

# Ammonia Removal Model Based on the Equilibrium and Mass Transfer Principles

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In air stripping of ammonia from the aqueous solution, a new removal model was presented considering the equilibrium principles for the ammonia in aqueous solution and between the aqueous and air phase. The effects of pH, temperature and airflow rate on the ammonia removal were evaluated with the model. In addition, the saturation degree of ammonia in air was defined and used to evaluate the effect of each experimental factor on the removal rate. As pH (8.9 to 11.9) or temperature (20 to 50 °C) was increased, the overall removal rate constants in all cases were appeared to be increased. Our presented model shows that the degrees of saturation were about the same (0.45) in all cases when the airflow condition remains the same. This result indicates that the effect of pH and temperature were directly taken into consideration in the model equation. As the airflow increases, the overall removal rate constants were increased in all cases as expected. However, the saturation degree was exponentially decreased with increasing the airflow rate in the air phase (or above-surface) aeration. In the subsurface aeration the saturation degree remains a constant value of 0.65 even though the airflow rate was increased. These results indicate that the degree of saturation is affected mainly by the turbulence of the aqueous solution and remains the same above a certain airflow rate.

**Key Words :** Ammonia removal model, pH, Temperature, Airflow rate

## Introduction

In the aqueous solution, ammoniac nitrogen can be classified into ammonium ion [ $\text{NH}_4^+$ ] and free ammonia [ $\text{NH}_3(\text{aq})$ ]. Of these, only free ammonia can move into the air phase because of its nature of volatility. This fact can be explained by comparing the Henry's law constants. If the ammoniac nitrogen in the aqueous solution is desired to be removed from the waste waters, two conditions should be considered for the effective removal. First, the fraction of the free ammonia in the aqueous solution should be increased by increasing pH and temperature. Second, the transfer rate from the aqueous to air phase should be increased by increasing the temperature and the airflow rate. Ammonia removal method applying these principles is called air contact process that can be classified into the airflow bubbling method and the stripping tower removal method.<sup>1-6</sup>

To estimate the ammonia removal by the air contact process from waste waters containing high concentration of ammoniac nitrogen, it is important to understand the behavior of ammonia species in the aqueous solution and to predict removal rate based on the experimental conditions as discussed above. This will provide valuable data for designing the effective ammonia removal process by aeration. Numerous researches have accomplished by many scientists to verify ammonia removal phenomena based on these essential experimental factors. Bayley<sup>7</sup> investigated that the chemical composition, the size of bubble, the rising speed of air bubble and the depth of aeration affected the ammonia removal efficiency. Schpirt,<sup>8</sup> however, stated that the depth of aeration did not affect the ammonia removal efficiency. Srinath and Loehr<sup>9</sup> reported the effect of air contact area,

contact time and the concentration of free ammonia. Liao and his coworkers<sup>6</sup> compared the ammonia removal efficiencies of air bubbling method with the stripping tower method packed with small plastic rings. Smith and Arab<sup>10</sup> reported that the air contact area and surface turbulence by air flows had an important role in ammonia removal and they hypothesized that the free ammonia between aqueous and gas phase reaches complete equilibrium instantaneously. Based on this hypothesis, Cheung<sup>11</sup> reported theoretical values of ammonia removal rate and compared with the experimental values. Unfortunately, the experimental values were much higher than the theoretical values, but they could not explain these unexpected results clearly. This hypothesis has not been proved until today.

Summarizing the above researches, the effects of essential parameters on the ammonia removal could only be explained qualitatively after the obtained experimental results. The reported ammonia removal rate models were frequently relied on the 1st order reaction kinetics.<sup>3,10,12,13</sup> In this kind of models, the ammonia concentration in the air contacting the aqueous phase assumed to be "zero", which is not correct. In addition, it should be pointed out that the model equation did not include the essential factors of pH, temperature and airflow rate. Although this type of models may be enough to evaluate the obtained experimental results indirectly, the effects of each experimental factor on the ammonia removal rate could not be directly evaluated.

In this research, a new ammonia removal model equation was presented utilizing the chemical equilibrium principles, mass balance and mass transfer theory. The model equation includes the pH, temperature and air flow rate as the essential parameters and thus the removal model can explain

the effect of each parameter on the ammonia removal rate quantitatively. The theoretical values for the ammonia removal rate were obtained and compared with the experimental data. To evaluate the completeness of ammonia equilibrium between the aqueous and air phase, the saturation factor was also introduced as a new concept and calculated by fitting the experimental data to the model. The presented model should also be applicable to the removal of any volatile species in the waste waters.

### Model Development

**Ammonia Removal Model.** When a container is not fully filled with aqueous solution, the inner part of the container can be divided into two regions of aqueous phase and air phase. As the ammonia is removed to the atmosphere, there are two processes of ammonia mass transfer. First process is the transfer of ammonia from the aqueous phase to the air phase in the container and second process is the removal from the air phase in the container to the outside of the container (or to atmosphere). Second process is the final removal process and can be divided into two mechanism; the removal process caused by gas diffusion and by airflow supplied into the system. In this process, if the gas diffusion can be ignored, the airflow provided into the system should only be the main removal process. Figure 1 shows that this type of system can be organized by closing the container with a cover and connecting between the air phase and the external air with a long tube of small inner diameter. In this system, the amount of ammonia removal can be expressed as a function of ammonia concentration in the air phase and the airflow rate provided into the aqueous phase. To model the ammonia removal rate, the following assumption should be first made.

1. Ammonia concentration in the aqueous phase is uniform.

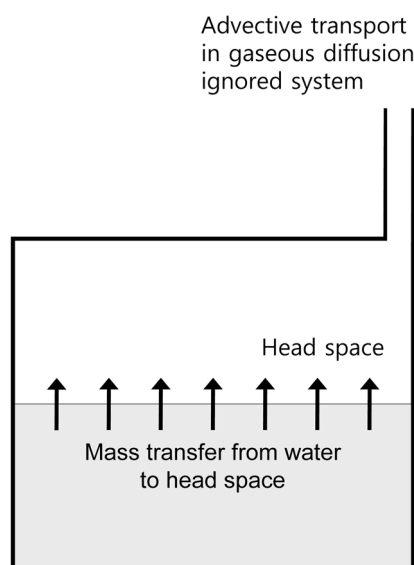


Figure 1. Schematic diagram of the ammonia removal system.

2. Ammonia concentration in the air phase is uniform.

3. Ammonia concentration in the air phase is in equilibrium with the aqueous phase. In other words, ammonia in the aqueous and air phase reaches equilibrium instantly.

Note that each ammonia concentration in the aqueous and air phase inside the container can be considered because the provided airflow normally makes enough turbulence. If the above all conditions are satisfied, the amount of ammonia removed from the container should be the same as the amount of ammonia contained in the airflow leaving the container. Therefore, the following equations can be written:

$$\Delta m_{out} = Q \cdot C_g \cdot \Delta t = Q \cdot \frac{m_g}{V_g} \cdot \Delta t \quad (1)$$

$$\frac{\Delta m_{out}}{\Delta t} = Q \cdot \frac{m_g}{V_g} \quad (1a)$$

$\Delta m_{out}$  = amount of ammonia removed from the container

$m_g$  = ammonia mass in the air phase inside the container

$Q$  = airflow rate

$C_g$  = ammonia concentration in the air phase inside the container

$V_g$  = volume of the air phase inside the container

$\Delta t$  = time increment

In the above equations,  $m_{out}$  can be expressed as a function of  $m_g$ . Since total amount of ammonia is always constant, the following mass balance equation can be written.

$$m_T = m_L + m_g + m_{out} \quad (2)$$

$m_T$  = total ammonia mass of interest

$m_L$  = ammonia mass in the aqueous phase

$m_g$  = ammonia mass in the air inside the container

$m_{out}$  = ammonia mass removed from the container or in the atmosphere

If the equilibrium between the aqueous and air phase is satisfied (Condition 3), the relationship between two phases can be expressed by using Henry's law.

$$H = \frac{C_g}{C_L \cdot \alpha_{NH_3}} \quad (3)$$

$H$  = Henry's law constant (unitless)

$C_L$  = total ammonia concentration in the aqueous phase

$C_g$  = ammonia concentration in the air phase inside the container

$\alpha_{NH_3}$  = fraction of  $NH_3(aq)$  in the aqueous phase

In the above, the concentration term ( $C_g$  and  $C_L$ ) can be changed to mass unit and thus  $m_L$  can be expressed as a function of  $m_g$  and other terms as follows.

$$m_L = \frac{V_L \cdot m_g}{\alpha_{NH_3} \cdot H \cdot V_g} \quad (4)$$

$V_g$  = volume of the air phase inside the container

$V_L$  = volume of the aqueous phase inside the container

After substituting equation (4) into equation (2), rearranging the equation for  $m_g$  yields the following equation.

$$m_g = \left( \frac{\alpha_{NH_3} \cdot H \cdot V_g}{V_L + \alpha_{NH_3} \cdot H \cdot V_g} \right) \cdot (m_T - m_{out}) \quad (5)$$

Substituting the above into equation (1), dividing both sides by  $\Delta t$ , and if  $\Delta t$  is assumed to be approach to zero, the differential equation (7) can be obtained.

$$\frac{\Delta m_{out}}{\Delta t} = \left( \frac{\alpha_{NH_3} \cdot Q \cdot H}{V_L + \alpha_{NH_3} \cdot H \cdot V_g} \right) (m_T - m_{out}) \quad (6)$$

$$\frac{dm_{out}}{dt} = \left( \frac{\alpha_{NH_3} \cdot Q \cdot H}{V_L + \alpha_{NH_3} \cdot H \cdot V_g} \right) (m_T - m_{out}) \quad (7)$$

By rearranging equation (7) and integrating the equation yields the final equation (9) for  $m_{out}$ .

$$\int_0^{m_{out}} \frac{dm_{out}}{(m_T - m_{out})} = \int_0^t \left( \frac{\alpha_{NH_3} \cdot Q \cdot H}{V_L + \alpha_{NH_3} \cdot H \cdot V_g} \right) dt \quad (8)$$

$$m_{out} = m_T - m_T \cdot \left( \exp \left[ \left( \frac{\alpha_{NH_3} \cdot Q \cdot H \cdot t}{V_L + \alpha_{NH_3} \cdot H \cdot V_g} \right) \right] \right)^{-1} \quad (9)$$

The above equation shows the theoretical maximum of the amount removed from the container as a function of time. In addition, the amounts of ammonia in the aqueous and air phase inside the container can be express as.

$$m_g = m_T \left( \frac{\alpha_{NH_3} \cdot H \cdot V_g}{V_L + \alpha_{NH_3} \cdot H \cdot V_g} \right) \left( \exp \left[ \left( \frac{\alpha_{NH_3} \cdot Q \cdot H \cdot t}{V_L + \alpha_{NH_3} \cdot H \cdot V_g} \right) \right] \right)^{-1} \quad (10)$$

$$m_L = m_T \left( \frac{V_L}{V_L + \alpha_{NH_3} \cdot H \cdot V_g} \right) \left( \exp \left[ \left( \frac{\alpha_{NH_3} \cdot Q \cdot H \cdot t}{V_L + \alpha_{NH_3} \cdot H \cdot V_g} \right) \right] \right)^{-1} \quad (11)$$

As shown above, the derived model equations contain all essential parameters of the pH, temperature, and airflow rate. Therefore, the theoretical amount of removed ammonia from the container can be adequately predicted by inputting the experimental parameters prior to experiment.

**Saturation degree.** In the above section, we assumed that the instantaneous equilibrium occurs between the aqueous and air phase. If this occurs, the equation (3) can be used to calculate the ammonia concentration in the air phase easily. However, if ammonia does not become saturated in the air phase, the ratio of ammonia concentrations in the air to the aqueous phase will be less than Henry's constant. In this research, the saturation degree ( $\beta$ ) was defined to account this difference by modifying the equation (3).

$$\frac{C_g}{(C_{aq} \cdot \alpha_{NH_3})} = \beta \cdot H$$

$$\beta = \frac{C_g}{H \cdot (C_{aq} \cdot \alpha_{NH_3})} \quad (12)$$

If  $\beta$  is "1" in equation (12), the ammonias in the aqueous and air phase are in equilibrium, indicating that the instantaneous equilibrium occurs between the aqueous and

air phase. If  $\beta$  is less than 1, it means that instantaneous equilibrium does not occur during the process. Generally, the Henry's Law constant can be obtained from a book and the concentration of ammonia in the aqueous phase can easily be measured. However, since it is difficult to accurately measure the concentration in the provided air into aqueous phase, the value  $\beta$  of cannot be directly obtained.

If the 'H' in equations (11) is substituted by ' $\beta H$ ', the following modified equation for  $m_L$  can be obtained.

$$m_L = m_T \left( \frac{V_L}{V_L + \alpha_{NH_3} \cdot (\beta \cdot H) \cdot V_g} \right) \left( \exp \left[ \left( \frac{\alpha_{NH_3} \cdot Q \cdot (\beta \cdot H) \cdot t}{V_L + \alpha_{NH_3} \cdot (\beta \cdot H) \cdot V_g} \right) \right] \right)^{-1} \quad (13)$$

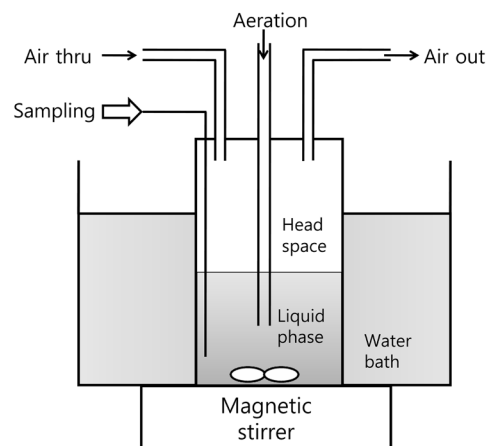
It is noted that all the parameters except  $\beta$  can be given prior to the experiment.

## Experimental

### Ammonia Removal Apparatus and Removal Method.

Figure 2 shows a schematic diagram for the ammonia removal system used in this research. The circular acrylic container (internal diameter of 15 cm; height of 20 cm) was installed inside the water bath. The height, width and length of the water bath were 30 cm, 50 cm, and 30 cm, respectively. The desired temperature was set and controlled by using the Samwon ENG company's U-105T heating device, circulating the water continuously with a submerged pump. The synthetic wastewater containing certain concentration of ammonia was poured into the acrylic container. To keep the constant temperature and uniform ammonia concentration, a magnetic stirrer was placed and operated at 60 rpm during the whole experiment.

The acrylic container was covered up tightly except for the air supplying inlet and the outlet. Constant airflow regulated by a flow meter (Dwyer Co.'s Rate-Master air flow meter) was supplied into the aqueous and air phase in the acrylic container through a 1 cm inner diameter tubing. The outlet was connected to a long tubing (1 cm inner diameter) in order to ignore the gas diffusion effect.



**Figure 2.** Schematic diagram of the system equipped with a submerged aerator, a headspace aerator and an outlet.

In the research, as the common experimental condition for ammonia removal process, ammonia concentration of 700 mg/L, alkalinity of 5000 mg/L CaCO<sub>3</sub>, pH 10, temperature of 30 °C, airflow 2.5 L/min to the aqueous phase were determined. When necessary, the only parameter of interest was changed from this initial experimental condition, keeping other parameters the same as the above initial condition unless otherwise specified.

The reagents used in this research are all first grades or greater qualities. The ammonium chloride (NH<sub>4</sub>Cl) was used to prepare ammonia synthetic samples. Sodium hydrogen carbonate (NaHCO<sub>3</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), and sodium hydroxide (NaOH) were used to regulate alkalinity and pH. Also, in all experiments performed in this research, alkalinity was fixed to the 5000 mg/L CaCO<sub>3</sub> in order to minimize pH change due to the introduction of atmospheric carbon dioxide while aeration.

**Analytical Method for Measurement of Total Ammonia.** The phenate method<sup>14</sup> was applied for the measurement of total ammonia in the aqueous solution. The reaction of ammonia with hypochlorite and phenol resulted in a blue indophenol that can be detected by a spectrophotometer. The reagents used for the ammonia analysis were 1 M phenolate solution, 0.35 M NaOCl, and 0.012 M sodium nitroprusside solution as a catalyst. The phenolate solution was prepared by dissolving phenol in the 0.8 M NaOH.

In this research, flow injection analysis system (Zellweger Analytics Co.'s QuickChem FIA+ 8000) was used. The system is consisted of a peristaltic pump for transferring reagents, a six-port rotary valve for the sample injection, a mixing coil with heater, and an 8 mm flow-cell for measuring absorbance. All parts of the system are controlled by a personal computer and the measured sample signals were converted to the concentrations by comparing the stored calibration data in the computer.

The prepared ammonia analysis reagents flowed into the analysis system at 1 mL/min, the samples were passed through reaction coil heated to a 60 °C for 2 min, and the absorbance responsible for the reaction products were measured at 630 nm. The applicable concentration range was determined 0.5-10 mg/L total ammonia. A correlation coefficient (R<sup>2</sup>) for the calibration curves in all measurements is greater than 0.999. In actual analysis, the collected samples from the container were appropriately diluted with deionized water prior to analysis. All samples were measured more than three times and the relative errors of less than 2 percent were obtained throughout the experiments.

## Results and Discussion

**Evaluation of Ammonia Removal Rate Based on 1st-Order Reaction Kinetics.** Numerous works have been carried out that free ammonia [NH<sub>3</sub>(aq)] in the aqueous solution can be removed by aeration and reported that the removal rate can be modeled by the 1st order reaction kinetics. Therefore, we have first applied the same model to our experimental data and the apparent rate constants were obtained (Table 1).

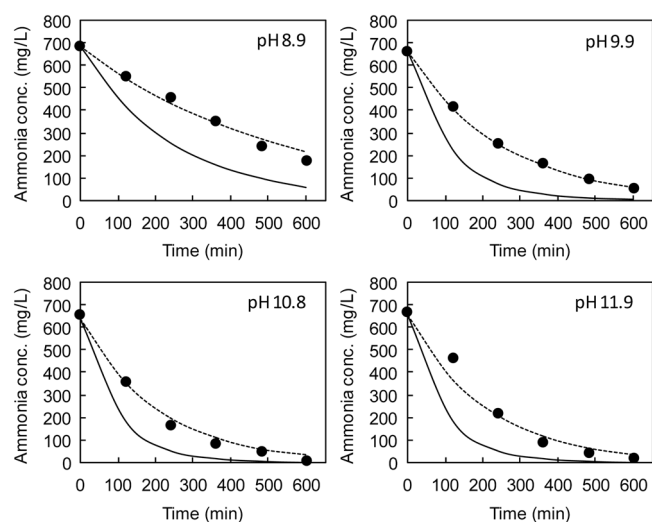
When the ammonia removal rate was evaluated with varying pH, the apparent ammonia removal rate was positively increased with increasing pH from 8.9 to 10.8, while no further significant removal rate was increased at pH 11.9. This result can be explained by the fact that the fraction of free ammonia is a function of pH. The fraction of free ammonia is exponentially increased until pH 11. Above pH 11, the fraction of free ammonia is reached to almost 100%, and thus no further increase in apparent ammonia removal rate occurs. The increase in temperature from 20 to 50 °C in the aqueous solution increased the apparent ammonia removal rate. This finding indicates that the temperature increases Henry's law constant, resulting in the increase of

**Table 1.** Summary of apparent ammonia removal rate constants in different experimental conditions

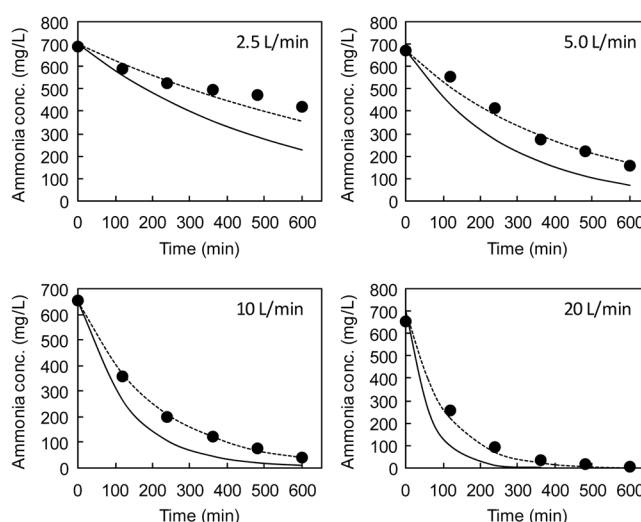
Purpose of experiment	pH	Temp. (°C)	Bubbled Airflow (L/min)	Headspace Airflow (L/min)	Rate Constant
pH Effect	<b>8.93</b>	30	2.5	10	<b>0.0021</b>
	<b>9.87</b>	30	2.5	10	<b>0.0040</b>
	<b>10.81</b>	30	2.5	10	<b>0.0055</b>
	<b>11.90</b>	30	2.5	10	<b>0.0056</b>
Temperature effect	10.0	<b>20</b>	2.5	10	<b>0.0016</b>
	10.0	<b>30</b>	2.5	10	<b>0.0040</b>
	10.0	<b>40</b>	2.5	10	<b>0.0070</b>
	10.0	<b>50</b>	2.5	10	<b>0.0097</b>
Submerged aeration effect	10.0	30	<b>2.5</b>	0	<b>0.0008</b>
	10.0	30	<b>5</b>	0	<b>0.0025</b>
	10.0	30	<b>10</b>	0	<b>0.0044</b>
	10.0	30	<b>20</b>	0	<b>0.0080</b>
Headspace aeration effect	10.0	30	2.5	<b>0</b>	<b>0.0008</b>
	10.0	30	2.5	<b>10</b>	<b>0.0041</b>
	10.0	30	2.5	<b>20</b>	<b>0.0051</b>
	10.0	30	2.5	<b>30</b>	<b>0.0070</b>
	10.0	30	2.5	<b>40</b>	<b>0.0073</b>

**Table 2.** Effect of experimental parameters on the ammonia removal

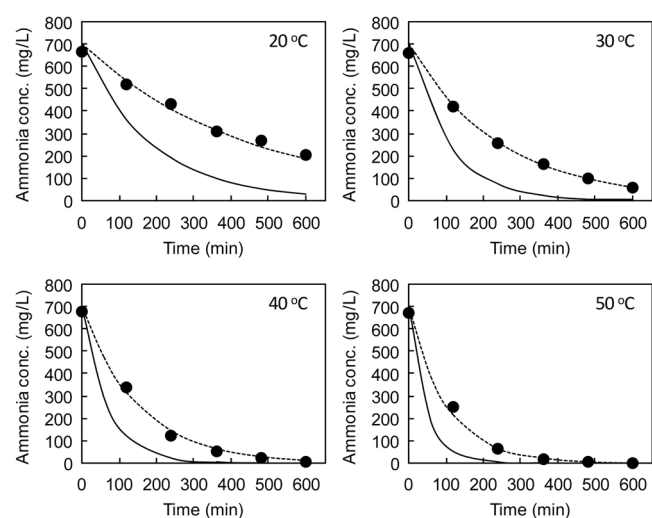
Change in Experimental Parameter	Direct Effect
pH increase	- Increase in the fraction of free ammonia in the aqueous solution
Temperature increase	- Increase in the fraction of free ammonia in the aqueous solution - Increase in the ratio of free ammonia in the air to aqueous phase
Airflow rate increase	- Increase in the transfer rate of free ammonia from the aqueous to air phase - Effect on the air-to-liquid contact area



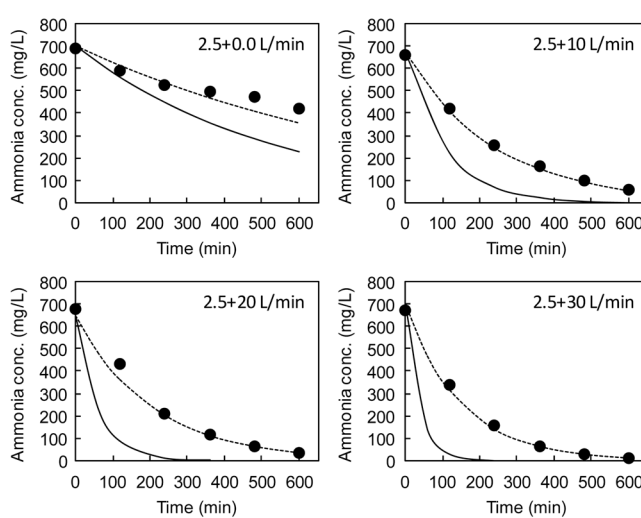
**Figure 3.** Dependence of the ammonia concentration in the aqueous phase on time at various pHs. ●: experimental data; ----: fitted to experimental data; —: instantaneous equilibrium model predicted.



**Figure 5.** Dependence of the ammonia concentration in the aqueous phase on time at various submerged aeration rates. ●: experimental data; ----: fitted to experimental data; —: instantaneous equilibrium model predicted.



**Figure 4.** Dependence of the ammonia concentration in the aqueous phase on time at various temperatures. ●: experimental data; ----: fitted to experimental data; —: instantaneous equilibrium model predicted.



**Figure 6.** Dependence of the ammonia concentration in the aqueous phase on time at various aeration rates. In all cases, submerged aeration rates were 2.5 L/min and additional headspace aeration rates were varied. ●: experimental data; ----: fitted to experimental data; —: instantaneous equilibrium model predicted.

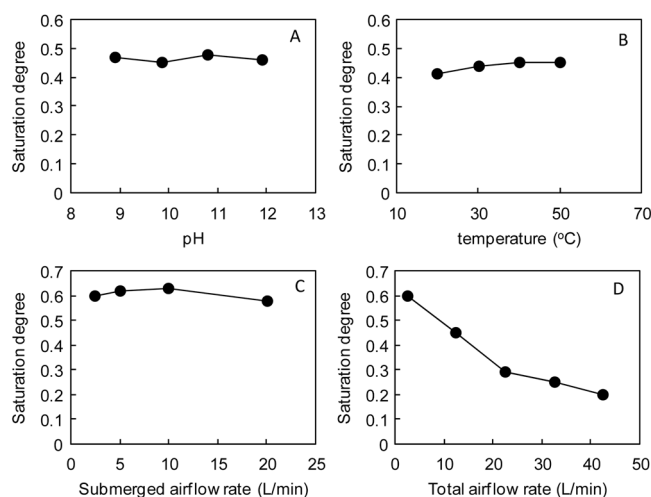
free ammonia fraction. The increase in the airflow rate increased the apparent ammonia removal rate positively because the mass transfer of ammonia increases as the airflow rate increases.

The effects of pH, temperature and the airflow rate on the ammonia removal rate are summarized in Table 2. As discussed above, since the increase in these essential parameters increased the ammonia removal rate, the application of the 1st order reaction kinetics appears to be appropriate. However, we can note that the model of 1st order reaction kinetics does not include any of the experimental parameters and the rate constant obtained from the experimental data can only be used to explain the difference of removal rate. Therefore, the 1st order reaction kinetics would not be used

as a prediction model for the ammonia removal process.

**Ammonia Removal Models Based on the Chemical Equilibrium Principle.** From Figure 3 to 6, the changes of ammonia concentration as a function of time were plotted with the experimentally obtained data (symbols) and the proposed model predicted data (solid line). As described in the previous section, the solid lines indicate the maximum removal rate theoretically, meaning that the air leaving the system is completely saturated with ammonia in the aqueous solution.

In all experiments carried out in this research, the ammonia removal rate did not reach the theoretical removal rate. These results indicate that during the bubbling the air,



**Figure 7.** Dependence of the saturation degree on various experimental conditions.

the instant equilibrium between the air and aqueous phase does not occur. This finding is important because the accepted hypothesis of instantaneous equilibrium<sup>10,11</sup> between the air bubble and aqueous phase during the aeration would not be correct.

**Saturation Degree.** With our revised model, the extent of equilibrium between the air and aqueous phase can be determined in terms of saturation degree as defined in the theoretical section. The saturation degree was determined by fitting the experimental data to the revised model equation (equation 13). Dotted lines in Figure 3-6 were the fitted data. The values of saturation degrees with different experimental parameters were depicted in Figure 7.

**Effects of pH and Temperature.** In all experiments varying pH and temperature in the aqueous solution, the saturation degrees were estimated at about 0.45 regardless of given experimental conditions. The reason why the degrees of saturation were measured the same is because all data are normalized. As noted in the introduction, ammoniac nitrogen in the aqueous solution is consisted of ammonium ion [ $\text{NH}_4^+$ ] and free ammonia [ $\text{NH}_3(\text{aq})$ ], and equilibrium occurs between  $\text{NH}_3(\text{aq})$  and  $\text{NH}_4^+$ . According to the equilibrium theory, the concentration fraction of  $\text{NH}_3(\text{aq})$  is a function of pH and temperature. Of these two species, only free ammonia is possible to transfer from the aqueous to the air phase. In our model, the parameters of pH and temperature are included to calculate the amount of free ammonia. And this free ammonia rather than total ammonia is considered as an only transferring species from the aqueous to air phase. Therefore, the pH and temperature would not affect the ammonia removal rate. Likewise, equilibrium between  $\text{NH}_3(\text{air})$  and  $\text{NH}_3(\text{aq})$  occurs, whose equilibrium can be explained by Henry's law. In this case, only temperature affects the equilibrium and the model takes this factor into consideration. Therefore, the saturation degrees would be the same for the given temperatures in this study.

**Effect of Airflow.** Two methods of aeration into the removal system were considered in this study. One method

was the solely submerged aeration into the aqueous solution and the other was the aeration above the surface of aqueous solution.

When the subsurface airflow rate was increased from 2.5 to 20 L/min without the headspace aeration, the saturation degree has shown to be about the same value of 0.6. This result is somewhat interesting because the extent of equilibrium between the aqueous and air phase are the same regardless of airflow rate. The reason may be explained by two ways. First, the extent of equilibrium between the air and aqueous phase would be affected by the liquid-to-air contact area due to the turbulence of aqueous solution. Second, the liquid-to-air bubble contact area was the same for the given airflow rate of 2.5 to 20 L/min, indicating that the apparent turbulence was not increased as the subsurface airflow rate was increased.

In order to investigate the effect of aeration to the headspace, the airflows were varied from 0 to 40 L/min, while subsurface aeration rate was adjusted to a constant value of 2.5 L/min. In this experiment, the saturation degree was 0.60 at the headspace airflow rate of 0 L/min, and decreased to 0.25 as the airflow rate increased to 40 L/min (Figure 7.D). This result can be expected because instantaneous equilibrium does not occur between the aqueous and air phase as stated in the above discussion. Thus, as increasing the headspace airflow caused less saturation before leaving the removal system. Considering that the saturation degree was decreased with increasing the air phase aeration, the subsurface aeration was shown to be more effective to remove ammonia than the air phase aeration.

## Conclusions

In this work, an ammonia removal model was presented utilizing the chemical equilibrium principles, mass balance and mass transfer theory. In addition, the saturation degrees were determined to evaluate the completeness of equilibrium after the modification of the initial model. The presented model was successfully used to predict the theoretically maximum ammonia removal rate by inputting the essential parameters of pH, temperature, and the airflow rate. The ammonia removal model based on the 1st order reaction kinetics was re-evaluated. Being consistent with other research works, the ammonia removal rate is increased with increasing the pH, temperature, and the airflow rate. However, we conclude that this model would not be used to explain the effect of above parameters systematically, because none of such parameters are included in the model equation. In most of air stripping of ammonia from the aqueous solution, the ammonia removal rate did not reach the theoretical removal rate. This result indicates that during the bubbling the air, the instant equilibrium between the air and aqueous phase does not occur. The experiment varying pH and temperature in the aqueous solution, the saturation degrees were estimated at about the same value (0.45) regardless of given experiment conditions. This result indicates that the presented model takes the pH and temperature

into consideration for the calculation of  $\text{NH}_3(\text{aq})$  in aqueous solution and the equilibrium of free ammonia between the aqueous and air phase. The saturation degree was decreased with increasing the airflow rate to the air phase above the aqueous solution, while the saturation degree remains about the same when the airflow was provided to the subsurface of the aqueous solution. This results show that the extent of equilibrium between the air to aqueous phase would be affected by the liquid-to-air contact area caused by the turbulence of aqueous solution. In addition, the subsurface aeration was shown to be more effective method to remove ammonia than the air phase aeration.

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