

# Aqueous Neutralizer as Reactive Solvents for Odorous Ammonia Removal

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## Abstract

Ammonia is an inorganic compound that may cause severe odor problem. In this study the effectiveness of applying natural neutralizer to destroy and remove the odor-causing compound from gas streams was studied. Experimental result evaluated with a bench-scale apparatus via the neutralization of gas phase. This indicates that the natural neutralization depends on the gas concentration, gas residence time, temperature and pH. Removal efficiency of ammonia from gas stream was achieved by 95% using the convection in the packed bed. This study proved the chemical neutralization technology was effective for controlling inorganic odor-causing compound.

*Keywords:* Ammonia, Convective velocity, Neutralization, Packed bed

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## 1. Introduction

In recent years, people have encountered lots of odor problems. If not appropriately handled, an odor problem may result in severe conflict between emitters and residents in the locality eventually. According to relevant statistics, odor-based complaints become one of the most common problems for public officials concerned with air pollution. The ammonia of numerous sources that may emit odors with a wide range of concentrations can be encountered in the locality such as landfills for waste disposal, livestock farming, and wastewater-treatment plants.

Traditional methods to control the emissions of gaseous odor-causing materials into the atmosphere include absorption of wet scrubbing, adsorption, thermal incineration, masking and bio-filtration.<sup>1-4)</sup> Nevertheless, all these technologies may have limitations in removing odor-causing substances from gas streams. Absorption and adsorption transfer odor-causing materials from the gas phase to scrubbing liquids or solid adsorbents, potentially causing other forms of pollution while resolving odor problems. Incineration can be effective in controlling odor-causing substances. However, the possibility of generating other air pollutants (such as CO, NO<sub>x</sub>, and particulate matter), potential poisoning of the catalyst, and relatively high cost associated with the technology should be taken into account. The effectiveness of odor masking is unpredictable since the odor concentration and at-

mospheric conditions may change rapidly. Relatively large space is essential for the effective removal of odor-causing materials with a biofiltration system, which may limit its use. Additionally, as the emission standards for these odor-causing substances become more stringent, the cost required to control odor problems also escalates. As a result, there is a motivation to develop innovative technologies to control odor problem in a more cost-effective and environmentally responsible manner.

This paper discusses an innovative gas-phase neutralization process that has the potential to remove ammonia from gas streams. This process uses chemical reaction to generate gas phase ions, such as hydroxyl ion and carboxyl ion, that can neutralize ammonia to form products which are less hazardous to the environment. Therefore, odor problems caused by ammonia may be alternately solved by applying this new concept. Natural absorption was chosen as a technology using convective velocity in the packed bed for this study because of easy operation and high efficiency in removing odorous compounds. The present paper has objectives to provide comprehensive experimental data for ammonia absorption from air into aqueous solution and to predict the convective effects in the chemical neutralization of the packed bed. In the following sections, gas-phase removal effects for ammonia using natural neutralization from gas streams and the dependence on relevant controlling parameters will be shown.

## 2. Material and Method

### 2.1. Experimental Apparatus

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A bench-scale experimental system has been designed and constructed to evaluate the effectiveness of applying natural neutralization to remove ammonia from gas streams. The experimental apparatus is composed of a continuous-flow gas generation system, laboratory-scale neutralization spray reactor, and gas-sampling and -detection system. The gas-generation system consists of a humidifier and compressed gas sources that are regulated by mass flow controller. The gas stream containing  $N_2$  and  $NH_3$  was initially passed through the humidifier to pick up water vapor. The resulting  $NH_3(g)$  of the gas stream was controlled by regulating the volume feed rates of the ammonia gas stream and the inert nitrogen gas stream. Specified amount of ammonia were then added to generate gas streams with specific gas composition and mass flow rates. The gas stream was maintained at atmospheric pressure and room temperature in the spray packed bed reactor for all tests.

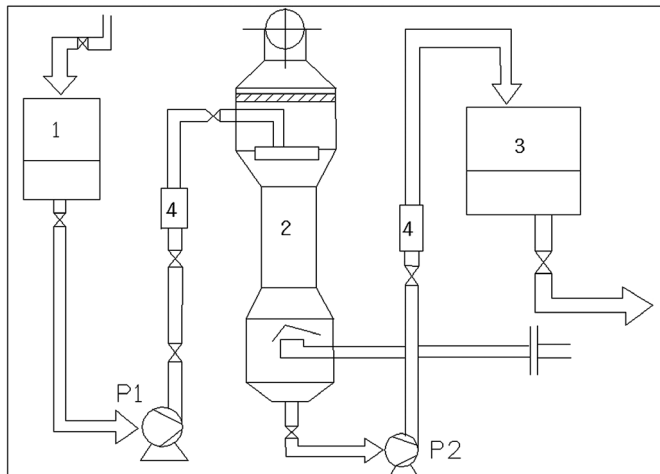
The packed bed reactor (see Fig. 1) was made of a SUS steel plate with 0.5 cm wall thickness. Spray nozzle on the top of reactor was made of a 2.4 mm diameter steel and nozzle size of 0.1 mm. The kinetic experiments were performed using the integrated packed bed. As shown in Fig. 1, the apparatus comprises a packing materials equipped with Raschig ring, mass flow controller, a peristaltic liquid pump (Perkin), a gas blower, and five K-type thermocouples. The integrated packed bed has 1 meter height of packed Raschig ring with a diameter of 0.4 m, as shown in Fig. 1. The active mass transfer area for this arrangement is  $2.2 \text{ m}^2$ . The characteristic active length of the packed bed is 2.5 m. The absorption bed was operated in countercurrent mode with liquid flow from top to bottom and gas flow in the opposite direction. The set-up was equipped with thermocouples at the inlet and outlet of both phases and inside the chamber. The liquid and gas flows can be adjusted independently using a liquid pump and gas blower, respectively. The flow of the blower was controlled by a Master frequency transmitter.

The ammonia gas (10%  $NH_3$ ) from a gas cylinder with inner pressure of 6 MPa was diluted with compressed nitrogen gas and supplied downward to the scrubber. The inlet concentration of ammonia was fixed by controlling flow rate, the initial concentration of ammonia was kept over 100 ppm for experimental period. After that, the load of ammonia was increased gradually by changing the inlet concentration. Ammonia gas passed through the chamber equipped with heating jacket to supply the constant temperature to the scrubber.

The parameters measured in this experiment were inlet and outlet concentration of ammonia, pressure drop, and outlet concentration of ammonia, and gas flow rate. Ammonia gas detector (Gastec, Model 3L) was used to measure concentrations of ammonia in air samples taken at the inlet and outlet sampling ports. The detection limit of the ammonia gas is 1%.

## 2.2. Materials

The leaves collected from pine and fir tree in the northern region of Kyungki province were used to examine the effects of their extracts on the removal efficiency of  $H_2S$  gas associated with neutralization reaction. The air-dried leaves were extracted



(a) 1: absorbent, 2: packed bed, 3: collection tank, 4: flow meter



(b) Picture of pilot plant

Fig. 1. Schematic diagram of experimental apparatus to remove ammonia.

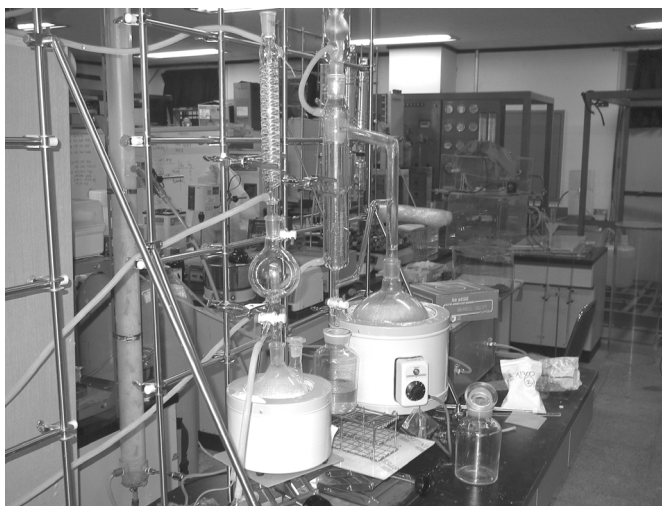


Fig. 2. Picture of experimental apparatus to extract natural solvent.

with 10% ethanol for 3 hr and evaporated to gain the extract. The extracts were obtained by placing 900 g of conifer leaves of pine's and fir's trees into 10 L of a 10.0% w/w ethanol / water

solution into a sealed 25 L Erlenmeyer flask, as shown in Fig. 2. The resulting extract was partitioned successively with ethanol using organic solvents with different polarities. Both aqueous and organic phases were analyzed by gas chromatography (GC, Hewlett Packard Model 4060).

### 2.3. Chemical Analysis

The chemical composition of the natural second metabolites was measured by GC (HP, Singapore) using a CBP-20 column. The operating temperature conditions was increased from 40°C - 200°C at a rate of 7°C/min, followed by an increase to 190°C at a rate of 9°C/3min. The detector temperature was maintained at 220°C, and N<sub>2</sub> gas was used as the carrier gas. The SPME fiber was used to measure the chemical compositions with 65 μm PDMS/DVB (polydimethylsiloxane-Divinylbenzene) fiber (Supelco Inc., Bellefonte, PA, USA). The adsorption of SPME was carried out 30 min.

## 3. Results and Discussion

### 3.1. Composition of Absorbent Neutralizer

The essential oils, such as monoterpenes, are known to be secondary metabolites that play direct roles in the processes of photosynthesis, respiration, solute transport, protein synthesis, and nutrient assimilation. They have been suggested to have important ecological functions in plants: they protect plants from being eaten by herbivores and against being infected by microbial pathogens. These terpenes have chemical functional groups such as alcohol, ketone, aldehyde, and esters (see Table 1) which react with ammonia.

The volatility of an aqueous solution of essential oils must be significantly less than that of ethanol in order to facilitate separation

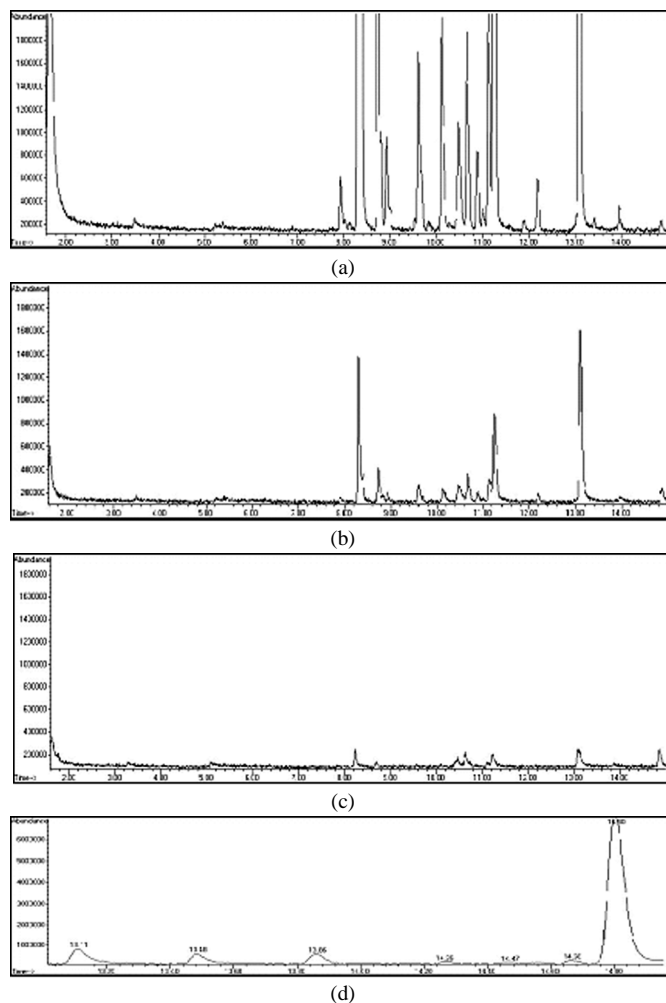


Fig. 3. A Chromatogram of extracted essential oil by GC-MS ((a) first extract by alcohol (b) second alcohol-extract of residue remained from 1st extract (c) third alcohol-extract of residue remained from 2nd extract) (d) extract by water.

Table 1. Chemical composition of terpenes in the extracts of conifer trees

Terpenes	Compounds	Essential oil composition (%)
monoterpene	eucalyptol	21.85
	L-fenchone	0.63
	L-linalool	0.443
	fenchol	0.537
	terpinolene	5.395
	cyclohexanemethanol	1.677
	pinocarvone	2.698
	linalool	1.630
	longicamphenylone	7.321
	β-eudesmol	5.620
caryophyllene oxide	3.989	
miscellaneous	terpineol	8.187
	bicyclo(2.2.1)heptane-2-ol	5.384
	cyclopropazulen-7-ol	5.014
	3-cyclohexen-1-ol	2.911
	naphthalene	1.679

in a solvent recovery evaporation column as shown in Fig. 2. The solubility of the extracted essential oil in water usually is high enough to make it necessary to remove and recover the residual solvent from the aqueous raffinate leaving the extractor. According to chemical analysis of the extracts, the residual composition can be compared with the essential oil extracts. The monoterpenes in pine and fir trees were extracted and their composition was analyzed by GC-MS, as shown in Fig. 3(a). The essential oils extracted were composed of several terpenes, ( $\alpha$ -pinene, eucalyptol and terpineol), as shown in Table 1. The important solvent properties are related to its volatility in a solvent-recovery evaporation column, the residual amounts of solvent can be evaporated and recovered from the raffinate by stripping.  $\alpha$ -pinene was the first chemical extracted and had a concentration of 29.2%. Fig. 3(b) and Fig. 3(c) show the results of GC-MS analysis of the second and third extract using the residual of the first extract. The total residual amount of  $\alpha$ -pinene from the second and third extracts was increased to 29.4% and 29.6%, respectively. The extracts from water instead of ethanol contained few monoterpenes as shown in Fig. 3(d).

### 3.2. Effect of Concentration

The reaction of terpenes in the liquid phase and ammonia in the gas phase creates an zwitterions structure which can remove ammonia as shown in Table 2. It is based on this idea, that terpene containing solutions can absorb ammonia, that we believe a natural amine product can be created. The absorption of ammonia was achieved with the concentration of essential oil as shown

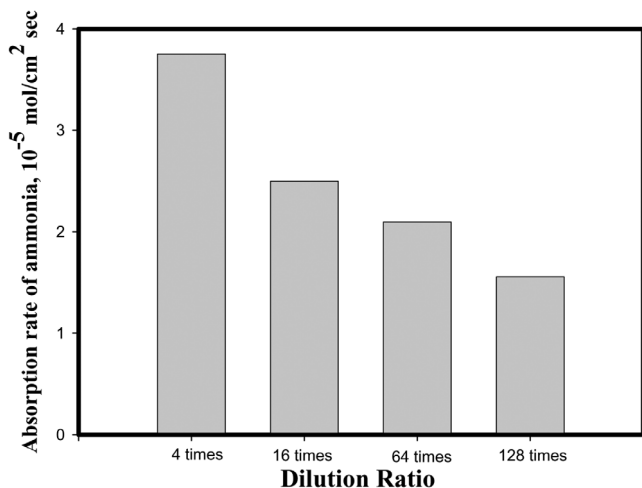


Fig. 4. Adsorption rate of ammonia gas in the aqueous solution.

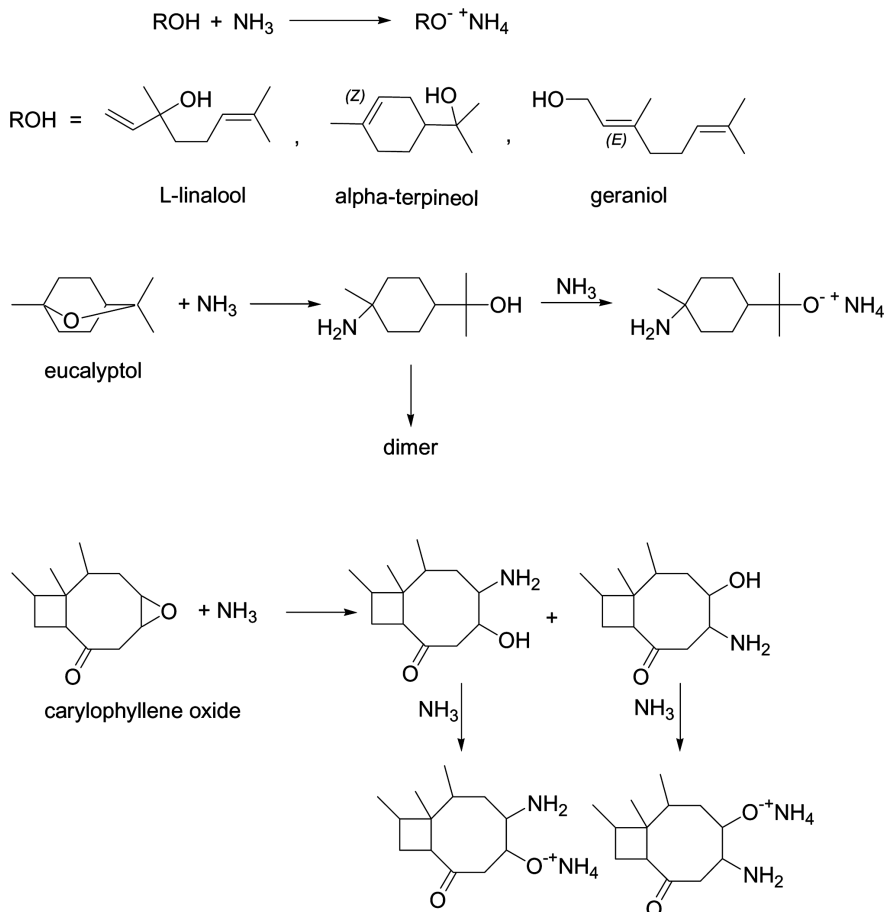
by Fig. 4. This indicates that higher absorption rate in the liquid phase occurs in more concentrated solution of essential oil. Fig. 4 shows that the absorption rate of ammonia by 4 times diluted essential oil is two times higher than that by 128 times diluted essential oil.

Most absorption analysis has been based on odor intensity. An essential oil sufficiently neutralized with chemical functional group of terpenes relative to ammonia as shown in Table 2. Fast reaction must be coupled with mass transfer in the absorption to achieve high removal efficiencies of ammonia. It is shown in Fig. 6 that high initial concentration of ammonia in the aqueous solution is low in mass transfer coefficient. In chemical absorption, the rate of a reaction cannot be neglected with respect to the mass transfer. The absorption flux is, therefore, enhanced because of the chemical reaction, and the average absorption flux is given by<sup>5)</sup>

$$\frac{1}{A} \frac{dn}{dt} = N_A = k_L (c_A^* - c_A) \quad (1)$$

where  $A$  is the interfacial area of gas-liquid phase and  $c_A^*$  is the concentration of ammonia gas in the interphase between gas and liquid,  $c_A$  is the concentration of ammonia gas in the solution.  $N$  is the mole number of absorbed ammonia gas and  $k_L$  is the mass

Table 2. Chemical reaction of ammonia with an essential oil<sup>9)</sup>



transfer coefficient. The following equation can be derived as follows<sup>4)</sup>

$$\left. \frac{dV}{dt} \right|_{t=0} = \frac{ART}{P - P^{\text{vap}}} k_L c_A^* \quad (2)$$

where  $P$  is the atmospheric pressure,  $P^{\text{vap}}$  is the vapor pressure.  $R$  is the universe gas constant,  $t$  is time and  $T$  is the temperature

in Kelvin.  $\left. \frac{dV}{dt} \right|_{t=0}$  has a lower value at a higher initial ammonia concentration (higher value of  $c_A^*$ ).  $c_A$  is the concentration of ammonia in the interphase between gas and liquid,  $c^*$  is the concentration of ammonia in the solution.  $V$  is the mole number of absorbed ammonia and  $P$  is an atmospheric pressure.  $P^{\text{vap}}$  is the vapor pressure and  $R$  is a gas constant. As shown in Equation (2), a positive intercept in Fig. 5 indicates a driving force for mass transfer. The mass transfer coefficient,  $k_L$  can be obtained by Equation (2). Therefore, the mass transfer coefficient,  $k_L$ , becomes lower in the high initial concentration of ammonia. The removal efficiencies depending upon initial concentrations of ammonia significantly varied from 40% to 90% as shown in Fig. 6. This indicates that the mass transfer coefficient is signi-

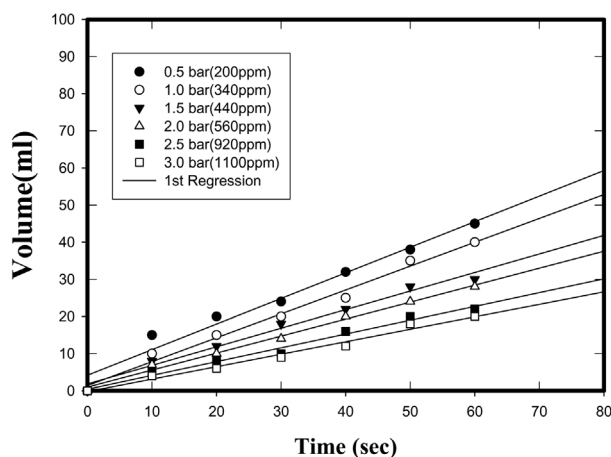


Fig. 5. Variation of collected volume depending on concentration of ammonia gas under experimental condition of 25°C, pH=7.

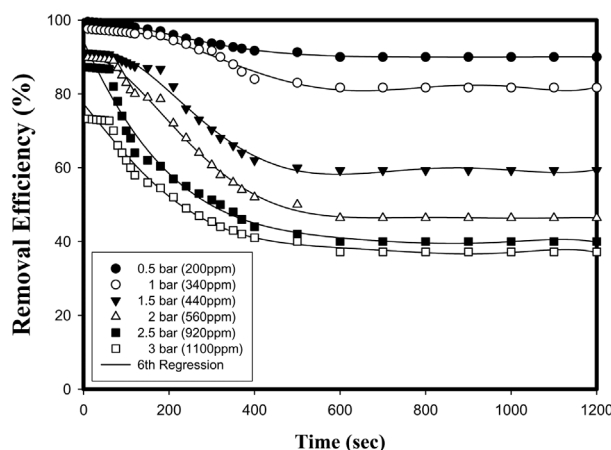


Fig. 6. Effect of initial gas concentration for the removal efficiency of ammonia gas under experimental condition of 25°C, pH=7.

ficantly dependent upon initial concentration of ammonia in the aqueous solution.

### 3.3. Effect of Convective Velocity

The convective flow rate in the packed bed was operated between 185 mL/min and 850 mL/min giving an acceleration. Fig. 7 shows the removal efficiency of ammonia varied for the investigated ammonia concentrations at different convective flow rates. It is believed that the higher convective velocity causes a subsequent rise to the interstitial velocity among Raschig rings throughout the packed bed. This fact in conjunction with a large specific area causes the creation of more contact between gas and liquid, and hence, the overall result has a better mass transfer performance. According to Park,<sup>6)</sup> the effect of the convective velocity in the packed column is more efficient at the higher flow rate due to the decrease in mal-distribution in the packed column and the quantitative effect of the forced convection on the reaction performance.

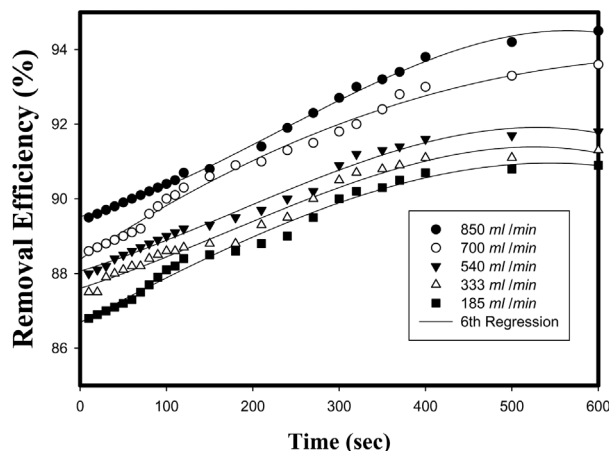


Fig. 7. Effect of convective velocity for the removal efficiency of ammonia gas under experimental condition of 25°C, pH=7.

In chemical absorption, the convective velocity cannot be neglected when determining the rate of reaction. Therefore, the absorption flux is enhanced by the chemical reaction and convection.<sup>6)</sup> Mass transfer resistance disappears because the rate of convection increases the internal active surface. However, for a given flow rate, however, the convection in the packed column may significantly improve the performance of liquid phase reactions.<sup>7)</sup> It should be noticed that high performance at a sufficiently large convective velocity is possible in the case of packed materials exposed to a rapid external flow. After all, the removal efficiency of ammonia increased more than 5% between 185 mL/min and 850 mL/min.

### 3.4. Temperature and pH Dependence

The sharp performance enhancement might be attributed to accelerate absorption kinetics especially when coupled with higher temperature. Because reaction rates are a function of temperature, these parameters were systematically altered to

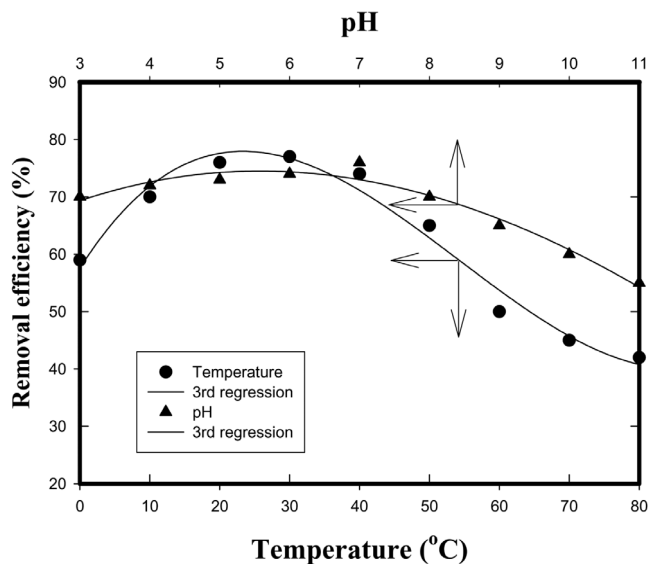


Fig. 8. Removal efficiencies of ammonia gas depending on temperature and pH under initial concentration of ammonia of 400 ppm.

determine their effect on ammonia neutralization (pH 3-11, temperature 20-40°C). rate cons between  $k/[\text{NH}_4\text{OH}]$  and  $1/T$ . For example, the solubility of ammonia gas in the aqueous solution decreases as a temperature elevates,<sup>7,8)</sup> but the reaction rate constant,  $k$ , increases with elevated temperature by Arrhenius equation. As shown in Fig. 8, a significant increase in the removal rate of ammonia with an essential oil as temperature were increased to 40°C. But the removal efficiency of ammonia gas in higher temperature slightly decreases due to the evaporation of terpenes in the extract and low solubility of ammonia in an aqueous solution. Therefore, the optimal condition exists in the removal efficiency of ammonia gas due to the correlation between the solubility and chemical reaction rate. As shown in Fig. 8, the optimal temperature to remove the ammonia gas in the packed bed has 30°C.

These data suggest that the removal efficiency of the ammonia in rendering emissions depends upon pH, that is, an ammonia gas potentially provides similar removal efficiencies at low pH in comparison with pH=7 due to the generation of an ammonium ion ( $\text{NH}_4^+$ ). And removal efficiency of ammonia in case of high pH significantly reduced due to a low solubility of ammonia than that in the neutral point of pH=7. This indicates that the acid-base reaction behavior for neutralization occurs f pH moves to acid region rather than alkali region, and the neutralization does not fully occur due to the decrease of nucleophilicity. The optimal condition for removing ammonia reacting with an essential oil occurs at low neutral region of pH as shown in Fig. 8. Therefore, the removal efficiency at optimal temperature and pH to remove ammonia gas via neutralization reaches 81%.

However, the optimal conditions to remove the ammonia can be achieved by different flow rate and initial condition of ammonia. The highest removal efficiency with best conditions of flow rate in the column and initial concentration of ammonia was achieved by 94.4%. This experimental result proves to affect the removal efficiencies by temperature, pH, flow rate as well as initial concentration of ammonia.

#### 4. Conclusion

The reaction of terpenes extracted from conifer trees and ammonia in the gas phase creates an zwitterions structure via neutralization, which can remove ammonia gas of odor compounds. Natural absorbent contributes to remove the odor gases, it provides a removal efficiency of 94% and their experimental results are as follows.

The high initial concentration of ammonia in the aqueous solution is low in mass transfer coefficient. In chemical absorption, the rate of a reaction cannot be neglected with respect to the mass transfer. This mass transfer for the chemical absorption occurs following physical variables such as convective velocity, temperature and pH. Higher convective velocity in the spray reactor causes a subsequent rise to the interstitial velocity among Raschig rings packed in the bed and may enhance the performance of chemical reaction. This fact is more efficient at higher flow rate and the removal efficiency of ammonia increased more than 5% depending upon convective flow velocity. The optimal temperature to remove the ammonia gas in the packed bed has 30 oC and the optimal condition for removing ammonia reacting with an essential oil provides a maximum point at neutral region of pH in the removal efficiency of ammonia.

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