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Insights into the formation of PCDD/Fs during the treatment of organo-chlorinated compounds by means of Fenton oxidation

The concern about water pollution has augmented during the last few years due to the increasing domestic and industrial activities together with growing population (A. Detomaso et al., 2003). Among the possible compounds found in wastewaters, chlorinated organic compounds include some of the most toxic and largest groups of hazardous chemicals. Chlorophenols (CPs) comprise a group of organic compounds that can be found in the environment as consequence of their widespread and long-term use in industry and daily life. Owing to their high toxicity and low biodegradability, CPs have been listed by the U.S. EPA and by the European Commission as priority pollutants. Furthermore, CPs are known to be precursors of the highly toxic polychlorodibenzo-*p*-dioxins and polychlorodibenzofurans (PCDD/Fs) that are also considered as priority pollutants. Among the 210 possible congeners of PCDD/Fs, the 17 congeners having the positions 2,3,7,8 chlorinated have received the greatest attention owing to the fact that the human exposure is related with different diseases and cancer, as it has been considered by the U.S. EPA in the case of 2,3,7,8-TCDD (H. Fiedler, 2003).

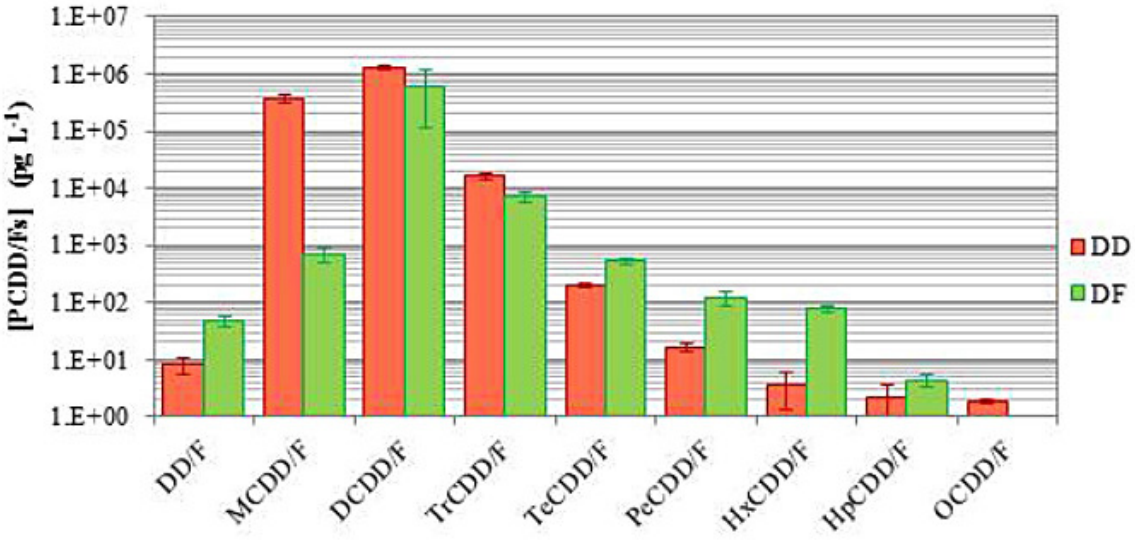

Fig. 1. Polychlorinated-p-dibenzodioxins (DD) and dibenzofurans (DF) profile from non-chlorinated DD/Fs to octachlorinated DD/Fs (OCDD/Fs) after 4 h Fenton oxidation of 15.56 mM 2-CP. [Fe2+]0= 0.18 mM; [H2O2]0= 40.44 mM; [NaCl]0=56.34 mM; pH0=3; Room temperature.

As a result of their low solubility in water almost all the studies regarding PCDD/Fs are focused on gas phase. However, the wide use of compounds such as CPs in insecticides, biocides, etc. has resulted in an increase of the presence of these pollutants in aqueous streams, whose treatment may result in the generation of PCDD/Fs (A. Detomaso et al., 2003). Both CPs and PCDD/Fs are characterized by their resistance towards chemical and biological degradation, so more effective technologies are needed. Advanced oxidation processes (AOPs) postulate as viable technologies to treat recalcitrant wastewaters by means of generating reactive oxygen species (ROS; P. Fernández-Castro et al., 2015). Hydroxyl radical (·OH) is the

most powerful ROS, which is non-selective and reacts rapidly with organic/inorganic pollutants. Among different AOPs, Fenton oxidation is proposed as a feasible technology to convert a broad range of contaminants to harmless or biodegradable products, or even to mineralize them, by using relatively non-expensive reagents which are easy to handle and environmentally safe. Nevertheless, it has been observed that depending on the treatments conditions, the partial mineralization of CPs led to the formation of PCDD/Fs, especially under theoretical substoichiometric ratios of the oxidant ([H2O2]theoretical/[2-CP]0: 20%), room temperature and with a chlorine source, as it is portrayed in Figure 1 (M. Vallejo et al., 2014).

Due to the price and difficulties to analyze the samples containing PCDD/Fs as well as the risks associated to its toxic character, several studies have been carried out to assess and predict the formation mechanisms of PCDD/Fs from 2-CP in gas phase by means of computational calculations, although theoretical studies related to their generation in aqueous solutions are lacked. A preliminary reaction pathway for the formation of PCDD/Fs in aqueous phase is proposed based on theoretical results for gas phase; besides the eight groups of homologues from non-chlorinated to OCDD/Fs have been experimentally quantified in aqueous phase in order to verify the mechanisms involved. Owing to the fact that 2-CP is a molecule composed by one chlorine atom, it could be expected the generation of PCDD/Fs with up to two chlorine atoms. Nevertheless, higher chlorinated PCDD/Fs were observed as displayed in Figure 1 (from TrCDD/F to OCDD/F).

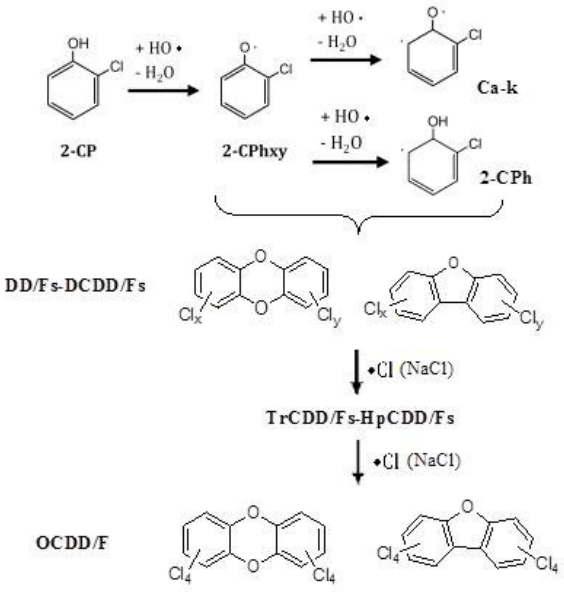

Fig. 2. Mechanistic proposal for the formation of PCDD/Fs during the Fenton oxidation of 2-CP in aqueous phase.

The formation of PCDD/Fs is thermodynamically favored through the formation of radical species such as chlorophenoxy (CPhxy), chlorophenyl (CPh) and α-ketocarbene (Cα-k), leading mainly to the formation of MCDD, DCDD and DCDF (W. Pan et al., 2013). From the results portrayed in Figure 1, it can be infrared that further chlorination reactions of PCDD/Fs are occurring due to the presence of chlorine (as NaCl) in the medium, and since no other phenolic compounds of higher chlorinated degree such as di-CPs were observed, which could serve as precursors of higher chlorinated DD/Fs. Figure 2 shows the mechanistic proposal

schematically: the hydroxyl radical generates the formation of aromatic radicals whose condensation reactions lead to the formation of PCDD/Fs that are sensitive to further chlorination.

Therefore, in spite of our big effort to deep in the comprehension of the mechanisms involved in the generation of PCDD/Fs from model and real solutions, we encourage further experimental and theoretical studies in aqueous phase as a consequence of the great relevance of this toxic pollutants and the increase of the use of chemical products in daily life.

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