

Removal of mono-chlorophenols by slow sand filtration and UV irradiation

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ABSTRACT

We attempted to remove mono-chlorophenols (MCPs) with a slow sand filter and UV irradiation, and compared the removability and the structure. The phenols examined are 2-chlorophenol (2-CP), 3-chlorophenol (3-CP) and 4-chlorophenol (4-CP). MCPs were also examined for removal under ultra-violet (UV) lamp irradiation and the relationship between degradability and molecular orbital properties of the phenols was estimated. The order of removability with a slow sand filter of the examined phenols was 4-CP > 3-CP ≥ 2-CP. Only 4-CP was removed without acclimation. After 5 min of UV irradiation, the initial concentration of MCPs of 20 mg L⁻¹ was decreased to approximately 0 mg L⁻¹, and the stoichiometric amount of chloride ions was released. A decrease in the concentration of dissolved organic carbon (DOC) suggested mineralization of MCPs. The degradability of 2-CP and 3-CP was slightly lower than 4-CP. Molecular orbital calculation suggests that the electrophilic frontier density and HOMO energy may be related to the degradability of MCPs under UV irradiation.

Keywords: 2-chlorophenol; 3-chlorophenol; 4-chlorophenol; Slow sand filtration; UV irradiation

1. Introduction

Slow sand filter is easy to build and operate to obtain tap water. The International Reference Centre for Community Water Supply and Sanitation published a brochure, in which slow sand filtration was reported to be a suitable technique for water supplies in developing countries [1,2].

Chlorophenols (CPs) are chlorinated aromatic compounds found in synthetic chemicals such as insecticides, herbicides and fungicides. They are also found in the natural chlorination of organic materials, biodegradation of chemicals and drinking water as by-products of disinfection [3–9]. Because of their toxicity, the U.S.

Environmental Protection Agency has classified them as priority pollutants [10]. Degradation of CPs occurs by photo-catalysis including photolysis and ultra violet (UV) irradiation, pulsed high-voltage discharge [11,12] and biological degradation [13,14].

UV light breaks down chemical bonds by production of hydroxyl radicals derived from ozone as well as photolysis. Photo-oxidation by UV has been investigated to remove micropollutants in water [15,16].

In previous experiments, we examined the removal of eight types of bisphenols by a slow sand filter and found that an attached group next to a hydroxyl group may inhibit phenol hydroxylation [17]. In this study, we tried to remove three isomers of mono-chlorophenols (MCPs), namely 2-CP, 3-CP and 4-CP, by slow sand filtration and compared

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the removal and the chemical structure. MCPs with low removal were also examined the removal of MCPs under UV irradiation, and estimated the relationship between degradability and molecular orbital properties of each MCP.

2. Materials and methods

2.1. Experimental conditions

We examined the removal of MCPs, shown in Fig. 1, in water by slow sand filtration and under UV light irradiation. A slow sand filter was prepared using a 10 cm × 10 cm × 30 cm plastic bottle, completely submerged and operating in down-flow mode (Fig. 2). The filter column was filled with filter sand of an effective diameter of 0.43 mm and uniformity coefficient of 2.00 [2]. The height of the sand and ponding water was 10 cm and 5 cm, respectively. The filter was operated at filtration rates of 3–4 m per day. Prior to the experiment to remove of phenols, local river water was applied to the sand filter to develop biofilms for 2 weeks. Two weeks after river water filtration, removal rates went around 80%. We took it that biofilms were developed. After biofilm development, we filtered each of the phenols added to river water at the concentration of 20 µg L⁻¹. Properties of the river water are as follows: BOD 0.6–2.0 mg L⁻¹, ammonium nitrogen 0.02–0.32 mg L⁻¹, phosphate ions 0.12–0.20 mg L⁻¹, heterotrophic plate count 1,050–17,500 CFU mL⁻¹, turbidity 3–10 NTU.

Fig. 3 shows the experimental set up for UV irradiation, and Fig. 4 shows the spectrum of the UV lamp, which emitted UV light of wavelengths of 200–400 nm. The properties of the lamp are as follows: input voltage 120 ± 10 V, electric energy 1,500 W, irradiance at 280 mm under the lamp for UV-25

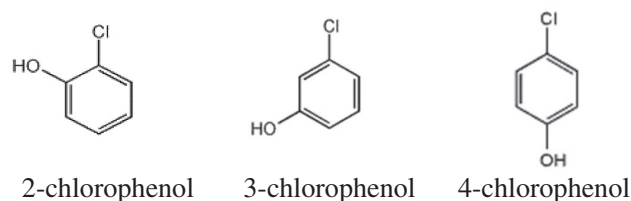


Fig. 1. Mono-chlorophenols examined.

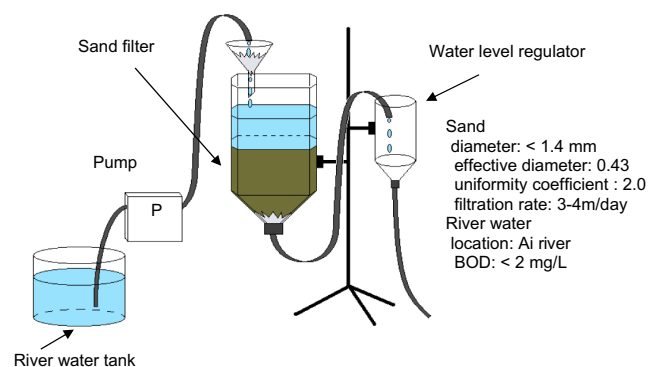


Fig. 2. Experimental set-up for a slow sand filter.

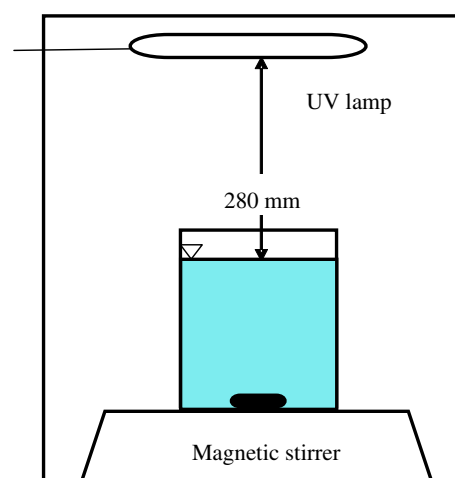


Fig. 3. Experimental set up for UV irradiation.

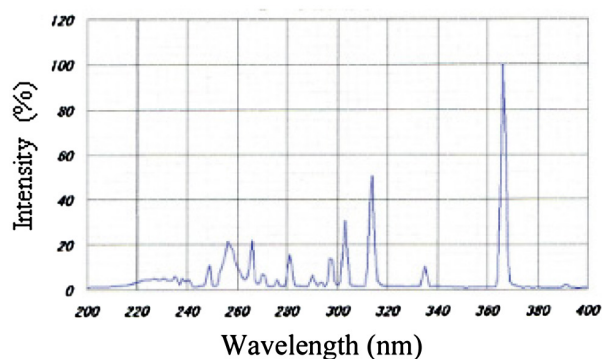


Fig. 4. Spectrum of the UV lamp.

(240–280 nm), UV-31 (280–360 nm) and UV-35 (300–390 nm), 41.8, 37.5 and 46.2 mW cm⁻², respectively. The reaction mixture was 300 mL of initial MCP concentration of 20 mg L⁻¹ in a glass beaker, and it was continuously mixed with a magnetic stirrer. The initial pH of reaction mixtures was adjusted to 5, 7 or 10. Sample water was taken periodically. The distance between the water surface and the UV lamp was kept the same by changing the height of the magnetic stirrer.

2.2. Analytical methods

The concentration of MCPs was determined by high-performance liquid chromatography (HPLC). The conditions for HPLC were as follows: column, XBridge C18 5 µm 4.6 mm i.d. × 250 mm (Waters, Mass., USA); eluent, methanol/water = 70/30, pH 4.0, adjusted with phosphoric acid; flow rate, 1 ml min⁻¹; detector, Hitachi L-2455 Photo Diode Array Detector; temperature, 40°C. Chloride ion was determined by ion chromatography (IC). The conditions for IC were as follows: column, Waters IC-Pak Anion HR (Waters, Mass., USA) 4 mm i.d. × 150 mm; eluent, 0.75 mM potassium biphthalate; flow rate, 1 mL min⁻¹; detector HITACHI L-3700 Conductivity Detector; temperature, 40°C. Sodium chloride was used as the standard sample. Dissolved organic carbon (DOC) was analysed by a TOC analyser (Shimadzu TOC Analyser 5000).

The semiempirical molecular orbital calculation using a PM5 Hamiltonian was performed in MOPAC Version 6 with a CAChe package (Fujitsu Co. Ltd., Tokyo).

3. Results and discussion

3.1. The removal of MCPs by slow sand filtration

Fig. 5 shows the removal percentage profile of CPs during experimental periods of 2 weeks. Full removal is during the filtration periods. The removal (%) of 2-CP, 3-CP and 4-CP during filtration period was 4%–100%, 50%–100% and 100%, respectively. The removal (%) of 2-CP was lower than 3-CP and 4-CP at the initial period of filtration.

The tendency, degradation of 4-CP may be higher than 2-CP or 3-CP, has been shown by researchers [17–21]. Knackmuss and Hellwig [22], and Knackmuss [23] have been investigated degradation of three isomers of chlorophenol through chlorocatechols in *Pseudomonas sp.* B13 and shown that the production of two types of chlorocatechols, i.e., 3- and 4-chlorocatechol from CPs, and suggested that the reaction may be catalysed by a same hydroxylase. A wide spectrum to degrade aromatic compound including CPs by phenol hydroxylase is also shown by other microbial strains [24–26]. Phenol hydroxylase catalyzes many substituted phenols, but an attached group next to a hydroxyl group may inhibit phenols' hydroxylation.

After 1 week of filtration, the removal (%) of 2-CP and 3-CP was gradually improved to 80% and 100%, respectively, suggesting acclimation. The order of removability of examined phenols was 4-CP > 3-CP ≥ 2-CP. Only 4-CP was removed without acclimation, then we tried to remove 2-CP and 3-CP by UV irradiation against unexpected loading of these CPs.

3.2. Removal of MCPs by UV irradiation

As removal of 2-CP and 3-CP was relatively low at the initial period of slow sand filtration, we tried to remove them by UV irradiation. UV light breaks down chemical bonds by producing hydroxyl radicals derived from ozone as well as photolysis. Ozone production is driven by UV irradiation of wavelengths less than 240 nm [27,28]. The UV lamp emitted UV light of wavelengths of 200–400 nm (Fig. 4). Hydroxyl radical is generated from degradation of ozone by UV as follows [28]:

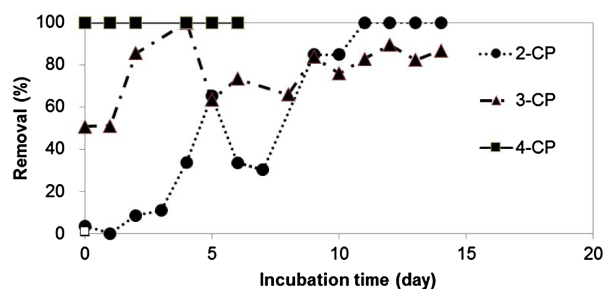
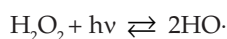
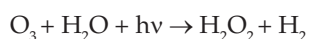


Fig. 5. Removal % profile of MCPs by a slow sand filter.

Decrease of MCPs under UV irradiation was immediate, and the technique was most effective at pH 10, rather than pH 5 or 7, because the production of OH radical is advantageous in alkaline condition. Using the first-order kinetic equation $\ln(C_0/C) = kt$, the rate constant k (min^{-1}) is calculated and summarized in Table 1. A higher rate constant was revealed for 4-CP at every pHs. The removal of 4-CP was rapid at every pH, and the rate constants given were almost the same (Table 1).

The removal (%) of each MCP after 2 min of UV irradiation at pH 10 was 81%, 96% and 100%, for 2-CP, 3-CP, and 4-CP, respectively. The order of degradability was 4-CP > 3-CP > 2-CP. After 5 min of UV irradiation, the initial concentrations of MCPs of 20 mg L^{-1} were decreased to 0. Chloride ions were released along with the decrease of MCPs, and the stoichiometric amount of chloride ions were released. Mineralization may occur after release of chloride ions because the decrease of DOC was slower than the release of chloride ions. As summarized in Table 2, after 60 min of UV irradiation, removal (%) of DOC and release (%) of chloride ions from each MCP were approximately 100%. MCPs were successfully degraded and mineralized by UV irradiation.

Table 1
Rate constant k (min^{-1}) of degradation of 2-CP, 3-CP and 4-CP under UV irradiation at pH5, 7 and 10 (initial concentration: 20 mg L^{-1})

		k (min^{-1})	$t_{1/2}$ (min)
2-CP	pH 5	0.41	1.69
	pH 7	0.44	1.58
	pH 10	0.82	0.85
3-CP	pH 5	0.49	1.41
	pH 7	0.51	1.36
	pH 10	0.95	0.23
4-CP	pH 5	3.67	0.19
	pH 7	3.71	0.19
	pH 10	3.69	0.19

Table 2
Removal (%) of DOC and release (%) of chloride ions from each MCP after 60 min of UV irradiation

		MCP removal (%)	DOC removal (%)	Chloride ions released (%)
2-CP	pH 5	100	100	89
	pH 7	100	100	100
	pH 10	100	100	94
3-CP	pH 5	97	97	99
	pH 7	100	100	98
	pH 10	100	100	97
4-CP	pH 5	100	100	99
	pH 7	100	100	99
	pH 10	100	99	96

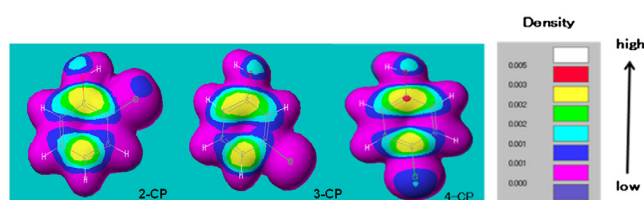


Fig. 6. Contour plot of electrophilic frontier density of 2-CP, 3-CP, and 4-CP.

3.3. Molecular orbital properties of MCPs

Fig. 6 shows contour plots of the electrophilic frontier density of 2-CP, 3-CP and 4-CP. The UV irradiation process produces ozone from O_2 . Hydroxyl radical is generated from degradation of ozone by UV [29]. The electrophilic frontier density is a probability density and a measure of the susceptibility of the substance to attack by an electrophile such as hydroxyl radical [30]. The density reveals reactive sites based on the electron distribution of active orbitals near the highest occupied molecular orbital (HOMO). In nucleophile such as phenols, larger absolute value of HOMO energy indicates lower reactivity [31,32].

As shown in Fig. 6, only 4-CP has a small pale blue area on the Cl atom. This is a more vulnerable area than blue and magenta. Degradation of 4-CP is quick because it has the highest density, shown as “red-” in the upper area of the molecule as well as a relatively higher electrophilic frontier density at the Cl atom. With regard to 2-CP and 3-CP, they have no red areas near the first carbon atom, and they have lower electrophilic frontier density at the Cl atom than that of 4-CP. HOMO energy of each MCP was -9.119 , -9.172 and -8.990 for 2-CP, 3-CP, and 4-CP, respectively. In addition, 2-CP and 3-CP have larger absolute values of HOMO energy than 4-CP.

Molecular orbital calculation of MCPs shows that removal of CPs under UV irradiation is partly explained on the basis of molecular orbital properties. The magnitude of decomposition of MCPs by UV irradiation may be related to the electrophilic frontier density of the Cl atom in MCPs and HOMO energy.

4. Conclusions

We attempted to remove MCPs with a slow sand filter and UV irradiation. The removal (%) of 2-CP, 3-CP and 4-CP during the filtration period was 4%–100%, 50%–100% and 100%, respectively, at an initial concentration of $20 \mu\text{g L}^{-1}$. Only 4-CP was removed without acclimation. An attached group next to a hydroxyl group may inhibit phenol hydroxylation.

The removal (%) after 2 min of UV irradiation at pH 10 was 81%, 96% and 100%, for 2-CP, 3-CP and 4-CP, respectively. The order of UV degradability was 4-CP > 3-CP > 2-CP. After 60 min of UV irradiation, removal (%) of DOC and release (%) of chloride ions from each MCP were approximately 100%. MCPs were successfully degraded and mineralized by UV irradiation.

The magnitude of decomposition of three isomers of MCP by UV irradiation may be related to the electrophilic frontier density of the Cl atom in MCPs and HOMO energy.

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