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Review

Degradation of chlorophenols and alkylphenol ethoxylates, two representative textile chemicals, in water by advanced oxidation processes: The state of the art on transformation products and toxicity

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HIGHLIGHTS

- Chlorophenols and alkylphenol ethoxylates as industrially important textile chemicals.
- Advanced oxidation processes could generate transformation products more toxic than parent compounds.
- Toxicity of chlorophenols and alkylphenol ethoxylates subjected to chemical oxidation.
- How is related toxicity to transformation products?

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ABSTRACT

Advanced oxidation processes based on the generation of reactive species including hydroxyl radicals are viable options in eliminating a wide array of refractory organic contaminants in industrial effluents. The assessment of transformation products and toxicity should be, however, the critical point that would allow the overall efficiency of advanced oxidation processes to be better understood and evaluated since some transformation products could have an inhibitory effect on certain organisms. This article reviews the most recent studies on transformation products and toxicity for evaluating advanced oxidation processes in eliminating classes of compounds described as "textile chemicals" from aqueous matrices and poses questions in need of further investigation. The scope of this paper is limited to the scientific studies with two classes of textile chemicals, namely chlorophenols and alkylphenol ethoxylates, whose use in textile industry is a matter of debate due to health risks to humans and harm to the environment. The article also raises the critical question: What is the state of the art knowledge on relationships between transformation products and toxicity?

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1. Introduction

The textile industry form a major part of manufacturing production, employment and trade in many developing countries. From the environmental point of view, the textile industry consumes high amounts of water (in some cases as high as 3000 $m^3 d^{-1}$) and generates high-strength and complex effluent streams which contain a very diverse range of contaminants with different intended use in the production train. The characteristics of wastewater from textile processing operations are closely related to the nature of the various industrial processes employed by the industry and the chemicals associated with these operations (Correia et al., 1994). Among the contaminants originated from different stages of the textile processing activities, chlorophenols and alkylphenol ethoxylates deserve special focus due to toxicological concerns associated with them and/or their metabolites. According to surveys of the textile industry in Canada, substituted alkylphenolics and phenols including nonylphenol ethoxylates and chlorophenols were expected to be found in untreated textile mill effluents (Rutherford et al., 2003), indicating that it is not unlikely to detect both of these compound classes in process waters and effluents originated from the textile industry.

In textile finishing, chlorophenolic chemicals are primarily used as biocides (specialty chemicals that control, inhibit or kill the growth of different kinds of microorganisms) in the antimicrobial after-treatment process. Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol), dichlorophen (2,2′-methylenebis(5-chlorophenol)), pentachlorophenol, trichlorophenols and chlorocresols such as 4-chloro-3-methylphenol are some to mention which are among the chlorophenolic textile biocides (Lacasse and Baumann, 2004). However, the majority of them are facing increasing srutiny in terms of their use and application levels or even prohibition due to their inhibitory properties and resistance to biodegradation (McCarthy, 1995). Since the biocidal finishing agents have been designed to act against microorganisms including algae, bacteria and fungi, they are the particular source of recalcitrance and toxicity in dyehouse effluent, and their proper management is becoming a challenging responsibility for the textile manufacturer (Arslan-Alaton and Alaton, 2007).

Alkylphenol ethoxylates are applied in textile industries in auxiliaries formulations (used in pretreatment operations) or in additives as detergents or wetting agents in wool scouring, hydrogen peroxide bleaching and dyeing processes. The alkylphenol ethoxylates, mainly nonyl- and octylphenol ethoxylates, are among the most common nonionic surfactants in textile industries (Lacasse and Baumann, 2004). While ultimate biodegradation results in the complete mineralization of the aromatic structure of alkylphenol ethoxylates, only primary biodegradation is known to be particularly rapid, producing more persistent, toxic and estrogenic metabolites than the parent compound (Mann and Boddy, 2000; Petrovic et al., 2003). The contamination of natural water resources by the persistent alkylphenol ethoxylate metabolites as influenced by the textile effluents has been already reported (Blackburn and Waldock, 1995; Berryman et al., 2004; Loos et al., 2007). Accordingly, a lot of companies even voluntarily stopped using alkylphenol ethoxylate-based chemicals in their household applications (Karahan et al., 2010). However, for industrial applications, alkylphenol ethoxylates are still being used because of their excellent performances and low production costs (Jonkers et al., 2001).

Chemical oxidation applications have been largely documented for the degradation of dyestuffs originating from the textile industry (de Souza et al., 2010; Tehrani-Bagha et al., 2010; Türgay et al., 2011). However, the chemical oxidation of other textile chemicals including alkylphenol ethoxylates has been paid less attention (Arslan-Alaton et al., 2012a, 2012b; Olmez-Hanci et al., 2011). Being free radical-mediated chemical oxidation processes, advanced oxidation processes (AOP) have the ability to successfully treat biologically difficult-to-degrade textile pollutants and oxidize textile wastewater (Tünay et al., 2010). Unfortunately, total mineralization of pollutants in industrial effluents by AOP may be really expensive due to the requirement of the consumption of too large amounts of expensive reactants (Oller et al., 2011). In this regard, significant cost reductions can be achieved by applying AOP as a pre-treatment stage, whose main role is the partial oxidation of the biologically persistent part to produce biodegradable reaction intermediates (Comninellis et al., 2008). However, the partial oxidation of organic contaminants may produce transformation products being more toxic than their parent compounds (Fatta-Kassinos et al., 2011). Accordingly, the collective environmental parameters such as chemical oxygen demand (COD) and total organic carbon (TOC) remain insufficient for the evaluation of the biocompatability of AOP-treated effluents before they can be safely discharged into receiving water bodies or transferred to a biological treatment. At this point, assessment of transformation products and toxicity gains importance in extending the understanding of the overall efficiency of AOP for degradation of industrial pollutants. In fact, the significance of transformation products in point of ecotoxicological view are increasingly attracting the interest of the scientific community. Fig. 1 reveals results of the literature search using the keywords "Advanced Oxidation Processes" and "Toxicity" where the substantial increase of the number of publications (whose full texts were accessible via Web of Science) treating ecotoxicological characterization of AOP can be clearly realized. It is even more worthwhile to conclude from Fig. 1 that the transformation products are increasingly being taken into account in studies relating to the ecotoxicological impact of AOP. Although it is clear that such a simple search underestimates the real number of relevant publications, it still serves to prove the general trend of an increasing interest of the scientific community.

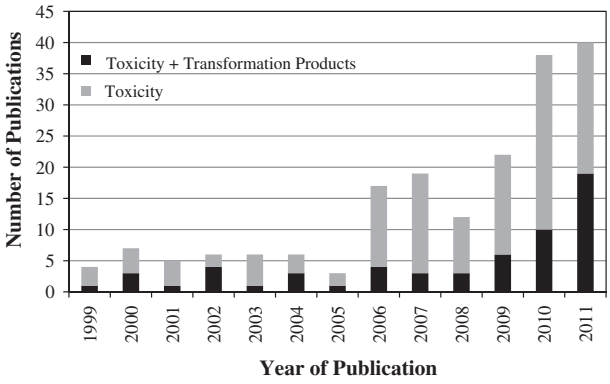

Fig. 1. Scientific studies covering toxicity during application of AOP with and without transformation products included.

In this article, findings being reported in the scientific literature in the last decade regarding the transformation product and toxicity evolution during application of the chemical oxidative treatment processes were critically reviewed for two originally recalcitrant pollutant classes deriving from the textile industry, namely chlorophenols and alkylphenol ethoxylates. Moreover, it tried to present current knowledge on the possible relationships between transformation products and toxicity. The compiled data were discussed in such a manner that the relevant knowledge gaps and research needs were highlighted. In order to provide the reader with some information about AOP and the test organisms involved in toxicity bioassays, a brief overview on them was first introduced.