Degradation of Iopamidol, a Commercial X-ray Contrast Chemical and Micropollutant, with ZVA and ZVI-activated, Common Oxidants: Investigation of Acute Toxicity and Anaerobic Inhibition

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Abstract The effect of nano-sized zero-valent aluminum (ZVA) and iron (ZVI) activation of hydrogen peroxide (HP) and persulfate (PS) oxidants on the treatment of aqueous iopamidol (IOPA, 2 mg/L), an iodinated organic X-ray contrast chemical and micropollutant, on acute toxicity and anaerobic digestion inhibition was examined. For this purpose, two different toxicity bioassays were conducted with *V. fischeri*-*P.subcapitata* and cumulative biogas production was monitored in batch anaerobic tests. The application of "activated" HP (1.00 mM) and PS (0.50 mM) treatment under acidic conditions (pH=3) resulted in complete IOPA removal. Acute toxicity results indicated that the untreated IOPA sample caused an inhibitory effect of 5% and 74% towards *V. fischeri* and *P. subcapitata*, respectively. The HP/ZVI- and PS/ZVA-treated IOPA samples exhibited toxic effects on *P. subcapitata*; the relative inhibition increased to 97% and 93% after 120 min HP/ZVI and PS/ZVA treatments, respectively. The freshwater microalgae *P. subcapitata* appeared to be more sensitive to IOPA and its degradation products than the photobacterium *V. fischeri*. Anaerobic digestion results indicated no meaningful change not only in the digestion performance but also in cumulative biogas production in the presence of untreated IOPA (2 mg/L) and HP/ZVI or PS/ZVA treated IOPA samples.

Keywords: Iopamidol (IOPA); zero-valent aluminum (ZVA) and iron (ZVI); persulfate (PS) and hydrogen peroxide (HP); acute toxicity; cumulative biogas production.

1. Introduction

Due to their widespread use and incomplete removal during conventional water and wastewater treatment, the presence of pharmaceuticals in aquatic environments has drawn increasing attention worldwide recently (Klavarioti et al., 2009). Among these, iodinated X-ray contrast chemicals (ICC) are usually administrated to patients at high doses and have been detected in municipal effluents, surface water and even drinking water at concentrations reaching 16 □g/L (Hirsch et al., 2000; Perez and Barcelo, 2007; Kormos et al., 2010). IOPA is the most frequently used ICC and hence acts as the major contributor to the formation of iodinated disinfection by-products and organically bound iodinated organics in discharged effluent (Bichsel and von Gunten, 2000; Fent et al., 2006; Duirk et al., 2011). It was reported that in the presence of IOPA, the cyto- and genotoxicity of drinking waters induced by chlorination increased dramatically (Bichsel and von Gunten, 2000; Fent et al., 2006; Duirk et al., 2011). Because of the biological recalcitrance of IOPA, several advanced physicochemical methods including ozonation, UV-C irradiation and ultrasound have been applied to remove IPM from water, but with rather limited efficiency (20-55%). Advanced oxidation processes (AOPs) including combinations of ozone, ultrasound and UV treatments as well as heterogeneous photocatalysis, Fenton and Photo-Fenton-like processes have also been explored to remove IOPA (Doll and Frimmel, 2004; Jeong et al., 2010; Arslan-Alaton et al., 2017a). More recently, sulfate radical ($SO_4^{\bullet-}$)-based AOPs acting as potential alternatives to $HO^{\bullet}$-mediated process were found to be effective in the treatment of refractory contaminants present in soils, surface- and ground waters (Ferronato et al., 2014; Cheng et al., 2015). The $SO_4^{\bullet-}$ has a redox potential in the range of 2.5-3.1eV and reacts with organic compounds primarily through an electron transfer mechanism at a second-order rate constant of 10^6-10^9 $M^{-1}s^{-1}$ (Neta et al., 1988). The $SO_4^{\bullet-}$ can be generated by activating persulfate (PS) or peroxymonosulfate (PMS) with UV-C light, heat (thermally), ultrasound or transition metals (Anipsitakis and Dionysiou, 2004; Ferronato et al., 2014; Fan et al., 2015; Qi et al., 2016). Among these activation methods, transition metal activation possesses the inherent advantage of high efficiency, low costs and energy demand. In particular, activation with zero-valent iron (ZVI) and zero-valent aluminum (ZVA) micro-or nano-scale particles offers a sustainable option since these metals are abundant, economically attractive and require minimal activation energies. Once corrosion on ZVI or ZVA surfaces occurs, Fe^{2+} and Al^{3+} ions are released into the reaction bulk and initiate a series of Fenton and Fenton-like processes leading to the oxidative destruction of pollutants (Girit et al., 2015; Cai et al., 2015; Cheng et al., 2015; Arslan-Alaton et al., 2017a and b);

Activation of HP with ZVI or ZVA:

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \quad (1)$$

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

$$Al^0 + 3H_2O_2 \rightarrow Al^{3+} + 3HO^{\bullet} + 3OH^- \quad (3)$$

Activation of PS with ZVI or ZVA:

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \quad (3)$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet-} \quad (4)$$

$$2Al^0 + S_2O_8^{2-} + 6H^+ + 1.5O_2 \rightarrow 2Al^{3+} + 2SO_4^{\bullet-} + 3H_2O \quad (5)$$

Since ICC exhibit a low volatility, high polarity and are very persistent towards microbial degradation (Hirsch et al., 2000) it could only be poorly removed (by 30-50%) under anaerobic conditions recently (Yangin-Gomec et al., 2016). It is also important to note that since AOPs promptly induce chain reactions that are difficult to control, examination of their ecotoxicological safety is important. Considering the above mentioned issues, the present study mainly focused on the potential toxic/inhibitory effects of IOPA and its degradation products. For this purpose, aqueous IOPA solutions that were treated with ZVA and ZVI-activated PS and HP oxidants, have first been subjected to acute toxicity tests employing the photobacteria *V. fischeri* and the freshwater microalga *P. subcapitata*. In the second part of the study, the inhibitory effect of the original and treated IOPA solutions on anaerobic digestion and biogas production was investigated by an anaerobic batch bioassay.

2. Materials and Methods

2.1. Materials

IOPA (molecular formula:$C_{17}H_{22}I_3N_3O_8$; molecular weight: 777 g/mol) is a non-ionic radiographic contrast agent commercially available as "Pamiray 300/370" (Ankara, Turkey). Analytical grade HP (35% w/w) and chromatographic grade acetonitrile were obtained from Merck (Germany). PS (potassium salt; purity >99.5%; Sigma-Aldrich, USA) was used as received without purification. HPLC mobile phases were purchased from Sigma-Aldrich (USA) at high purity (>99.9%). Commercial nano-scale ZVI (average particle size 50 nm; BET surface area 20-25 m^2/g; purity>99.5%) was obtained from Nanofer Star, Nano Iron (Czech Republic). High purity (> 99.5%) ZVA nanoparticles (average particle size 100 nm; specific surface area 10-20 m^2/g) were purchased from US Research Nanomaterials, Inc. (Houston, USA).

2.2. Analytical Procedures

IOPA analysis was performed on a 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. Details of the instrumental procedure were described elsewhere (Arslan-Alaton et al., 2017a). Residual HP and PS concentrations were traced by employing colorimetric methods according to Klassen et al. (1994) and Villegas et al. (1963). Acute toxicity bioassays were conducted with *V. fischeri* and *P. subcapitata* before and during treatment with the selected oxidation systems (HP/ZVI, PS/ZVA) as described in earlier work (Girit et al., 2015; Arslan-Alaton et al., 2017a and b).

2.3. Anaerobic Inhibition Experiments

Anaerobic digestion experiments were conducted as three sets of bioreactors containing 2 mg/L aqueous IOPA solution, HP/ZVI and PS/ZVA-treated reaction solutions plus a control bioreactor. The substrate in the control reactor was the biological sludge taken from the secondary sedimentation tank of a municipal WWTP with a capacity of 500.000 m^3/day serving to 2,500,000 people. Advanced treatment for the removal of organic materials and nutrients was applied in the biophosphorus and aeration tanks at the WWTP. The inoculum was taken from the mesophilic anaerobic internal circulation reactor treating the wastewater of a pulp/cardboard industry (TS≅48 g/L; TSS≅45 g/L; VSS/TSS≅59%). Since the inoculum was in the granular form, it was added (v/v=1/5) into all reactors after grinding about 30s. A background reactor was run at the same operating conditions including the seed only, as well as a control reactor made up of a mixture of 550 mL biosludge sample, 150 mL distilled water (IOPA=0 mg/L), and the seed (150 mL). Three other reactors were set up with 150 mL distilled water bearing untreated 2 mg/L aqueous IOPA, HP/ZVI and PS/ZVA-treated reaction solutions together with 550 mL biosludge sample and 150 mL seed sludge. In order to investigate the initial condition (t=0 day), 100 mL samples were taken from the complete mixture of all bioreactors. Hence, the effective volume (V_{eff}) was 750 mL in the entire digestion period (V_{total}=1000 mL). The experimental setup was designed to monitor the anaerobic digestion performance at different digestion times. For this purpose, four bioreactors of the first set were opened (except the seed reactor) at the 7^{th}, 21^{st}, and 50th d of operation, respectively. Total COD (TCOD), Soluble COD (SCOD), Total Solids (TS), Total Volatile Solids (VS), Suspended Solids (TSS), Volatile Suspended Solids (VSS), pH and alkalinity were measured at the beginning and at the end of the incubation period according to Standard Methods (APHA, 2005). Additionally, gas productions in the bioreactors during anaerobic digestion were daily monitored using a Lutron PM-9107 manometer. All reactors were flushed with N_2 before incubation in the dark at 35°C and they were stirred twice a day manually. The bioreactors were maintained till daily biogas productions ceased.

3. Results and Discussion

3.1. Treatment of IOPA with Activated HP and PS

In all experimental runs, the initial IOPA concentration was selected as 2 mg/L (2.6 □M) to enable more intense kinetic assessment of the results. Figure 1 presents percent IOPA removal efficiencies obtained for ZVI-activated HP and PS oxidation systems (at pH3), whereas the *Figure Insert* comparatively depicts % IOPA removals obtained for the PS (0.50 mM)/ZVA (1 g/L) oxidation system that was representing the best treatment results for ZVA-activation obtained in previous work (Arslan-Alaton et al., 2017a). Control experiments demonstrated that IOPA removals without activation remained poor (< 5% for HP only and <

20% for PS only), as expected. Figure 1 compares the activated oxidations systems (HP/ZVI and PS/ZVI) with ZVI treatment only (in the absence of oxidants). It is evident that with increasing HP concentration the immediate Fenton reaction resulting from the formation of H_2O_2 and release of Fe(II) ions was appreciably enhanced resulting in a prompt IOPA reduction (13%, 40%, 57% and 65% IOPA removal for 0, 0.25, 0.50 and 1.00 mM HP, respectively), that reached a stagnant condition after t5, t20 and t90 min for 0.25, 0.50 and 1.00 mM HP, respectively. Obviously, faster reactions might also accelerate the accumulation of Fe(II-III)oxides, IOPA degradation products, complexation reactions on and passivation of the ZVI surface. Complete IOPA removal was only achieved in the presence of 1.00 mM HP for HP/ZVI treatment. In the case of ZVI-activated PS treatment, similar patterns were observed in terms of IOPA abatements that increased with increasing PS concentrations. However, the accelerating effect was relatively poor as compared to the HP/ZVI oxidation system; the addition of 0.25 mM PS had practically no influence on IOPA removals as compared to ZVI only (Figure 1). On the other hand, the addition of 0.50 mM PS enhanced the initial IOPA degradation from 13% to 43% at t0, to 49% at t20 and ultimately to 52% after 120 min PS/ZVI treatment speaking for the dominating involvement $SO_4^{\bullet-}$-based reactions. IOPA removal profiles obtained in the presence of ZVI activation appreciably differed from those achieved when the oxidants were activated with nano-ZVA; in the HP/ZVA treatment combination IOPA removal was limited to 40% and did not improve when elevating the HP concentration from 0.25 mM to 0.50 mM.

On the other hand, as is clear from the *Insert* of Figure 1, the interaction between ZVA and PS was more attractive; a slow but regular degradation pattern was observable for IOPA reduction and IOPA removal reached 100% at the end of the reaction period, revealing that not only the initial Fenton-like oxidation, but also the surface-dependent redox reactions between the oxidant and the ZVI oxides affected IOPA removal rates with the studied oxidation systems as we have already demonstrated in previous works (Arslan-Alaton et al., 2017a).

3.2. Acute Toxicity

The marine photobacterium *V. fischeri* and the freshwater microalgae *P. subcapitata* were employed to evaluate the ecotoxicological risks of IOPA treatment with the HP/ZVI and PS/ZVA processes under optimized reaction conditions (IOPA=2 mg/L, PS=0.50 mM, HP=1.00 mM, ZVA=ZVI=1 g/L, pH3). Figure 2 delineates percent relative inhibitions observed at the treatment times where IOPA was completely removed (t5 min for HP/ZVI and t120 min for PS/ZVA). Acute toxicity of untreated IOPA solution towards *V. fischeri* and *P. subcapitata* were also included in Figure 2. According to Figure 2, the original IOPA solution was non-toxic towards *V. fischeri* (5% inhibition), whereas an inhibitory effect of 74% was observed on *P. subcapitata*. Neither HP/ZVI- nor PS/ZVA-treated IOPA solutions exhibited toxicity on *V. fischeri*. On the other hand, relative *P. subcapitata* inhibition increased from 74% to 97% and 93% at the end of 120 min HP/ZVI and PS/ZVA treatments, respectively. Results revealed the formation of degradation products being more toxic than IOPA. It was also concluded that *V. fischeri* was not sensitive to IOPA and its degradation products.

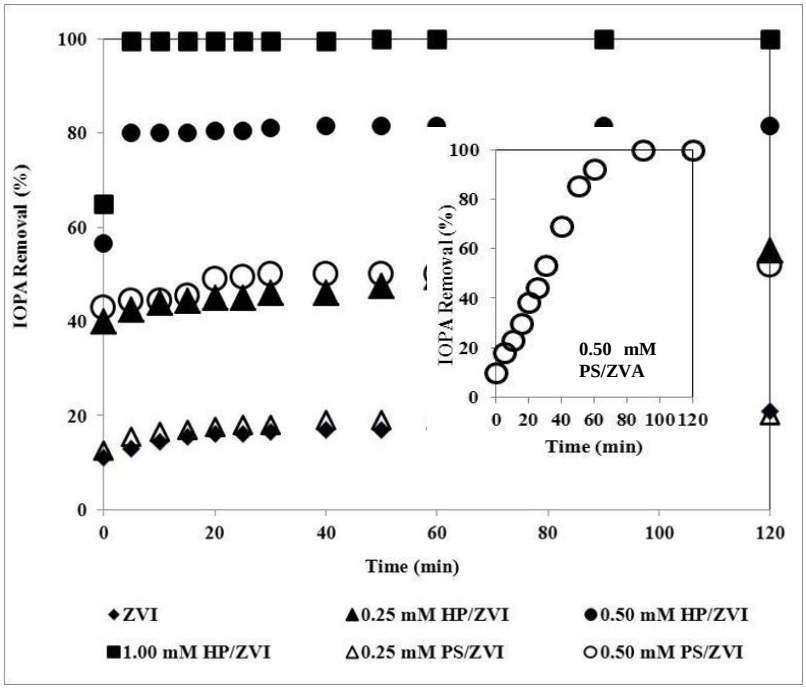

Figure 1. IOPA removals obtained during ZVI-activated HP and PS treatments at different HP,PS concentrations. The ***Figure Insert*** shows the best result for PS/ZVA treatment. $IOPA_o$=2 mg/L; ZVA=ZVI=1 g/L; pH=3; T=25°C.

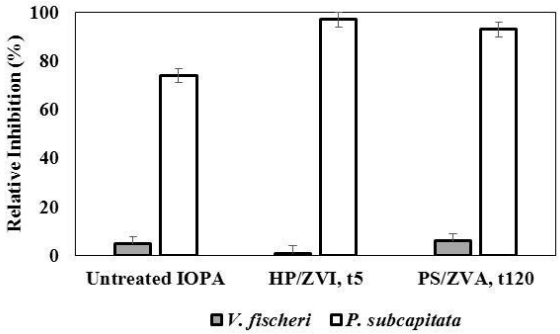

Figure 2. % *V. fischeri* and *P. subcapitata* inhibitions obtained for ZVI-activated HP and PS treatments. IOPA=2 mg/L, PS=0.50 mM, HP=1.00 mM, ZVA=ZVI=1 g/L, pH3.

a. Anaerobic Inhibition

Results of the anaerobic inhibition tests indicated that untreated and HP/ZVI or PS/ZVA-treated IOPA did not result in any appreciable decrease in the anaerobic treatment performance of the biosludge compared to the control reactor. The initial pH and alkalinity values of the batch reactors were 6.81-6.88 and 1850-2720 mg $CaCO_3$/L, respectively. A slight pH decrease was observed at the end of the first week in the first set of bioreactors as a consequence of the acidification phase following the hydrolysis step. Thereafter, pH values re-increased to 7.16-7.24 in all bioreactors indicating achievement of stability, whereas alkalinity reached 4250 mg $CaCO_3$/L at the end of the digestion period. TS (a), VS (b), and SCOD (c) as well as the biogas profiles (d) are depicted in Figure 3. It could be demonstrated that the highest VS removal (37%) was observed in the untreated and HP/ZVI-treated IOPA samples compared to control reactor having no IOPA (33%), whereas 34% VS removal was achieved in the PS/ZVA-treated IOPA sample. The biogas profiles implied that there was no meaningful difference between the untreated, original IOPA (2 mg/L) and the HP/ZVI-or PS/ZVA-treated samples. Cumulative biogas productions were determined in the range of 1170 mL (control)-1220 mL (untreated IOPA solution) excluding the seed contribution (Figure 3d). The biogas yield for the bioreactor bearing the untreated IOPA solution was calculated as around 92.4 L/kg VS_{fed} speaking for a minor increase as compared to the control reactor (≈90.2 L/kg VS_{fed}). The average daily biogas production rates in the bioreactors were found very close to each other; 23 mL for the control and 24 mL for the untreated, HP/ZVI-treated and PS/ZVA-treated IOPA samples, respectively, at the end of digestion. The obtained findings demonstrated that IOPA and its degradation products did not cause any significant inhibition which is in accord with our previous acute toxicity and genotoxicity findings (Arslan-Alaton et al., 2017a).

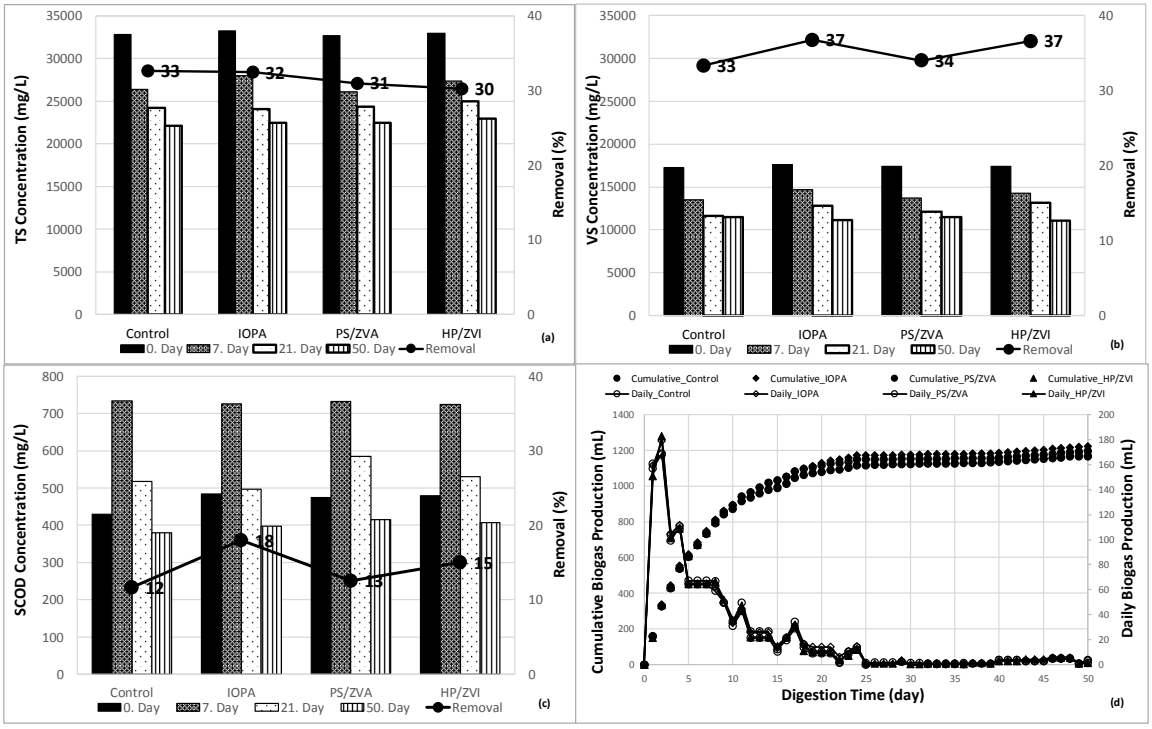

Figure 3. TS (a), VS (b), SCOD (c) removals and the biogas profile (d) obtained during anaerobic digestion of the biosludge for untreated and HP/ZVI or PS/ZVA-treated IOPA solutions. IOPA=2 mg/L, PS=0.50 mM, HP=1.00 mM, ZVA=ZVI=1 g/L, pH3, t5 for HP/ZVI, t120 for PS/ZVA treatment; T=35°C; digestion time=50 d.

4. Concluding Remarks

Our experimental findings have highlighted that HP/ZVI and PS/ZVA treatments are viable options for the removal of the X-ray contrast agent and refractory micropollutant iopamidol. The effectiveness of iopamidol oxidation with HP and PS arouse from their activation with zero-valent nanoparticles promoting the formation of reactive hydroxyl and sulfate radicals thereby initiating a series of Fenton-like chain reactions. Our investigation also emphasized the importance of conducting bioassays with different toxicity test organisms as well as following the performance of anaerobic digestion by measuring biogas formations which all serve to evaluate the ecotoxicological hazard risks of the proposed treatment systems in more detail. Currently, the feasibility of HP/ZVI and PS/ZVA are also questioned by genotoxicity analyses with the Umu Chromo test.

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