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Ozonation for source treatment of pharmaceuticals in hospital wastewater – Ozone lifetime and required ozone dose

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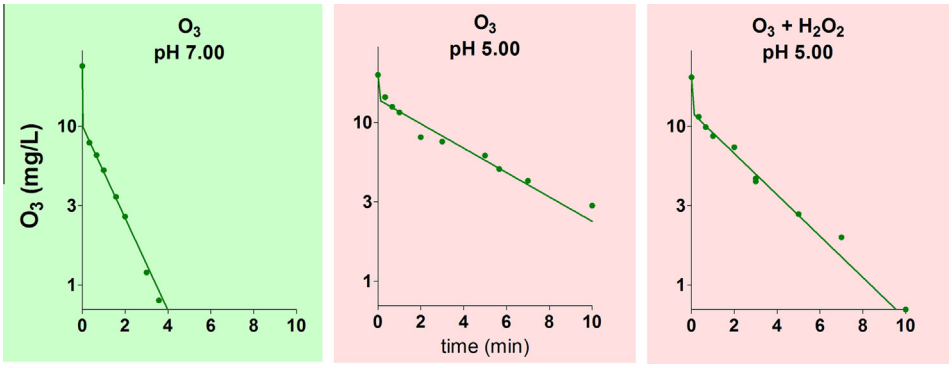
HIGHLIGHTS

- Ozone dosage was determined for pharmaceuticals removal in hospital wastewater.
- The ozone dosage required varied 2-fold with both DOC and pH experienced over time.
- DOC normalized ozone dosage for 90% removal of 32 pharmaceuticals was determined.
- At low pH, pharmaceuticals need less ozone while ozone lifetime increased to 20 min.
- H_2O_2 dosing shorten the ozone lifetime at low pH to 5 min similar to neutral pH.

GRAPHICAL ABSTRACT



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ABSTRACT

Ozonation aimed at removing pharmaceuticals was studied in an effluent from an experimental pilot system using staged moving bed biofilm reactor (MBBR) tanks for the optimal biological treatment of wastewater from a medical care unit of Aarhus University Hospital. Dissolved organic carbon (DOC) and pH in samples varied considerably, and the effect of these two parameters on ozone lifetime and the efficiency of ozone in removing pharmaceuticals were determined. The pH in the effluent varied from 5.0 to 9.0 resulting in approximately a doubling of the required ozone dose at the highest pH for each pharmaceutical. DOC varied from 6 to 20 mg-DOC/L. The ozone required for removing each pharmaceutical, varied linearly with DOC and thus, ozone doses normalized to DOC (specific ozone dose) agreed between water samples (typically within 15%). At neutral pH the specific ozone dose required to remove the easiest degradable pharmaceutical, sulfadiazine, was 0.50 ± 0.04 mg-O_3/mg-DOC and the most recalcitrant, diatrizoic acid, required 4.7 ± 0.6 mg-O_3/mg-DOC. The lifetime of ozone increased drastically in the higher end of the indicated dosage. At the lowest observed pH of 5.0, its lifetime was quadrupled to 20 min which influences the design of the reaction tank. The addition of 0.1 mg-H_2O_2 per 1 mg-O_3 mitigated the prolonged lifetime without a corresponding influence in the pharmaceutical removal efficiency of ozone.

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1. Introduction

The occurrence of pharmaceutical compounds in the aquatic environment is a known environmental issue, which cause a major concern as regards their potential impact on the environment and

Abbreviations: DDO_3, decadic dose of ozone, required ozone dose needed to remove 90% of a pharmaceutical; DO_3, delivered ozone dose; DOC, dissolved organic carbon; MBBR, moving bed biofilm reactor; WWTP, wastewater treatment plant.

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human health. Wastewater has been pointed out as the main route of entry of pharmaceuticals into the environment [1]. Pharmaceuticals utilized by humans are excreted either unchanged or as metabolites through feces or urine and transported with wastewater to WasteWater Treatment Plants (WWTPs) where some pharmaceuticals are totally or partly removed before the effluent is discharged [2]. Although, the pharmaceuticals are found in low concentrations, they might adversely affect humans and living organisms [3].

Since several pharmaceuticals are poorly removed by conventional WWTP, various advanced tertiary treatments have been investigated [4]. The integration of ozone as an additional treatment step in the existing WWTP has become a widely accepted polishing technology for removing pharmaceuticals and other micro-pollutants in wastewater effluents [5–10]. Furthermore, treatment with ozone was found to be more cost effective than UV or UV/H_2O_2 in the removal of estrogens in effluent from biologically treated wastewater [7,11] and it is more easily applied than activated carbon. During ozonation, micro-pollutants are oxidized either by a direct reaction with ozone (Eq. (1)) or indirectly by the non-selective, highly reactive hydroxyl radicals (Eq. (4)) [12]. Hydroxyl radicals are produced during the decomposition of ozone (Eq. (2)) and the rate of decomposition increases with increasing pH [12]. Addition of H_2O_2 prior to ozonation, which is known as peroxone, accelerates the decomposition of ozone to the non-selective hydroxyl radical (Eq. (3)) [12]. Ozone efficiency against miscellaneous compounds is described by the reaction rate constants of micro-pollutants with these two, k_{O3} and k_{OH} [13,14].

$$R + O_3 \rightarrow R_{ox} \quad (1)$$

$$H_2O + O_3 \rightarrow O_2 + 2HO^{\cdot} \qquad (HO^{-}\text{catalyzed}) \quad (2)$$

$$H_2O_2 + 2O_3 \rightarrow 3O_2 + 2HO^{\cdot} \quad (3)$$

$$R + HO^{\cdot} \rightarrow R_{ox} \quad (4)$$

Wastewater from hospitals are often mixed with municipal wastewater and treated at the municipal WWTPs. Several studies have shown that the contribution of hospitals to the overall input of pharmaceuticals to the municipal WWTPs is minor [15–17]. Despite the debate on the importance of hospital wastewater as a significant point source for pharmaceuticals in scientific literature, Danish hospitals are required to make plans for a reduction in concentrations of pharmaceuticals occurring in their wastewater due to political interest in hospital wastewater.

If biological treatment (for example using activated sludge or biofilms) followed by ozonation is applied for point source treatment of micropollutants at a hospital, certain challenges can be envisaged in the water chemistry when compared with a system operation on municipal wastewater, owing to the lack of mixing with other sources of wastewater: Firstly, pH might systematically deviates more from neutral pH than the wastewater of the entire municipal system would, or it fluctuates considerably due to absence of mixing with many other sources. Additionally, a small source treatment system, intended for a single hospital building might not use denitrification for its biological treatment, as any nitrate released will be consumed in the sewer system. Thus, alkalinity in the water is consumed through the nitrification of ammonia and this might be particularly significant in hospital wastewater which is known to contain more reduced nitrogen than municipal wastewater [18,19]. At lower pH, ozone is converted slowly to hydroxyl radicals ($HO^{\cdot}$; Eq. (2)) and thus the lifetime increases for ozone. Secondly, the concentration of the matrix components in the effluent consuming ozone in competition with the targeted pharmaceuticals will inherently fluctuate due to single events in the hospital, which have proportionally more effect on the local treatment system than similar events that are averaged by dilution in a larger wastewater system prior to entering a municipal WWTP.

Thus, this work is aimed at quantifying the variation in ozone requirement necessary for the removal of pharmaceuticals in a biological pre-treated wastewater from a single medical section of a hospital which is caused by the smaller system. We addressed the special problem associated with the single source character majorly because the ozone dosage for removal of each pharmaceutical is influenced by greater DOC and pH variation. Experiments on the variations of each parameter are performed while determining the ozone kinetic and the ozone dosage required for removing a range of pharmaceuticals. Additionally, we investigated the extent of the expected increase in ozone lifetime at low pH and if it can be mitigated through the application of a small dose of hydrogen peroxide.

2. Methods

2.1. Chemicals

All pharmaceutical reference standards of analytical grade (>98%) were purchased from different suppliers (Table S1 and [20]). A stock solution of the pharmaceuticals was prepared in methanol (Merck, Darmstadt, Germany). All other chemicals were purchased from Sigma–Aldrich Denmark ApS and were used as received. The experimental set-up for the ozonation was based on a 20 g/h ozone generator from O3-Technology AB, Vellinge, Sweden, which was supplied with dry oxygen gas. To create an ozone stock solution, the generated ozone was dispersed through a diffuser in a collection bottle containing ultra-pure water which was immersed in an ice bath in order to increase ozone solubility. To further increase the solubility of the ozone a manometer and a valve were placed after the collection bottle and a pressure at 1.4 barG was established. Based on these experimental conditions, the concentration of ozone in the stock solution was between 70 and 90 mg/L.

2.2. Analytical Techniques

2.2.1. Determination of ozone concentration

Ozone concentration was quantified using the indigo method [21]. The reagents used were 0.5 M phosphate buffer at pH 2 and 1.00 g/L potassium indigotrisulfonate dissolved in 20 mM phosphoric acid. For the ozone decomposition profile, the volumes from Bader and Hoigné [21] were downsized to fit into a 3 mL cuvette. Specifically, 0.100 mL indigotrisulfonate (1.0 g/L) and 0.250 mL phosphate buffer (0.5 M at pH 2) were added to the cuvette. Ultra-pure water and sample were then added, so the total volume became 2.5 mL. The quantity of sample and ultra-pure water was varied depending on the ozone concentration. The absorbance of the unreacted indigotrisulfonate was measured at 600 nm. By comparing the absorbance of a blank with the sample and using $\Delta A = -20{,}000$ 1/(cm mol ozone added per L), the ozone concentration was determined.

The delivered ozone dose was determined by adding a sufficient amount of indigotrisulfonate and 10 mL phosphate buffer into 100 mL sample. For example, a water sample (100 mL) was ozonated with an ozone dose of 2 mg/L. To determine the delivered ozone dose, 4.0 mL indigotrisulfonate (1.0 g/L) and 10 mL phosphate buffer were added into a 100 mL volumetric flask and it was filled to the mark with ultra-pure water and then poured into a glass bottle. The same amount of ozone stock solution was then added to the glass bottle as was added to the water sample. The absorbance of the unreacted indigotrisulfonate was measured at

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