Addressing Global Antibiotic Contamination: Effective Degradation of Ciprofloxacin with Ozone Microbubbles—A Comprehensive Study of Spectroscopic, Kinetic, and Antibacterial Effects

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Introduction

The shared goal of one health and global health is to optimize health outcomes for individuals, communities, and ecosystems worldwide through collaborative and interdisciplinary approaches. A critical challenge within this framework is antimicrobial resistance (AMR), where microorganisms adapt to antibiotic exposure, posing significant threats to public health. Of particular concern is the high concentration of antibiotics and their residues found in the hospital wastewater (HWW) due to inadequate treatment technologies [1]. Ciprofloxacin [CIP; $C_{17}H_{18}FN_3O_3$] **(Fig. 1)** is one of the most reported antibiotic pollutants in the environment [2,3]. CIP was detected at concentrations of 2,6 mg/L and 28–31 mg/L in the effluent of HWW [4] and pharmaceutical manufacturing unit [5], and reported with values as high as 6.5 mg/L in two Brazilian lakes [6,7], but it is worth noting that this low level micro-pollutant increased the possibility of resistance development in HWW [8,9].

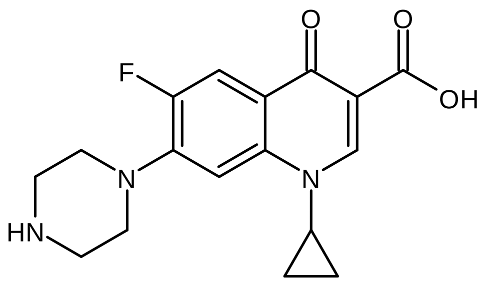

Fig. 1. Chemical structure of CIP.

In countries like Indonesia, limited resources exacerbate these challenges, emphasizing the urgent need for comprehensive action within the one health and global health paradigm. In response to this challenge, innovative wastewater treatment methods such as ozonation have been proposed as a means to mitigate the presence of antibiotic. Besides being a potent oxidiser (E° = 2.07 V) [10], ozone is also an environmentally friendly oxidizer, making it a sustainable solution to emerging contaminant (EC) problems. However, ozone has a low solubility in water, with Henry's law solubility constant (H^{CP}) being $1.0 \times 10^{-6} - 1.3 \times 10^{-4}$ mol/m^3.Pa [11], and may result in a low mineralization capability.

Methods

Ozonation alone is inadequate to treat persistent contaminants in wastewater. Ozonated-micro- and nano-bubbles can be generated by a simple aerator pump. Ozonated-micro- and nano-bubbles have an extra small diameter and a super low Rayleigh number in water [12]. These properties enable them to rise slowly toward the water surface [13]. Therefore, they show a prolonged persistence when dispersed in treated water, thus enhancing the mass transfer between the ozone and the water containing the pollutants [14,15]. This study used a scaled-up volume of 10 mg/L CIP solution (10 L) placed inside an opened-up acrylic tub with dimensions of 37 × 24 × 15 cm^3. Into this solution, the ozone generated by a double dielectric barrier discharge (DDBD) plasma generator was injected continuously for 600 mins. The ozone was injected in two different ways, i.e., through diffused ozonation using a stone diffuser (d = 1.2 cm and h = 2.9 cm) or through an enhanced ozonation by an aerator pump, which is a pressurized dissolution method to generate microbubbles. This aerator had a propeller perpendicular to the intake ozone [16,17] and a pump system for the flow of the CIP solution. The pump moves the aqueous solution of CIP at a speed of 50 L/mins, and the propeller rotates this solution at a high speed. Thus, the pressure of the flowing solution is considerably lower than the pressure of the inlet ozone around the propeller. Based on the different ozonation techniques, the degradation of CIP was then investigated under conventional ozonation (FO system) and ozonated microbubbles (APO system) for every 30 mins.

Results and Discussion

The number of captured microbubbles in the same sampling area in the APO system (34 microbubbles out of 94 bubbles) was higher compared with that in the FO system (0 microbubbles out of 49 bubbles). The diameter of the microbubbles was in the range of 62–306 μm in the APO system compared with 109–2719 μm in the FO system. This result aligned with the average dissolved ozone (C_{DO_3}) in distilled water in the APO and FO systems, which were 0.43 and 0.31 mg L^{-1}, respectively. The best fitting lines revealed that the APO system reached saturation at 20 mins, which was faster than that of the FO system (40 mins).

The CIP degradation, in the other section, shows the time-dependent absorption spectra of the CIP solution treated using the APO and FO systems. The degradation efficiency of CIP upon ozone treatment injected through the APO was 83.5%, which was significantly higher than that obtained during the treatment by the FO system (60.9%). With the post-treatment by ozonated bubbles using the APO system, the inhibition zone decreased to 6 mm for *E. coli* and *S. aureus* strains. These results suggested that the ozonated bubbles in the APO system reduced the antibacterial activity of CIP against *E. coli* and *S. aureus* by 14 and 8 mm, respectively. These values were higher than those of the ozonated bubbles in the FO system, which reduced 7 and 5 mm of the antibacterial activity against *E. coli* and *S. aureus*, respectively.

The MIC values of the CIP solution before ozone treatment in the APO and FO systems were 0.043 and 0.035 g mL^{-1} against *E. coli* and 0.093 and 0.085 g mL^{-1} against *S. aureus*. Such decrement in the antibiotic activity of the remaining CIP and their by-products was reported by Zhai et al. (2021) and De Witte et al (2010). This finding offers an interpretation that ozone disintegrates the piperazinyl moiety of CIP [20], which is responsible for its antibacterial activity against Gram-negative and Gram-positive bacteria [21]. It is also noteworthy that the piperazinyl moiety of CIP has a large electron density, making it susceptible to attack by free radicals, such as $OH^{\cdot-}$, $O_2^{\cdot-}$, and $HO_2^{\cdot-}$ [22,23]. In most reports, these ROS would likely attack the fluorine group first with substitution or hydrolysis reactions [20,23,24], although the cleavage of the C—F bond in the fluorine group requires more energy than the breakage of the C—H or C—N bonds [24].

Conclusion

The APO system demonstrated superior performance in all tested parameters compared to the FO system, highlighting its potential as an effective solution for degrading antibiotics like ciprofloxacin in wastewater. This study shows that advanced technology can be both simple and scalable, offering promising opportunities for countries like Indonesia to become more self-reliant in addressing hospital wastewater treatment challenges. As the global threat of antimicrobial resistance (AMR) continues to grow, it is essential to invest in and further develop technologies like ozonated microbubbles, which can help eliminate micro-pollutants from wastewater. By doing so, we can support Indonesia's Vision 2045 and contribute to achieving global health and sustainability goals.

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