

Characterization of Ammonia Removal from Municipal Wastewater Using Microwave Energy: Batch Experiment

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Abstract

This study investigates the characteristics of ammonia removal from municipal wastewater using microwave radiation (MW). Synthetic and real wastewater samples were heated in batch reactors by MW radiation and ammonia removal efficiency was tested under variable conditions. The effects of initial ammonia concentration, pH, and radiation time on ammonia removal efficiency were investigated. Radiation time and pH showed significant influence on the removal of ammonia nitrogen with lower influence of the initial ammonia concentration. The highest ammonia removal efficiency achieved was $91.1 \pm 0.8\%$ and $90.5 \pm 1.2\%$ for synthetic and real wastewaters, respectively. The highest efficiency in both cases was achieved at a pH of 11 with 4 minutes of MW radiation. Comparing the results of this study with the work of others, it was found that ammonia removal efficiency from municipal wastewater that normally has low initial ammonia concentration is less than its removal efficiency from industrial wastewater that has initial ammonia concentrations in the range of 500-12000 mg NH₃-N/L. It is concluded from this study that MW radiation is an effective method for the removal of ammonia nitrogen from municipal wastewater.

Keywords: microwave radiation, ammonia nitrogen, pH, municipal wastewater, heating

1. Introduction

Ammonia nitrogen is a hazardous contaminant that should be removed from wastewater before reuse or disposal to the environment. The typical ammonia nitrogen concentration in the raw municipal wastewater is in the range of 30 to 100 mg NH₃-N/L (CMWU, 2010). Globally, reclaimed wastewater quality standards specify the maximum allowable ammonia concentration according to the reuse purposes. For example, the Jordanian standards limit the maximum ammonia concentration to 5mg NH₃-N/L for wastewater reuse in recharge to groundwater (JSIM, 2006). Several technologies are applied to remove ammonia nitrogen from wastewater, such as biological processes (Holman & Wareham, 2005), ammonia-stripping (Guštin & Logar, 2011), chemical precipitation (Huang et al., 2012) and ion exchange (Jorgensen & Weatherley, 2003). Biological processes are the most commonly used process for ammonia removal from municipal wastewater. However, this process requires high capital and running costs. Moreover, this process is highly sensitive to environmental conditions such as temperature and pH. Ammonia stripping requires high energy supply in running the stripping towers (Lin et al., 2009). Chemical precipitation is effective to some extent, but it is based on adding chemical reagents, which may produce other pollutants in water (Huang et al., 2012).

Microwave (MW) radiation is a promising technique for wastewater treatment that had attracted a number of researchers to explore its unknown effects on wastewater pollutants. Lin et al. (2009) used MW radiation to remove high-concentrated ammonia nitrogen from both simulated and real industrial wastewater samples through a bench-scale study. The concentrations ranged from 500 mg NH₃-N/L to 12,000 mg NH₃-N/L. They investigated four affecting factors: radiation time, initial pH, initial ammonia concentration and aeration. The experiment results showed that higher pH and MW radiation time resulted in larger ammonia removal, with minute effect of aeration. They achieved a removal efficiency of 98.2% in 3 min of radiation with initial concentration of 500 mg NH₃-N/L. Lin et al. (2009) explained in details the mechanism of ammonia removal from wastewater which was mainly attributed to the generated heat in the solution due to MW radiation. They stated that by increasing the MW radiation, the solution temperature becomes higher and the random water molecular motion increases. This stimulates the escape of molecular ammonia from solution by volatilizations.

Zieliński et al. (2013) studied the possibilities for improving wastewater treatment by applying MW radiation, compared to convective heating of trickling filters. They delivered the microwaves to the biofilm in a continuous and intermittent way, having temperatures of 20, 25, 35 and 40°C. The authors found that the presence of organic compounds in the continuous influent exposed to MW resulted in 10% higher efficiency and 20% higher rate of nitrification compared to intermittent MW radiation and convective heating. In addition, they observed that the absence of organic carbon in the influent induced a significant increase in ammonium oxidation efficiency at 20-35°C.

Yang et al. (2009) explored an advanced oxidation process based on sulfate radical SO_4^{2-} to degrade organic pollutants in wastewater. They used a MW-activated persulfate oxidation with or without active carbon. The experiment were conducted to examine whether MW heating is an effective method to activate persulfate and then to decompose biorefractory organic compounds in wastewater by using an Azo Dye Acid Orange 7 (AO7) (up to 1,000 mg/L) as a model compound. It was found that AO7 was completely decolorized within 5-7 min. By adding 1.0 g/L of active carbon as catalyst, 100% decolorization of AO7 (500 mg/L) was achieved within 3 min.

Jothiramalingam et al. (2010) used MW heating for the stabilization of industrial wastewater sludge and reported significant increase of sludge stabilization efficiency compared to conventional heating by heat exchangers. Eskicioglu et al. (2009) investigated the enhancement of thermophilic anaerobic digestion of thickened waste activated sludge by combined microwave heating and alkaline pretreatment. They found that methane production was increased by 27% due to MW heating compared to traditional heating methods.

After literature review, it was found that the use of MW radiation in removing ammonia from municipal wastewater is not yet investigated. Hence, this study was initiated to fill this gap by determining the characteristics of this process and to specify its optimum operating conditions.

2. Materials and Methods

Figure 1 shows a schematic diagram of the experimental apparatus. A domestic microwave oven (700 W, 2450 MHz, Dura brand XB2316, UK) with multiple power settings was used as the source of the MW radiation. A hole was drilled on its top cover, with copper pipe inserted to prevent MW emission (Yang et al., 2009).

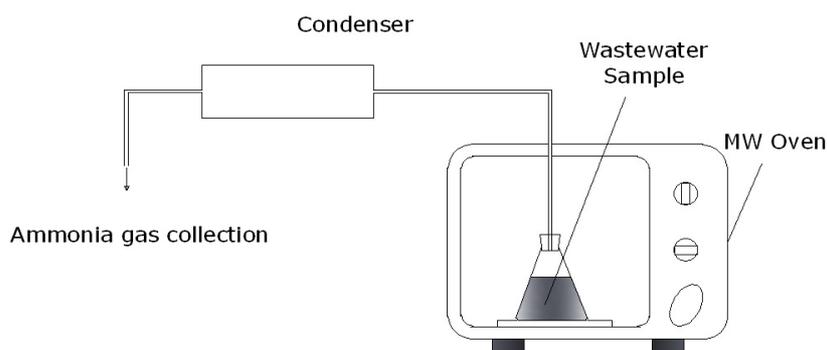


Figure 1. Schematic diagram of the experimental apparatus

To make sure that there was not any harmful radiation leakage, the radiation exposure rate of the MW oven was tested before starting experiments, using electric and magnetic field measurement device (EMR-21C, Safety Test Solutions, Germany), and it was completely safe.

A 250-ml Erlenmeyer flask containing 100 ml of wastewater was placed in the oven and radiated under different conditions. The flask was connected to a condensing system. The temperature was measured by a thermometer and the final concentration of the ammonia nitrogen was measured using Nessler standard method (APHA, AWWA, & WEF, 1989).

Synthetic wastewater solution was prepared with ammonium chloride (99.5%, analytical reagent, HiMedia Laboratories, Mumbai, India) and distilled water. The initial pH of the solution was adjusted using sodium hydroxide solution (NaOH, 2.0 mol/L, 97.5%, Chemie, Mumbai, India).

After heating each sample, the volume of wastewater slightly decreased due to evaporation of water. Thus, after

heating each sample, the volume was adjusted with deionized water, using a 100-ml Erlenmeyer flask, to keep the same initial volume of the samples. In all experiments, for statistical purposes, each condition was tested 5 times and an average value was reported together with its corresponding standard deviation.

As a comparison, the same experiment was applied on real municipal wastewater samples, which were obtained from Gaza Wastewater Treatment Plant. The removal efficiencies of ammonia nitrogen were compared with those resulted from synthetic wastewater.

3. Results and Discussion

In order to achieve the best removal of ammonia nitrogen from municipal wastewater, the affecting factors, including initial ammonia concentration, pH, and radiation time were investigated. In this research, no aeration was applied, since it has a minute effect on ammonia nitrogen removal as illustrated elsewhere (Lin et al., 2009).

3.1 Effect of Initial Ammonia Concentration

In this experiment, six initial ammonia concentrations were tested (25, 40, 55, 70, 85, and 100 mg NH₃-N/l) at pH values of 9, 10, and 11 and at radiation times in the range of 1 to 5 minutes. Figure 2 represents the effect of initial ammonia concentration on residual ammonia concentration at pH=11 and radiation times of 1,2,3,4, and 5 minutes.

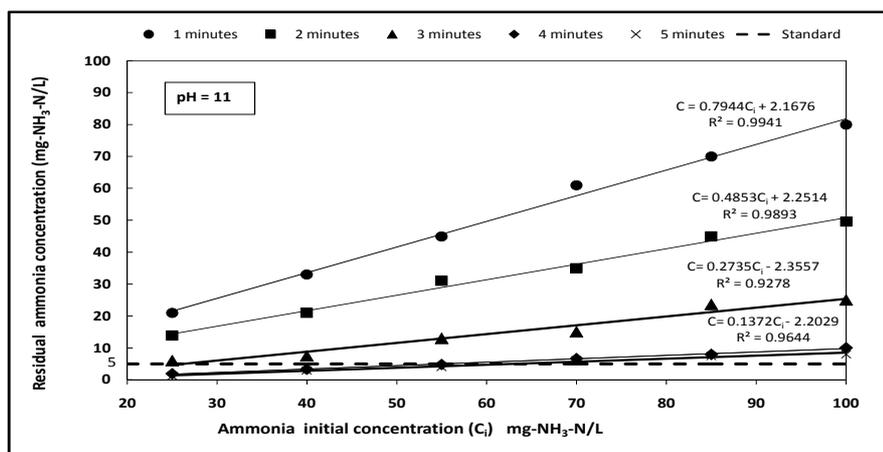


Figure 2. Effect of initial ammonia concentration on residual ammonia concentration (pH=11)

It is interpreted from the figure that the value of the residual ammonia concentration (C) increased linearly with the increase of initial ammonia concentration (C_i) as illustrated by the regression equations presented on Figure 2. For example (at a pH value of 11 and a radiation time of 3 minutes), when (C_i) was 25 mg NH₃-N/l (C) was 6.2 mg NH₃-N/l, and when (C_i) was 85 mgNH₃-N/l (C) was 23.5 mgNH₃-N/l. The same behavior was detected for other radiation times (i.e. 1, 2, 3, and 5) and other values of pH (i.e. 9 and 10). The benefit of this finding is the ability to determine the initial ammonia concentrations at which a specific residual ammonia concentration can be achieved. For example, a maximum residual ammonia concentration of 5 mg NH₃-N/l is required by the Jordanian standards so that the treated wastewater can be recharged to groundwater (Jordanian Standards, 2006). In this work, as interpreted from Figure 2, a residual ammonia concentration of 5 mg NH₃-N/l is achieved when the initial ammonia concentration was 55 mg NH₃-N/l or less (at a pH value of 11 and a radiation time of 4 minutes).

Another finding of this part of the experiment is that the ammonia removal percent (r) was not significantly affected by the value of the initial concentration (C_i). The linear correlation between (r) and (C_i) is indicated by the regression equations given in Figure 3 for radiation times of 1, 2, 3, 4, and 5 minutes. The slope of these lines are close to zero (0.0285, 0.0655, -0.0567, -0.0604, -0.0426) and the lines are almost parallel to the x-axis. This verifies that the initial concentration of ammonia has minor effect on ammonia removal percent (r) for the (C_i) concentrations range studied in this work. For example (at pH of 11 and radiation time of 4 minutes), when the initial concentrations were 25, 40, 55, 70, 85, and 100 mgNH₄-N/l, the removal percents were 92.2, 91.70, 91.3, 90.5, 90.6, and 90.1%, respectively. The average removal rate (r_{average}) in this case is 91.1% with a standard

deviation (STD) of ±0.8% (small deviation around r_{average}). Similar results were obtained for other radiation times as given in Table 1 and as interpreted from Figure 3.

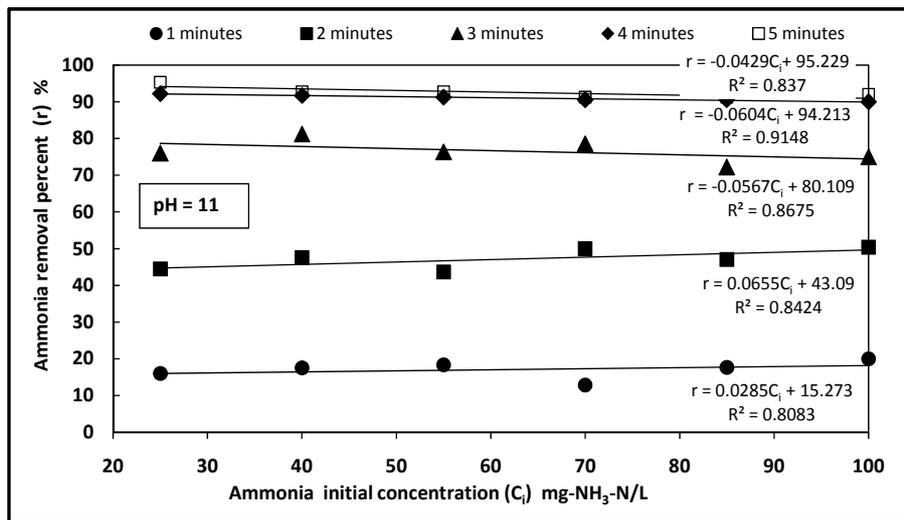


Figure 3. Effect of initial ammonia concentration on ammonia removal percent at pH 11

It should be clarified at this point that there is no contradiction that C_i affects C in direct proportion (as illustrated by Figure 2) while it doesn't significantly affect (r) (as illustrated by Figure 3). This can be explained by looking at the ammonia removal percent formula:

$$r = \frac{C_i - C}{C_i} \times 100$$

What keeps (r) almost constant is that when C_i increases, C increases proportionally, as illustrated above, and the right hand term of the formula doesn't significantly change. Similar conclusion was reached by Cheung et al. (1997) while commenting on mass transfer of ammonia from liquid to air in their experiments on ammonia stripping from landfill leachate.

Hence, the main conclusion of this part of the experiment is that for each radiation time (t) and pH value there is an average removal percent (r_{average}) regardless of the value of the initial ammonia concentration. The main factors that affect (r) are the pH value and the radiation time rather than C_i as illustrated by Figure 3 and Table 1.

Table 1. Ammonia average removal percent for initial concentrations in the range of 25-100 mg/L at pH =11 and radiation times in the range of 1 to 5 minutes

Item	Radiation time (minutes)				
	1	2	3	4	5
% r_{average}	17.1	47.2	76.6	91.1	92.5
STD (\pm)	1.2	1.8	1.3	0.8	0.5

3.2 Effect of Initial pH

To study the effect of pH, the initial ammonia concentration (C_i) and the microwave radiation time (t) were fixed at specific values while pH was varied to the values 9, 10, and 11. The general observed trend was that ammonia removal rate increased with the increase of pH as illustrated by Figure 4. For example, when the pH was 9 and C_i was 100 mgNH₃-N/l and after 4 minutes of radiation, the residual ammonia concentration (C) was 67 mg NH₃-N/l (33% removal) while it was reduced to 35 mg NH₃-N/l (65% removal) and 9 mgNH₃-N/l (91% removal) when the pH was increased to 10, and 11, respectively. So there was a considerable increase of ammonia removal efficiency per each additional pH unit. Similar results were observed for all C_i values tested in this experiment

(i.e. 25, 40, 55, 70, 85, and 100 mg NH₃-N/l) and for all radiation times in the range of 1 to 5 minutes. In all cases, the highest removal rates were achieved at a pH value of 11 compared to pH values of 10 and 9.

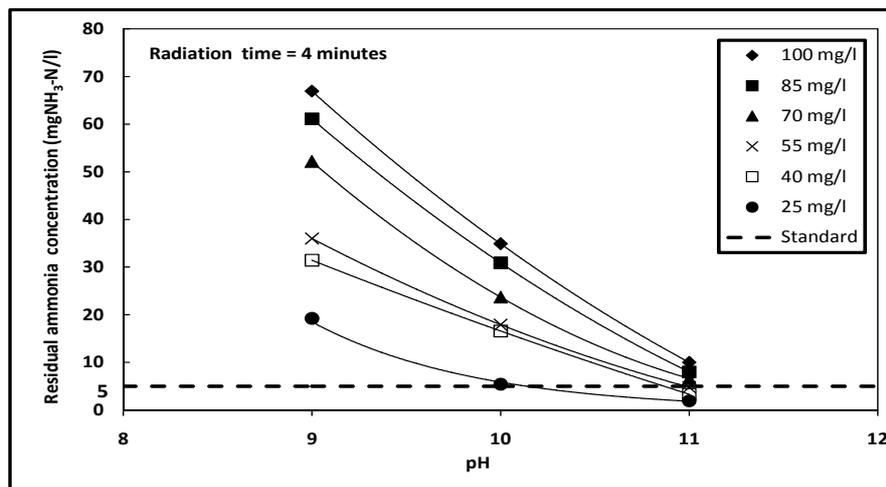


Figure 4. Effect of pH on ammonia residual (MW radiation time = 4)

Lin et al. (2009) achieved 98% ammonia removal from industrial wastewater with pH 11 and after 3 min of radiation. In the Lin et al. (2009) work, the steady state removal percent of 98% was achieved in a shorter time (3 minutes versus 4 minute in this research). This is attributed to the higher microwaves' power input that they used (750 W versus 700 W in this research). Moreover, Lin et al. (2009) achieved higher steady state ammonia removal efficiency at a pH of 11 compared to the efficiency achieved in this work (98% versus 91%). This may be attributed to the higher initial concentration range that they worked with (in the range of 500-12000 mg NH₃-N/l) compared to the low initial concentrations dealt with in this research (in the range of 25 to 100 mg NH₃-N/l). This may be attributed to the higher ammonia mass transfer rate resulting from higher driving force created by the high difference between initial and final ammonia concentrations (i.e. $C_i - C$). For example, the driving force in Lin et al. (2009) work with a C_i value of 12000 mg NH₃-N/l and a C value of 473 mgNH₃-N/l was 11563 mg NH₃-N/l, while the maximum driving force in this research was 91 mg NH₃-N/l ($C_i=100$ mg NH₃-N/l, $C=9$ mg NH₃-N/l). So it can be concluded that the ammonia removal characteristic at lower concentrations as those existing in municipal wastewater (in the range 25 to 100 mg NH₃-N/l) are different from the removal characteristic at higher concentrations as those found in industrial wastewater (up to 12000 mg NH₃-N/l).

The increased ammonia removal rate with the increase of pH value is attributed to the increase of the concentration of NH₃, the unionized volatilizing form of ammonia. In basic solution, non-volatile NH₄⁺ converts to volatile NH₃. The equilibrium equation of these two ammonia species is:



When the percentage of the volatile NH₃ increases, the efficiency of ammonia removal by heating increases. The percent of volatile NH₃ in solution is given by the following formula (USEPA, 1999b):

$$\% \text{ volatile } NH_3 = \frac{100}{1 + 10^{(pka - pH)}}$$

Where, pka is the ammonia dissociation coefficient.

Applying this formula at pH values of 9, 10, 11 and 12, and using a pka value of 9.34 (at $T=22^\circ C$, the initial temperature of solution before heating), the volatile NH₃ percents in solution are calculated as 31, 82, 98, and 99.7%, respectively. So, the available volatile NH₃ at pH 11 is considerably higher than that at pH of 9 and 10. This explains the higher ammonia removal percents at a pH of 11 compared to that at pH values of 9 and 10. It is also understood from the formula that increasing pH from 11 to 12 did not add a significant increase on the available volatile NH₃ percent (increased from 98% to 99.7% only). Hence, increasing the pH from 11 to 12 is not economically justified since this will require the addition of significant amount of alkaline such as NaOH to the solution while not adding significant improvement on the removal efficiency of ammonia. Based on that, pH

11 is suggested to be the optimum pH value for removing ammonia from wastewater.

3.3 Effect of Radiation Time

To study the radiation time effect, the initial pH value and the initial ammonia concentration were fixed at specific values while the value of radiation time was increased in the range of 1 to 5 minutes. The general observed trend was that ammonia concentration decreased nonlinearly with the increase of radiation time as illustrated by Figures 5, 6, and 7. For example, as shown in Figure 7, when the initial pH was fixed at 11, and the initial ammonia concentration was fixed at 55 mg NH₃-N/l, the ammonia concentration decreased to 36 mg NH₃-N/l after 1 minute of radiation while it decreased to 4.9 mg NH₃-N/l after 4 minutes. It is interpreted from these figures that the relation between the residual ammonia concentration (C) and the MW radiation time (t) can be modeled by a third degree polynomial formula as the following:

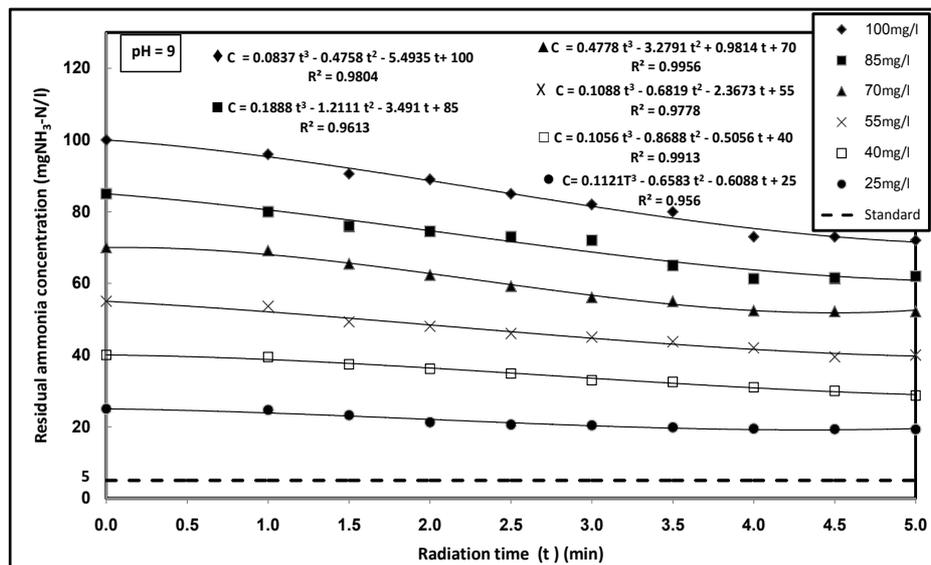


Figure 5. Effect of microwave radiation time on ammonia nitrogen removal (pH = 9)

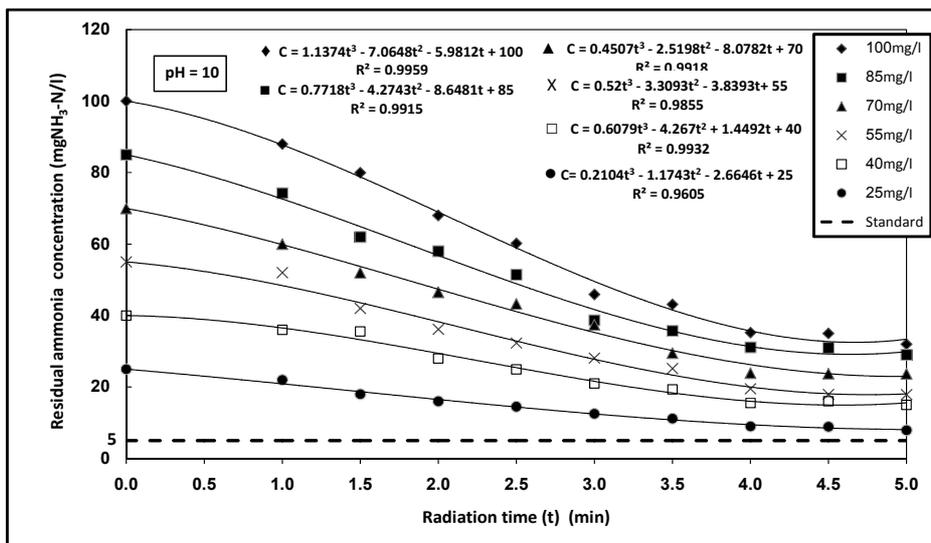


Figure 6. Effect of radiation time on of ammonia nitrogen removal (pH = 10)

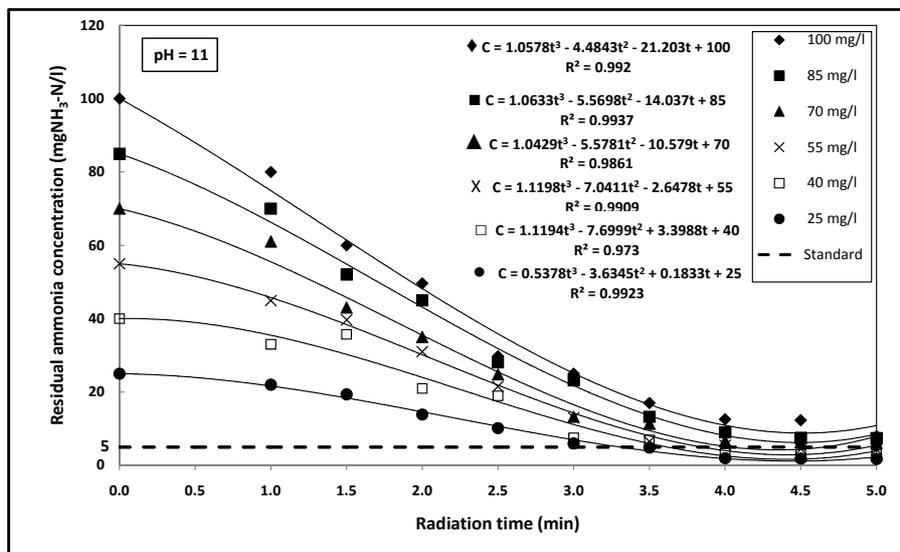


Figure 7. Effect of radiation time on ammonia nitrogen removal (pH = 11)

$$C = Kt^3 - Lt^2 \pm Mt + C_i$$

Where,

C_i = initial ammonia concentration, mg NH_4-N/l .

K, L, M = constant coefficients.

The polynomial formulae of each pH value and ammonia initial concentration are illustrated on Figures 5, 6 and 7. The values of the coefficients K, L and M depend on pH and initial ammonia concentration. These formulae are valid for radiation time (t) in the range of 1 to 5 minutes and for initial ammonia concentration (C_i) in the range of 25 to 100 mg NH_3-N/l .

It is also interpreted from the data that no significant reduction of ammonia concentration was achieved when the radiation time was increased beyond 4 minutes regardless of the pH value or the initial ammonia concentrations (Figures 5, 6, and 7). For example, as shown in Figure 7, for an initial ammonia concentration of 55 mg NH_3-N/l , the residual ammonia concentrations were 4.96, 4.50, and 4.35 mg NH_3-N/l at radiation times of 4, 4.5 and 5 minutes, respectively. This indicates that a steady state residual ammonia concentration is achieved after 4 minutes of radiation. Consequently, it is concluded that the optimum radiation time for the removal of ammonia is 4 minutes for the pH range 9 to 11 and for initial ammonia concentrations in the range of 25 to 100 mg NH_3-N/l .

4. Treatment of Real Wastewater

In order to confirm the results obtained from the synthetic wastewater experiments, a similar experiment was applied on three real wastewater samples that were collected from the treated effluent of Gaza Wastewater Treatment Plant. The samples were collected in Nov. 17th, Dec. 15th 2011 and Feb. 18th 2012. Table 2 presents the main characteristics of each sample.

Table 2. Characteristics of the real wastewater samples

Sample #	Collection date	pH	BOD ₅ (mgO ₂ /L)	TSS (mg/L)	NH ₃ (mgNH ₃ -N/L)	Fecal Coliform Cell/100 ml
1	Nov. 17 th , 2011	7.2	130	105	52.30	3500
2	Dec. 15 th , 2011	7.5	90	75	67.50	2750
3	Feb. 18 th , 2012	7.4	110	92	86.70	3230

The samples were heated by microwave radiation in the range of 1 to 5 minutes at the optimum pH value of 11 as found in the experiments performed on synthetic wastewater. Figure 8 shows the results obtained from treating the real wastewater samples for ammonia removal. The general observed trend (as illustrated by Figure 8) was that ammonia concentration decreased nonlinearly with the increase of radiation time following a third degree polynomial regression model indicating a similar behavior to that observed with synthetic wastewater treatment. The steady state residual ammonia concentration (C) was attained after 4 minutes of radiation in good agreement with the synthetic wastewater samples results. Moreover, the ammonia removal efficiency was also similar to that obtained with synthetic wastewater as illustrated in table 3. As shown in the table (at radiation of 4 min.), when the initial ammonia concentrations were 52.30, 67.50 and 86.70 mg NH₃-N/l, the removal efficiencies were, 91.50, 90.10, and 91.1%, respectively. The average removal efficiency (r_{average}) in this case is $90.9 \pm 0.7\%$ which is comparable to the (r_{average}) value of the synthetic wastewater which was $91.10 \pm 0.8\%$ (pH =11, t=4 minutes) as reported in Table 1. The similar ammonia removal efficiencies indicate that other constituents in the treated wastewater effluent such as organic matter and suspended solids has no significant effect on the ammonia removal efficiency by MW radiation.

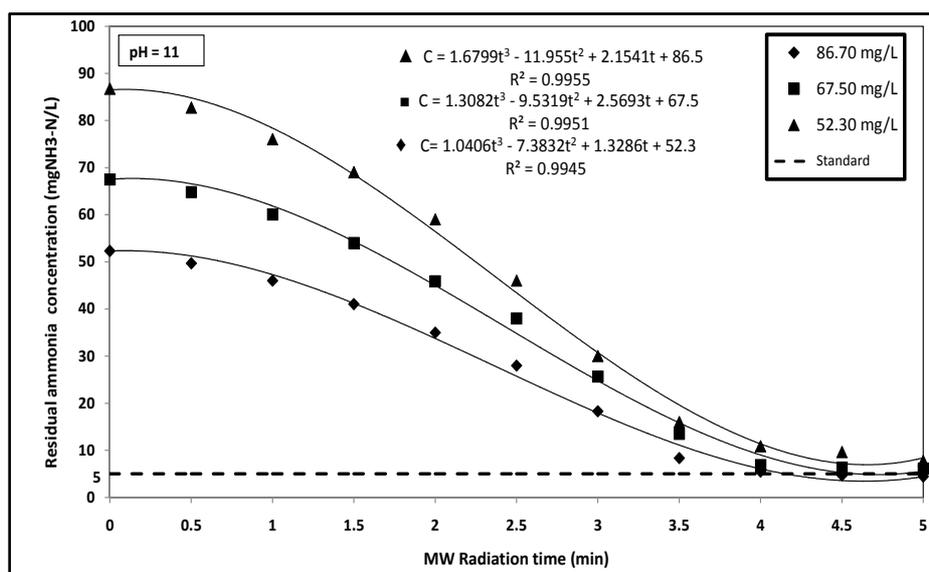


Figure 8. Residual ammonia in municipal wastewater versus MW radiation time (pH=11)

Table 3. Final ammonia concentration after 4 min radiation

Initial concentration (mg/l)	Final concentration (after 4 min) (mg/l)	Percentage of removal (r %)
52.3	4.45	91.5
67.5	6.08	90.1
87.6	9.54	89.1

5. Conclusion

This research was carried out to explore the ammonia nitrogen removal from municipal wastewater using MW energy. The effects of initial concentration, pH, and radiation time, were investigated. Increasing radiation time together with pH had the most significant effect on ammonia nitrogen removal. Using 700W MW energy, and 100 ml synthetic wastewater samples, $91.10 \pm 0.8\%$ ammonia nitrogen removal was achieved after 4 min radiation at a pH value of 11. Similar ammonia nitrogen removal efficiency ($90.5 \pm 1.2\%$) was achieved with real municipal wastewater samples that were treated under the same conditions of pH and radiation time. Thus, the optimum ammonia removal from municipal wastewater by MW is achieved at a pH of 11 and radiation time of 4 minutes. The ammonia removal efficiency in the lower range concentration (25-50 mg NH₃-N/l) is found to be lower than the removal efficiency in the higher range (500-12000 mg NH₃-N/l). MW radiation is proved to be an effective alternative method for the removal of ammonia nitrogen from municipal wastewater.

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