# Effects of Ultraviolet-Enhanced Ozonation on Degradation of Ammonia and Urea in Fertilizer Plant Wastewater

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# Effects of Ultraviolet-Enhanced Ozonation on Degradation of Ammonia and Urea in Fertilizer Plant Wastewater

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**Abstract**. Ammonia and urea contained in fertilizer plant wastewater are pollutants to the environment. High concentration of ammonium and urea in wastewater can affects algae blooms in ecosystem which will generate various diseases in aquatic biota. It is known that there are many methods for degradation of ammonium and urea contained in fertilizer plant wastewater. One of potential method is ultraviolet-enhanced ozonation. Ozonation is oxidation with $O_3$ that generates hydroxyl radicals which subsequently react with organic contaminants, while UV irradiation can break down $O_3$ molecules and produce radical ions $OH^*$. The objectives of this study were to examine the effects of the utilization of the ultraviolet-enhanced ozonation method in degradation of various initial ammonium (100-300 ppm) and urea concentration (100-300 ppm) in inlet feed of ozonation-UV irradiation combination system. Some important variables such as contact time (0-120 minutes) and ozone feed rate of 0.2, 0.6, and 1.21 g/h were evaluated. Degradation process was carried out in two steps; ozonation and UV irradiation. Ozonation process was carried out in a contacting tank at constant feed flow rate of 1.5 l/min and at room temperature, while UV irradiation process was conducted in pipeline equipped with UV lamp at various contact time. The ultraviolet-enhanced ozonation could degraded ammonium and urea nitrogen up to 83.6% and 63.8%, respectively, at ozone feed rate 1,21 g/h, contacting time 60 and 120 min, initial feed concentration of ammonia (100 ppm) and urea (40 ppm).

## 1. Introduction

Some compounds contained in fertilizer industry wastewater are ammonia and urea. The urea production need 12 $m^3$ water consumed per ton of product and produced 2.3 $m^3$ of wastewater [1]. This wastewater is collected in temporary storage ponds and need further processing to reduce the concentration of urea and ammonium by neutralizing pH using chemicals and aeration treatment [2]. Wastewater from urea plant contains ammonium 2-9%, urea 0.3-1.5% and carbon dioxide around 0.8-6% by weight of wastewater [3]. There are several conventional processes have been developed to reduce ammonia in fertilizer plant wastewater i.e.; ammonia stripping tower aeration combined with biological treatment. Unfortunately, these methods are relatively not effective in fertilizer industry which produced a large capacity of wastewater per day and need rapid residence time for degradation

process [4]. Hydrolysis is one process in which low concentration of urea solution will come into contact with high pressure steam (18-25 Kg/cm$^2$) under high operating temperature (200-220 $^o$C) [5]. The use of chemical solvents of sulfuric acid ($H_2SO_4$) is also one of popular methods. The process of separating ammonia from sulfuric acid as an acidic reactive compound to ammonia under alkaline to be decomposed [2]. The application of the ammonia separation process depends on several factors, type of contamination, system security, availability of heating sources and chemicals. These methods have their own characteristics, limitations, and has a different equipment's, high operating costs and secondary pollution. Therefore, it is necessary to develop an efficient and practical method of ammonia removal [6].

One method that has great potential to eliminate ammonia and urea levels in liquid waste is the ozonation method. Ozone ($O_3$) is a gas molecule discovered by Van Marum in 1785 using electrical equipment. Ozone gas can barely dissolve in water (0.03 mg/100 ml), at 200 $^o$C decomposed into oxygen rapidly. This method will produce $OH^-$ which can shift the equilibrium reaction or produce $OH^*$ radicals to promote degradation of ammonia and urea nitrogen. Due to ozone is known as strong disinfectant and oxidant, it is often used by industry to deodorize, decolouration, and to produce structural changes in organic compounds [7]. Ozone also proven in reducing COD by 27% which is 2.5 folds greater than oxidation of ordinary organic compounds or biological treatment. $O_3$ will undergo an oxidation process which results in the formation of hydroxyl radicals which are very strong oxidizers [8]. OH, radicals formed from this ozone transformation react with ammonium hydroxide, as shown in equation (1).

$$NH_4OH + O_3 \rightarrow NH_3 + H_2O + 1.5O_2 \quad (1)$$

Ozonation will dominate at high pH (> 9) [9]. The results of the study explain overall stoichiometry as shown in equation (2):

$$2NH_3 + 4O_3 \rightarrow 4O_2 + H_2O + NH_4NO_3 \quad (2)$$

In the electrode chamber, there is a plasmanization process that is the process of exposure of the feed gas in a high voltage electric field which will then undergo ozone formation so that $OH^*$ radicals and OH-ions will degrade waste [10]. The OH radicals formed then attack ammonia on the reactions in equations (4), (5), and (6):

$$HO^- + NH_3 \rightarrow NH_2^* + H_2O \quad (4)$$

$$NH_2 + H_2O_2 \rightarrow NHOH^* + H_2 \quad (5)$$

$$NH_2^* + HO^- \rightarrow NH_2OH \quad (6)$$

UV irradiation at a wavelength of 185 nm can be used to produce ozone, using the corona/electric field discharge method or also called plasma corona discharge [11]. Contact times of 10-30 seconds are often used in commercial UV units, with doses of 60-75 mWs/cm$^2$ known to eliminate ozone residues of 0.5 mg/L. The objective of this study was to evaluate the effectiveness of the ozonation method and its combination with UV irradiation and to determine the performance of the process in reducing the concentration of ammonia nitrogen and urea nitrogen in fertilizer wastewater.

## 2. Materials and Method

### *2.1. Materials*

The raw material used in this experiment was ammonia-containing wastewater directly taken from the Process Condensate Treatment (PCT) unit in urea plant of PT. Pupuk Iskandar Muda (PIM) (Persero), Lhokseumawe, Indonesia. Ammonium chloride, mercuric iodide, potassium persulfate, and hydrochloric acid were of analytical grade obtained from central laboratory of PT. PIM and used

without any further purification; ozone was provided by LH-YT-10G ozone generator BNP OZ-3G 3 gr/h; pH and absorbance values were determined by REX PHS-3C pH meter and UV Steriligh S5QPA 6 watt; spectrophotometer shimadzu UV-1601, respectively. The experimental apparatus is a cylindrical reactor made of transparent glass, and the oxidation system comprises several operation units as shown in schematic flowchart of experimental apparatus in Figure 1.

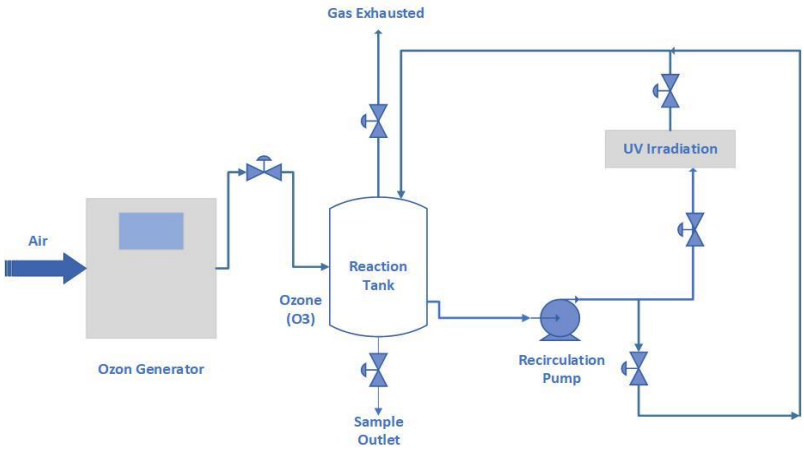


**Figure 1.** Flowchart of experimental apparatus

*2.2. Method*

Prior to running the experiment, the productivity of ozone generator was examined using iodometric method (PT.PIM standard method). By setting up $O_3$ generator loaded by 100 mA, 150 mA, and 200 mA, which generated $O_3$ in solution with concentration of 0.2, 0.6 and 1.2 g/h, respectively. Ammonia-containing wastewater was prepared from fertilizer plant condensate wastewater with various initial solution concentration i.e: ammonia100 ppm-urea 40 ppm, ammonia 150 ppm-urea 50 ppm, ammonia 200 ppm-urea 60 ppm, ammonia 250 ppm-urea 70 ppm, ammonia 300 ppm-urea 80 ppm. At room temperature (about 25 °C), 500 mL of wastewater sample was added into the reactor after the adjustment of pH, then ozone was pumped in. The reaction solution was sampled every 30 min to analyze the changes of pH values, concentrations of ammonia nitrogen ($NH_4^+$-N), urea nitrogen $(NH_2)_2CO$. The concentrations of chemicals were measured by Nessler's reagent spectrophotometry methods and pH value was measured by pH meter [12]. Ozone flow rate, contact time, and pH values were the main effects considered in the experiment of ammonia removal by ultraviolet-enhanced ozonation method. There are two processes of ammonia removal was evaluated, including oxidation by ozone, and UV irradiation combined with ozonation for simultaneous ammonia nitrogen and urea nitrogen removal. The combination of UV irradiation and ozonation treatment was carried out by recirculation outlet flow of the reaction solution to be constantly exposed by UV irradiation. The UV-exposed solutions were then sampled at various contact time (30, 60, 90 and 120 m) to analyze ammonium concentration in the reaction solution.

## 3. Results and Discussion

*3.1. Decrease in ammonia concentration*

Figure 2 shown the decreasing of ammonia concentration in wastewater is significant, especially in the first 30 minutes. The longer ozone residence time contact time gives a significant effect due to under alkaline conditions allow $O_3$ to be decomposed into OH- radicals which then subsequently reacted with ammonium in the solution. The highest ammonia reduction can be seen in the 100 ppm wastewater solution, which is 83.6% to 16.42 ppm. In the wastewater sample solution of 300 ppm the rate of ammonia reduction is lower as 21.5%. It fact presumably due to ozone will be very reactive

under alkaline pH conditions (>10) [9]. The lower the ammonia concentration, the lower the pH. In experimental testing, the use of raw and synthetic wastewater given no comparable difference in ammonia removal.

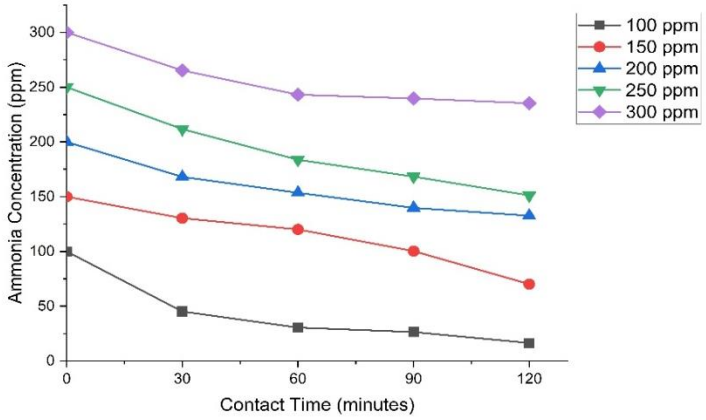


**Figure 2.** Effect of Time on decreasing ammonia concentration with 200 mA ozone loads

*3.2. Decrease in the concentration of urea*

The process of reducing urea nitrogen in liquid wastewater solution proceeded by the reaction of $O_3$ and urea as can be seen in the following equation (7):

$$CO(NH_2)_2 + O_3 \rightarrow N_2 + CO_2 + 2H \quad (7)$$

The synthetic sample solution with 60 ppm urea was reduced to 21.73 ppm with a decrease of 57.8%. This evidence shows the ozonation combined with UV irradiation greatly affects the decrease in urea concentration. Conversely the raw waste samples at 40 ppm urea concentration decreased to 58.3% while at 50 ppm urea concentration the concentration reduction reached 61.4%.

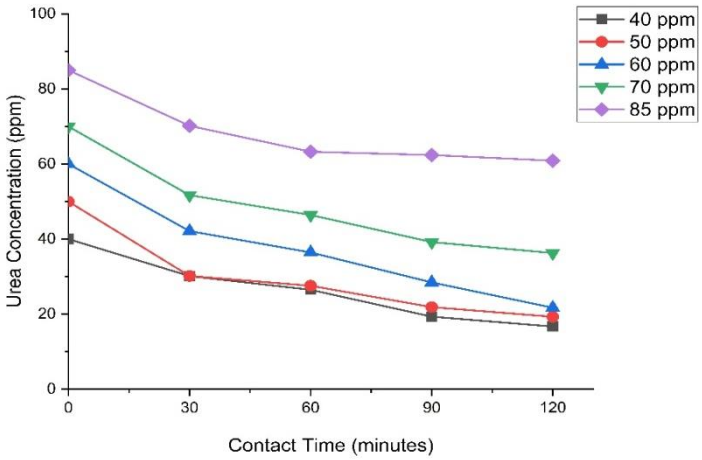


**Figure 3.** Effect of contact time on decreasing urea concentration with 200 mA ozone loads

*3.3. Effect of the amount of ozone concentration and UV irradiation on the reduction of waste concentration*

Figure 4 showed the addition of various ozonator loads (100, 150, and 200 mA) would affected the increase in $O_3$ production in the solution to 1.21 g /h. The higher concentration of $O_3$ in the solution,

the greater the formation of hydroxyl radicals ($OH^*$), the more ammonia and urea reacted with $O_3$. The UV irradiation removed $O_3$ residue that did not react in the solution (catalyzing conversion of $O_3$into $O_2$).

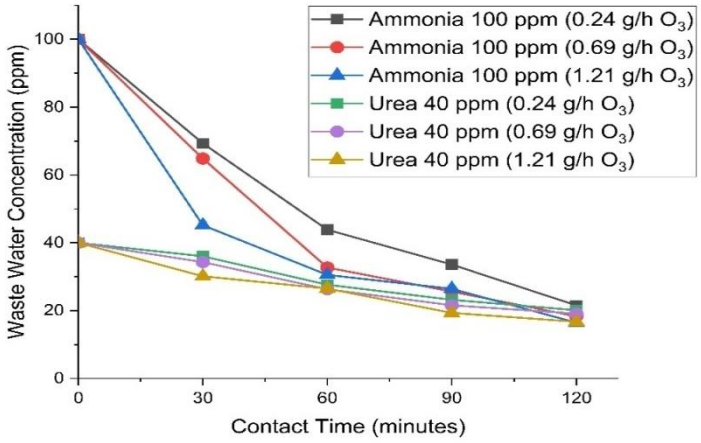


**Figure 4.** Effect of ozonator load and UV light on decreasing the concentration of ammonia and urea

Ozone generator load by increasing the current supplied from 100, 150 and 200 mA would increase $O_3$dose in the solution to 0.24, 0.69 and 1.21 g/h, respectively. UV light irradiation removed the unreacted $O_3$(promoted catalytic conversion of $O_3$ into $O_2$). This phenomenon is dependent on wavelength and strength of energy transmitted [13]. In Figure 4, it can be seen that at 100 mA $O_3$ load (0.24 gr/hr) ammonia concentration reduced from 100 ppm to 21.53 ppm with 78.47% removal occurred. At $O_3$ load 150 mA (0.69 g/hr) ammonia concentration reduced from 100 ppm to 18.3 ppm or 81.7% removal. For $O_3$ load of 200 mA (1.21 g/h), ammonia dropped to 16.42 ppm or 83.6% decreased. Urea concentration in solution also decreased at various ozone load. For 100mA ozone load the decrease reached 49.73% from 40 ppm to 20.11 ppm, at 150 mA the decrease reached 52.25% from 40 ppm to 19.1 ppm and at 200 mA ozone loads revealed the highest decrease occurred was 53.8% where 40 ppm of urea concentration decreased to 16.7 ppm. The oxidation process using ozone is predicted involved in two reaction pathways, oxidized by ozone and oxidation by hydroxyl radicals ($OH^*$)[14]. The formation of ($OH^*$) is resulted from a series of ozone transformational reactions due to its strong oxidizer property even stronger than ozone itself.

### *3.4. Effect of pH on ozonation and UV processes*

The pH output of the waste solution is influenced the whole ammonia removal operation. This fact occurs due to the ozone reaction in the solution that produce acidic ammonium nitrate.

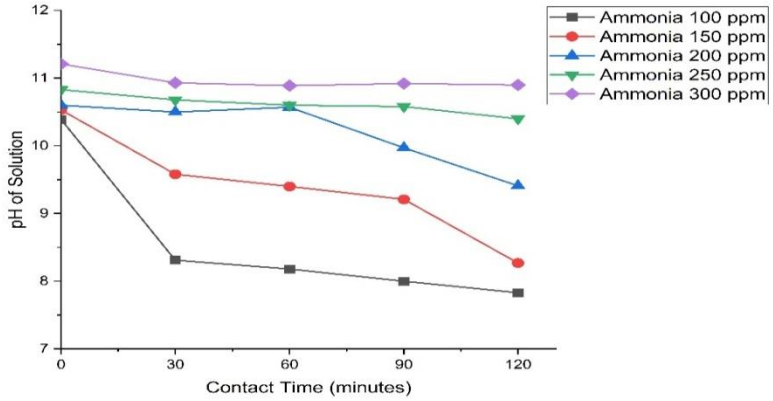


**Figure 5.** Effect of decreasing pH solution on combination of ozonation and UV irradiation

Figure 5 showed that the longer the ozonation time the more ammonia and urea were oxidized to $N_2$ and $NO_3$. Decreasing the pH of the solution (the greater the concentration of OH- ions) will be inversely proportional to the ability of ozonation, where ozonation is very effective in very alkaline conditions. pH decreased by the increase of contact time and ammonia concentration [10]. It also can be seen that the effectiveness of 200 mA load (ozone concentration 1.21 g/h in solution) is optimum in 100 ppm ammonia concentration reduced the pH of the solution up to 7.59. At certain operating times, the higher the pH of ammonia solution (the more alkaline) will affect the faster the $NH_3$ concentration decreased promoting the amount of $NH_3$ removal increase. The same trend also applies that the higher the initial concentration of the solution, the lower the concentration of $NH_3$ would affect lower amount of ammonia removal.

## 4. Conclusion

The ammonia and urea removal in wastewater using the ozonation method can remove ammonia nitrogen by 72.3% and urea by 50.8%. The combination of ozonation and UV irradiation in ammonia nitrogen removal process can increase efficiency of ammonia nitrogen removal up to 83.6% and urea by 63.4% at prolonged recirculation time from 60 minutes and 120 minutes with ozone feed rate 1,21 g/h, initial feed wastewater concentration contained ammonia 100 ppm and urea 40 ppm.

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