

Degradation of endocrine disrupting chemicals by heat-activated persulfate

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The presence of endocrine disrupting compounds (EDCs) at the ng/L- μ g/L level in waters and treated wastewaters has been well-documented. EDCs are designed to be bioresistant and, therefore, they are only partially removed by biological processes. As a consequence, they are released in the water cycle and may pose a potential danger to fish and other aquatic organisms, even at trace concentrations of 0.1-10 ng/L. Bisphenol A (BPA) is predominantly used in plastics manufacturing (epoxy and polycarbonate resins) as binder, plasticizer and hardener, while it may also be employed as additive in flame retardants, brake fluids and thermal papers. BPA is known to have estrogenic activity at concentrations as low as 1 ng/L (Auriol et al., 2006). In recent years, various efforts are being made to eliminate or effectively remove xenobiotics in the environment; among them, advanced oxidation processes (AOPs) are a viable alternative option for water/wastewater treatment (Klavarioti et al., 2009). The sulfate radical-AOP has recently been discussed in the literature as an efficient and affordable process. Sodium persulfate (SPS) ($\text{Na}_2\text{S}_2\text{O}_8$) has attracted the attention of the scientific community as a promising source of sulfate radicals because of its moderate cost (i.e. the wholesale price is in the order of 1000 USD/tn) and its high redox potential of 2.01 V (Gao et al., 2012). Other advantages of persulfate over other oxidants include the fact that it is solid at ambient temperature, thus facilitating its storage and transport, as well as its high stability and aqueous solubility.

In this work, BPA was chosen as a representative model compound of the EDCs family to investigate its degradation by heat-activated persulfate oxidation. The main scope was to evaluate the effect of various operating conditions such as initial BPA and SPS concentrations, reaction time, pH, temperature and water matrix on kinetics.

Oxidation reactions were conducted in a 120 mL thermostated reactor made of pyrex glass. The vessel was open to the atmosphere without gas sparging since preliminary runs showed that the effect of aeration on degradation was negligible. Certain volumes of BPA and SPS stock solutions were mixed to a predefined volume of ultrapure water in order to get the desired concentration of each reactant (i.e. $[\text{BPA}]_0=110\text{--}440\ \mu\text{g/L}$; $[\text{SPS}]_0=10\text{--}650\ \text{mg/L}$). SPS was added after the working BPA solution had reached the desired temperature (i.e. up to 70°C). All experiments were performed un-buffered at their inherent pH. Samples periodically drawn from the reactor were immediately cooled down at 4°C in an ice bath for about 5 min to quench the reaction and then analyzed to assess the degradation of BPA by means of high performance liquid chromatography (Waters Alliance 2695).

In order to demonstrate the effect of temperature on BPA (200 $\mu\text{g/L}$) degradation, a series of experiments were conducted at an initial persulfate concentration of 625 mg/L and an initial pH of 6 in the temperature range of 40–70 °C. Increasing the reaction temperature from 40 °C to 70 °C enhanced BPA conversion significantly. Complete degradation of BPA was observed in 120, 30, 7 and 3 min when the reaction was carried out at 40 °C, 50 °C, 60 °C and 70 °C, respectively. The process appears to be favored at neutral pH; for example, the removal of 220 $\mu\text{g/L}$ of BPA after 45 min and $[\text{SPS}]=167\ \text{mg/L}$, $T=50\ \text{°C}$ was 100%, 74% and 51% at pH 6, 3 and 9, respectively. For the range of concentrations studied, the reaction order with respect to BPA shifts from first to zeroth as initial concentration increases from 110 $\mu\text{g/L}$ to 440 $\mu\text{g/L}$. Moreover the role of water matrix is critical and has a negative effect on process efficiency, i.e. it decreases with increasing matrix complexity from ultrapure water (UPW) to secondary treated wastewater (WW). This can be explained taking into account that (i) the radicals are competitively consumed in reactions involving the organic fraction inherently present in WW but not in UPW, and (ii) sulfate and hydroxyl radicals may be scavenged by bicarbonates and chlorides present in WW.

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