Ecotoxicology and Environmental Safety 157 (2018) 441–456

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Review

Ecotoxicity of phenol and cresols to aquatic organisms: A review

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ARTICLE INFO

Keywords:
Phenol
Cresols
Ecotoxicity
Aquatic organisms
Biodegradation

ABSTRACT

With the development of industrial production and continuous demand for chemicals, a large volume of wastewater containing phenols was discharged into the aquatic environment. Moreover, chemical leakage further increased the emission of phenols into aquatic systems. Phenol and its methylated derivative (cresols) were selected due to their extensive use in industry and ecotoxicity to freshwater and marine organisms. This review focused on the ecotoxicity of phenol and *m*-, *o*-, and *p*-cresol on aquatic systems. The mechanism of action of phenols was also discussed. The aim of this literature review was to summarise the knowledge of the behaviour, and toxicity on marine and freshwater organisms, of phenols as well as to try to select a series of sensitive biomarkers suitable for ecotoxicological assessment and environmental monitoring in aquatic environments.

1. Introduction

Phenol, a colourless-to-white solid with a characteristic odour, is the simplest monatomic phenol. Cresols, methylated derivatives of phenol, are composed of three isomers [meta-(*m*-), ortho-(*o*-), and para-(*p*-)]. Phenolic compounds are extensively used as materials for organic synthesis and also used in different industries, such as pesticides, dyes, coatings, and oil refining (ASTDR, 2008a, 2008b; Michałowicz and Duda, 2007) and hence, they are ubiquitous in the wastewater from these industries (Jiang et al., 2006; Saravanan et al., 2008; Surkatti and El-Naas, 2017).

Moreover, leakage accidents further increased the possibility of the emission of phenols into the environment. Accidental spills of phenol, which happened in the Port of Gothenburg (Sweden) and Xin'an River (China), caused leakage of a significant amounts of phenol, posing a threat to water quality and aquatic systems (China Chemical Safety Association, 2011; HELCOM, 2002). Due to their high water-solubility (phenol, 8.28 g/100 mL; cresols, 2.15–2.60 g/100 mL), phenol and cresols can persist at a high concentration in aquatic environments (Wei et al., 2016). Water pollution in China is mainly caused by discharged wastewater from dozens of types of industrial pollution source (Zhou et al., 1991). Phenol and *m*-cresol, as priority pollutants of many industrial point source, such as oil processing industry, insecticide factory, and chemical trades, have been named on the list of priority pollutants (68 substances) held by the China Environmental Priority Monitoring Research Group (Zhou et al., 1989). Currently, phenol has been named on a list of the top 20 chemicals likely to pose the highest risk of being involved in an HNS (hazardous and noxious substance) incident held by International Maritime Organization (IMO) (ITOPF, 2011).

In this study, a literature review of the ecotoxicological effects on aquatic organisms and their environmental behaviour in the aquatic environment was conducted for phenol and cresols (including three isomers of cresol). Besides, the effects of environmental factors relating to chemical toxicity and the mechanism of action of phenols on aquatic life were discussed in detail.

2. Current situation: phenol pollution in the aquatic environments

To understand the status of pollutant phenols in aquatic systems, information about the concentrations of phenol and cresols in natural waters was compiled in Table 1. The maximum concentration of surface waters was 2110 μg/L for phenol (Table 1) based on the available studies. Ayeni (2014) concluded that indiscriminate disposal of wastewaters into the aquatic environment and abrogation of the responsibility to manage industrial wastewater before point of discharge caused higher level concentrations of phenol in water systems. As for seawater, the concentrations of volatile phenols (including phenol and cresols) in Maoming onshore fishery (China) were greater than 10 μg/L, and thus were classified as a Class IV pollutant according to Sea Water Quality Standard (SEBC, 1997). Moreover, accidental leakages of phenol and cresols, to sea or a river, may give rise to a significant increase of phenol and/or cresols concentrations in aquatic systems, causing high toxicity

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https://doi.org/10.1016/j.ecoenv.2018.03.089
Received 22 November 2017; Received in revised form 29 March 2018; Accepted 29 March 2018

Table 1
The concentration of phenols in natural waters.

Place	Matrix	Range detected (μg/L)[a]	References
Dzierżązna river and Ner river, Poland	Spring and river	Phenol: ND-0.853	Michałowicz et al. (2008)
Netherlands	Surface water	Phenol: 2.6–5.6	Michałowicz and Duda (2007)
Poland	Runoff	Phenol: 0.1203–0.9116	Grynkiewicz et al. (2002)
Isebo River, Nigeria	River	Phenol: 50–2110	Ayeni (2014)
A perennial freshwater stream, Florida	Surface water	*m*-Cresol: 3.1 *o*-Cresol: 4.7 *p*-Cresol: 2.2	Middaugh et al. (1991)
Seven streams of Arkansas, USA	Surface water	Phenol: 0.110–0.990 (0.260) *p*-Cresol: 0.031–0.150 (0.053)	Haggard et al. (2006)
Three Gorges Reservoir, China	Surface water	Phenol: 0.00001–1.31884 *m*-Cresol: ND-0.16979 *o*-Cresol: ND-0.14753 *p*-Cresol: ND-0.07144	Wu et al. (2012)
Taizihe River, China	River	Monophenols: 8.31–20.86	Bi et al. (2016)
Qiantang River, China	River	Phenol: ND-12.10 (2.06)	Chen et al. (2005)
Taihu Lake, China	Lake	Phenol: ND-0.2056 (0.075) *m*-Cresol: ND-0.0654 (0.0057) *o*-Cresol: ND-0.1995 (0.0301)	Zhong et al. (2010)
Jiaozhou Bay, China	Seawater	Volatile phenols: 0.50–2.39	Qiao et al. (2006)
Meizhou Bay, China	Seawater	Volatile phenols: 1.60–5.60 (3.70)[a]	Chen et al. (1999)
Maoming onshore fishery, China	Seawater	Volatile phenols: 14–26	Yang et al. (2003)

[a] Mean value is inserted in brackets when possible; ND means not detected.

of phenols to aquatic organisms (see below). For example, a total of 400 t of phenol entered the seawater in the Port of Gothenburg, Sweden in 1973 (HELCOM, 2002).

3. The environmental behaviour of phenols in the aquatic environments

The physico-chemical properties of pollutants determine their behaviour upon entering the water (ITOPF, 2011). The Standard European Behaviour Classification (SEBC) codes enshrined a set of criteria for theoretical behaviour according to physico-chemical properties (*i.e.* physical state, density, solubility in water, and vapour pressure). Sink solids (density > seawater) with a solubility of 10% (or less) and sink liquids (density > seawater) with a solubility of 0.1–5% are classified as sinker (S) and sinker/dissolver (SD) by SEBC, respectively (Le Floch et al., 2012). The physico-chemical properties of phenol and cresols were listed in Table 2: the properties of phenol, *o*-cresol, and *p*-cresol (with a density of 1.03–1.05 g/cm^3, and a solubility of between 2.15 and 8.28 g per 100 mL of water) indicate that they will, in theory, behave as S (ATSDR, 2008a, 2008b); however, *m*-cresol and mixed cresol (with a density of 1.03–1.038 g/cm^3 and a solubility of 2.27–2.59 g per 100 mL of water) will behave as SD (ATSDR, 2008b; CAFÉ database, 2017).

Phenol is not expected to volatilise or be adsorbed by sediments and suspended particulates in the aquatic environment (ATSDR, 2008a). Biodegradation and indirect reactions with photochemically produced hydroxyl radicals and peroxyl radicals are expected to be important transport mechanisms (ATSDR, 2008a). For cresols, volatilisation may be the dominant process (ATSDR, 2008b). Yet, these pathways may be influenced by environmental factors *in situ*. The results of microcosm experiments conducted with seawater under simulated marine conditions showed that volatilisation was the dominant attenuation type for phenol, *o*-cresol, and *p*-cresol, and photolysis dominated for *m*-cresol, with half-lives of 4.3–7.9 days for phenol and three isomers of cresol (Wang et al., 2017). The Henry's Law constant for *m*-cresol is the lowest (8.6×10^{-7} atm·m^3/mol) (Lyman et al., 1990), which indicates that the rate of evaporation of *m*-cresol inferior to the others. Experimental bioconcentration factors (BCFs) of 0.28–39 indicated that phenol and the isomers of cresol would not bioconcentrate in aquatic organisms (ATSDR, 2008a, 2008b; NCBI, 2017); however, sound evidence could be concluded, from this review, that the effects of phenol and cresols showed high toxicity and potential sub-acute toxicity to aquatic systems (see below). Hence, the toxicity of phenol and cresols to aquatic organisms is more likely to be a direct effect rather than via their transfer through the food chain (Rocha et al., 2016).

Table 2
Physic-chemical properties of phenol and cresols. Sources: ATSDR (2008a, 2008b) and CAFÉ database (2017).

Chemical name	CAS No.	Physical state	Density (g/cm^3)	Solubility in water (g/100 mL)
Phenol	108-95-2	Solid	1.05	8.28
m-Cresol	108-39-4	Liquid	1.03	2.27
o-Cresol	95-48-7	Solid	1.05	2.60
p-Cresol	106-44-5	Solid	1.03	2.15
Mixed cresol	1319-77-3	Liquid	1.030–1.038	2.59

Based on the available research, bacteria, fungi, and microalgae were able to biodegrade phenol and cresols, and bacteria isolated from polluted environments were the most commonly investigated (Basha et al., 2010; Semple and Cain, 1996). The removal efficiency of phenol by bacteria ranged from 46% to 100%, depending on species type, initial concentration of the chemical, degradation time, and environmental factors (Table 3). The strain *Alcaligenes faecalis*, isolated from diluted activated sludge, could degrade phenol entirely at 1600 mg/L within 76 h (Jiang et al., 2007). The phenol degradation ability of microalgae had been proven (El-Sheekh et al., 2012; Lovell et al., 2002; Werner and Pawlitz, 1978). Among these algae, one marine diatom *Thalassiosira* sp. was reported to have the ability to degrade phenol by using phenol as a carbon source for growth (Lovell et al., 2002). According to Table 3, studies on the biodegradation of isomers on cresol were rarely compared with those on phenol. A concentration of *p*-cresol (100 mg/L) and *m*-cresol (280 mg/L) could be degraded completely (Hamitouche et al., 2014; Jiang et al., 2006). A higher concentration of *m*-cresol (1600 mg/L) could be degraded to 97.81% within 48 h by the bacterium isolated from coking wastewater (Yu and Mao, 2015). Besides, the degradation performance of microorganisms was studied while considering the coexistence of phenol and isomers of cresol. *o*-Cresol degradation was inhibited in the presence of *p*-cresol and/or *m*-cresol (Kar et al., 1997; Surkatti and El-Naas, 2017) and *m*-cresol degradation was inhibited at higher phenol concentrations (Saravanan et al., 2008). One marine organism, *Synechococcus* PCC 7002, had the ability to completely degrade a certain concentration of phenol (Wurster et al., 2003). In conclusion, the biodegradation ability of