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Environmental aspects of photooxidative treatment of phenolic compounds

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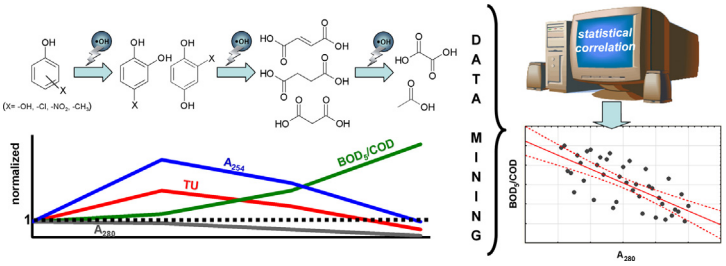
HIGHLIGHTS

- We study the environmental aspects of phenols when treated by UV/H_2O_2 process.
- We investigate the pollutant chemical structure and water quality relationship.
- Structurally defined degradation pathway influence biodegradability and toxicity.
- Water quality varies regarding the formation and distribution of by-products.

GRAPHICAL ABSTRACT



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ABSTRACT

The study was aimed at evaluation of environmental aspects on photooxidative treatment of phenolic compounds by UV/H_2O_2 process. Hydroxy-, chloro-, nitro- and methyl-phenols substituted in *ortho* and *para* positions were used as model pollutants. The influence of pollutant chemical structure on variations of water quality during the photooxidative treatment was investigated. In that purpose, we monitored the changes of total organic carbon (TOC); chemical oxygen demand (COD); aromaticity, measured as absorbance at 280 (A_{280}) and 254 nm (A_{254}); biodegradability, estimated over ratio of biochemical and chemical oxygen demand (BOD_5/COD); and toxicity, estimated on inhibition of *Vibrio fischeri* luminescence (TU). It was found that changes of monitored parameters are influenced by the type and position of substituent. Studied pollutants share sequence in degradation pathway and consequently some of the formed by-products are the same as well. However, their distribution and the formation of specific by-products with characteristic functional groups play significant role in observed variations of water quality, which was particularly reflected in biodegradability and toxicity. The cross-correlation between recorded sum-water parameters is assessed on the basis of calculated Spearman rank coefficients.

1. Introduction

A sizable fraction among single-benzene ring compounds generated by man-made activities pertains to phenols [1]. They are found to be one of the most prevalent contaminants of wastewater streams from petrochemical, polymeric resins, pharmaceuticals, coal conversion plants and chemical industries [2]. Due to their high aqueous solubility and weak adsorption to soils, phenolic compounds are common pollutants in natural waters [3]. They are characterized by low biodegradability making them difficult to remove from the environment by natural occurring processes. Accordingly, they can be found in drinking water reservoirs. The accumulation of these compounds leads to the contamination of the environment and causes many deleterious effects on the living systems. Phenols are toxic to microorganisms, animals and

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humans [2], possessing potential mutagenic and carcinogenic effect as well [2,4]. Considering their negative impact to the environment in general, phenols are recognized by both U.S. EPA [5] and European Commission [6], as priority pollutants, while the World Health Organization recommended the permissible concentration of phenolic contents in potable waters to be $\leq 1\ \mu g\ L^{-1}$ [7].

Toxic and non-biodegradable organic compounds cannot be effectively removed from industrial wastewaters by common treatment technologies [8]. Advanced oxidation technologies (AOTs) have received increased interest due to their potential to oxidize the majority of persistent organics present in the water [4,9–11]. However, total mineralization of organic contaminants using AOTs could be very costly. Thus, AOTs could serve as an oxidative pretreatment method converting non-biodegradable or low-biodegradability organic pollutants to more readily biodegradable contaminants [12,13].

The environmental effect of wastewater originated from chemical production sector, besides biodegradability, should be assessed on toxicity as well. The prediction of the biodegradability and toxicity on the basis of concentration of particular organic pollutant and other parameters with summarizing characteristics which can be easily determined by simple and rapid analytical techniques such as total organic carbon (TOC), chemical oxygen demand (COD), aromaticity (A_{280} and A_{254}), may be a valuable tool in ecological risk estimation [14].

The aim of the study is to evaluate the environmental aspects of photooxidative treatment of eight phenolic pollutants by the means of sum-water quality parameters. The changes of overall organic carbon content, aromaticity, biodegradability and toxicity during UV/H_2O_2 processes were correlated with the structural characteristics of parent pollutants and their degradation pathways, while their relationship was estimated using Spearman rank coefficient.

2. Materials and methods

2.1. Chemicals

Model pollutants: *ortho*-hydroxy-phenol (*o*-HP); *ortho*-chlorophenol (*o*-CP); *ortho*-nitro-phenol (*o*-NP); *ortho*-methyl-phenol (*o*-MP); *para*-hydroxy-phenol (*p*-HP); *para*-chloro-phenol (*p*-CP); *para*-nitro-phenol (*p*-NP); *para*-methyl-phenol (p-MP); were purchased by Sigma–Aldrich, USA. The chemical structures, formulas, physical properties and activities toward $HO^{\bullet}$ and *Vibrio fischeri* of parent pollutants are summarized in Table 1 [15–20]. Methanol (Sigma Aldrich, USA) was used as mobile phase in HPLC analysis. Hydrogen peroxide (H_2O_2, $w = 30\%$), sodium hydroxide (NaOH, p.a.), sulfuric acid (H_2SO_4, >96%), sodium chloride (NaCl, p.a.), sodium sulphite (Na_2SO_3, p.a.), and ammonium metavanadate (NH_4VO_3, p.a.) were purchased from Kemika, Croatia. All experiments were performed with deionized water with conductivity less than $1\ \mu S\ cm^{-1}$.

2.2. Experimental procedure

All experiments were performed with the model solutions containing 1 mM of phenols (Table 2) in the glass water-jacketed batch reactor equipped with UV-C lamp, located in the middle of the reactor in a quartz tube (Fig. S1, Supplementary Material). The value of incident photon flux at 254 nm, $I_0 = 5.12 \times 10^{-6}$ Einstein s^{-1}, was calculated on the basis of H_2O_2 actinometry [21]. The total volume of treated solution was 1.4 L, while its homogeneity was provided by magnetic stirring. Temperature was maintained at $25.0 \pm 0.2\ ^{\circ}C$ by circulating the water through the jacket around the photoreactor. The experimental conditions; initial pH values and $[H_2O_2]$, were determined as optimal regarding the type of pollutant in

Table 1
Chemical structures, properties and activities of studied phenols.

Compound #	1	2	3	4	5	6	7	8
Structure								
Name	Catechol	*o*-Chlorophenol	*o*-Nitrophenol	*o*-Cresol	Hydroquinone	*p*-Chlorophenol	*p*-Nitrophenol	*p*-Cresol
IUPAC name	Benzene-1,2-diol	2-Chlorophenol	2-Nitrophenol	2-Methylphenol	Benzene-1,4-diol	4-Chlorophenol	4-Nitrophenol	4-Methylphenol
CAS number	120-80-9	95-57-8	88-75-5	95-48-7	123-31-9	106-48-9	100-02-7	106-44-5
Formulas								
Chemical	$C_6H_4(OH)_2$	C_6H_4ClOH	$C_6H_4NO_2OH$	$C_6H_4CH_3OH$	$C_6H_4(OH)_2$	C_6H_4ClOH	$C_6H_4NO_2OH$	$C_6H_4CH_3OH$
Molecular	$C_6H_6O_2$	C_6H_5ClO	$C_6H_5NO_3$	C_7H_8O	$C_6H_6O_2$	C_6H_5ClO	$C_6H_5NO_3$	C_7H_8O
Properties								
Molecular weight ($g\ mol^{-1}$)	110.1	128.56	139.11	108.14	110.1	128.56	139.11	108.14
Density: at 20 °C ($g\ mL^{-1}$)	1.344	1.264	1.495	1.047	1.3	1.3	1.5	1.035
Melting point (°C)	105	9.4	44–45	31	172	43–45	113–114	35.5
Boiling point (°C)	245.5	174.9	214–217	191	287	220	279	201.8
Solubility: H_2O, 25 °C ($g\ L^{-1}$)	430	20	2	25	59	27	16	19
Extinction coefficient: at 254 nm ($M^{-1}\ cm^{-1}$)	409	340	1987	462	184	186	1023	263
Quantum yield: at 254 nm (mol Einstein^{-1})	0.0069	0.0221	0.0108	0.007	0.0095	0.0237	0.0049	0.0141
Activity								
Reaction rate constant with $HO^{\bullet}$ ($\times 10^9\ M^{-1}\ s^{-1}$)	11[a]	12[a]	3.4[b]	11[a]	21[a]	9.3[c]	3.8[a]	12[a]
Toxicity (EC_{50}): to *Vibrio fischeri* ($mg\ L^{-1}$)	87.86 (47.7–86.2)[d]	27.49 (22.3–33.8)[d]	52.49 (29.6–53.9)[e]	29.54 (21.5–27.1)[d]	0.088 (0.08)[d]	5.654 (1.07–8.30)[d]	16.32 (9.85–38.2)[d,e]	5.71 (5.53)[f]

Sources: (a) [15]; (b) [16]; (c) [17]; (d) [18]; (e) [19]; (f) [20].