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Review

Photo-degradation of chlorophenols in the aqueous solution

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Abstract

The review presents the chlorophenols photo-degradation kinetics and mechanism in the aquatic environment under UV–vis in the presence of hydroxyl radicals and singlet oxygen. The influence of experimental parameters e.g. pH, dissociation degree, presence of oxidants in solution, number and position of Cl atoms on the quantum yield and reaction rate constant of chlorophenols are discussed. Mechanisms of photolysis, reaction with hydroxyl radicals, singlet oxygen and secondary reactions for mono-, di-, tri-, tetra- and pentachlorophenol are proposed. The pathways for intermediate reactions e.g. dechlorination, oxidation, dimerization for chlorophenols are also presented.

Keywords: Chlorophenols; Photo-degradation; Kinetic study; Mechanisms

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Contents

Abbreviations: CP, chlorophenol; 2-CP, 2-chlorophenol; 2,3-DCP, 2,3-dichlorophenol; 2,4-DCP, 2,4-dichlorophenol; 2,5-DCP, 2,5-dichlorophenol; 2,6-DCP, 2,6-dichlorophenol; 3-CP, 3-chlorophenol; 3,5-DCP, 3,5-dichlorophenol; 4-CP, 4-chlorophenol; 4-Cl-2-MP, 4-chloro-2-methylphenol; 2,3,4-TCP, 2,3,4-trichlorophenol; 2,3,6-TCP, 2,3,6-trichlorophenol; 2,4,5-TCP, 2,4,5-trichlorophenol; 2,4,6-TCP, 2,4,6-trichlorophenol; DMPO, 5,5′-dimethylpyrroline *N*-oxide; k_n, reaction rate constant of the corresponding equations; PCP, pentachlorophenol; S, substrate

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1. Introduction

Chlorophenols (CP) occurs in all components of the natural environment. They result from a variety of sources: the natural chlorination of organic material, biodegradation of phytodefensive chemicals, or the large-scale disinfection of drinking water [1–6]. Chlorophenols are weakly acidic, so in the aquatic environment they occur in both dissociated and undissociated forms. The main photochemical processes involving chlorophenols are: photo-dissociation, photo-isomerization, photo-substitution, photo-rearrangement, photo-oxidation and photo-reduction. In general, the photo-degradation of any substance in the natural environment is a superposition of reactions of several or all of these types, and its rate and quantum yield depend on a variety of factors. The maximum absorption level of the compound, wavelength of radiation, duration of radiation exposure and physical state of the compound undergoing the transformation process play central roles in determining the photochemical processes.

Because of the ubiquitous presence of chlorophenols in the natural environment and their toxic properties, understanding the kinetics and mechanisms of the process of photo-degradation of these compounds is critically important. The results of the investigations concerning this subject are presented below. Despite a great number of publications, however, some questions concerning the mechanisms of reaction during photo-degradation require further investigations.

2. Quantum yield of the photolysis

The quantum yield of a photochemical reaction depends on maximum light absorption of compounds undergoing the process, wavelength of the radiation, the properties of the solvent used [7] and the pH [8–10] of the solution. Boule et al. [9] point out the impact of chlorophenol speciation – dissociated or undissociated – on the quantum yield for photolysis of monochlorophenols upon 254 nm irradiation. Various papers show that photolysis of the anionic forms of these compounds results in a higher quantum yield than that of other molecular forms [10–13]. Some of the results concerning the quantum yield of photo-degradation of various chlorophenols have been taken from the literature and are presented in Table 1.

3. Kinetic study

The ability to undergo chemical transformation upon photon absorption is an intrinsic molecular property and may drastically differ among various compounds. Also, in the aquatic environment, the possibility of photo-induced transformation of the intermediate products of the primary reactions increases when the dissolved organic material has absorbed a high proportion of photons and can act as a potential photosensitizer. In the aquatic environment, singlet oxygen, superoxide ions, hydroperoxyl radicals, hydroxyl radicals and peroxy organic radicals may arise [14–28]. Under these circumstances photo-degradation processes may include direct photolysis and reactions with of reactive species. The kinetics and mechanism of these reactions is highly dependent on experimental conditions such as the wavelength of irradiation, pH of solution, concentration of dissolved oxygen and the presence of sensitizers. The kinetic results of chlorophenol transformation upon direct photolysis and reactions with $^{\bullet}$OH radicals and singlet oxygen are presented below.

3.1. Direct photolysis

The law describing light absorption in an aqueous environment is the Lambert–Beer law for liquid phase, expressed by the equation:

$$\log\left(\frac{E_{\lambda}^{0}}{E_{\lambda}^{I}}\right) = \varepsilon_{\lambda} c_{i} l \qquad (1)$$

where E_{λ}^{0} and E_{λ}^{I} are the light intensities, l the distance in the environment (optical path) [cm], ε the extinction coefficient [$\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$] and c_i is the concentration [M] of component i.

The absorbance at wavelength λ is the product $\varepsilon_{\lambda} c_{i} l$.

The rate constant k for direct photolysis is defined by equation:

$$k = 2,3\phi_{\mathrm{A}}^{\mathrm{A}} I_0 \varepsilon_{\mathrm{A}} l \qquad (2)$$

where $\phi_{\mathrm{d},\lambda}$ is the quantum yield of the reaction, $I_{0,\lambda}$ the light intensity, ε_A the molar extinction coefficient of substance S at wavelength λ, and l is the optical path.

The results from Eq. (2) show that the rate of the direct photolysis of chlorophenols is proportional to the irradiation intensity.

Table 1
Quantum yields (ϕ) for chlorophenols, pH 7

Compounds	ϕ	λ (nm)	Reference
2-Chlorophenol molecular form	0.03	296	[9]
2-CP anionic form	0.20	296	
3-Chlorophenol molecular form	0.09	296	[9]
3-CP anionic form	0.13–0.15	296	
4-Chlorophenol	0.25	296	[9]
	0.75	266	[10]
	0.44	266	[11]
4-Chloro-2-methylophenol	0.66	280	[12]
2,4,5-Trichlorophenol	5.9×10^{-2}	254	[13]
Pentachlorophenol	0.06	185–436	[8]