

Comparative Analysis of Chlorinated Intermediates Formed During Electrochemical and Photo(electro)catalytic Degradation of 4-Ethylphenol in Saline Media

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Abstract

Formation of toxic by-products, such as chlorinated intermediates, is one of the major drawbacks of advanced oxidation processes for saline wastewater treatment. Here a comparative analysis of electrochemical oxidation and photocatalytic degradation of 4-Ethylphenol, a *non*-chlorinated starting model compound of the group of alkylphenols, is presented. Main intermediates have been identified and quantified for brackish [$0.03 \text{ mol} \cdot \text{L}^{-1}$] and sea water [$0.6 \text{ mol} \cdot \text{L}^{-1}$] salt concentrations representative for the salt levels in various industrial effluents. Our comparison indicates that photocatalytic treatment (using TiO_2 photocatalysts) might be favorable over electrochemical treatments with Pt or BDD anodes due to the minor role of chlorination and the limited formation of chlorinated compounds in photocatalysis. Finally, using photoelectrochemical degradation an external surface recombination mechanism of photogenerated charge carriers will be presented explaining the absence of chlorinated compounds during photocatalytic wastewater treatment.

Keywords: advanced oxidation process, photocatalytic degradation, electrochemical oxidation, chlorination, intermediates

1. Introduction

Industrial wastewater treatment is essential for the development of sustainable processes. In particular Advanced Oxidation Processes (AOP) are promising for the removal of organic pollutants and their implementation might enable the reuse of industrial wastewater streams (Dewil et al., 2017). Salts, such as sodium chloride are frequently present in wastewater (Lefebvre et al., 2006). Whereas chloride is supportive for the degradation process in electrochemical treatments due to the formation of reactive chlorine species (Sires et al., 2014), photocatalytic degradation is usually strongly inhibited (Azevedo et al., 2004). Unfortunately, the supportive effect of chloride in electrochemical treatments is accompanied by the formation of undesirable toxic chlorinated intermediates (Saylor et al.,

2012; Jasper et al., 2017). Degradation studies usually focus on either photocatalytic or electrochemical treatments, therefore a comparative study using the same non-chlorinated model compound 4-ethylphenol (4EP) has been performed for direct comparison.

2. Results

Electrochemical degradation (ECD) studies using a platinized Ti electrode (Ti/Pt) or a Boron doped diamond electrode have been performed at a constant current density of $15 \text{ mA} \cdot \text{cm}^{-2}$. For photocatalytic degradation (PCD) suspensions containing anatase TiO_2 [$0.5 \text{ g} \cdot \text{L}^{-1}$] were constantly illuminated with UVA light ($\approx 375 \text{ nm}$, $0.32 \text{ mW} \cdot \text{cm}^{-2}$). In both cases the initial concentration of 4EP was $50 \text{ mg} \cdot \text{L}^{-1}$ and a maximum treatment time of 5 h has been used.

Table 1. Maximum concentration of the chlorinated intermediates 2-Chloro-4-ethylphenol (2C4EP) and 2,6-Dichloro-4-ethylphenol (26DC4EP) detected during ECD (Ti/Pt or BDD electrode) or PCD (TiO_2) of 4EP in low ($0.03 \text{ mol} \cdot \text{L}^{-1}$) and high ($0.6 \text{ mol} \cdot \text{L}^{-1}$) saline water. The detection limit (D.L.) was $0.05 \text{ mg} \cdot \text{L}^{-1}$.

NaCl [$\text{mol} \cdot \text{L}^{-1}$]	2C4EP [$\text{mg} \cdot \text{L}^{-1}$]		
	ECD-Ti/Pt	ECD-BDD	PCD-TiO ₂
0.03	23.4	23.9	< D.L.
0.6	14.1	16.4	0.2
NaCl [$\text{mol} \cdot \text{L}^{-1}$]	26DC4EP [$\text{mg} \cdot \text{L}^{-1}$]		
	ECD-Ti/Pt	ECD-BDD	PCD-TiO ₂
0.03	8.5	10.7	< D.L.
0.6	7.0	5.7	< D.L.

The supportive effect of reactive chlorine species has been clearly observed in ECD and a faster removal of the parent compound 4EP with degradation rates of $37 \text{ mg} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$ and $460 \text{ mg} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$ in the presence of low ($0.03 \text{ mol} \cdot \text{L}^{-1}$) and high ($0.6 \text{ mol} \cdot \text{L}^{-1}$) NaCl

concentrations has been determined with Ti/Pt anodes. Compared to similar experiments performed in "inert" NaNO₃ electrolytes, degradation in NaCl proceeded up to 100 times faster. In contrast, PCD was strongly inhibited by NaCl, especially in conditions of high salinity. For example PCD without salt additives resulted in a 4EP degradation rate of 56 mg*L⁻¹*h⁻¹ and was reduced by more than half for suspensions containing 0.6 mol*L⁻¹ NaCl (25 mg*L⁻¹*h⁻¹).

Using LC-MS 2-Chloro-4-ethylphenol (2C4EP) and 2,6-Dichloro-4-ethylphenol were identified as main aromatic intermediates, formed in NaCl containing electrolyte in significant amounts during ECD (up to 23.9 mg*L⁻¹, Table 1). Furthermore, their formation was found to be independent of NaCl concentration and type of the anode (Figure 1). For the PCD experiments the formation of these chlorinated intermediates was strongly suppressed. Only at high salt concentrations small amounts of 2C4EP were detected (0.2 mg*L, Table 1). Importantly for low salt conditions the concentration of 2C4EP was below the

detection limit and the dichlorinated intermediate was not observed at all during PCD treatments. Instead, 4-Hydroxyacetophenon was identified as main intermediate.

Photoelectrochemical degradation using a TiO₂/Ti electrode illuminated by a 365 nm LED at a small bias potential (0.1 V vs. Ag/AgCl) resulted in the formation of significant amounts of 2C4EP (9 mg*L⁻¹) and 26DC4EP (17 mg*L⁻¹) even in low NaCl concentration conditions, evidencing that reactive chlorine can be easily formed on TiO₂ surfaces. However, in contrast to PCD experiments the bias-induced charge separation leads to the formation of chlorinated intermediates. We therefore propose a short-circuit mechanism where Cl⁻ on (close to) the TiO₂ surface acts as a recombination center for photogenerated charge carriers (Sunada et al., 1998). This mechanism is in agreement with the observed lower degradation rates and the negligible formation of chlorinated intermediates.

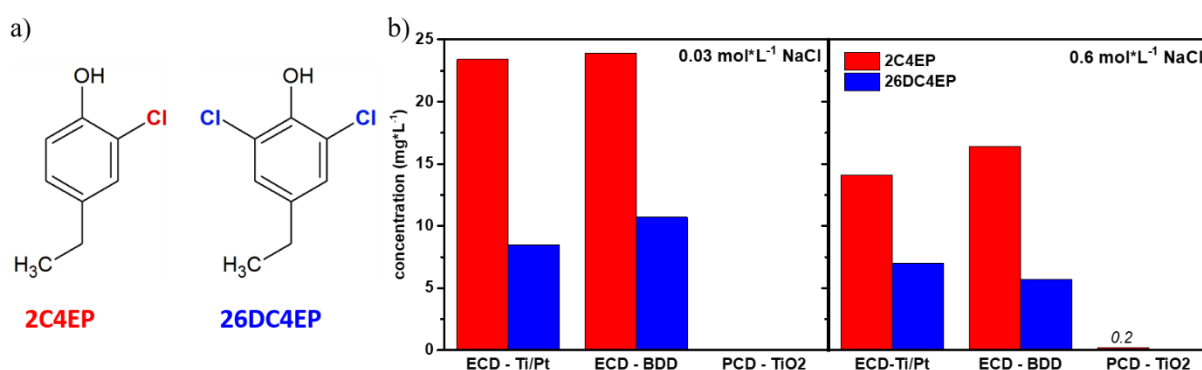


Figure 1. a) Chemical structure and b) maximum concentration of the monochlorinated intermediate 2-chloro-4-ethylphenol (2C4EP) and dichlorinated intermediate 2,6-dichloro-4-ethylphenol (26DC4EP) formed during ECD (using either Ti/Pt or BDD electrode) or PCD (using TiO₂) of 4EP in low (0.03 mol*L⁻¹) and high (0.6 mol*L⁻¹) saline water.

References

- Azevedo E.B., de Aquino Neto F.R. and Dezotti M. (2004), TiO₂-photocatalyzed degradation of phenol in saline media: lumped kinetics, intermediates, and acute toxicity, *Applied Catalysis B: Environmental*, **54**, 165–173.
- Dewil R., Mantzavinos D., Poullos I. and Rodrigo M.A. (2017), New perspectives for advanced oxidation processes, *Journal of Environmental Management*, **195**, 93-99.
- Jasper J.T., Yang Y. and Hoffmann M.R. (2017), Toxic by-product formation during electrochemical treatment of latrine wastewater, *Environmental Science and Technology*, **51**, 7111-7119.
- Lefebvre O. and Moletta R. (2006), Treatment of organic pollution in industrial saline wastewater: a literature review, *Water Research*, **40**, 3671-3682.
- Saylor G.L., Chen L. and Kupferle M.J. (2012), Using toxicity testing to evaluate electrochemical reactor operations, *Environmental Toxicology and Chemistry*, **31**, 494-500.
- Sires I., Brillas E., Oturan M.A., Rodrigo M.A. and Panizza M. (2014), Electrochemical advanced oxidation processes: today and tomorrow. A review, *Environmental Science and Pollution Research*, **21**, 8336-8367.
- Sunada F. and Heller A. (1998), Effects of water, salt water, and silicone overcoating of the TiO₂ photocatalyst on the rates and products of photocatalytic oxidation of liquid 3-octanol and 3-octanone, *Environmental Science and Technology*, **32**, 282-286.