

Removal of Nonylphenol and Octylphenol from Aqueous Solutions by a Novel Nano-Composite (ZVI/Fullerene) [†]

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Abstract: Nonylphenol (NP) and octylphenol (OP) are considered as endocrine disrupting compounds and they restrict the reuse potential of wastewater. Therefore, innovative and reliable technologies are required for elimination of these compounds from waste streams. In this study, we consider use of iron nanoparticles (nZVI) (0.1 mM; 2 mM) and also a composite of nZVI/fullerene nanoparticles (aq-nC₆₀) (0.1 mM nZVI/2.5 ppm aq-nC₆₀; 2 mM nZVI/2.5 ppm aq-nC₆₀) for the removal of 25 µg/L NP and OP concentrations. The nano-composite was synthesized according to chemical reduction method and was characterized using XRD, particle size distribution and zeta potential measurements. NP and OP concentrations were quantified with a GC-MS. The results demonstrated that 0.1 mM nZVI alone resulted in 6% and 17% decrease in NP and OP concentrations, respectively. However, when the nZVI concentration was increased to 2 mM, the removal efficiency increased to 59% for NP and 32% for OP. When compared with NP, lower removal rates were achieved for OP regardless of the nZVI concentration. Although NP and OP have similar chemical structures, OP has a branched arrangement and this structure is anticipated to cause a decrease in the active adsorption sites and lower removal efficiency for OP. Highest removal was obtained with 0.1 mM nZVI/2.5 ppm aq-nC₆₀ for both NP and OP. Our results show that nZVI/aq-nC₆₀ holds a potential for elimination of NP and OP from wastewater sources.

Keywords: nano-composite; nZVI; Fullerene; nonylphenol; octylphenol

1. Introduction

Nonylphenol (NP) and octylphenol (OP) are micropollutants that are among surface active materials and have been widely used in domestic and industrial applications. Either these substances themselves or metabolites of their ethoxylated forms that form during biological processes in wastewater treatment plants are have toxic properties [1–3].

Complete elimination of these compounds with conventional treatment plants is not possible because they have not been designed for their removal [4,5]. In addition, it's possible that the existence of various micropollutants together might cause an undesired synergistic effect. Since

nonylphenol and octylphenol have high log K_{ow} values, these compounds tend to *accumulate in the solid phase rather than remaining in the liquid phase*. For this reason, even though their concentration in the effluent of the treatment plant seems to be reduced, they actually accumulate in the wastewater sludge [6]. This limits the land application of wastewater sludge. Therefore, innovative and economic technologies are required for maximum removal of micropollutants such as nonylphenol and octylphenol in wastewater treatment plants, so that wastewater reuse and sludge land utilization can be achieved.

The decomposition-resistant and toxic structure of nonylphenol and octylphenol has led to the evaluation of advanced oxidation processes (ozone, photocatalytic processes, UV, etc.) as an alternative to conventional treatment processes which have relatively low removal efficiency for micropollutants. However, the most important disadvantages encountered in advanced oxidation processes are the high initial investment and operating costs as well as the formation of toxic intermediate products. For instance, it was noted the formation of much more toxic intermediates after chlorination of a water sample containing nonylphenol with NaOCl [7]. Especially when wastewater reuse is concerned, chlorination can be preferred due to the fact that it is a cheap and effective method. However, it is more important that nonylphenol content of the water should be eliminated before chlorination is applied to avoid the risks in such a case.

Nanotechnology is an interdisciplinary science and one of its main application areas is environmental pollution control. Zero-valent iron nanoparticles (nZVI) are among the first-generation nano materials investigated in the field of nanotechnology and have advantages such as being relatively easy to synthesize compared to other nanoparticles and not being toxic in concentrations used for remediation purposes. In this study, removal of nonylphenol and octylphenol with two different nZVI concentrations (0.1 mM and 2 mM) under aerobic conditions was investigated. Also a composite of nZVI/fullerene was synthesized and evaluated for the same purpose.

2. Experimental

2.1. Chemicals and Solutions

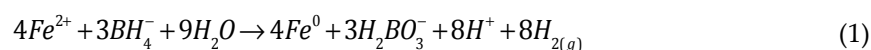
Technical grade nonylphenol mixed isomers (purity 100%), 4-*N*-octylphenol (purity 99.5%), internal standard anthracene d10 (98% D) and surrogate 4-*N*-nonylphenol 2,3,5,6-d4, OD (98.9% D) was purchased from Dr. Ehrenstorfer (Darmstadt, Germany). Chromatography (GC) grade (Suprasolv) hexane, methanol, and acetone were obtained from Merck (Darmstadt, Germany). Stock standard solutions of nonylphenol and octylphenol were prepared separately by weighing 10 mg of each compound and diluting them into acetone to obtain 1000 mg/L concentration. The concentration of each compound detected was corrected by using Anthracene d10 as internal standard. 4-*N*-nonylphenol 2,3,5,6-d4, OD (98.9% D) was used as surrogate.

2.2. GC-MS Analysis

The samples were analyzed by GC-MS using a Shimadzu GCMS-QP2010 Gas Chromatograph fitted with mass spectrometer (Shimadzu, Kyoto, Japan). The analytes were chromatographically separated by injecting a 1 μ L of sample onto a Trb-5 ms capillary GC column (30 m \times 0.25 μ m \times 0.25 μ m); electron impact spectra were obtained at 70 eV.

2.3. Synthesis of Iron Nanoparticles (nZVI)

ZVI nanoparticles were synthesized immediately before use by aqueous-phase reduction of ferrous sulfate with sodium borohydride according to the following chemical reaction:



Briefly 10 mM $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was mixed with 100 mM NaBH_4 at a stoichiometric ratio of 1:2.5 [8]. This reaction resulted in the formation of a black-colored suspension of ZVI nanoparticles along with hydrogen, which was allowed to escape.

2.4. Preparation of Fullerene Nanoparticles (aq- nC_{60}) and Preparation of nZVI/aq- nC_{60} Nanocomposite

Fullerene was purchased in powder form (C_{60} ; purity 99.9%) (MER, Tucson, AZ, USA). Since fullerene is a highly hydrophobic substance it was subjected to a long-term sonication process in order to be dispersed in water [8]. Size distribution and total organic carbon (TOC) content of the stock solution were determined using Malvern ZS90 (Malvern, Worcestershire) and TOC (Sievers, GE, Trevose, Pennsylvania), respectively.

2.5. Experimental Setup

40 mL glass vials were used for the removal studies carried out in the acetone phase. Since aq/ nC_{60} nanoparticles are light sensitive, it was planned to increase their activity by UV/Vis LED light. For control studies, experiments in the absence of C_{60} were conducted. Orbital shaker was used for homogeneous mixing of nanoparticles in the vials. The photoreactor was constructed as a cylindrical chamber with 21 cm diameter and 25 cm height. LED lamps (visible light) were mounted on 13 aluminum strips. The amount of light emitted from the photoreactor was controlled by an adjustable mechanism. Samples were taken at predetermined times and they were filtered by nylon membrane filters with 0.22 μm pore size to separate nanoparticles.

3. Results and Discussion

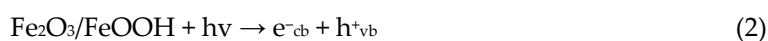
3.1. Characterization of Nanoparticles

The crystal structure analysis of the synthesized nanoparticles was performed with an XRD instrument (Rigaku Corp., Neu-Isenburg, Germany). The diffractograms obtained for the iron nanoparticle (nZVI) and aq/ nC_{60} -ZVI composite showed a sharp peak at 44.9° , characteristic for ZVI. The peak at 30° in aq/ nC_{60} -ZVI sample confirmed the presence of aq/ nC_{60} in the nanocomposite. Suspensions of the nZVI and nZVI-aq/ nC_{60} nanoparticles had number-average hydrodynamic diameters of 33 nm and 34 nm, respectively.

3.2. Effect of Iron Nanoparticle (nZVI) Concentration on the Removal of Nonylphenol and Octylphenol

In this study, the removal efficiencies of two different concentrations of iron nanoparticles on nonylphenol were investigated in both dark (Figure 1a) and in the presence of visible light (UV/Vis) (Figure 1b). The same conditions were also applied for octylphenol (Figure 2a,b). The concentrations of iron nanoparticles were 0.1 mM (5.6 ppm Fe equivalent) and 2 mM (102 ppm Fe equivalent). As seen in Figure 1a, the nonylphenol removal yield increased to 60% as the iron concentration increased. Increased removal rates at higher iron concentration suggested that adsorption would be the main removal mechanism is adsorption. Zero-valent iron corrodes under oxic conditions producing iron oxides such as hematite ($\alpha\text{-Fe}_2\text{O}_3$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and iron oxyhydroxides such as lepidocrocite ($\gamma\text{-FeOOH}$). These corrosion products are compounds with high adsorption capacity and give successful results in the removal of different pollutant molecules with organic and inorganic nature. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) acts as a photocatalyst in addition to its adsorption property.

Corrosion products such as hematite/oxyhydroxide carry n-type semiconductor properties and can be activated with visible light. Therefore, two types of carriers [electrons (e^-) and voids (h^+)] are formed after visible light is absorbed by the corrosion products. The band gap of the hematite/iron oxyhydroxides is about 2.2–2.6 eV and they can absorb light energy at a wavelength lower than 564 nm. As the electrons in the conductivity band are released by the incoming light energy, the gaps in the valence band travel to the metallic surface. It is predicted that the reaction is as follows [9]:



The electrons released in this way, have strong reducing property and supply the reduction of oxygen. As a result of oxygen reduction the formation of ROS such as superoxide and hydroxyl radicals is concerned. However, since the reaction solution is acetone, although strong oxidants such as the hydroxyl radical may occur, it is possible that these radicals might have reacted with acetone before nonylphenol/octylphenol. On the other hand, iron oxidation accelerates the formation of hematite/iron oxyhydroxide, forming a layer around the metallic core. As the thickness of this layer increases, the diffusion of oxygen into the interior is restricted. Thus, iron nanoparticles probably cannot be completely oxidized and magnetite is formed.

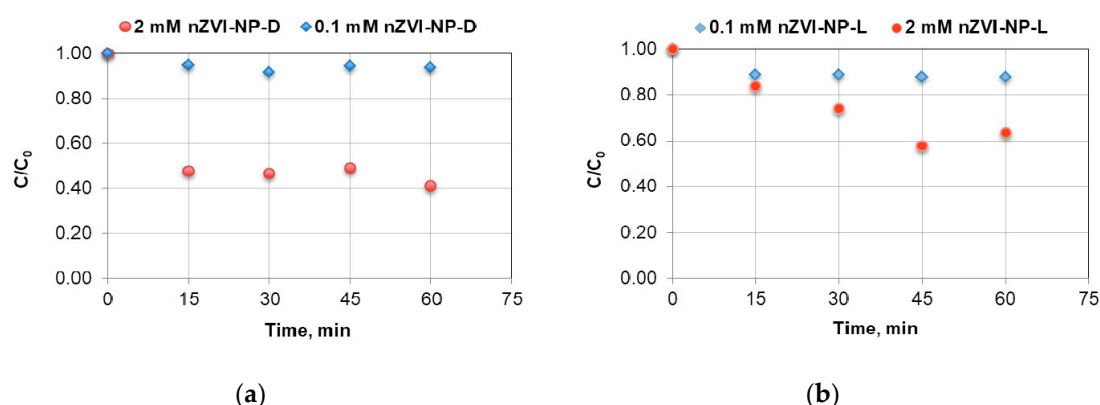


Figure 1. Effect of nZVI concentration on the removal of nonylphenol under: (a) Dark (b) Light conditions.

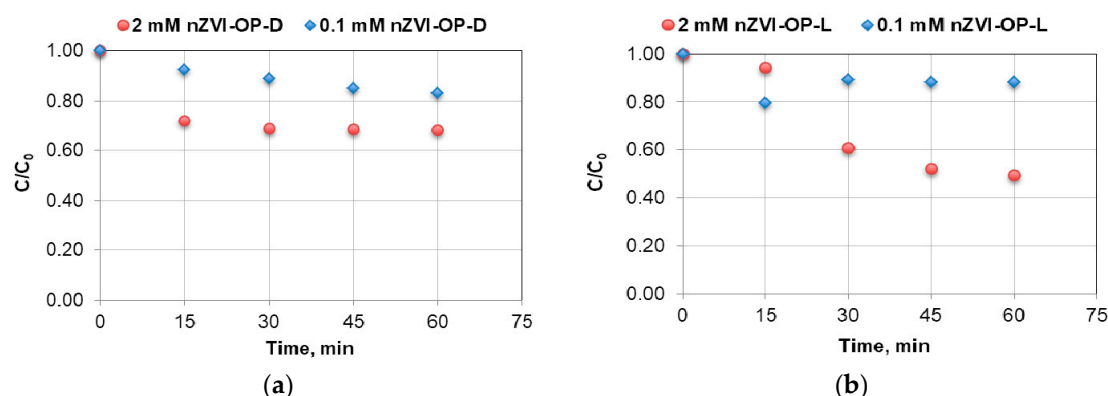


Figure 2. Effect of nZVI concentration on the removal of octylphenol under: (a) Dark (b) Light conditions.

With a concentration of 0.1 mM nZVI, octylphenol removal (Figure 2a) showed a similar tendency to nonylphenol, resulting in negligible elimination. Although higher octylphenol removal was achieved with 2 mM nZVI compared to 0.1 mM nZVI, this removal (30%) remained at a lower level (60%) than nonylphenol. Nonylphenol ($C_{15}H_{24}O$) and octylphenol ($C_{14}H_{22}O$) are molecules with similar chemical structures but the active sites on the nanoparticles where octylphenol can be adsorbed might be reduced due to the branching structure of octylphenol.

The effect of different concentrations of iron nanoparticles on the removal of octylphenol in the presence of visible light is shown in Figure 2b. Under dark conditions 2 mM nZVI performed slightly better than 0.1 mM nZVI, which might be explained by higher amount of corrosion products in case of 2 mM nZVI. Under light conditions 0.1 mM nZVI showed almost the same removal efficiency as was observed under dark conditions. However, a noticeable increase was observed for 2 mM nZVI under light conditions, which is possibly linked to the higher ROS generation associated with higher amount of corrosion products. When 2 mM nZVI was used, the OP removal reached equilibrium in the first 45 min. Slightly higher octylphenol removal (50%) than nonylphenol removal (40%) with 2

mM nZVI in the presence of light might indicate that photoactive forms of corrosion products may interact more easily with octylphenol.

3.3. Effect of Light on Removal of Nonylphenol and Octylphenol

Nonylphenol removal by 2 mM nZVI was compared in dark and light conditions (Figure 3). At the end of the 60-min reaction period, there was a marked difference in light and dark conditions for nonylphenol removal.

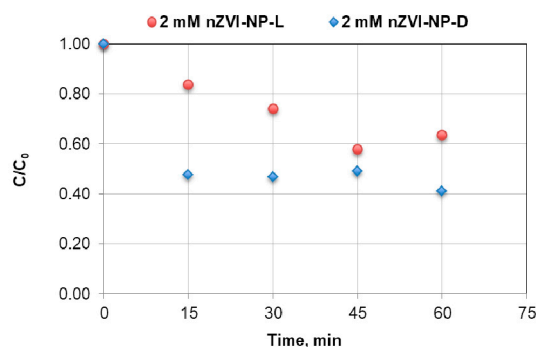


Figure 3. Effect of light (L) and dark (D) conditions on nonylphenol removal by 2 mM nZVI.

The ROS formation potential due to the reduction of molecular oxygen in the presence of light is higher than that in dark conditions. Considering the reaction rate constants of ROS species with acetone, it is possible that these compounds reacted with acetone before nonylphenol. Thus, lower nonylphenol removal efficiencies were obtained under light when compared to dark conditions. Nonylphenol removal at 0.1 mM nZVI concentration was compared in dark and light conditions (data is not shown). It is suggested that the nonylphenol removal observed at the negligible level in both conditions is provided by the adsorption mechanism.

Octylphenol removal with 2 mM nZVI concentration was compared in dark and light conditions (Figure 4). Nearly 50% of octylphenol removal was achieved in the light conditions, while only 30% removal was obtained in the dark conditions. It is thought that iron oxide/hydroxide species, which are the result of corrosion reactions of iron nanoparticles, make this difference by photocatalytic effect in the presence of light. Octylphenol removal at a concentration of 0.1 mM nZVI was compared in dark and light conditions (data is not shown). It is suggested that the removal of octylphenol, which is observed in the negligible level (about 10%) in both conditions, is provided by the adsorption mechanism.

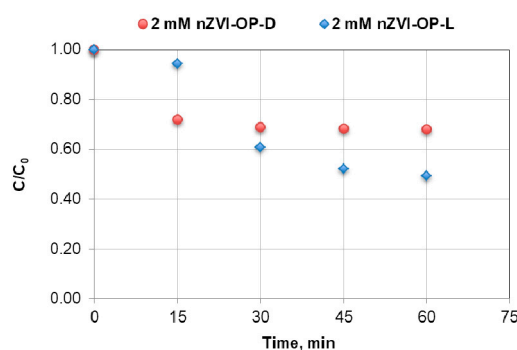


Figure 4. Effect of light (L) and dark (D) conditions on octylphenol removal by 2 mM nZVI.

3.4. Effect of aq/nC₆₀-nZVI Composite on Nonylphenol and Octylphenol Removal

The nZVI/fullerene nanocomposite is prepared to increase the concentration of hydroxyl radicals that iron nanoparticles can form in solution under aerobic conditions. Fullerene nanoparticles are photosynthetic and are known to be excited by UV/Vis or UV-A light. Considering

the energy consumption, UV/Vis (visible wavelength light) was preferred to excite fullerene nanoparticles in this study. It is possible to form reactive oxygen species (ROS), such as singlet oxygen and superoxide radical as a result of the reactions between the excited species of fullerene particles and the molecular oxygen in the solution. On the other hand, when an electron donor such as nZVI is present in the environment, the hydroxyl radical formation occurs by the Fenton reaction between nZVI and hydrogen peroxide which is protonated species of superoxide. It is therefore possible to obtain more hydroxyl radicals in the same iron nanoparticle concentration.

Nonylphenol removal obtained under different conditions with 2 mM nZVI is shown in Figure 5. It is observed that fullerene nanoparticles do not significantly increase the yield of nonylphenol removal as it was expected. Under dark conditions, using the nanocomposite prepared with 2.5 ppm C₆₀ the obtained removal was close to 40% after 60 min. It was observed that the removal was slightly increased under light. This result indicates that fullerene nanoparticles can be activated with UV/Vis light. On the other hand, it is thought that that fullerene nanoparticles couldn't be effective in the composite, since the concentration of nZVI (2 mM) was too intense. Previously, similar results were obtained while studying the potential of this composite to form superoxide [8]. The octylphenol removal obtained under different conditions with 2 mM nZVI is shown in Figure 6. As in the case of nonylphenol, no significant effect of the aqC₆₀/nZVI composite was observed for the octylphenol removal. However, in the case of light application, the removal percent was slightly increased, confirming that the fullerene nanoparticles can be activated by UV/Vis light. Nonylphenol removal obtained under different conditions with 0.1 mM nZVI was also evaluated (data is not shown). Although 0.1 mM nZVI (5.6 ppm Fe equivalent) was a rather low concentration and did not show any significant effect on nonylphenol removal when it was applied alone, the removal yield increased from 10% to 50% when aq/nC₆₀-nZVI was applied. Factors affecting this situation are thought to be the formation of reactive oxygen species formation. Octylphenol removal in different conditions with 0.1 mM nZVI was similar to nonylphenol removal data. 0.1 mM nZVI alone did not show any significant effect on octylphenol removal, but when the nZVI composite was formed with aqC₆₀, the removal yield increased from about 10% to about 55%.

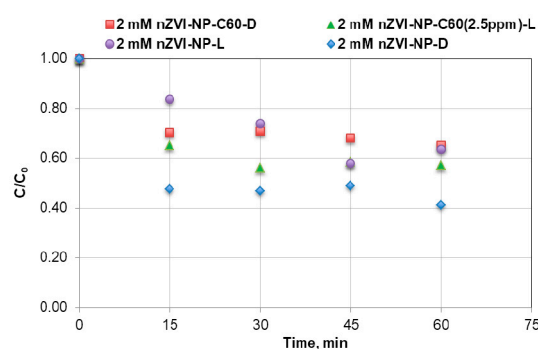


Figure 5. Nonylphenol removal by aq/nC₆₀-nZVI composite (2 mM nZVI, 2.5 ppm aq/nC₆₀).

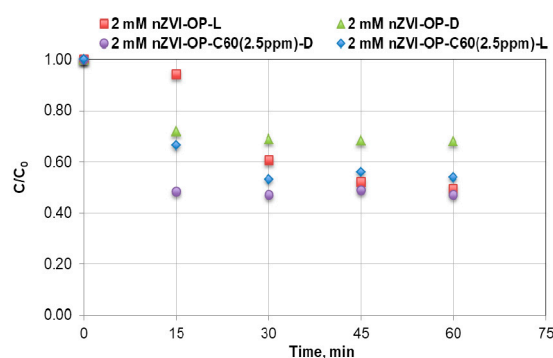


Figure 6. Octylphenol removal by aq/nC₆₀-nZVI composite (2 mM nZVI, 2.5 ppm aq/nC₆₀).

4. Conclusions

Two different concentrations (0.1 mM and 2 mM) of iron nanoparticles (nZVI) along with a nano composite of nZVI/fullerene particles were assessed for the removal of nonylphenol and octylphenol. The removal percents for both nonylphenol and octylphenol increased with the increase in the nZVI concentration. The substantial dependency on nZVI concentration suggests that the removal is mainly due to adsorption. Although the formation of reactive oxygen species (ROS) is possible in the presence of light and in oxic conditions, the removal of nonylphenol/octylphenol with 2 mM nZVI was lower under light when compared to the dark conditions. Fullerene nanoparticles (aqC₆₀) are photosynthetic materials and known to be excited by UV/Vis or UV-A light. In this study, UV/Vis (visible wavelength light) was used to excite the fullerene nanoparticles, considering the energy consumption. In the study, the highest nonylphenol/octylphenol removal was about 50% and was obtained with 0.1 mM nZVI-C₆₀ nanocomposite. It is suggested that C₆₀ nanoparticles were easily dispersed in low iron concentration and protected their active surfaces.

Author Contributions: Esra Erdim conceived and planned the experiments. Gül Gülenay Haciosmanoglu and Zeynep Yücesoy-Ozkan carried out the experiments. Zehra Semra Can contributed to the interpretation of the results and took the lead in GC-MS measurements. Elif Soyer aided in interpreting the results. Seval Genc assisted in characterization of the nanomaterials. Elif Pehlivanoglu Mantas helped supervise the project. Esra Erdim performed the analysis, drafted the manuscript and designed the figures. Gul Gulenay Haciosmanoglu wrote the manuscript in consultation with Esra Erdim and Zehra Semra Can.

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Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Servos, M.R. Review of the aquatic toxicity, estrogenic responses and bioaccumulation of alkylphenols and alkylphenol polyethoxylates. *Water Qual. Res. J. Can.* **1999**, *34*, 123–177.
2. Soares, A.; Guieysse, B.; Jefferson, B.; Cartmell, E.; Lester, J. Nonylphenol in the environment: A critical review on occurrence, fate, toxicity and treatment in wastewaters. *Environ. Int.* **2008**, *34*, 1033–1049, doi:10.1016/j.envint.2008.01.004.
3. Staples, C.; Mihaich, E.; Carbone, J.; Woodburn, K.; Klecka, G. A weight of evidence analysis of the chronic ecotoxicity of nonylphenol ethoxylates, nonylphenol ether carboxylates, and nonylphenol. *Hum. Ecol. Risk Assess.* **2004**, *10*, 999–1017, doi:10.1080/10807030490887122.
4. Can, Z.S.; Fırlak, M.; Kerç, A.; Evcimen, S. Evaluation of different wastewater treatment techniques in three wwtps in istanbul for the removal of selected edcs in liquid phase. *Environ. Monit. Assess.* **2014**, *186*, 525–539, doi:10.1007/s10661-013-3397-7.
5. Wang, L.; Wu, Y.; Sun, H.; Xu, J.; Dai, S. Distribution and dissipation pathways of nonylphenol polyethoxylates in the yellow river: Site investigation and lab-scale studies. *Environ. Int.* **2006**, *32*, 907–914, doi:10.1016/j.envint.2006.06.012.
6. Heidler, J.; Halden, R.U. Meta-analysis of mass balances examining chemical fate during wastewater treatment. *Environ. Sci. Technol.* **2008**, *42*, 6324–6332, doi:10.1021/es703008y.
7. Fan, Z.; Hu, J.; An, W.; Yang, M. Detection and occurrence of chlorinated byproducts of bisphenol a, nonylphenol, and estrogens in drinking water of china: Comparison to the parent compounds. *Environ. Sci. Technol.* **2013**, *47*, 10841–10850, doi:10.1021/es401504a.

8. Erdim, E.; Badireddy, A.R.; Wiesner, M.R. Characterizing reactive oxygen generation and bacterial inactivation by a zerovalent iron-fullerene nano-composite device at neutral pH under UV-a illumination. *J. Hazard. Mater.* **2015**, *283*, 80–88, doi:10.1016/j.jhazmat.2014.08.049.
9. Qiu, P.; Chen, Z.; Yang, H.; Yang, L.; Luo, L.; Chen, C. The transformation of corrosion products on weathering steel by visible-light illumination under simulated marine atmospheric condition. *Int. J. Electrochem. Sci.* **2016**, *11*, 10498–10510, doi:10.20964/2016.12.76.



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