

# Oxidation-Reduction Potential and Peroxone Process in Antibiotic Residues Removal from Hospital Wastewater

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Peroxone is an advanced oxidation process for the removal of antibiotics in hospital wastewater. In this study, ORP monitor was combined into the system to obtain the optimum ratio of H<sub>2</sub>O<sub>2</sub> to O<sub>3</sub> by automatically adjusting the dosage of H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>. Relationships between ORP, pH, and H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> concentrations were observed during the process. The effectiveness of the peroxone process for antibiotics removal was investigated by using ofloxacin as a model substance. An ORP between 200 mV and 900 mV is used for H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> control. The correlation between ORP and the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> shows potential for use as a parameter to control the peroxone process. The working optimal range of ORP was determined to control the most effective removal of ofloxacin. The experiment results show ORP between 250 mV and 300 mV or 800 mV and 900 mV is suitable for H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> control. The study investigated the feasibility of using ORP as a parameter to control antibiotic removal in hospital wastewater by the peroxone process.

## 1. Introduction

Ozonation or catalytic ozonation is an environmentally friendly wastewater treatment technology. Ozone has an oxidizing potential for a wide variety of organic pollutants. The ozone molecule can directly decompose organic pollutants. Compounds such as antibiotics, the ozonation process cannot completely mineralize the antibiotics (Ahmad et al., 2020). This is an important drawback to ozonation alone, as these low molecular weight byproducts can exhibit more acute toxicity than the primary pollutants. The simultaneous use of hydrogen peroxide in ozonation can help improve the process efficiency, as the reaction of O<sub>3</sub> with H<sub>2</sub>O<sub>2</sub> leads to the generation of •OH hydroxide radicals (Cuerda-Correa et al., 2020). Oxidation systems that combine O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> are called peroxone. In recent years, peroxone oxidation for antibiotics has been of great interest due to its high efficiency, no production of by-products and little influence of environmental factors. Lakovides et al. (2019) studied the peroxone process to remove antibiotics from domestic water, many antibiotics were tested including ampicillin, azithromycin, clarithromycin, erythromycin, ofloxacin, sulfamethoxazole, tetracycline, trimethoprim. The treatment efficiency is always over 70 %, especially for ofloxacin antibiotic, the efficiency is over 98 %. Chen and Wang (2021) studied the degradation and mineralization of ofloxacin by peroxone, the obtained results showed that the treatment efficiency was always above 90 % and the mineralization process was over 55 %.

Oxidation-Reduction Potential (ORP) is a measure of the oxidizing or reducing ability of a solution (Igboamalu et al., 2020), ORP has the unit of mV. In the field of environmental remediation, the ORP index is a measure of the degree of oxidation or reduction of pollutants, a positive ORP number indicates an oxidizing solution, while a negative ORP indicates a reducing solution. In water treatment by oxidation, the ORP index is considered very important. In the wastewater sector, ORP is also used as an indicator of the level of disinfectant in the effluent wastewater. The positive ORP values in the presence of chlorine and the negative ORP values in the presence of hydrogen sulfide. ORP has been used in groundwater quality monitoring to characterize groundwater geochemistry. If the sample water contains a dominant oxidation/reduction system, the ORP value provides a clue as to the ratio of the oxidizing agent to the reducing agent, such as Fe<sup>2+</sup> ions under reduced conditions compared to Fe<sup>3+</sup> ions under oxidizing conditions (Stramarkou et al., 2022). ORP is also used as a tool to assess the likelihood of oxidation/reduction biological reactions. In wastewater treatment systems, there

are important oxidation/reduction reactions: nitrification, denitrification, biological phosphorus removal and cBOD removal (Yaser et al., 2015). These reactions involve changing the states of carbon, phosphorus, sulfur and nitrogen. The reciprocal change holds the oxidation state (containing oxygen) such as nitrate ( $\text{NO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) and the reduced state (containing hydrogen) such as ammonia ( $\text{NH}_3$ ) and sulfide ( $\text{H}_2\text{S}$ ) (Myers, 2019). Redox reaction monitoring is the best application of ORP measurement. When an oxidation-reduction reaction ends, there is usually a large change in the ORP (Yao et al., 2014). The typical purpose of using ORP is to ensure that the ORP reaction is complete.

In this study, the relationship between ORP and peroxone process for antibiotic treatment in hospital wastewater was determined. The results suggest the possibility of using ORP as an indicator to control the peroxone process.

## 2. Material and methods

### 2.1 Analysis method

The concentration of OFL was determined by high-performance liquid chromatography equipped with mass spectrometry (LC-MS). The antibiotics extracted from the wastewater were determined using an Agilent HPLC System (Model 1200 Series) with the Agilent 6130 Series Quadrupole LC-MS System. Zorbax SB-C18 column (150 mm  $\times$  4.6 mm) packed with a C18 stationary phase with a particle size of 5  $\mu\text{m}$  used for chromatographic separation. The mobile phase includes solvent A (0.1 % formic acid (v/v) in deionized water) and solvent B (0.1 % formic acid (v/v) and acetonitrile). The flow rate is 0.5  $\text{mL}\cdot\text{min}^{-1}$ . The InPro 4260/120/PT1000, Mettler Toledo, USA was used for pH determination as well as multi-parameter analysis. A ozone meter (DOZ-6000) and an ORP meter (Hanna - BL932700/probe HI2003/5) are used to directly measure  $\text{O}_3$  and ORP values of wastewater in the tank.

### 2.2 Experimental design and procedure

Figure 1 shows a schematic diagram of the wastewater recovery system used in this study. A glass bath 5 L was used as the bubble  $\text{H}_2\text{O}_2/\text{O}_3$  reaction vessel (R1). Synthetic wastewater is continuously fed into the bubble reactor from above with a flow rate from 0.5  $\text{L}\cdot\text{min}^{-1}$  to 2  $\text{L}\cdot\text{min}^{-1}$ , and the  $\text{O}_3$  generated from the R2 device is fed to the tank. overreaction of the gas dispersion tube system. The gas flow rate varies from 1 to 4  $\text{L}\cdot\text{min}^{-1}$  and the rated output of the ozonator is 10  $\text{mg}\cdot\text{min}^{-1}$ . The feeding rate of  $\text{H}_2\text{O}_2$  is adjusted automatically by the PID controller based on the measured ORP values. Approximately 0.1  $\text{L}\cdot\text{h}^{-1}$  wastewater from R1 was used to measure TOC (of ofloxacin). The remaining water flows into a glass bath (R2; effective volume, 10 L), and can be further treated with  $\text{O}_3$  discharged from R1 through a nozzle. The recirculation rate for the nozzle varies between 0 and 1  $\text{L}\cdot\text{min}^{-1}$ . An on-line TOC meter is installed for post-treatment TOC measurement. Synthetic wastewater (20  $\mu\text{g}\cdot\text{L}^{-1}$  ofloxacin) was prepared by dissolving the ofloxacin standard in ultrapure water. The inlet TOC concentration was adjusted by controlling the ratio between the feeding rate of the stock solution and the ratio of the ultrapure water. Each condition was tested for 6 h, and 2 to 3 samples were taken at intervals of 30 min for each condition. The pH, ORP,  $\text{O}_3$ , TOC values, are read at the same time.

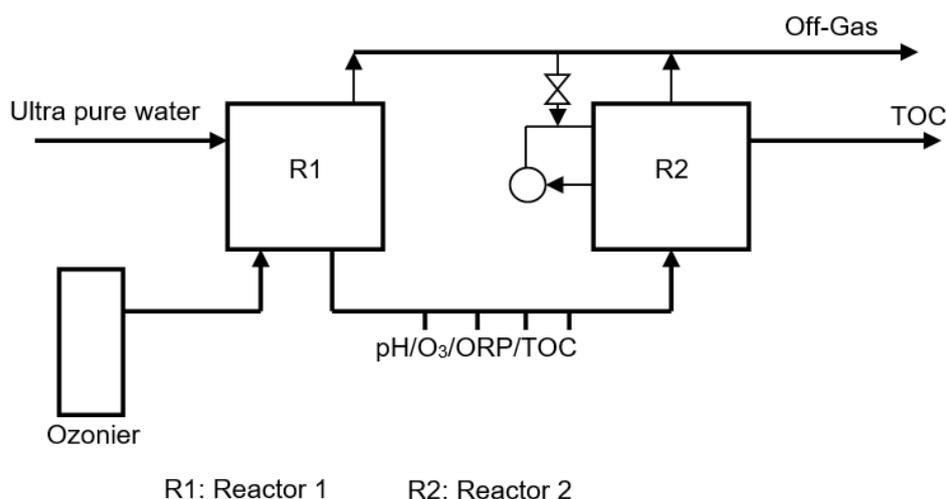


Figure 1: Schematic diagram of experimental setup

### 3. Results and discussion

#### 3.1 Possibility of using ORP for H<sub>2</sub>O<sub>2</sub> dosing control

Optimizing the ratio of H<sub>2</sub>O<sub>2</sub> to O<sub>3</sub> for an oxidation reaction varies the perfume option used. The main reason for the variation of the optimal ratio may be the existence of O<sub>3</sub> consumers, including proprietors such as antibiotics and our oxidizing intermediates, in country. When water is treated with a certain ratio of H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> it is not reasonable. To find a number of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> with the high sensor, ORP and O<sub>3</sub> balance of water after process are track contact and parsing H<sub>2</sub>O<sub>2</sub> balance by hand. OFL has been using quality samples. The experimental conditions are as follows: TOC<sub>in</sub> (TOC input) 5,000 ppb; pH 7-9; effect O<sub>3</sub>/TOC (O<sub>3</sub> value rate of O<sub>3</sub> is used to TOC<sub>in</sub>) 10-20; R2 is not operated. ORP can variable, O<sub>3</sub> balance and O<sub>3</sub>, and TOC<sub>out</sub> ratio (TOC water) to TOC<sub>in</sub> with H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> (is the mean here is gH<sub>2</sub>O<sub>2</sub> is plug-in / gO<sub>3</sub> absorption) for R1 are shown in Figure 2.

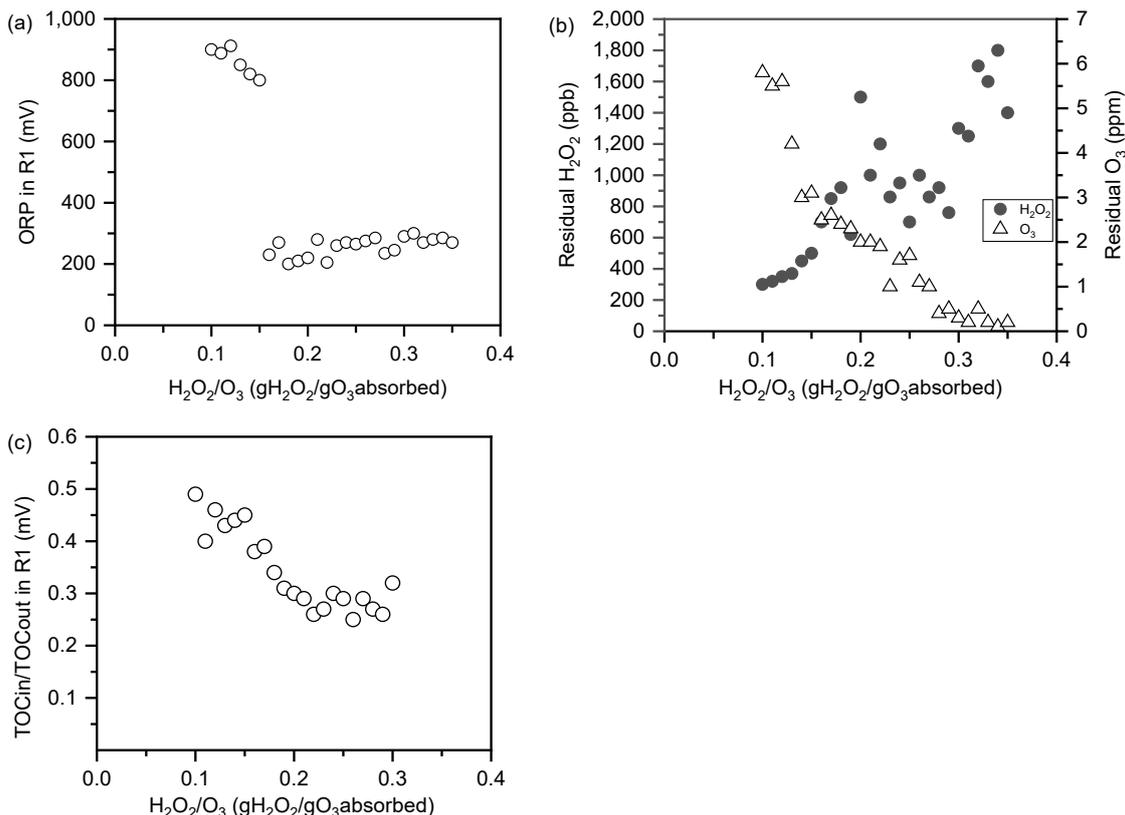


Figure 2: Effects of H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> on TOC decomposition: (a) ORP in R1 (mV), (b) Residual H<sub>2</sub>O<sub>2</sub> (ppb) and Residual O<sub>3</sub> (ppm), (c) TOC<sub>in</sub>/TOC<sub>out</sub> in R1 (mV)

Figures 2a and 2b show that ORP and residual O<sub>3</sub> decrease as the amount of H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> increases, and the amount of residual H<sub>2</sub>O<sub>2</sub> increases simultaneously. The variation of the residual amounts of H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> is continuous. An inflection point appeared for ORP with the increase of H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>. ORP decreased from ca. 800 mV to a little over 200 mV around H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> is 0.15. Figure 2c indicates that the minimum TOC<sub>out</sub>/TOC<sub>in</sub>, i.e. the best TOC degradation performance, is also achieved near the inflection point of the ORP. By comparing Figure 2c with Figure 2a, it is clear that the ORP sensitively reflects the state of the oxidation reaction in the reactor, and the reflectance point of the ORP suggests that it may be the point of the optimal H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>. The ORP reflectance point can be used to control the dose of H<sub>2</sub>O<sub>2</sub>, treatment under controlled ORP conditions has been performed. In this test, the ORP value used to adjust the feed rate of H<sub>2</sub>O<sub>2</sub> and effective O<sub>3</sub>/TOC ranges from 10 to 15.

Both TOC<sub>out</sub>/TOC<sub>in</sub> and TOC after R2 treatment are shown in Figure 3a. TOC<sub>out</sub>/TOC<sub>in</sub> and TOC were lowest when the ORP was between 250 mV and 800 mV. It is almost impossible to keep the ORP constant in the 300 mV < ORP < 800 mV range. The TOC removal efficiency decreased significantly when the ORP was reduced by about 200 mV. That is to say, overdosing on H<sub>2</sub>O<sub>2</sub> is not only wasteful, but also harmful to the oxidation reaction. Processing even at ORPs as high as 900 mV has little effect on the TOC degradation efficiency, which provides a very wide range of ORPs to choose from.

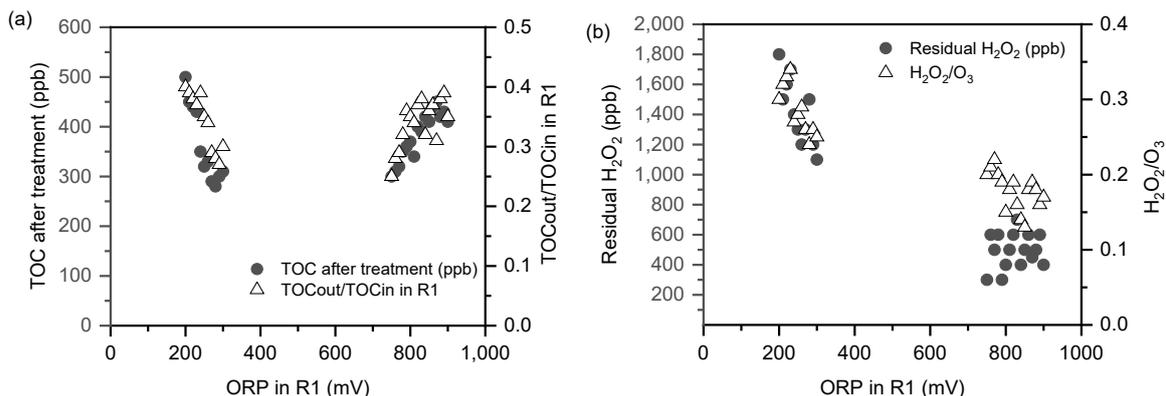


Figure 3: TOC removal under controlled ORP: (a) TOC after treatment (ppb) and TOCout/TOCin in R1, (b) Residual H<sub>2</sub>O<sub>2</sub> (ppb) and H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>

The ORP from 250 mV to 300 mV (low range) or from 800 mV to 900 mV (high range) are suitable for effective H<sub>2</sub>O<sub>2</sub> dosing. Two ranges of ORP can be selected according to need, which is very convenient in some cases. For example, a lower ORP range may be used when undesirable side effects occur within a higher ORP range. Figure 3a also indicates that nearly 70 % of the TOC was fully mineralized in R1 according to the appropriate ORP and ca. The remaining 80 to 85 % of TOC in R1 consists of organic acids, which are removed by the successive IER column. Figure 3b shows the transformation of residual H<sub>2</sub>O<sub>2</sub> with ORP. Residual H<sub>2</sub>O<sub>2</sub> is 750 ppb or less in the ORP 250–900 mV range. Elevating ORP can reduce residual H<sub>2</sub>O<sub>2</sub> to some extent. However, ORP is not the only factor associated with residual H<sub>2</sub>O<sub>2</sub>, effective O<sub>3</sub>/TOC is also an influencing factor. The value of H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> is also shown in Figure 4. H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> was between 0.15 and 0.25 in the ORP range of 250 mV to 900 mV in this experiment.

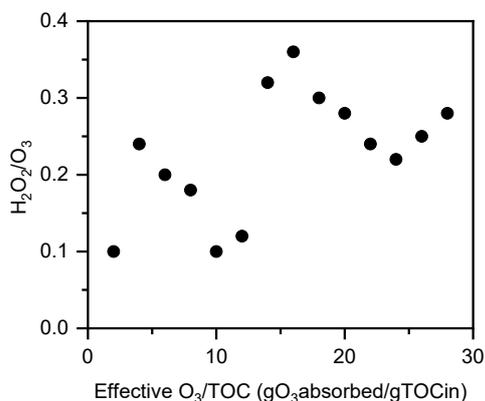


Figure 4: Effects of O<sub>3</sub> dosage on H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> ratio

Optimal H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> is not only related to ORP, it also varies with O<sub>3</sub> dosage as shown in Figure 4. Figure 4 data were obtained in controlled ORP (from 770 mV to 830 mV). Despite the dispersion of the data, it is clear that the H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> gradually increased with the increase of the effective O<sub>3</sub>/TOC ratio even though the ORP was controlled at a relatively constant value. The experiment was performed under 3 concentrations of TOC: 1,000 ppb, 3,000 ppb and 5,000 ppb, and the transformation of TOCin did not produce any significant difference. The results indicate that optimal H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> is not a fixed method, and an appropriate control method such as that used in this study is required for effective TOC (ofloxacin) removal.

### 3.2 Effects of antibiotics on their treatability

Figure 5 show the relationship between the TOC removal levels of the OFLs and their respective O<sub>3</sub> requirements under the following conditions: TOCin 3,000–5,000 ppb; pH 7-9; H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> 0.1–0.35; HRT 0.33–1.8 h; R2 is not operated. It has been found that both the logarithm of TOCout/TOCin and the post-IER TOC can be approximately linearly related to the logarithm of the effective O<sub>3</sub>/TOC.

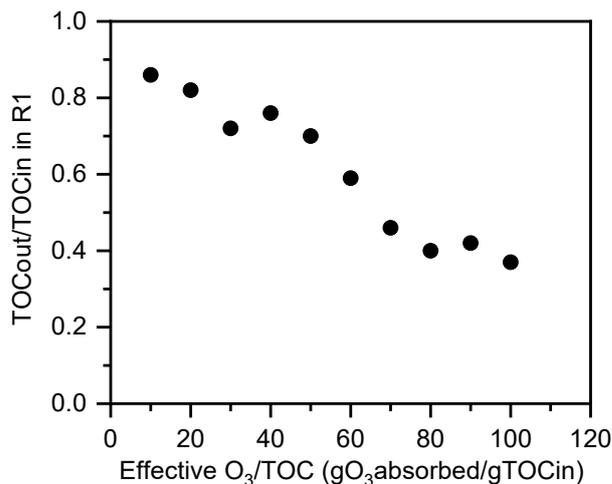


Figure 5: TOC removal and O<sub>3</sub> demand

The results show that the oxidation of the remaining TOC requires more O<sub>3</sub>. The TOCout/TOCin ratio indicates the degree of mineralization of TOC and TOC after R2 represents the binding fraction of TOCout. It is clear that the oxidation of R1 requires more O<sub>3</sub> than the other two methods, either from the point of view of complete TOC decomposition or from the point of view of TOC removal through the formation of organic acids. That is to say, compounds that are easily oxidized to organic acids are also prone to complete decomposition. It should be noted that the change of HRT from 1.8 h to 0.33 h did not significantly affect the TOC removal performance.

### 3.3 Effectiveness of waste gas utilization

The ratio of O<sub>3</sub> absorption of the bubble reactor to the Lv gas (linear velocity) over the entire experimental period is shown in Figure 6. The dispersion of the data is probably because they were obtained in the experiments. different experimental conditions. It is clear that O<sub>3</sub> absorption rate decreases as Lv increases. When the Lv of the gas increases from 2.8 m.h<sup>-1</sup> to 11.2 m.h<sup>-1</sup>, the rate of O<sub>3</sub> absorption decreases from a value of about 90 % to 70 %. That is to say, 10 % to 30 % of the O<sub>3</sub> produced is not used and must be decomposed in the flue gas treatment reactor. If dry air is used for O<sub>3</sub> production, the O<sub>3</sub> absorption rate will be much lower because the O<sub>3</sub> concentration in the gas is much lower (only 1/6 of the concentration used in this study). Since O<sub>3</sub> production accounts for a major proportion of the total initial and operating costs of the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidation, it is important to reduce the O<sub>3</sub> demand. One method to reduce O<sub>3</sub> requirements is to reuse O<sub>3</sub> waste gas. The second reactor (R2) is set up to further treat the wastewater from R1 with O<sub>3</sub> waste.

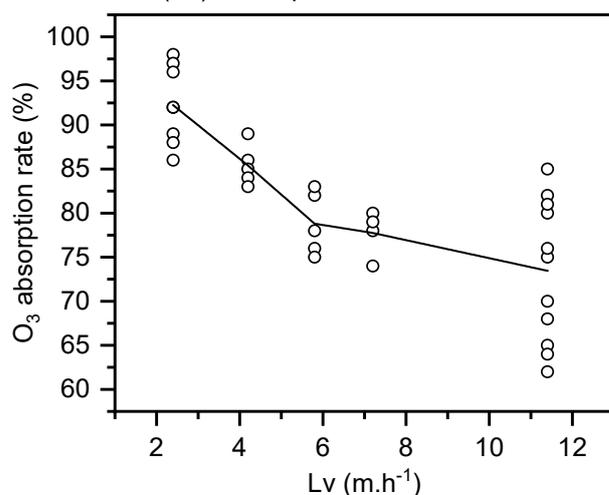


Figure 6: Effects of Lv on O<sub>3</sub> absorption rate

The exhaust O<sub>3</sub> gas is granted by a nozzle, it is difficult to directly measure the air flow speed. The flow rate of the pump received for the driving gas has been used. Figure 6 shows the effect of circulating speed on the elimination of TOC under the following conditions: ofloxacin = 7,000 ppb, pH = 6.6-6.8, O<sub>3</sub>/effective TOC of R1 = 15, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> = 0.2, water flow speed to R1 and R2: 120 L.h<sup>-1</sup> and 110 L.h<sup>-1</sup>; gas flow rate to R1 = 120 L.h<sup>-1</sup> (Lv gas at R1: 5.6 m.h<sup>-1</sup>). TOC after ion exchange resin decreased from more than 300 ppb to 200 ppb when the circulatory rate increased from 0 to more than 400 L.h<sup>-1</sup>. It is clear that the O<sub>3</sub> gas emissions from R1 has been effectively utilized in R2. From Figure 5, it is clear that the same effects can be achieved by increasing the effective O<sub>3</sub>/TOC from 15 to 20. The absorption rate O<sub>3</sub> in R1 is 80 %. It is not possible to lift the effective O<sub>3</sub>/TOC of two step oxidation system to 20 even when all the excess O<sub>3</sub> gas from R1 is absorbed into R2. The result indicates that the two-step processing system is developed in this study more effectively than the system if the same amount of O<sub>3</sub> is consumed. In this case, O<sub>3</sub> injection through multiple ports can be considered as many steps. The results showed the effect of two step oxidation in the controlled ORP conditions by comparing the results with the results obtained in a step processing. The conditions of two step processing are: ofloxacin = 7,000 ppb, ORP = 800 mV, HRT = 0.33 h, gas flow rate to R1 = 240 L.h<sup>-1</sup> (Lv gas at R1 = 11.2 m.h<sup>-1</sup>), the circulatory speed of R2 = 600 L.h<sup>-1</sup>, the dose of H<sub>2</sub>O<sub>2</sub> is equal to R2 = 2.95 mg.L<sup>-1</sup>. For one step processing, the following conditions: H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> = 0.15-0.35, HRT = 0.33-1.8 h. The effective O<sub>3</sub> absorption rate is not obtained, the terms of the dose ratio of O<sub>3</sub> (O<sub>3</sub> are supplemented/OFL) are used instead of O<sub>3</sub>/TOC. TOC after ion exchange resin 100 ppb can be obtained at the dose of O<sub>3</sub> 20 gO<sub>3</sub>/gTOC during two step processing. Without the ORP control in R1 and the second handling step, the percentage of O<sub>3</sub> dose for the same TOC target has increased to 35 gO<sub>3</sub>/gTOC, up 40 % compared to the previous case. The control of the dose of H<sub>2</sub>O<sub>2</sub> and the second step processing by using O<sub>3</sub> emissions from R1, the total efficiency of 40 % O<sub>3</sub> can be obtained.

#### 4. Conclusion

Peroxone oxidation system with ORP is combined to control the dosage of H<sub>2</sub>O<sub>2</sub> for antibiotic treatment in medical wastewater. The ORP was found to be very sensitive to the reaction state of the solution, and a very sharp reflection point of the ORP was observed near the point of the optimal H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>. The O<sub>3</sub> emitted from the first step is used efficiently in the second step, and the two-step treatment system is said to be more efficient than the single treatment system. By controlling the dosage of H<sub>2</sub>O<sub>2</sub> by ORP and reusing the waste O<sub>3</sub> in the second step, the system can save about 40 % O<sub>3</sub> compared with the conventional O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidation process.

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