Research Article

Removal of Antibiotics from Real Hospital Wastewater by Cold Plasma Technique

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Hospital wastewater contains a complex mixture of bioactive substances and microorganisms that are deleterious to humans and aquatic animals. In this study, four antibiotics, namely, ofloxacin, ciprofloxacin, cefuroxime, and amoxicillin, respectively, from the wastewater of seven hospitals in Ho Chi Minh City, Vietnam, were monitored. The results revealed that the wastewater from these hospitals is contaminated with at least one of the antibiotics. In addition, the degradation capacity of the antibiotics by the wastewater treatment plant at one of the hospitals by the cold plasma technique was investigated. Furthermore, effects of the variation in pH, interelectrode distance, applied voltage, and reaction time on the removal efficiency were investigated in terms of the reduction in antibiotics concentration, COD, and ammonia. Ciprofloxacin, cefuroxime, COD, and ammonia were almost eliminated, while ofloxacin and amoxicillin were reduced by more than 72% under optimum conditions (initial pH of 10, reaction time of 15 min, applied voltage of 30 kV, and interelectrode distance of 10 mm). All of these factors affected the removal efficiency. The removal efficiency was most robust in the first 5 min, and it increased with the increase in the reaction time. However, the removal efficiency tended to saturate over time, while it decreased with the increase in the reaction time. With an applied voltage of 30 kV onwards, the removal efficiency was not significantly different. Most of the pollutants were predominately eliminated under slightly alkaline conditions (pH of ~10). In addition, primary oxidants in the aqueous phase, such as O_3 , H_2O_2 , and $\cdot OH$, were generated. Besides, the obtained results also revealed that the decomposition of ciprofloxacin and cefuroxime follows the first-order reaction kinetics; meanwhile, the third-order reaction kinetics was most likely for the decomposition of ofloxacin and amoxicillin.

1. Introduction

As one of the sources of waste, hospital wastewater (HWW), which contains a high concentration of detergents, disinfectants, hormones, and even antibiotic compounds, causes severe environmental pollution. The presence of these compounds in HWW poses an adverse threat to living organisms. Several studies have reported that these antibiotics and their residues pose a substantial toxic risk to aquatic organisms [1]. Moreover, antibiotic residues can accelerate the production of antibiotic-resistant bacteria and

antibiotic-resistant genes even at low concentrations, which could be a major threat to public health globally [2, 3]. Extensive studies have reported that antibiotic compounds originating from HWW can be transported to ponds, rivers, and wastewater treatment plants [4]. Therefore, these compounds must be eliminated before their discharge into sewage systems. Several methods have been developed to eliminate these compounds in HWW. Conventional processes such as coagulation, aerotank, and adsorption have been applied for the treatment of real HWW; however, these methods are not adequate to remove contaminants [5–7].

Some advanced oxidation processes (AOPs), including photocatalysis [8, 9], ozone treatment [10], activated persulfate [11, 12], electro-Fenton process [13], and an electron-beam process [14–16], have successfully mitigated the pollutants present in synthetic HWW; however, these AOPs exhibit practical limitations when used on an industrial scale.

Recently, the application of cold plasma—one of the AOPs—has attracted considerable attention for wastewater treatment due to its efficiency, less chemical requirements, and low sludge production [17]. Cold plasma has been employed for the degradation of recalcitrant pollutants in the wastewater generated from pesticide production [18], a slaughterhouse [19], textiles [20], and pharmaceuticals [21–24].

Under aqueous conditions, cold plasma typically generates strongly reactive free radicals or molecules *in situ*, such as hydroxyl radicals ($\cdot\text{OH}$), hydrogen radicals ($\cdot\text{H}$), hydrated electrons (e^-), hydrogen peroxide (H_2O_2), ozone (O_3), and even UV light [18] by the following process [25].

The as-formed powerful oxidants can decompose and mineralize organic pollutants into carbon dioxide and water. Some studies have reported that cold plasma is an efficient technology for the removal of antibiotics. Lou et al. [26] have reported that the use of only dielectric barrier discharge (DBD), a type of cold plasma, can degrade >80% chloramphenicol in contaminated soil. Kim et al. [27] have employed a DBD system and reported the removal of 9 antibiotic compounds, namely, lincomycin, ciprofloxacin, enrofloxacin, chlortetracycline, oxytetracycline, sulfathiazole, sulfamethoxazole, sulfamethazine, and trimethoprim, respectively, from a synthesis solution, with removal efficiencies varying from 60% to 90%. In addition, Sarangapani et al. have employed cold plasma for the high-efficiency mitigation of two widely used antibiotics (i. e., ofloxacin and ciprofloxacin, respectively) from water and meat effluents [21]. The results revealed that cold plasma successfully degrades the examined antibiotics and that plasma treatment considerably reduces the activity of both antibiotics. The authors indicated that the advantages of cold plasma treatment include the oxidation or reduction of pollutants into biodegradable compounds without environmental risks, and the method can be an effective, ecofriendly, and economically promising technology for the treatment of wastewater in practical applications. Although these techniques can reduce the organic compounds in aqueous solutions, studies on removing these contaminants from real HWW are not available.

In this study, contamination by four widely used antibiotics (such as ofloxacin, ciprofloxacin, cefuroxime, and amoxicillin, respectively) from the wastewater of seven hospital treatment plants in Vietnam was investigated. Next, the application of cold plasma to eliminate these pollutants from the wastewater of one representative hospital was investigated. Furthermore, the effects of four factors, i. e.,

pH, interelectrode distance, voltage, and reaction time, respectively, were examined by reducing the antibiotic concentration, COD, and ammonia. To the best of our knowledge, this is the first study to discuss the application of cold plasma for the treatment of hospital wastewater in Vietnam.

2. Methodology

2.1. Wastewater and Chemicals. Wastewater was obtained from equalization tanks at seven hospital wastewater treatment plants (i. e., National Hospital of Odonto-Stomatology, Oncology Hospital, Thong Nhat Hospital, Hung Vuong Hospital, General Saigon Hospital, Binh Dan Hospital, and Gia Dinh Hospital, respectively) in Ho Chi Minh City, Vietnam (Figure S1). The wastewater was collected in glass containers and preserved at 4°C for treatment by cold plasma.

Analytical-grade standards of ofloxacin, ciprofloxacin, cefuroxime, and amoxicillin (>98% purity) were used. In addition, HPLC solvents, such as methanol, acetonitrile, ethyl acetate, ammonium hydroxide solution (NH_4OH), acetic acid (AcOH), formic acid (HCOOH), and other chemicals were of analytical grade. The chemicals and solutions were kept in the dark and stored at 4°C.

2.2. The Cold Plasma Reactor Model. Figure 1 shows the schematic of a plasma reactor model, including plumbing, a reaction chamber, sewage tanks, water pumps, gas pumps, flowmeters, pump control valves, and switches. A gas mass flow meter and controllers were used to introduce air into the reactor chamber. The height and volume of the reaction chamber were 30 cm and 1500 mL, respectively, which was designed with one inlet and one outlet. The water inlet was placed 12 cm from the bottom, and water was allowed to flow from the bottom up—the volume of the reaction zone was 600 mL. The experiment was designed with plasma electrodes, including two SUS304 stainless-steel electrodes and a pointed tip anode electrode submerged in water. A rectangular design (30 × 25 × 3 mm) on a perforated electrode plate with a diameter of 4 mm served as the negative electrode. The top of the reaction chamber was a threaded lock cap comprising an insulating plastic, which fixed two electrodes of the model. A rectangular box composed of acrylic plastic with a volume of 2000 mL served as the reservoir for the output effluent.

2.3. Experimental Design and Procedure. Plasma treatment experiments were conducted on the basis of the single-factor design, i. e., in every series of experiments; only one independent factor was varied, whereas all other factors were maintained constant. Table S1 shows the parameters and their value ranges with the following initial conditions: initial pH of 6.7, the reaction time of 15 min, the distance between two electrodes of 20 mm, and applied voltage in the range of 15–35 kV at constant antibiotic concentrations for the examination of the wastewater from the General Saigon hospital. A total of four series were conducted to evaluate all

FIGURE 1: The cold plasma reactor chamber.

factors. Moreover, the formation of O_3 , H_2O_2 , and $\cdot OH$ were investigated by the variation in the pH and reaction time under optimum conditions (the distance between the two electrodes was 10 mm, and the applied voltage was 30 kV).

In each run, 600 mL of the wastewater from General Saigon hospital (which was adjusted to the desired pH) was added to the reaction chamber at the established gap between two electrodes, followed by locking the two valves at the bottom and the cooling tower. Then, the air was fed into the chamber at a constant flow rate of 4 L/min, the power supply was switched on, and the applied voltage was adjusted to the required values. After the desired reaction time, aliquots of the treated wastewater were sampled through the bottom discharge and analyzed.

2.4. Analysis Method. A Shimadzu HPLC system (Model 20AT) equipped with a UV detector was utilized to monitor the antibiotics extracted from the wastewater using solid-phase microextraction method as follows. About 5 μL of the analyte solution was injected into the HPLC valve using a 25 mm Puradisc syringe (sterile and free of endotoxins, 0.2 μm PES Filter Media) and a Terumo syringe (5 mL) at room temperature ($25 \pm 2^\circ C$). The target analyzed compounds were separated on a Phenomenex Luna reverse phase (RP-18) column (250 mm $\times$ 4.6 mm) packed with a C18 stationary phase having a particle size of 5 μm .

The pollution and pathogenic microorganism parameters in HWW before and after treatment, such as pH, COD, TSS, sulfide, ammonium, nitrate, phosphate, plant and animal fats and oils, coliforms, *Salmonella*, *Shigella*, and

Vibrio cholera, were analyzed according to the American Public Health Association [28]. Meanwhile, O_3 , H_2O_2 , and $\cdot OH$ generated in wastewater also were determined by standard methods [28–30]. Results were expressed as the mean of triplicate measurements, and statistical analyses were performed using Microsoft Excel software release 2010 (Microsoft Corp., USA).

3. Results and Discussion

3.1. Characteristics of Hospital Wastewater. All of the HWW samples were contaminated with COD in the range from 191 to 539 mg/L, while coliforms ranged from 1.5×10^5 to 1.4×10^7 CFU/100 mL, and the other parameters were above the stipulated standards in some hospitals. Some antibiotics were detected in the wastewater; in particular, all four parameters were detected in the wastewater of the General Saigon hospital. These results revealed that contaminants are detected in most surveyed hospitals and are deleterious to residents (Table S2). Owing to the presence of all four contaminant antibiotics, the wastewater from the General Saigon hospital was selected for the plasma treatment experiment. The degradation efficiencies of the antibiotics from the hospital's wastewater treatment plant by the cold plasma technique were evaluated via the investigation of the effects of applied voltage, reaction time, pH, and the interelectrode distance of the plasma reactor on the concentration of the four antibiotics in the effluents. In addition, the formation of oxidizing species, such as O_3 , H_2O_2 , and $\cdot OH$, was investigated to clarify the degradation mechanism of cold plasma.

3.2. Plasma Treatment

3.2.1. Effect of Applied Voltage. The effect of the applied voltage on the degradation of the antibiotics was investigated by conducting experiments at applied voltages of 15, 20, 25, 30, and 35 kV by maintaining the distance between two electrodes at 20 mm and the initial pH value at ~ 6.7 (background value of the General Saigon hospital wastewater) for a reaction time of 15 min. With the increase in the applied voltage, the removal efficiency of antibiotics, COD, and ammonia by cold plasma treatment increased (Figure 2); however, the efficiencies were different for each antibiotic. Ciprofloxacin, cefuroxime, COD, and ammonia were mostly eliminated at an applied voltage of ≥ 25 kV, while no clear difference in the removal efficiency was observed with the further increase in the applied voltage to 35 kV (Figures 2(b)–2(f)). The finding might be related to the low concentration of ciprofloxacin (1.052 mg/L) and cefuroxime (0.273 mg/L) and the facile oxidizing substances that contribute to the COD in the HWW sample. That is, an applied voltage of 25 kV is adequate to release sufficient oxidants ($\cdot\text{OH}$, O_3 , and H_2O_2) for eliminating ciprofloxacin, cefuroxime, COD, and ammonia during the plasma process [31]. On the contrary, at an applied voltage of 35 kV, the highest removal efficiencies of 50.22% and 35.40% were observed for ofloxacin and amoxicillin, respectively (Figures 2(a) and 2(d)). The highest applied voltage can be attributed to the generation of an increased number of reactive species at a higher applied voltage. However, the low removal efficiencies mentioned above may be explained by inadequate oxidant products for removing high concentrations of ofloxacin (41.23 mg/L) and amoxicillin (23.58 mg/L). The increase in the removal efficiency with an adequate increase in the applied voltage is consistent with the results reported by Sarangapani et al. [21]; in their study, the authors have reported that with the rise in the voltage from 70 to 80 kV, the plasma degradation efficiency increased from 75% to 89% for ciprofloxacin and from 88% to 92% for ofloxacin. Even at an applied voltage of 35 kV, the highest removal efficiency was observed for ofloxacin and amoxicillin; however, the difference in removal efficiencies was not significant between the applied voltages of 30 kV and 35 kV. Moreover, to optimize the experimental conditions and reduce energy for plasma treatment (saving time and safety), an applied voltage of 30 kV was selected for subsequent experiments.

3.2.2. Effect of Reaction Time. Experiments were conducted at reaction times of 5, 10, 15, 20, and 25 min with a distance between two electrodes of 20 mm, an applied voltage of 30 kV, and a natural pH value (6.6). With the increase in the reaction time, the degradation efficiency increased (Figure 3); however, similar to the effect of the applied voltage, the results revealed that ciprofloxacin and cefuroxime are rapidly degraded in the first 10 min ($>90\%$) and reach a plateau until the reaction is completed (Figures 3(b) and 3(c)); this trend also was observed in the case of COD and ammonia at a reaction time of 15 min (Figures 3(e) and 3(f)).

This result is consistent with the following theory: the reaction time exhibited a positive effect on the degradation of organic compounds in the plasma process. With the increase in the reaction time, the disturbing process is strong, the reaction occurs rapidly, and organic substances are exposed to strong oxidizing substances [32]. However, with the increase in the reaction time to greater than 15 min, the degradation efficiency remained stable. It is hypothesized that with the further increase in the reaction time, the number of intermediate products (between the formed oxidants and antibiotics) increases, which are competing with antibiotics; hence, the degradation efficiency decreases. Meanwhile, a different trend in degradation efficiencies was observed in the case of ofloxacin and amoxicillin (Figures 3(a) and 3(d)), where their efficiencies reached peak values at a reaction time of 30 min. This might result in the presence of inadequate concentrations of oxidants (such as $\cdot\text{OH}$, O_3 , and H_2O_2) to remove high concentrations of ofloxacin and amoxicillin from wastewater. This pattern of results is consistent with the previous study of Kim et al. [27], where plasma was used to degrade enrofloxacin in an aqueous solution. The author revealed that the decomposition of 1 mg/L of enrofloxacin could be completed only within 20 min, while around 30 min is required to reduce the concentration of the same compound from 5 mg/L to 1 mg/L. In terms of removal efficiency, a reaction time of 30 min was optimum for subsequent experiments. However, excluding ofloxacin and amoxicillin, all of the six parameters and *coliforms* (data not shown) were entirely eliminated during 15 min. Furthermore, the shortened reaction time ensures savings in operational costs. Hence, a reaction time of 15 min reaction is selected for subsequent experiments.

3.2.3. Effect of the Initial pH. Effects of the initial pH on the removal of antibiotics by cold plasma were investigated in the range from 7 to 10. The distance between the two electrodes and applied voltage was maintained constant at 20 mm and 30 kV, respectively, during a reaction time of 15 min for all experiments. With the increase in the initial pH from 7 to 10, the overall removal efficiencies increased for all pollutants by cold plasma treatment (Figure 4). These results are in agreement with those reported in recent studies where an increase in the pH accelerates the formation of $\cdot\text{OH}$ due to the decrease in the $\cdot\text{OH}$ redox potential according to the Nernst equation [33, 34]:

$$E^0 = E_{\text{HO}^\cdot/\text{H}_2\text{O}_2}^0 - 0.059 \text{ pH}. \quad (2)$$

In other words, the redox potential of $\cdot\text{OH}$ might slightly decrease from 2.39 to 2.21 with the increase in the pH from 7 to 10 [33]. At a constant applied voltage, the decrease in the redox potential can enhance $\cdot\text{OH}$ production; hence, the oxidant can react with an increased amount of pollutants in wastewater, leading to increased removal efficiencies. Panorel et al. [24] have reported that the oxidation efficiency of paracetamol under alkaline conditions (52 g/kW·h) is substantially greater than that under acidic conditions (28 g/kW·h). With the increase in the initial pH, even the overall removal efficiencies of

FIGURE 2: Effect of the applied voltage on the degradation efficiency of the four antibiotics, i.e., (a) ofloxacin, (b) ciprofloxacin, (c) cefuroxime, and (d) amoxicillin, respectively, as well as (e) COD and (f) ammonia removal.

FIGURE 3: Continued.

FIGURE 3: Effect of the reaction time on the degradation efficiency of four antibiotics, namely, (a) ofloxacin, (b) ciprofloxacin, (c) cefuroxime, and (d) amoxicillin, respectively, as well as (e) COD and (f) ammonia removal.

FIGURE 4: Effect of the pH on the degradation efficiency of four antibiotics, namely, (a) ofloxacin, (b) ciprofloxacin, (c) cefuroxime, and (d) amoxicillin, respectively, as well as (e) COD and (f) ammonia removal. Effect of the interelectrode distance of the plasma reactor.

these antibiotics, COD, and ammonia increased. Three trends were observed during this treatment. In the case of ofloxacin and amoxicillin (Figures 4(a) and 4(d)), the variation in the removal efficiencies or breakpoint at pH 8 (ofloxacin 31.18%) and 9 (amoxicillin 41.63%) was possibly related to the existing forms of the two antibiotics [35]. Notably, at pH values of 8 and 9, the two antibiotics were dominated by negatively charged forms due to their higher pH values than the pKa values of the compounds. These forms could ineffectively react with $\cdot\text{OH}$; hence, removal efficiencies decrease [35, 36]. All of the ciprofloxacin, cefuroxime, and COD (Figures 4(b)–4(e)) were completely degraded ($\sim 90\%$) at pH 8; the further increase in the pH led to the slight reduction in the removal efficiency because, at a higher pH of 8, the two antibiotics could be negatively charged forms, leading to decrease in the removal efficiency [37]. With the increase in the pH, ammonia in the wastewater was eliminated extremely rapidly ($>90\%$) (Figure 4(f)). Two mechanisms were involved; first, the extent of oxidation of ammonia to nitrite or nitrate is increased by the produced oxidants under alkaline conditions as mentioned above; second, N-NH_4^+ can be transformed easily to NH_3 , which can evaporate under alkaline conditions during cold plasma treatment. These complex trends with the variation in pH during cold plasma treatment were in good agreement with those reported in previous studies [18, 27, 32]. A pH of 10 satisfied all parameters to attain the highest removal efficiency; therefore, this pH is selected for subsequent experiments.

A previous study has reported that the interelectrode distance in the plasma reactor can determine the amount of the formed $\cdot\text{OH}$ [38], thereby affecting the degradation efficiency. The experiment was conducted by utilizing various electrode distances of 10–30 mm, pH 10, and an applied voltage of 30 kV for a reaction time of 15 min. Figure 5 shows the relationship between the pollutant concentration and removal efficiency to the electrode distance. The removal efficiency even slightly varied at an interelectrode distance of 25 mm for ofloxacin (Figure 5(a)) and at that of 30 mm for the other antibiotics (Figures 5(b)–5(d)); hence, the increase in the interelectrode distance leads to the significant decrease in the antibiotic removal efficiency. At an interelectrode distance of 10 mm, the highest antibiotic removal efficiencies reached 72.13%, 99.60%, 99.20%, and 75.80% for ofloxacin, ciprofloxacin, cefuroxime, and amoxicillin, respectively. The decrease in the removal efficiency with the increase in the electrode distances can be explained as follows: with the increase in the interelectrode distance, the possibility of electrical discharge is reduced, leading to the decrease in the electric-field energy generated to create the plasma and subsequently low production of oxidants during the plasma process. These results are consistent with those reported in some previous studies [17, 38, 39]; these studies indicated that a suitable two-electrode spacing from 8 to 20 mm not only improves the formation of oxidants but also accelerates the temperature during the plasma process, leading to the mitigation of a high concentration of pollutants. In the case of COD and ammonia, with the increase in the interelectrode distance, even the removal efficiency decreased, albeit with an insignificant decrease. The highest removal efficiencies of 84.23% and 98.60% for COD and ammonia were

observed at an interelectrode distance of 10 mm, respectively, while the lowest values of 73.17% and 76.40%, respectively, were observed at an interelectrode distance of 30 mm. These results demonstrated the effectiveness of the plasma process for the disinfection of HWW. Hence, an interelectrode distance of 10 mm may be a suitable alternative for subsequent experiments for oxidant formation during the plasma process.

3.3. Formation of Oxidizing Agents O_3 , H_2O_2 , and $\cdot\text{OH}$.

As mentioned above, cold plasma generates several oxidizing species, such as radicals ($\cdot\text{OH}$, $\cdot\text{H}$) and molecules (O_3 and H_2O_2); among these species, the hydroxyl radical is considered to be a powerful nonselective oxidant [25]. The process formed free $\cdot\text{OH}$ as O_3 was dissolved in water-based eqs (3)–(10):

Hydroxyl radicals were formed by a collision between energetic electrons and H_2O vapour molecules.

In addition, $\cdot\text{OH}$ radicals were formed by the reaction between oxygen and water vapour molecules.

Recombination of free radicals also possibly decreased the mitigation capacity according to the following equations (14) and (15) [40].

Experiments were conducted to investigate the effects of pH and reaction time on the formation of O_3 , H_2O_2 and $\cdot\text{OH}$.

3.4. Effect of pH on the Formation of O_3 , H_2O_2 , and $\cdot\text{OH}$.

The content of oxidizing agents generated by variation in the pH value (4, 6, 8, 10, and 12) while simultaneously

FIGURE 5: Effect of the interelectrode distance in the plasma reactor on the degradation efficiency of four antibiotics, namely, (a) ofloxacin, (b) ciprofloxacin, (c) cefuroxime and (d) amoxicillin, respectively, as well as (e) COD and (f) ammonia removal.

maintaining the other parameters constant, i. e., an applied voltage of 30 kV, a reaction time of 15 min, and an inter-electrode distance of 10 mm. As can be observed in Figures 6(a) and 6(b), with the increase in the pH from acidic to alkaline conditions (3.4 mM and 0.05 mM), the highest concentrations of ozone and H_2O_2 were observed, with the highest detected under acidic conditions (4.8 mM and 0.18 mM), and the decomposition rate of these compounds sharply increased. These results are in good agreement with those reported by Kuo et al. [41], where the author reported that in the plasma process, with the increase in pH, the reaction between ozone and H_2O_2 can be accelerated to produce $\cdot\text{OH}$ (a stronger oxidant), as shown in equation (11), leading to the decrease in the concentrations of ozone and H_2O_2 in the aqueous phase. These explanations can be confirmed by the predominant formation of $\cdot\text{OH}$ under alkaline conditions (Figure 6(c)): with the increase in the pH from 4 to 6, the $\cdot\text{OH}$ concentration only slightly increased from 0.052 mM to 0.06 mM. Nevertheless, with the increase in the pH to 10 (0.215 mM), the $\cdot\text{OH}$ concentration dramatically increased. The sudden drop in the $\cdot\text{OH}$ concentration to 0.17 mM at pH 12 may be explained by the fact that most of the $\cdot\text{OH}$ reacted with pollutants in the wastewater.

These results also again demonstrated the enhanced formation and removal efficiency of $\cdot\text{OH}$ under alkaline conditions by the Nernst equation [33].

3.5. Effects of the Reaction Time on the Formation of O_3 , H_2O_2 , and $\cdot\text{OH}$. Reaction time was directly related to the formation of active radicals; hence, its effect on the production of radicals is examined. The reaction time was adjusted from 2 min to 10 min while simultaneously maintaining an applied voltage of 30 kV, a pH of 10, and an interelectrode distance of 10 mm. At a long reaction time, the O_3 concentration increased (Figure 7(a)). At a reaction time of 2 min, the ozone concentration was 1.2 mM, which slightly increased at a reaction time of 3 min. The generated ozone concentration was 3.9 mM (greater than 3.2 times), while the reaction time increased only by 1 min. At a reaction time of 10 min, the ozone concentration was 8.0 mM (6.7 times greater than that observed in 2 min). Similar trends observed for the formation of H_2O_2 (Figure 7(b)): the H_2O_2 concentration notably increased from 0.076 mM at 2 min to 0.23 mM at 5 min. The H_2O_2 concentration was 0.076 mM at a reaction time of 2 min. With the further increase in

FIGURE 6: Effect of pH on the formation of (a) O_3 , (b) H_2O_2 , and (c) $\cdot OH$.

FIGURE 7: Continued.

FIGURE 7: Effect of the reaction time on the formation of (a) O_3 , (b) H_2O_2 , and (c) $\cdot OH$.

TABLE 1: Reaction kinetics models for the decomposition of four antibiotics.

Antibiotics	Initial conc. (mg/L)	Reaction order	Regression equation	R^2	Rate constant	$t_{1/2}$ (min)
Ofloxacin	41.23	1	$y = 0.0333x + 0.0993$	0.9214	0.0333 (1/min)	20.82
		2	$y = 0.0014x + 0.0258$	0.9737	0.0014 (L/mg.min)	17.32
		3	$y = \mathbf{0.0001x + 0.0005}$	0.9896	5×10^{-5} (L ² /mg ² .min)	1.76
Ciprofloxacin	1.052	1	$y = \mathbf{0.2332x - 0.082}$	0.9790	0.2332 (1/min)	2.97
		2	$y = 0.6232x + 0.2062$	0.8349	0.6232 (L/mg.min)	1.53
		3	$y = 4.2432x - 6.4031$	0.6643	2.122 (L ² /mg ² .min)	0.64
Cefuroxime	0.273	1	$y = \mathbf{0.2421x - 0.0918}$	0.9626	0.2421 (1/min)	2.86
		2	$y = 2.6828x + 0.234$	0.7739	2.683 (L/mg.min)	1.37
		3	$y = 79.501x - 131.03$	0.5925	39.75 (L ² /mg ² .min)	0.51
Amoxicillin	23.58	1	$y = 0.0319x + 0.195$	0.9107	0.0319 (1/min)	21.73
		2	$y = 0.0026x + 0.0498$	0.9711	0.0026 (L/mg.min)	16.31
		3	$y = \mathbf{0.0004x + 0.002}$	0.9826	2×10^{-4} (L ² /mg ² .min)	13.49

reaction time up to 10 min, the H_2O_2 concentration only reached 0.25 mM, indicating that when the reaction time is doubled, the concentration increase of H_2O_2 is only about 0.02 mM. Compared to H_2O_2 or O_3 , the $\cdot OH$ concentration increased almost linearly with the reaction time and reached the highest concentration of 0.8 mM at 10 min (Figure 7(c)). These results are apparently in agreement with those reported previously on the use of plasma to eliminate pollutants from aqueous solutions [17, 21–23].

3.6. Reaction Kinetic Models for the Decomposition of Antibiotics. To obtain further insights into the reaction kinetics for the decomposition of the antibiotics by cold plasma treatment, the change in the concentration of substances over the reaction time under optimum conditions was carefully investigated. The investigated reaction kinetics models included first-order kinetics, second-order kinetics, and third-order kinetics as reported in our previous studies [15, 16]. Table 1 and Figure S2 show the results obtained, i. e., rate constants, reaction orders, and squared correlation coefficients. The first-order reaction kinetics model revealed the highest squared correlation coefficient for the

decomposition of ciprofloxacin and cefuroxime (0.9790 and 0.9626, respectively). Meanwhile, these squared correlation coefficients were the highest for the third-order kinetics reaction of the decomposition of ofloxacin and amoxicillin (0.9896 and 0.9826, respectively).

Table 2 below summarizes the removal efficiencies for antibiotics using cold plasma reported in recent studies. In addition to the Corona plasma systems similar to those used herein, other plasma systems such as DBD were utilized. Specifically, only this study discussed real wastewater containing a high concentration, as well as mixed contaminants, of antibiotics compared to a single antibiotic in an aqueous solution or synthetic wastewater in the references. In a shorter time, this study reaches a suitable result as compared with other reference studies. The removal efficiencies of all antibiotics were extremely high (>99% for cefuroxime and ciprofloxacin and >72% for amoxicillin and ofloxacin). These values are greater than the treatment efficiencies of tetracycline (61.9%) and β -oestradiol (70%) reported in studies by He et al. [23] and Panorel et al. [24], respectively. The lower removal results for mixed compounds compared to individual compounds using AOPs can be found in some previous studies [42, 43].

TABLE 2: Some recent findings of cold plasma treatment for the elimination of antibiotic compounds in water or wastewater.

Antibiotics	Matrix	Plasma conditions	Efficiency (%)	References
Ofloxacin ciprofloxacin	Synthetic meat effluent (10 mg/L antibiotics)	DBD reactor (25 mL), applied voltage of 80 kV, degradation kinetics: first-order, during a reaction time of 25 min	Ofloxacin 92% Ciprofloxacin 89%	[21]
Carbamazepine clofibric acid iopromide	Aqueous solution and synthetic landfill leachate carbamazepine (23.6 mg/L), clofibric acid (21.5 mg/L), iopromide (79.1 mg/L)	DBD-rotating drum reactor (1000 mL), discharge power of 500 W during, reaction time of 60 min	Carbamazepine 94% Clofibric acid 100% Iopromide 98%	[22]
Tetracycline	Aqueous solution (50 mg/L)	Corona with gas bubbling (250 mL), discharge power of 36 W during a reaction time of 24 min	61.9%	[23]
Paracetamol β -oestradiol	Aqueous solution of paracetamol (100 mg/L) β -oestradiol (3 mg/L)	Corona with liquid shower (40 L), discharge power of 250 W during a reaction time of 30 min	Paracetamol 80% β -Oestradiol 70%	[24]
Lincomycin, ciprofloxacin, enrofloxacin, chlortetracycline, oxytetracycline, sulfathiazole, sulfamethoxazole, sulfamethazine trimethoprim	Aqueous solution (5 mg/L antibiotics)	Cylindrical DBD reactor (1000 mL), supplied O ₂ , discharge power of 6.8 W corresponding energy requirements: 0.39–2.06 kJ/mg antibiotic during a reaction time of 30 min	Over 90%	[27]
Amoxicillin cefuroxime ofloxacin ciprofloxacin	Real HWW amoxicillin (23.58 mg/L), cefuroxime (0.273 mg/L), ofloxacin (41.23 mg/L), ciprofloxacin (1.052 mg/L)	Corona with a liquid discharge system (600 mL), applied voltage of 30 kV, initial pH of 10, and an interelectrode distance of 10 mm during a reaction time of 15 min	Amoxicillin 75.80% Cefuroxime 99.20% Ofloxacin 72.13%, ciprofloxacin 99.60%	This study

4. Conclusions

In this study, the cold plasma technique was demonstrated to be a simple, efficient method for eliminating antibiotic contaminants from real hospital wastewater in Ho Chi Minh City, Vietnam. The degradation efficiency of these antibiotic compounds was considerably dependent on the initial pH and reaction time as it possibly affected the formation of oxidants (such as O₃, H₂O₂, and ·OH) during the plasma process. The obtained results also indicated that the applied voltage and electrode distance affect the treatment process. Under the optimum conditions (initial pH of 10, electrode distance of 10 mm, reaction time of 15 min, and applied voltage of 30 kV), the removal efficiencies of all antibiotics were high (>72% for ciprofloxacin and cefuroxime and >99% for amoxicillin and ofloxacin), in addition to the complete removal of COD and ammonia. The significant formation of ·OH and rapid decomposition of O₃ and H₂O₂ under alkaline conditions might prove to play a key role in the production of OH during this plasma treatment for such contaminants. In this study, contamination by the four antibiotics also was detected in the effluent of seven hospitals in Ho Chi Minh City, directly leading to the environment. Such environmental pollution could be alarming due to the antibiotic pollutants from the hospital wastewater in Vietnam.

Data Availability

The data used are included in the manuscript.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

Supplemental Table. Table S1: Evaluated factors and their established ranges for the plasma tests. Table S2: Characterization of wastewater from the seven hospitals. Supplemental Figure. Figure S1: The study area and regional map (a). Ho Chi Minh City area (b), and Hospital sampling site in Ho Chi Minh City (c). Figure S2: Third-order reaction kinetics models of (a) ofloxacin and (b) amoxicillin, and first-order reaction kinetics models of (c) ciprofloxacin and (d) cefuroxime. (*Supplementary Materials*)

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