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Degradation characteristics of metoprolol during UV/chlorination reaction and a factorial design optimization

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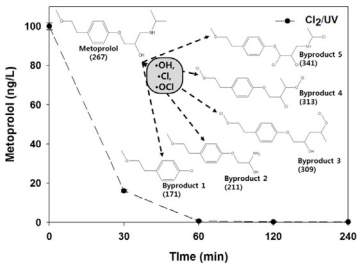
HIGHLIGHTS

- UV/chlorine reaction effectively removed metoprolol in water.
- DOM mainly affected the removal of metoprolol during UV/chlorination reaction.
- The established model using a factorial design was well fitted to experimental data.
- Five transformation byproducts were identified during UV/chlorination reaction.
- OH and chlorine radicals mainly transformed metoprolol into its byproducts.

GRAPHICAL ABSTRACT



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ABSTRACT

Metoprolol (MTP), a hypertension depressor, has been increasingly detected even after conventional water treatment processes. In this study, the removal of MTP was compared using chlorination (Cl_2), UV–C photolysis, and UV/chlorination (Cl_2/UV) reactions. The results showed that the UV/chlorination reaction was most effective for MTP removal. MTP removal during UV/chlorination reaction was optimized under various conditions of UV intensity (1.1–4.4 mW/cm^2), chlorine dose (1–5 mg/L as Cl_2), pH (2–9), and dissolved organic matter (DOM, 1–4 mg C/L) using a two-level factorial design with 16 experimental combinations of the four factors. Among the factors examined, DOM scavenging by OH radicals was the most dominant in terms of MTP removal during UV/chlorination reaction. The established model fit well with the experimental results using to various water samples including surface waters, filtered and tap water samples. The optimized conditions (UV intensity = 4.4 mW/cm^2, [Cl_2] = 5 mg/L, pH 7, and [DOM] = 0.8–1.1 mg C/L) of the model removed more than 78.9% of MTP for filtered water samples during UV/chlorination reaction. Using LC–MS/MS, five byproducts of MTP (molecular weight: 171, 211, 309, 313, and 341, respectively) were identified during UV/chlorination reaction. Based on this information, the MTP transformation mechanism during UV/chlorination was suggested. Our results imply that applying UV/chlorination process after filtration stage in the water treatment plant (WTP) would be the most appropriate for effective removal of MTP.

1. Introduction

Metoprolol (MTP) is a representative β-blocker used to treat cardiovascular diseases such as hypertension, angina, and arrhyth-

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mias [1,2]. MTP is soluble in water and is an aromatic compound with various chemical functional groups such as hydroxy-(—OH), methoxy-(—O—CH_3), and -amine (—NH—). These complicated chemical properties of MTP may limit its elimination using conventional water treatment techniques such as coagulation, filtration, and biological degradation. MTP has been detected in wastewater treatment plants (WWTPs) and water treatment plants (WTPs). Huggett et al. [3] measured MTP in WWTP effluents in 34 states across the United States, and reported average concentrations up to 74 ng/L. Lee et al. [4] also detected MTP (257 ng/L) in seven Canadian sewage treatment plants.

The persistence of MTP in conventional water treatment systems has been continuously reported. Schriks et al. [5] also reported high MTP levels of 2100 ng/L in drinking water, even after treatment, in the Netherlands. Vieno et al. [6] showed that MTP (<10%) was ineffectively removed in pilot-scale water treatment processes using coagulation and sand filtration processes. Therefore, recent studies have focused on the efficient elimination of MTP during water treatment processes [1,2,7,8]. These studies mainly applied ozonation (O_3), ultraviolet (UV) radiation, UV/ozonation (UV/O_3), and ozonation/chlorination (O_3/Cl_2) for MTP removal during disinfection stage in WTPs, because strong oxidation with disinfectant (e.g., chlorine, ozone, and UV) is known to remove refractory pollutants.

Disinfection effectively oxidizes refractory contaminants in WTPs. However, conventional disinfection is not designed to remove micropollutants, but rather to eliminate microbial activity in WTPs. Considering the sustainability of disinfection for drinking water, chlorine is a more appropriate disinfectant than other methods such as UV and ozonation. Von Gunten [9] discussed that ozone is unstable in water and reacts with natural organic matter (NOM). UV radiation can also be used in disinfection processes in WTPs; however, this process also causes photochemical reaction depending on the photosensitivity of the compounds along with disinfection reaction [10,11].

Recently, it was reported that the oxidation of MTP by chlorination is ineffective [12]. However, a combination of disinfectants with advanced oxidation processes (AOPs) can be used to remove MTP [2,13] because oxidants such as the hydroxyl radical (·OH) non-selectively oxidize organic compounds. Huerta–Fontela et al. [7] showed that >50% of MTP was removed during the O_3/Cl_2 process. Šojić et al. [2] also showed that 84% of MTP was degraded using the UV/O_3 reaction.

Many studies reported effective elimination when the parent compounds were reduced using only the suggested water treatment. However, the transformation byproducts must be identified because the byproducts can be more toxic than the parent compounds [8,14–16]. For these reasons, the optimization of MTP removal and the identification of byproducts are important when the selected process is applied in WTPs.

In this study, we evaluated the MTP removal efficiency using UV photolysis, chlorination-only, and UV/chlorination reactions. The selected processes were then optimized according to various parameters (UV light intensity, chlorine dose, pH, and DOM) using the two-level factorial design of experiments (DOE). For the suitability of the optimization, the established model was then applied to various water samples unclosing surface and filtered waters. Finally, MTP ddegradation byproducts during the UV/chlorination reaction were identified using liquid chromatography tandem mass spectrometry (LC–MS/MS), and the possible degradation pathways of MTP were constructed.

2. Material and methods

2.1. Chemicals

Metoprolol (MTP, $C_{15}H_{25}NO_3$) was obtained from Sigma–Aldrich. Table 1 summarizes the physicochemical properties of MTP. The stock solution for MTP was prepared by dissolving 1 g/L MTP in methanol (Fisher Scientific, Pittsburgh, PA, USA), which was diluted as necessary. The stock solution was refrigerated at 5 °C in the dark to prevent biological degradation. All tested solutions (with the exception of samples collected from surface waters and WTPs) were prepared in deionized water obtained from a Milli-Q water generator (R = 18.2 MΩ/cm, Millipore, Billerica, MA, USA).

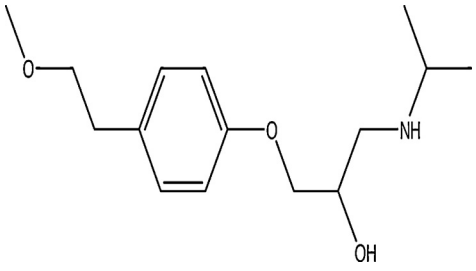
Sodium hypochlorite solution (NaOCl), and sodium thiosulfate ($Na_2S_2O_3$) were purchased from Sigma–Aldrich and used as chlorine disinfectant and its quencher, respectively. Humic acid (Sigma–Aldrich Co., Ltd., USA) was used as an indicator for dissolved organic matter (DOM). The stock solution of humic acid was prepared by dissolving humic acid in deionized water. To adjust the initial pH of solutions, 0.5 N sodium hydroxide (NaOH, Mallinckrodt, St. Louis, MO, USA) and 0.5 N hydrochloric acid (HCl, Sigma–Aldrich Co., Ltd., USA) were used.

Ammonium acetate ($CH_3CO_2NH_4$, Sigma–Aldrich Co., Ltd., USA), ammonium formate (HCO_2NH_4, Sigma–Aldrich Co., Ltd., USA), and formic acid (HCOOH, Fluka, Buchs, Switzerland) were used as buffers in the analytic mobile phase when we measured MTP using LC–MS/MS.

2.2. Water samples.

Surface water was collected from the Han River near Seoul, Korea in the summer of 2012. Two samples (Surfaces A and B) were collected at the site, and other samples were collected from a

Table 1
Physicochemical properties of metoprolol.

Chemical structure	Investigated contents	
	Molecular formula:	$C_{15}H_{25}NO_3$
	Molecular weight:	267.4
	Log K_{ow}:	1.88[a]
	pKa:	9.6[b]

[a] [42].
[b] [14].