given in the below reactions (Yan et al. 2013; Cheng et al. 2015).

ZVA/ H^+ / O_2

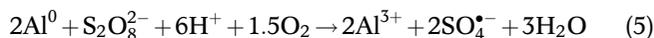


It has been reported that the degradation of micropollutants by the ZVA/ H^+ / O_2 process is a relatively slow and thus inefficient treatment system (Cheng et al. 2015; Lin & Lin 2016; Arslan-Alaton et al. 2017a, 2017b). More specifically, depending on the surface properties of ZVA as well as the pH of the reaction solution, an induction period (a lag-phase) is typically being observed for the degradation of pollutants with the ZVA/ H^+ / O_2 treatment system. Therefore, external addition of common oxidants such as HP or persulfate (PS) is expected to enhance pollutant removal rates and efficiencies. Upon activation of ZVA with HP (reaction Equation (4)*) or PS (reaction Equation (5)) oxidants, HO^\bullet and sulfate radical ($SO_4^{\bullet-}$) formations are accelerated, since the electron transfer from the ZVA surface to the oxidants starts directly with Fenton-like redox reactions (Cheng et al. 2015; Dogan et al. 2016; Arslan-Alaton et al. 2017a, 2017b);

ZVA/HP (same as reaction Equation (4) shown above, but with external HP addition)



ZVA/PS



Activated PS has a widespread application range for environmental remediation (Chen et al. 2014; Wang et al. 2014; Wang & Liang 2014; Zhao et al. 2014; Wang et al. 2016), as formed $SO_4^{\bullet-}$ reacts with organic chemicals causing either partial or complete mineralization (Ding et al. 2013; Paul et al. 2014; Zhang et al. 2015). In-situ remediation with activated PS oxidation may be preferred over HP-induced, HO^\bullet -based oxidation processes, as the PS anion is more stable and may be transported further in the subsurface before being activated for contaminant degradation (Waldermer et al. 2007; Yan et al. 2013). For effective pollutant removal with ZVA activation of HP or PS, an acidic pH environment ($pH < 4$) is essential because a high pH slows down ZVA surface corrosion, which is critical for the surface redox reaction (Bokare & Choi 2009; Lien et al. 2010; Cheng et al. 2015; Zhang et al. 2015).

Considering the above mentioned potential of ZVA-activated oxidation of micropollutants found in water and wastewater, the present study focused on the degradation of aqueous BPA, selected as the model EDC and micropollutant, with the ZVA/HP and ZVA/PS treatment systems. HP and PS were selected as they are common oxidizing agents and activated with nano-scale ZVA to enhance BPA oxidation. In order to question the real-world application and practical integration potential of ZVA oxidation process for water and wastewater treatment, experiments were also conducted in pure water (PW) and real SW samples. Moreover, the ecotoxicological risk of the treatment systems was examined by conducting toxicity tests with the marine photobacteria *Vibrio fischeri* (*V. fischeri*) and the freshwater microalgae *Pseudokirchneriella subcapitata* (*P. subcapitata*). The sustainability and reuse potential of the proposed material was also questioned within the scope of this experimental study. It should be emphasized that so far the reuse potential of ZVA as well as the ecotoxicological safety of the ZVA/HP and ZVA/PS treatment processes have not been investigated. These issues are thought to be important criteria to evaluate the feasibility and real-scale applicability of these water treatment systems for micropollutant removal.

MATERIALS AND METHODS

Materials

High purity (>99.5%) ZVA nanoparticles with an average particle size of 100 nm and a specific Brunauer-Emmett-Teller (BET) surface area of 10–20 m²/g were purchased from US Research Nanomaterials, Inc. (Houston, Texas). BPA (228 g/mol; C₁₅H₁₆O₂; CAS No. 80-05-7; 99.9%), potassium persulfate (PS; 270 g/mol; CAS No. 7727-21-1; >99.5%), H₂O₂ (HP; 34 g/mol; CAS No. 7722-84-1; 30%, w/w) were obtained from Merck (Germany). An initial BPA concentration of 2 mg/L was selected in this work for several reasons. Firstly, 2 mg/L is an appropriate concentration to easily and accurately follow BPA abatement kinetics via instrumental analyses; secondly, it is a suitable working range that could easily be compared with previous related work and thirdly, it has been reported in the scientific literature that BPA concentrations in the ‘mg/L’ range are the highest concentrations being encountered in natural/engineered systems such as in landfill leachate (Yamamoto & Yasuhara 1999; Yamamoto *et al.* 2001). Hence, 2 mg/L can be considered as a worst-case scenario in terms of BPA concentration. The real SW sample was taken from the influent of a local water treatment plant located in Istanbul, Turkey. The environmental characteristics of the SW sample are presented in Table 1. The SW sample contained 6.4 mg C/L dissolved organic carbon (DOC) and the added BPA (2 mg/L) only contributed to 10% of the reaction solution’s total DOC content.

Experimental procedures

Several control (ZVA only, HP and PS only experiments) and treatability (optimization) experiments were carried out in 500 mL-capacity glass beakers under continuous stirring at 150 rpm to ensure uniform ZVA dispersion, mixing and oxygen saturation. Firstly, aqueous BPA solution (2 mg/L, 8.8 μM) was prepared in PW, and its pH was adjusted to 3 with concentrated H₂SO₄ solution. Finally, the oxidant (HP or PS) was introduced at an appropriate concentration to initiate the oxidation reaction. Experimental conditions such as an acidic reaction pH (=3) and ZVA concentration (1 g/L) were selected considering our previous works (Dogan *et al.* 2016; Arslan-Alaton *et al.* 2017a, 2017b) and former related studies (Bokare & Choi 2009; Lien *et al.* 2010; Zhao *et al.* 2010; Ding *et al.* 2013; Cheng *et al.* 2015). BPA-spiked, real SW samples were subjected to ZVA/HP and ZVA/PS treatment under optimized

Table 1 | Characteristics of the real SW sample

Parameter	Unit	Value
TOC	mg/L	6.78
DOC	mg/L	6.42
Alkalinity	mg CaCO ₃ /L	115
Hardness	mg CaCO ₃ /L	110
Colour	Pt-Co Units	48
SS	mg/L	12
UV ₂₅₄	cm ⁻¹	0.202
UV ₂₈₀	cm ⁻¹	0.154
UV ₃₅₀	cm ⁻¹	0.051
Cl ⁻	mg/L	21
Br ⁻	mg/L	0
F ⁻	mg/L	0.08
NO ₂ ⁻	mg/L	0
NO ₃ ⁻	mg/L	2.2
SO ₄ ²⁻	mg/L	15.5
PO ₄ ³⁻	mg/L	0.17
pH	-	7.9

reaction conditions. Every experiment was conducted in duplicate and whenever unusual or erroneous results were obtained, the experiment was repeated.

Analytical procedures and instrumental analyses

The real SW sample was characterized in terms of conventional environmental parameters according to APHA (2005). All samples containing ZVA were immediately filtered through 0.22 micron Millipore membranes (Millipore Corp., USA) to separate the ZVA nanoparticles from the treatment solution and cease the reaction. Thereafter, samples were directly analyzed for remaining BPA, DOC, HP and PS concentrations. The pH of the original and treated samples was adjusted to neutral (7.0 ± 0.2) values with concentrated NaOH solution and the formed Al(OH)₃ flocs were removed by filtration with 0.22 micron syringe membranes before conducting the bioassays. BPA analysis was performed on a high performance liquid chromatography (HPLC) (Agilent 1100 Series, Agilent Technologies, USA) equipped with a diode array detector (G1315A, Agilent Series) and a Symmetry C18 (3.9 mm × 150 mm, Waters, USA) reversed phase column. The detection wavelength and column temperature were set as 214 nm and 25 °C, respectively. The mobile phase consisted of acetonitrile/water (50/50, v/v) used at a flow rate of

1.0 mL/min. The calibration curve indicated a good linear correlation for BPA concentrations in the range of 0.025–2 mg/L ($R = 0.999$), with limit of detection of 8 $\mu\text{g/L}$ for the lowest injected standard that gave a signal-to-noise ratio of at least three and an accuracy of 80–95%. The quantification limit of BPA for an injection volume of 100 μL was calculated as 10 times the signal-to-noise ratio (28.0 $\mu\text{g/L}$). The organic carbon (total organic carbon (TOC) and dissolved organic carbon (DOC)) contents of the samples were measured on a V_{PCN} analyzer (Shimadzu, Japan). Residual HP and PS concentrations were traced by employing colorimetric methods according to Klassen *et al.* (1994) and Villegas *et al.* (1963), respectively.

Toxicity bioassays

The toxicity experiments were conducted with untreated and treated BPA in PW and real SW samples. Toxicity towards the photobacterium *V. fischeri* was measured using a commercial bioassay kit (BioToxTM, Aboatox Oy, Finland) according to the ISO 11348-3 test protocol (2008). Percent relative photoluminescence inhibition rates were calculated after 15 min incubation on the basis of a toxicant-free control.

The toxicity towards the freshwater microalgae *P. subcapitata* was examined using Algaltoxkit FTM (MicroBioTests, Inc., Belgium) microbiotests according to ISO 8692 (2012). At the start and after 24, 48 and 72 h, the cell density in the test replicates was measured on 10 cm path-length cuvettes at 670 nm, using a Jenway 6300 model spectrophotometer (Bibby Scientific, USA). Percent relative growth inhibition rates were calculated after an incubation period of 72 h on the basis of a toxicant-free control.

In order to eliminate their effect on toxicity measurements, residual PS was removed with sodium thiosulfate (158 g/mol; $\text{Na}_2\text{S}_2\text{O}_3$; CAS No. 7772-98-7; >97%; Merck, Germany), which was found to be the most suitable quenching agent to eliminate the interference of PS in the *V. fischeri* and *P. subcapitata* bioassays (Olmez-Hanci *et al.* 2014).

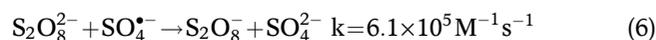
RESULTS AND DISCUSSION

BPA treatability experiments

Preliminary baseline experiments have indicated that in the absence of either ZVA (1 g/L) or oxidants (0.5 mM HP or 0.5 mM PS), only poor and slow BPA removals were obtained ($\text{pH} = 3$, $t = 120$ min). BPA degradation was limited to <5% and <10% at the end of HP or PS oxidations

and ZVA/ H^+/O_2 treatment, respectively (data not shown). That the ZVA/ H^+/O_2 treatment process as well as HP, PS oxidations in the absence of activation are not appropriate for effective micropollutant removal has already been confirmed in our previous studies (Dogan *et al.* 2016; Arslan-Alaton *et al.* 2017a, 2017b). Some preliminary optimization experiments were also carried out in PW at varying HP and PS concentrations (0–2.5 mM) activated with 1 g/L ZVA for a reaction period of 120 min at $\text{pH} 3$. The effect of increasing the oxidant (HP and PS) concentrations from 0 mM (e.g. 1 g/L ZVA only) to 2.5 mM is presented in Supporting Figures S1 and S2, respectively (available with the online version of this paper). From these figures it is evident that optimum HP and PS concentrations exist on the basis of BPA removal. Figure 1 shows time-dependent BPA abatements for the ZVA/HP (a) and ZVA/PS (b) treatment systems at two different oxidant concentrations (0.25 mM and 0.50 mM) for which the highest BPA removals were obtained.

Similar to the well-known inhibitory effect of excessive HP concentrations on pollutant removal rates, high concentrations of PS could act as $\text{SO}_4^{\bullet-}$ scavengers and compete with BPA and its degradation products for ROS (Ding *et al.* 2013; Xiong *et al.* 2014):



From Figure 1(a), showing the results for ZVA/HP treatment, it is evident that complete BPA removal could only be achieved with 0.5 mM HP at $t = 60$ min, whereas in the presence of 0.25 mM HP, prolonged treatment times would be required for the same target removal. In the case of ZVA/PS treatment, both 0.25 mM and 0.50 mM PS are capable of 100% BPA removal in 40–60 min. Moreover, BPA abatements are slightly faster for ZVA/0.25 mM PS treatment as compared with ZVA/0.50 mM PS treatment. It has been postulated that $\text{SO}_4^{\bullet-}$ has a longer lifetime ($3\text{--}4 \times 10^{-5}$ s) than HO^{\bullet} (2×10^{-8} s), therefore, $\text{SO}_4^{\bullet-}$ radicals have more chances of reacting with organic pollutants (Ghanbari *et al.* 2016). The obtained results revealed that the $\text{SO}_4^{\bullet-}$ -based oxidation system (ZVA/PS) outperformed the HO^{\bullet} -based oxidation system (ZVA/HP), since BPA removal was faster and occurred at a lower PS concentration. In previous experimental work carried out with free radical probe chemicals (secondary and tertiary alcohols), it could be demonstrated that HO^{\bullet} (ZVA/HP)- and $\text{SO}_4^{\bullet-}$ (ZVA/PS)-driven oxidation systems exhibited different reactivities and selectivities for different model pollutants and their degradation products (Arslan-Alaton *et al.* 2017a, 2017b), which could explain the differences in BPA and DOC

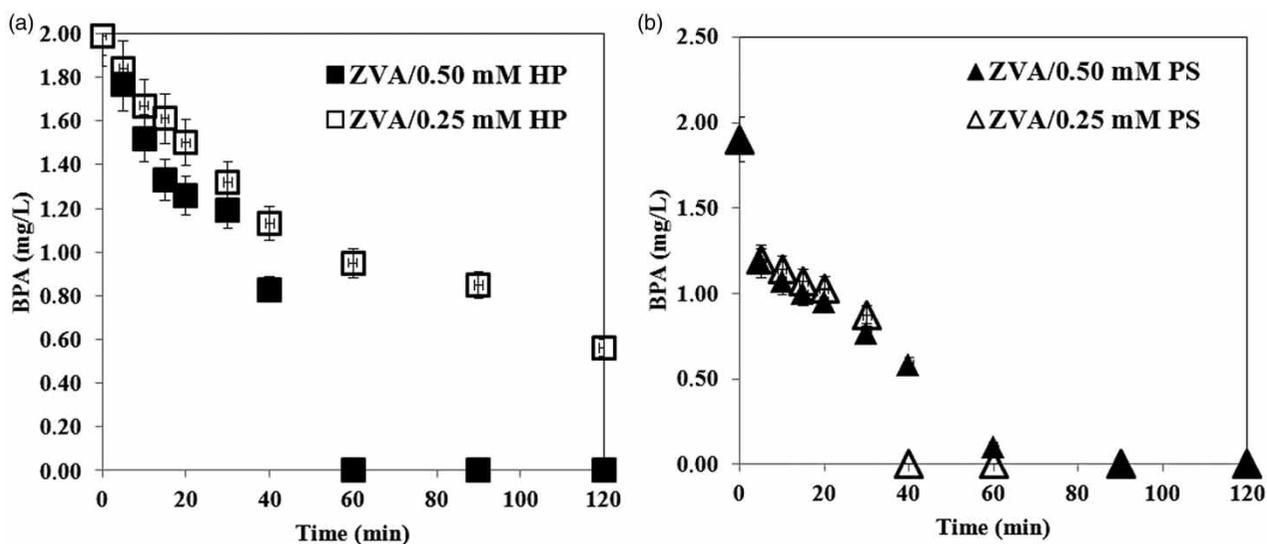


Figure 1 | Changes in BPA concentrations during (a) ZVA/HP (0.25 mM and 0.50 mM HP) and (b) ZVA/PS (0.25 mM and 0.50 mM PS) treatments. Experimental conditions: BPA = 2 mg/L; ZVA = 1 g/L; pH = 3.0; t = 120 min.

removals being observed during ZVA/HP and ZVA/PS treatment processes.

Changes in HP and PS concentrations were also followed during ZVA/HP and ZVA/PS treatments, respectively. The relationship between BPA removals and oxidant (HP, PS) consumptions was also evaluated for varying HP (0.25–2.5 mM) and PS (0.25–2.5 mM) concentrations for 1 g/L ZVA; pH3; t = 120 min. From the obtained findings, it could be concluded that a fairly positive correlation existed for percent BPA removals and percent HP consumptions (see Supporting Figure S3 for details, available with the online version of this paper), while no relationship was evident between percent BPA removals and percent PS consumptions (see Supporting Figure S4 for details, available online). This could be attributed to the fact that HP and PS reactivities and decomposition rates corresponding to reduction in their concentrations do not necessarily indicate that their consumption is due to BPA oxidation; obviously, BPA degradation does not involve direct HP or PS oxidation but indirect, free radical-based degradation reactions which are much more complex (Girit et al. 2015; Diao et al. 2016).

For the forthcoming treatability experiments in real water samples, it was decided to work under the following reaction conditions: 0.25 mM PS, 0.50 mM HP, 1 g/L ZVA, pH = 3 and t = 120 min.

BPA treatability in real SW

Figure 2 depicts ZVA-mediated BPA abatements observed during ZVA/HP and ZVA/PS treatments of BPA in PW

and real SW. For both treatment systems, 100% BPA removal was obtained under optimized treatment conditions (0.50 mM HP, 0.25 mM PS, 1 g/L ZVA, pH3; 120 min). In the SW samples, BPA removals remained high (96% after 120 min) with the ZVA/HP treatment system, although at an appreciably slower rate than in the PW sample. However, BPA removals dramatically decreased from 100% to 51% for the ZVA/PS treatment combination. Different from PW, the SW sample contains a variety of organic and inorganic compounds (humic materials, sulfate, chloride, phosphate, etc.), which are all known to mostly inhibit (slow down) the removal rates and efficiencies of target pollutants (Wang et al. 2016). The inhibitory effect might change according to the dominant ROS in the reaction medium. In other words, for more selective treatment systems such as the $\text{SO}_4^{\bullet-}$ -based ZVA/PS process, competition of BPA molecules with organic/inorganic constituents of the water matrix could hinder its effective degradation (Diao et al. 2016; Wang et al. 2016; Arslan-Alaton et al. 2017a, 2017b), as in the present study.

On the other hand, a different profile was observed in terms of the DOC parameter, which was also followed during BPA treatment with ZVA/HP and ZVA/PS in SW; DOC removals were found to be 9% and 29% at the end of 120 min treatment with ZVA/HP and ZVA/PS, respectively (Figure 3). This observation could be explained as follows: BPA removal was retarded most probably by the organic carbon content of the SW sample (see Table 1), which was preferentially oxidized instead of BPA and/or its degradation products during ZVA/PS treatment. However, during the relatively less selective, HO^{\bullet} -based ZVA/HP process, BPA

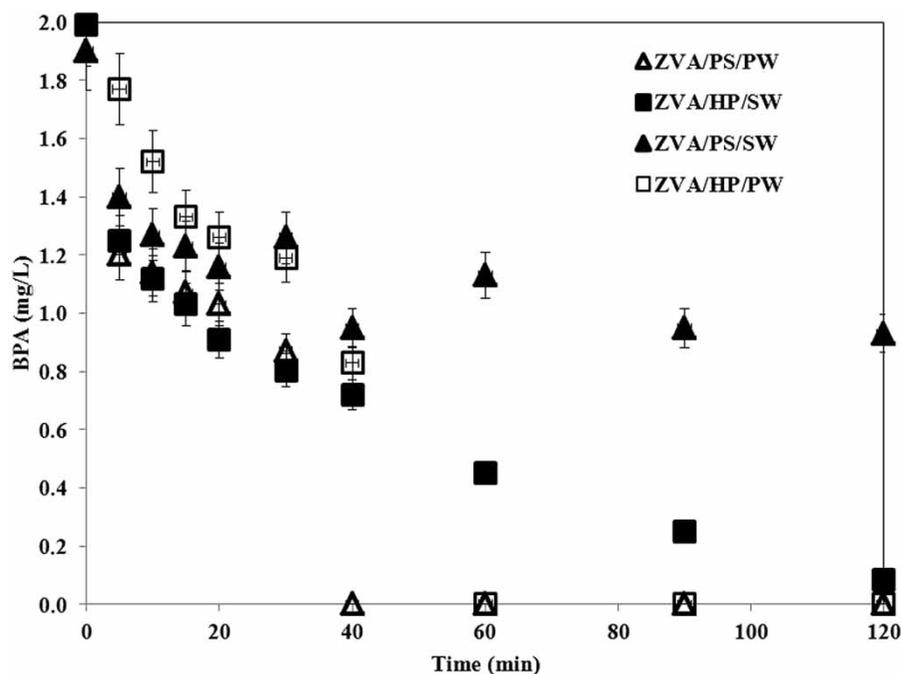


Figure 2 | Changes in BPA concentrations during ZVA/HP and ZVA/PS treatments in PW and SW samples. Experimental conditions: BPA = 2 mg/L; HP = 0.50 mM; PS = 0.25 mM; ZVA = 1 g/L; pH = 3.0; t = 120 min; original DOC of the SW = 6.4 ± 0.2 mg/L.

degradation products and DOC were competing for ROS- HO^\bullet in this case, resulting in only 9% DOC removal when BPA is being subjected to ZVA/HP treatment in SW. Consequently, performance in target pollutant (BPA) and mineralization

abatement is strongly influenced by the type of treatment process (dominant ROS type) and the effluent matrix (water sample characteristics), which has also been evidenced in former related works (Diao *et al.* 2016; Wang *et al.* 2016;

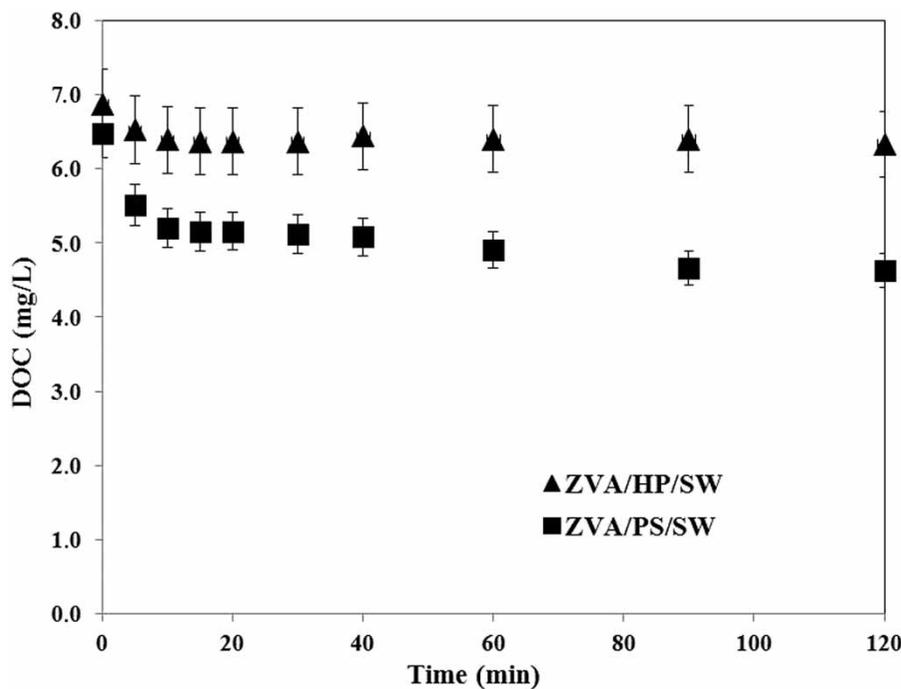


Figure 3 | Changes in DOC concentrations during ZVA/HP and ZVA/PS treatments in SW samples. Experimental conditions: BPA = 2 mg/L; HP = 0.50 mM; PS = 0.25 mM; ZVA = 1 g/L; pH = 3.0; t = 120 min; original DOC of the SW = 6.4 ± 0.2 mg/L.

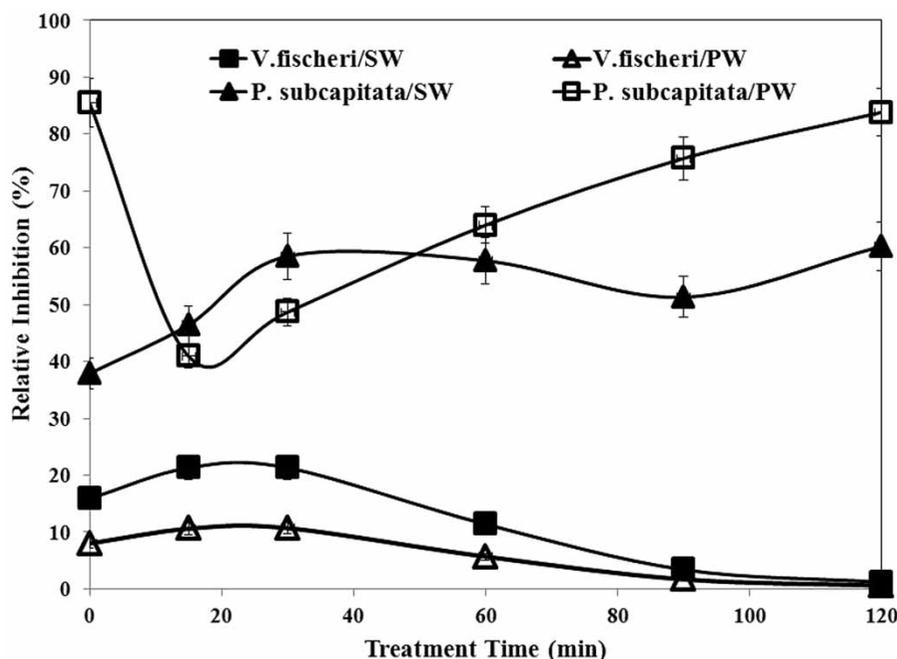


Figure 4 | 15 min-*V. fischeri* and 72 h-*P. subcapitata* toxicity evolution based on percent relative inhibition rates observed during ZVA/PS treatment of BPA in PW and SW samples. Experimental conditions: BPA = 2 mg/L; PS = 0.25 mM; ZVA = 1 g/L; pH = 3.0; t = 120 min; original DOC of the SW = 6.4 ± 0.2 mg/L.

Arslan-Alaton et al. 2017a, 2017b). For example, in Wang et al. (2016), natural organic matter (NOM), the major component of DOC in SWs greatly inhibited the degradation of alachlor in the ZVI/PS treatment system, with removal rates of 97.8%, 90.0%, 79.7% and 78.6% at concentrations of 0, 1, 3 and 5 mg/L NOM, respectively.

For the inhibitory effect of inorganic ions, Tan et al. (2013) claimed that the interference of Cl^- and other anions exhibited correlation with the generation rate of $\text{SO}_4^{\bullet-}$. According to their study, when the concentration of Cl^- was ≥ 100 mmol/L, $\text{SO}_4^{\bullet-}$ was quenched to a great extent. Similar findings were reported for the inhibitory effect of other ions such as sulfate and phosphate (Yang et al. 2016).

Ecotoxicological assessment

Bioassays and battery tests provide essential information about the ecotoxicological safety of AOPs (Olmez-Hanci et al. 2014). There are only few papers reporting toxicity assessment for the ZVA/HP and ZVA/PS treatment systems (Temiz et al. 2016; Xu et al. 2016; Arslan-Alaton et al. 2017a, 2017b). Typically, an increase is observed at the initial stages of treatment due to the accumulation of oxidation byproducts that are more inhibitory/toxic than the original pollutant (Temiz et al. 2016; Xu et al. 2016; Arslan-Alaton et al. 2017a, 2017b). In this work, toxicity studies were

conducted for ZVA/PS treatment of BPA in PW and SW samples. The ZVA/PS treatment system was preferred as an example for the ecotoxicological risk assessment of ZVA activated treatment systems. Figure 4 displays changes in percent relative inhibition values being obtained during BPA treatment with the ZVA/PS system in both water samples. BPA toxicity appeared to be substantially higher for *P. subcapitata* (in the range of 38–85%) than for *V. fischeri* (in the range of 10–20%), indicating that *P. subcapitata* was more sensitive to BPA and its degradation products than *V. fischeri*. As is also apparent from Figure 4, the toxicity patterns depended upon the type of water (whether PW or SW matrix). For example, the percent relative inhibition rate of the untreated BPA sample was as high as 85% in SW, but only 38% in PW for *P. subcapitata*, whereas it dropped from 16% in SW to 8% in PW for *V. fischeri* in the untreated BPA sample. Ultimately, the toxicity towards *P. subcapitata* could not be eliminated during ZVA/PS treatment in PW and SW samples. Moreover, at the end of treatment, *P. subcapitata* toxicities remained high and even increased, most speculatively due to the inhibitory effect of incomplete mineralization (BPA oxidation) products. Percent relative inhibition rates (*P. subcapitata* toxicities) in treated SW and PW were determined as 60% and 84%, respectively.

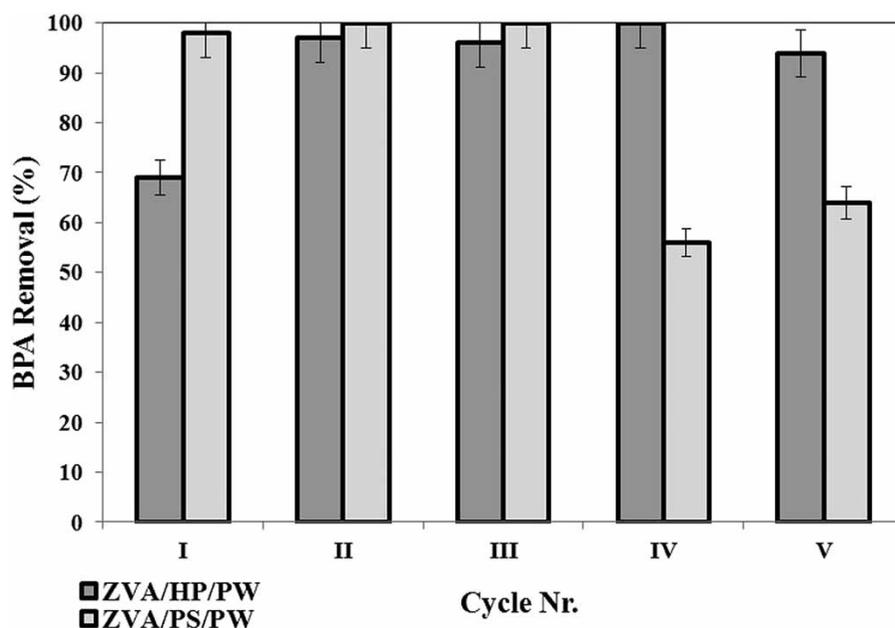


Figure 5 | BPA removal efficiencies (%) obtained after ZVA/PS treatment in PW with ZVA being reused for five consecutive cycles. Experimental conditions: BPA = 2 mg/L; HP = 0.50 mM; PS = 0.25 mM; ZVA = 1 g/L; pH = 3.0; t = 120 min.

It should also be noted here that in both cases the toxic response was neither attributable to Al ions, which were entirely removed in the form of $\text{Al}(\text{OH})_3$ flocs after a pH-re-adjustment, precipitation and filtration step, nor to the accumulation of sulfate or other forms of S (sulfur) during ZVA/PS treatment experiments, as was already confirmed in our previous works (Arslan-Alaton *et al.* 2017a, 2017b).

ZVA reuse potential

The possibility of ZVI and ZVA reuse after several cycles has already been examined in related work for activation of HP and PS as well (Zhang *et al.* 2016). In order to explore the sustainability of the process, ZVA was re-used in five consecutive cycles for BPA treatment with the ZVA/HP and ZVA/PS processes in PW after thorough rinsing with deionized water, 0.22 micron-filtration and drying at 110 °C for 5 h. Figure 5 displays percent BPA removal efficiencies obtained after each step of the reuse cycle. As can be seen in Figure 5, BPA removals remained in the range of 90–100% after ZVA/HP treatment for five consecutive cycles in the presence of 0.50 mM HP, whereas in the case of ZVA/PS treatment with 0.25 mM PS, BPA removal dropped from 100% to around 60% after the 4th and 5th reuse cycles. From the above findings, it is obvious that during ZVA/HP treatment it would be possible to reuse ZVA more often than during ZVA/PS which is an important

criterion for the examination of real-scale process integration and feasibility.

CONCLUSIONS AND RECOMMENDATIONS

In the present study, the treatability of BPA, which was selected as a model micropollutant and endocrine disrupting chemical, with ZVA-activated HP and PS oxidation in PW and SW samples, was investigated. Treatability (BPA, DOC removal) performance, oxidant consumption, ecotoxicological assessment and ZVA reuse potential in the presence of HP and PS have demonstrated that both proposed treatment systems (ZVA/HP and ZVA/PS) have their advantages and limitations depending upon different factors affecting these processes. In this respect, the following main conclusions could be drawn from this study:

- In terms of BPA abatement rates and efficiencies in PW, the ZVA/PS treatment system outperformed ZVA/HP treatment; complete BPA removal was achieved within a shorter treatment period (40 min instead of 60 min) and at a lower oxidant concentration (0.25 mM PS instead of 0.50 mM HP).
- The situation was different in the real SW sample; the ZVA/HP treatment system was more robust to the water sample matrix (organic and inorganic ingredients) than the ZVA/PS treatment system. After a treatment

period of 120 min, 96% and 51% BPA removals were achieved with the ZVA/HP and ZVA/PS treatment processes, respectively.

- Regarding the DOC profiles being obtained during ZVA/HP and ZVA/PS treatment of BPA in real SW samples; the ZVA/PS system was superior in terms of mineralization rates. After 120 min, 9% and 29% DOC removals were obtained with the ZVA/HP and ZVA/PS treatment systems, respectively.
- *P. subcapitata* toxicity could not be reduced and remained high after 120 min ZVA/PS treatment of BPA. Ultimate percent relative *P. subcapitata* inhibitions were obtained as 60% in SW and 84% in PW. On the other hand, BPA exhibited low *V. fischeri* toxicities (16% in SW and 8% in the PW). Percent relative *V. fischeri* inhibitions decreased to non-toxic values ($\approx 2\%$) after 120 min ZVA/PS treatment.
- The reuse potential of ZVA after ZVA/HP and ZVA/PS treatments of BPA in PW was examined for five consecutive cycles. It appeared that the ZVA/HP process was superior to the ZVA/PS process in terms of ZVA reuse for BPA removal; even after five cycles, BPA removal was 94%, whereas it varied between 56% and 64% after the fourth and fifth cycles of ZVA/PS treatment.

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REFERENCES

- APHA 2005 *Standard Methods for the Examination of Water and Wastewater*, 21st edn. American Public Health Association, Washington, DC.
- Arslan-Alaton, I., Olmez-Hanci, T., Khoei, S. & Fakhri, H. 2017a Oxidative degradation of Triton X-45 using zero valent aluminum in the presence of hydrogen peroxide, persulfate and peroxymonosulfate. *Catal. Today* **280**, 199–207.
- Arslan-Alaton, I., Olmez-Hanci, T., Korkmaz, G. & Sahin, C. 2017b Removal of iopamidol, an iodinated X-ray contrast media, by zero-valent aluminum-activated H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ oxidation. *Chem. Eng. J.* **318**, 64–75.
- Bokare, A. D. & Choi, W. 2009 Zero-valent aluminum for oxidative degradation of aqueous organic pollutants. *Environ. Sci. Technol.* **43**, 7130–7135.
- Chen, W. S., Jhou, Y. C. & Huang, C. P. 2014 Mineralization of dinitrotoluenes in industrial wastewater by electro-activated persulfate oxidation. *Chem. Eng. J.* **252**, 166–172.
- Cheng, Z., Fu, F., Pang, Y., Tang, B. & Lu, J. 2015 Removal of phenol by acid-washed zero-valent aluminium in the presence of H_2O_2 . *Chem. Eng. J.* **260**, 284–290.
- Crane, R. A. & Scott, T. B. 2012 Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. *J. Hazard. Mater.* **211–212**, 112–125.
- Diao, Z.-H., Xu, X.-R., Jang, D., Kong, L.-J., Sun, Y.-X., Hua, Y.-X., Hao, Q.-W. & Chen, H. 2016 Bentonite-supported nanoscale zero-valent iron/persulfate system for the simultaneous removal of Cr(VI) and phenol from aqueous solutions. *Chem. Eng. J.* **302**, 213–222.
- Ding, Y., Zhu, L., Wang, N. & Tang, H. 2013 Sulfate radicals induced degradation of tetra-bromobisphenol A with nanoscaled magnetic CuFe_2O_4 as a heterogeneous catalyst of peroxymonosulfate. *Appl. Catal. B Environ.* **129**, 153–162.
- Dogan, M., Ozturk, T., Olmez-Hanci, T. & Arslan-Alaton, I. 2016 Persulfate and hydrogen peroxide-activated degradation of bisphenol A with nano-scale zero-valent iron and aluminum. *J. Adv. Oxid. Technol.* **19**, 266–275.
- Ghanbari, F., Moradi, M. & Gohari, F. 2016 Degradation of 2,4,6-trichlorophenol in aqueous solutions using peroxymonosulfate/activated carbon/UV process via sulfate and hydroxyl radicals. *J. Water Process Eng.* **9**, 22–28.
- Girit, B., Dursun, D., Olmez-Hanci, T. & Arslan-Alaton, I. 2015 Treatment of aqueous bisphenol A using nano-sized zero-valent iron in the presence of hydrogen peroxide and persulfate oxidants. *Water Sci. Technol.* **71** (12), 1859–1868.
- Gu, C., Jia, H. Z., Li, H., Teppen, B. J. & Boyd, S. A. 2010 Synthesis of highly reactive subnano-sized zero-valent iron using smectite clay templates. *Environ. Sci. Technol.* **44**, 4258–4263.
- He, F., Zhao, D. Y. & Paul, C. 2010 Field assessment of carboxymethyl cellulose stabilized iron nanoparticles for in situ destruction of chlorinated solvents in source zones. *Water Res.* **44**, 2360–2370.
- Hu, L. J., Chen, X., Tao, G. & Kekred, K. 2007 Fate of endocrine disrupting compounds in membrane bioreactor systems. *Environ. Sci. Technol.* **41**, 4097–4102.
- ISO 11348-3 2008 *Water Quality-Determination of the Inhibitory Effect of Water Samples on the Light Emission of *Vibrio fischeri**. International Organisation for Standardization, Geneva.
- ISO 8692 2012 *Water Quality-Freshwater Algal Growth Inhibition Test with Unicellular Green Algae*. International Organisation for Standardization, Geneva.
- Johnson, R. L., Nurmi, J. T., O'Brien Johnson, G. S., Fan, D., O'Brien Johnson, R. L., Shi, Z. Q., Salter-Blanc, A. J., Tratnyek, P. G. & Lowry, G. V. 2013 Field-scale transport and transformation of carboxymethylcellulose-stabilized nano zero-valent iron. *Environ. Sci. Technol.* **47**, 1573–1580.
- Kasprzyk-Hordern, B., Dinsdale, R. M. & Guwy, A. J. 2009 The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters. *Water Res.* **43**, 363–380.
- Klassen, N. V., Marchington, D. & McGowan, H. C. E. 1994 H_2O_2 determination by the I_5^- method and by KMnO_4 titration. *Anal. Chem.* **66**, 2921–2925.

- Li, S., Zhang, G., Wang, P., Zheng, H. & Zheng, Y. 2016 Microwave-enhanced Mn-Fenton process for the removal of BPA in water. *Chem. Eng. J.* **294**, 371–379.
- Lien, H. L., Yu, C. C. & Lee, Y. C. 2010 Perchlorate removal by acidified zero-valent aluminum and aluminum hydroxide. *Chemosphere* **80**, 888–893.
- Lin, K.-Y. A. & Lin, C.-H. 2016 Simultaneous reductive and adsorptive removal of bromate from water using acid-washed zero-valent aluminum (ZVA). *Chem. Eng. J.* **297**, 19–25.
- Nie, Y., Qiang, Z., Zhang, H. & Ben, W. 2012 Fate and seasonal variation of endocrine-disrupting chemicals in a sewage treatment plant with A/A/O process. *Sep. Purif. Technol.* **84**, 9–15.
- Olmez-Hanci, T., Arslan-Alaton, I. & Dursun, D. 2014 Investigation of the toxicity of common oxidants used in advanced oxidation processes and their quenching agents. *J. Hazard. Mater.* **278**, 330–335.
- Paul, J., Naik, D. B., Bhardwaj, Y. K. & Varshney, L. 2014 Studies on oxidative radiolysis of ibuprofen in presence of potassium persulfate. *Radiat. Phys. Chem.* **100**, 38–44.
- Qiu, X. Q., Fang, Z. Q., Liang, B., Gu, F. L. & Xu, Z. C. 2011 Degradation of decabromodiphenyl ether by nano zero-valent iron immobilized in mesoporous silica microspheres. *J. Hazard. Mater.* **193**, 70–81.
- Sharma, J., Mishra, I. M. & Kumar, V. 2016 Mechanistic study of photo-oxidation of Bisphenol-A (BPA) with hydrogen peroxide (H₂O₂) and sodium persulfate (SPS). *J. Environ. Manage.* **166**, 12–22.
- Shi, L. N., Zhang, X. & Chen, Z. L. 2011 Removal of chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron. *Water Res.* **45**, 886–892.
- Tan, C., Gao, N., Deng, Y., Rong, W., Zhou, S. & Lu, N. 2013 Degradation of antipyrine by heat activated persulfate. *Sep. Purif. Technol.* **109**, 122–128.
- Temiz, K., Olmez-Hanci, T. & Arslan-Alaton, I. 2016 Zero-valent iron-activated persulfate oxidation of a commercial alkyl phenol polyethoxylate. *Environ. Technol.* **37**, 1757–1767.
- Villegas, E., Pomeraz, Y. & Shellenberger, J. A. 1963 Colorimetric determination of persulfate with Alcian Blue. *Analyt. Chim. Acta* **29**, 145–148.
- Waldemer, R. H., Tratnyek, P. G., Johnson, R. L. & Nurmi, J. T. 2007 Oxidation of chlorinated ethenes by heat-activated persulfate: kinetics and products. *Environ. Sci. Technol.* **41**, 1010–1015.
- Wang, C.-W. & Liang, C. 2014 Oxidative degradation of TMAH solution with UV persulfate activation. *Chem. Eng. J.* **254**, 472–478.
- Wang, X., Wang, L. G., Li, J. B., Qiu, J. J., Cai, C. & Zhang, H. 2014 Degradation of acid orange 7 by persulfate activated with zero valent iron in the presence of ultrasonic irradiation. *Sep. Purif. Technol.* **122**, 41–46.
- Wang, W., Li, S. L., Lei, H., Pan, B. C. & Zhang, W. X. 2015 Enhanced separation of nanoscale zero valent iron (nZVI) using polyacrylamide: performance, characterization and implication. *Chem. Eng. J.* **260**, 616–622.
- Wang, Q., Yisheng, S., Gao, N., Chu, W., Deng, J., Xiang, S., Lu, X., Zhu, Y. & Wei, X. 2016 Degradation of alachlor with zero-valent iron activating persulfate. *J. Taiwan Inst. Chem. Eng.* **63**, 379–385.
- Xiong, X., Sun, B., Zhang, J., Gao, N., Shen, J., Li, J. & Guan, X. 2014 Activating persulfate by Fe⁰ coupling with weak magnetic field: performance and mechanism. *Water Res.* **62**, 53–62.
- Xu, Y., Ai, J. & Zhang, H. 2016 The mechanism of degradation of bisphenol A using the magnetically separable CuFe₂O₄/peroxymonosulfate heterogeneous oxidation process. *J. Hazard. Mater.* **309**, 87–96.
- Yamamoto, T. & Yasuhara, A. 1999 Quantities of bisphenol A leached from plastic waste samples. *Chemosphere* **38**, 2569–2576.
- Yamamoto, T., Yasuhara, A., Shiraishi, H. & Nakasugi, O. 2001 Bisphenol A in hazardous waste landfill leachates. *Chemosphere* **42**, 415–418.
- Yan, N., Liu, F. & Huang, W. Y. 2013 Interaction of oxidants in siderite catalyzed hydrogen peroxide and persulfate system using trichloroethylene as a target contaminant. *Chem. Eng. J.* **219**, 149–154.
- Yang, Y., Pignatello, J. J., Ma, J. & Mitch, W. A. 2016 Effect of matrix components on UV/H₂O₂ and UV/S₂O₈²⁻ advanced oxidation processes for trace organic degradation in reverse osmosis brines from municipal wastewater reuse facilities. *Water Res.* **89**, 192–200.
- Zhang, B. T., Zhang, Y., Teng, Y. H. & Fan, M. H. 2015 Sulfate radical and its application in decontamination technologies. *Crit. Rev. Env. Sci. Tec.* **45**, 1756–1800.
- Zhang, X., Feng, M., Qu, R., Liu, H., Wang, L. & Wang, Z. 2016 Catalytic degradation of diethyl phthalate in aqueous solution by persulfate activated with nano-scaled magnetic CuFe₂O₄/MWCNTs. *Chem. Eng. J.* **301**, 1–11.
- Zhao, J., Zhang, Y., Quan, X. & Chen, S. 2010 Enhanced oxidation of 4-chlorophenol using sulfate radicals generated from zero-valent iron and peroxydisulfate at ambient temperature. *Sep. Purif. Technol.* **71**, 302–307.
- Zhao, L., Hou, H., Fujii, A., Hosomi, M. & Li, F. S. 2014 Degradation of 1,4-dioxane in water with heat- and Fe²⁺-activated persulfate oxidation. *Environ. Sci. Pollut. R.* **21**, 7457–7465.
- Zhao, L., Ji, Y., Kong, D., Lu, J., Zhou, Q. & Yin, X. 2016 Simultaneous removal of bisphenol A and phosphate in zero-valent iron activated persulfate oxidation process. *Chem. Eng. J.* **303**, 458–466.

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