Ammonia removal mechanism by the combination of air stripping and ultrasound as the function of pH

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Abstract. Ammonia removal mechanism by the combination of air stripping and ultrasound (AU) as the function of pH was investigated. The synergistic effects were observed for air stripping and ultrasound, which was obviously enhanced with the decrease in pH. Ammonia degradation and ammonia stripping were the ammonia removal pathways by AU. Ammonia degradation was the main ammonia removal pathway at the pH of lower than 8, but at a higher pH, ammonia stripping was the main pathway. Air stripping strengthens ammonia degradation by ultrasound in two ways of providing reactive radicals and more cavitation bubbles for pyrolysis. Ammonia degradation depended on the oxidation of radicals at a pH of lower than 8 and did on pyrolysis at a higher pH. Ultrasound also strengthens ammonia stripping by increasing mass transfer coefficient and accelerating the shift of the equilibrium of free ammonia and ammonium ions, which resulted in more strongly strengthening effect at a lower pH.

1. Introduction
Air stripping has been used to treat wastewater, based on the principle that dissolved volatile compounds can be carried away by a gas stream that shifts the equilibrium from aqueous to gaseous phase [1-3]. Removal of ammonia from waste water using air stripping has been reported [4,5]. Ultrasound has also been used to treat wastewater containing ammonia and high removal of ammonia was obtained [6,7]. The chemical effects of ultrasound are due to the phenomenon of acoustic cavitation, which involves the formation and subsequent collapse of microbubbles generating localized, transient high temperatures (roughly 5000°C) and pressures (about 500 atm) [8,9]. Therefore, the ultrasonic energy influences the chemical reactions by providing huge heat (pyrolysis) or producing reactive free radicals, and ultrasonic waves increase the mass transfer rate in an aqueous solution via turbulence [10,11].

Ultrasonic treatment is highly energy intensive and relatively inefficient with respect to total input energy and therefore is not economically attractive alone. Coupling of ultrasound with other type of energy presents attractive advantages and has been widely studied [12]. It was reported the synergistic effects of combined ultrasound and air stripping for the removal of carbon tetrachloride and 1,1,1-trichloroethane from water, attributing to the effect of ultrasound on the mass transfer process [13]. Moreover, ammonia removal at pH 11 was studied by the combination of ultrasound and air stripping and the decomposition of free ammonia was found by pyrolysis but not by oxidation of hydroxyl free radicals [14]. However, it was less studied about the effect of pH on ammonia removal mechanism in solution by the combination of ultrasound and air stripping.
Generally with higher pH, the removal efficiency was higher by the airstripping or ultrasound for higher free volatile ammonia. Therefore, pH is a critical factor for ammonia removal. The ammonia removal mechanism by airstripping or ultrasound alone has been researched and reported [15].

Generally thinking, ultrasound can accelerate the speed of ammonia mass transfer in liquid phase and then strengthen the ammonia stripping. However, there has been little reported about the synergistic mechanism of ammonia removal by the combination of ultrasound and air-stripping, especially as a function of pH. Except for increasing ammonia mass transfer in liquid phase, there are more details to know about ultrasound’s chemical effects for ammonia removal.

In this study, the primitive objective was to examine the synergy of combined ultrasound and air-stripping treatment in the removal of ammonia from aqueous solutions, especially to explore the ammonia removal mechanism as the function of pH.

2. Experimental

2.1. Materials and methods

2.1.1. Ammonia-containing solution preparation. The ammonia-containing solution of 504.3mg L\(^{-1}\) TNH\(_3\) (total dissolved ammonia concentration in the liquid phase) was prepared by dissolving a known amount of ammonium chloride in deionized water.

2.1.2. Experimental apparatus. Experiments were conducted at temperature of 40±2°C in a 250ml double-surrounded cylindrical glass reactor in which the ultrasonic reaction and air-stripping take place (figure 1). The tailing gas from the reactor was introduced to the two sealed 250 ml cylindrical absorption glass bottle with H\(_2\)SO\(_4\) (0.1 mol L\(^{-1}\)) solution in series.

The reactor was placed in the ultrasonic bath tank. Sonication frequency was set at 20 kHz and input power at 200W. In order to control reaction temperature, water circulation was provided.

Meanwhile, the air stripping process was ensured by a diffuser from which a compressed air flow was bubbled into the solution. The air flow rate was adjusted to 300 L min\(^{-1}\) by a flow meter.

The batch ultrasonic-air stripping apparatus (figure 1) included a constant-temperature water bath, an ultrasonic power supply with a generator, glass tube gas diffusers, a 250 ml double-surrounded cylindrical glass reactor, and two 250 ml cylindrical absorption glass bottle with H\(_2\)SO\(_4\) (0.1 mol L\(^{-1}\)) solution. The 200 W ultrasound power supply has a 20 kHz acoustic frequency. The reactor was placed in the ultrasonic bath tank. The temperature inside the reactor was controlled and maintained constantly at 40±2°C via thermos state bath and water circulation system. For air stripping, air was supplied by a compressor and the vent tube was inserted into the solution. The tailing gas containing...
ammonia was introduced to the two sealed absorption glass bottle in series. When N\textsubscript{2} was substitute for air, N\textsubscript{2} was supplied by the high-pressure cylinder. Using a bubble flow meter, air flow rates were adjusted to 10 \text{L min}^{-1} for all stripping experiments. For ultrasound experiments, a vent tube was inserted above the solution in the reactor and its air flow rates were adjusted to 0.1 \text{L min}^{-1} to measure ammonia stripping role. The reactor was sealed with the rubber plug and has one port for sampling.

2.2. Experimental procedure
Before an experiment was conducted, the ultrasound power supply system and deionized water (200 ml) was warmed up and then an appropriate amount of ammonium chloride was added into deionized water and mixed. The initial pH of the solution was adjusted to required value with \text{H}_2\text{SO}_4 (0.1 \text{ mol L}^{-1}) or \text{NaOH} (0.1 \text{ mol L}^{-1}) solution. At each sampling interval, about 1ml of treated liquid sample was withdrawn from the reactor using a sampling syringe and so did from the absorption bottle.

3. Results and discussion
3.1. Kinetics of the combination of air stripping and ultrasound
Figure 2 shows the ammonia removal at pH of 11 with the reaction time by AS, US and AU. The obtained data were fit to a general first-order expression shown as follows:

\[
\ln \frac{C}{C_0} = -kt
\]

where \(C_0\) and \(C\) are initial ammonia concentration and ammonia concentration in aqueous solution at any time, respectively, \text{mg L}^{-1}; \(t\) is reaction time (min) and \(k\) is the pseudo-first-order rate constant (min\(^{-1}\)).

![Graph showing removal of ammonia by AS, US, and AU](image)

**Figure 2.** Removal of ammonia from water by AS, US and AU at pH of 11. Reaction conditions: air flux 300L min\(^{-1}\), ultrasound power 200W, pH 11, [T\textsubscript{NH}_3]=504.3 \text{ mg L}^{-1}.

|       | AS   | US   | AU   |
|-------|------|------|------|
| \(k\) (min\(^{-1}\)) | 0.0188 | 0.0033 | 0.0622 |
| \(R^a\) | 0.9873 | 0.9303 | 0.9918 |

Table 1. Estimated \(k\) of ammonia removal kinetics.

where \(k\) represents pseudo-first-order rate constant (min\(^{-1}\)) and \(R^a\) represents linear regression coefficient for the plot of \(\ln(C/C_0)\) vs the reaction time (min) shown in figure 2.

The rate constant was measured and given in the table 1. Only ultrasound removed ammonia
weakly. The $k$ of the combination of air stripping and ultrasound was obviously greater than that of the air stripping, which indicates that the air stripping is intensified by ultrasound.

For an air stripping system, the efficiency of ammonia removal is strongly dependent on two thermodynamic equilibria, the Henry’s law equilibrium (equation (2)) and the ammonia dissociation equilibrium (equations (3) and (4)) [5,16].

$$p = -K_c c$$

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

$$\frac{[NH_3]}{[TNH_3]} \rightleftharpoons (1 + \frac{10^{-\rho p}}{10 - (0.09018 + 2729.92/T(K))})$$

Here, $p$ is the partial pressure of the ammonia gas, $c$ is its molar concentration in the liquid phase, and $K_c$ is the Henry’s law constant. $[NH_3]$ and $[TNH_3]$ represent the concentrations of free ammonia and the sum of free ammonia and ammonium ion, respectively. As shown in equation (4), the free ammonia concentration in the aqueous phase depends on the pH and temperature.

The mass transfer rate of volatile free ammonia in a batch stripping unit can be described as equation (5) [17].

$$\ln C_t/C_0 = -K_{La} at$$

Where $C_0$ and $C_t$ are the ammonia concentrations in aqueous solution at the beginning and at any time, respectively, mg L$^{-1}$; $t$ is reaction time (min) and $K_{La}$ is the overall liquid mass transfer coefficient, mmol m$^{-3}$ min$^{-1}$; $a$ is the interface area per unit volume of liquid, m$^2$m$^{-3}$.

At the higher pH, the free ammonia was the main component of total ammonia in solution. Then for air stripping, the mass transfer coefficient, $K_{La}$, is equal to the rate constant in equation (1). So ultrasound strengthens the air stripping by increasing the mass transfer coefficient, which has been tested in an autoclave reactor [18]. For the different concentration of free ammonia at different pH, pH strongly affected ammonia removal by air stripping.

3.2. Synergy of airstripping and ultrasound

Except for increasing the mass transfer rate, the ultrasound influences the chemical reactions by providing huge heat (pyrolysis) or producing reactive free radicals [8]. So for the AU system, ammonia stripping should be accompanied by ammonia degradation. When ultrasound irradiation was combined with aeration, aeration increases the concentrations of cavitation bubbles in solution, enhancing the effective utilization of ultrasound [14]. So air stripping could also strengthen ultrasound for ammonia removal.

Figure 3 shows the ammonia removal by AS, US and AU as the function of pH. Ammonia removal increased with the increase of pH from 7 to 11.5. The ammonia removal by AU was much higher than that by AS or US alone, which exhibits the synergy of air stripping and ultrasound. By using the following equation, the synergy could be measured.

$$S = \frac{R_{AU}}{R_{AS} + R_{US}} \times 100\%$$

where $R_{AU}$, $R_{AS}$ and $R_{US}$ are the ammonia removal for the AU, AS and US, respectively; $S$ is the synergistic factor.

The $S$ was calculated and shown in the figure 3 at the pH of lower than 6, only air stripping or ultrasound couldn’t remove ammonia, but ammonia removal occurred with the combination of air stripping and ultrasound. Then the synergistic factor is enormously high. As the function of pH, $S$ sharply decreases to 146% at pH of lower than 9 and then does slowly. Higher pH could obtain a better ammonia removal by air stripping, but the synergistic effect of the combination of air stripping and ultrasound becomes poor. At a higher pH for ammonia stripping, ammonia removal is decided
only by mass transfer, but at a lower pH, ammonia removal is decided by both of equations (3) and (5). The ultrasound could accelerate the shift of equilibrium between free ammonia and ammonium ions for free ammonia vaporizing into cavitation bubbles. Though free ammonia is a small component at a lower pH, more ammonium ions are shifted to free ammonia in solution by ultrasound. Moreover, sonochemical effect could play an important role in the synergy of air stripping and ultrasound.

\[ \text{Figure 3. The synergy of AS and US as the function of pH.} \]

3.3. Ammonia removal mechanism
The ultrasound can influence chemical reactions by providing huge energy (pyrolysis) or producing reactive free radicals and increasing the mass transfer rate via turbulence [19]. For ammonia removal, the pyrolysis and free radicals can influence ammonia degradation and mass transfer rate increasing can promote ammonia stripping. Here, ammonia stripping and ammonia degradation were discussed independently.

3.4. Ammonia stripping mechanism
As shown in figure 4, ammonia removal by AU, AS and US increases with the increase of pH and the ratio of free ammonia to the total ammonia. Ammonia stripping efficiency is much related to the ratio of free ammonia and mass transfer rate. As in equation (5), mass transfer coefficient is a constant for the stripping system, where the ratio of free ammonia is the only factor to influence ammonia removal in solution. Ammonia stripping by air stripping was strengthened by ultrasound and the synergistic factor for ammonia stripping was calculated in figure 5. The strong synergy of air stripping and ultrasound was got at a lower pH for ultrasound strengthens air stripping by accelerating the shift of the equilibrium of free ammonia and ammonium ions. At the pH of higher than 10, the major component of ammonia is almost free ammonia and the ammonia stripping synergistic factor is lower than 100%, which shows that the increase of mass transfer coefficient by ultrasound has less effect to strengthen air stripping at a higher pH.
3.5. Ammonia degradation mechanism

The ammonia in aqueous solution exists in two forms: ammonium ion and volatile free ammonia. At different pH, their ratio is completely different. In the sonochemistry, volatile, hydrophobic pollutants can undergo high-temperature pyrolysis in the gas phase inside the bubbles, while non-volatile, hydrophilic species can be degraded by •OH at the bubble surface or in the solution bulk [19-21]. Volatile ammonia should be able to be degraded by pyrolysis with ultrasound. In order to identify whether ammonia degradation by ultrasound is by pyrolysis or free radical oxidation, n-butyl alcohol was added to the solution. n-Butyl alcohol is effective scavenger of hydroxyl radicals [22]. It is evident from the experiments that the addition of n-butyl alcohol has little effect on the ammonia removal by ultrasound at any pH. It can be demonstrated that ammonia is almost not removed by the oxidation of hydroxyl free radicals, which amount may be so less that radical oxidation is negligible. So only by ultrasound, ammonia is degraded by pyrolysis in cavitation bubbles.

![Figure 4. Ammonia stripping from water by AS, US and AU at the function of pH.](image1)

![Figure 5. Synergistic effect for ammonia stripping and ammonia degradation respectively by the combination of air stripping and ultrasound at the function of pH.](image2)

![Figure 6. Ammonia degradation from water by AS, US and AU at the function of pH.](image3)

The presence of air in the liquid creates additional heterogeneity in the medium giving additional...
nuclei for the generation of cavitation events leading to enhanced cavitational activity [23]. With the combination of aeration and ultrasound, the role of pyrolysis would be enhanced. Figure 6 shows the effect of pH on ammonia degradation by AU and US. Only by ultrasound, ammonia degradation efficiency was very low and increased with the increase of pH from 5 to 9 and then slightly decreased. By the combination of aeration and ultrasound (AU), ammonia degradation efficiency was much higher and increased all along with the increase of pH from 5 to 11.5. Obviously, air aeration greatly promoted ammonia degradation, especially at the lower pH. At the pH of 5, free ammonia is less than 0.01% of the total ammonia and pyrolysis with ultrasound could not occur, which indicates there exists radical oxidation by the combination of air stripping and ultrasound. For air aeration, the N₂ scavenges the H•, O• and •OH radical to produce various species through the following reactions [24,25]:

\[
\begin{align*}
N₂ + &\rightarrow N· + NO \quad (7) \\
N₂ + &\cdot OH\rightarrow N₂H + O \quad (8) \\
N₂ + &\cdot OH\rightarrow N₂O + H· \quad (9) \\
N₂ + &\cdot OH\rightarrow NH + NO \quad (10) \\
N₂ + &H\rightarrow N₂H \quad (11) \\
N₂ + &3H·\rightarrow 2NH + H· \quad (12) \\
N + &\cdot OH\rightarrow NO + H· \quad (13) \\
N₂O + &O·\rightarrow 2NO \quad (14) \\
NO + &\cdot OH\rightarrow NO₂ + H \quad (15) \\
NH + &\cdot OH\rightarrow NH₂ + O· \quad (16) \\
NH₂ + &O·\rightarrow HNO + H· \quad (17)
\end{align*}
\]

However, O₂ reacts with these species to generate O• and •OH radicals through the following reactions:

\[
\begin{align*}
N + &O₂\rightarrow NO + O· \quad (18) \\
NO + &O₂\rightarrow NO₂ + O· \quad (19) \\
NH + &O₂\rightarrow HNO + O \quad (20) \\
NH + &O₂\rightarrow NO + •OH \quad (21) \\
N₂ + &O₂\rightarrow N₂O + O \quad (22)
\end{align*}
\]

Compared with the US, radicals increase greatly for the AU with air aeration. It is obvious that production of radicals by N₂ is very least for extensive scavenging of radical species by N₂ molecules. Therefore for the AU with N₂ substitute for air, ammonia degradation can be regarded as ammonia removal by pyrolysis. For the AU with air, ammonia degradation includes two parts: one by pyrolysis and the other by oxidation of radicals, which is equal to the total ammonia degradation that ammonia degradation by pyrolysis is deducted from. In figure 6, with the increase of pH, ammonia degradation by oxidation of radicals firstly slowly increased and then decreased while ammonia degradation by
pyrolysis increased all the way. Ammonia degradation was much related to ammonia state in aqueous solution. At pH of lower than 8, the major ammonia component was ammonium ion and oxidation of radicals was the main ammonia degradation route. With a higher pH and less ammonia ion, ammonia degradation by radical oxidation decreased and pyrolysis gradually became the main ammonia degradation route. It is demonstrated that ammonia ion can be oxidized by radicals but free ammonia is decomposed in cavitation bubbles.

Ammonia degradation by ultrasound was strengthened by air stripping and the synergistic factor for ammonia degradation was calculated in figure 5. S changed with pH for the different ammonia degradation mechanisms of radical oxidation and pyrolysis. At the pH of lower than 7, oxidation of radicals rarely occurred in the ultrasonic process alone. When with combination of air stripping, large amounts of reactive radicals were produced and a certain amount of ammonia degradation happened. Therefore at lower pH, the synergistic factor was largely higher, which attributed to air supplying. With the increase of pH and free ammonia ratio, pyrolysis plays a certain role and the synergistic factor decreases. However, at the pH of higher than 8, synergistic factor slightly increases with the increase of pH. It indicates that aeration strengthens ammonia degradation by ultrasound in two ways of providing reactive radicals and more cavitation bubbles for pyrolysis.

4. Conclusions
The air stripping was significantly strengthened by ultrasound and there existed synergistic effect, which was obviously enhanced with the decrease in pH. Ammonia degradation occurred mainly at the pH of lower than 8 by AU, but at a higher pH, ammonia stripping was the main ammonia removal mechanism. Air stripping strengthens ammonia degradation by ultrasound in two ways of providing reactive radicals and more cavitation bubbles for pyrolysis. Ammonia degradation depended on the oxidation of radicals at a pH of lower than 8 and did on pyrosislation at a higher pH. Ultrasound strengthens ammonia stripping by increasing mass transfer coefficient and accelerating the shift of the equilibrium of free ammonia and ammonium ions, which resulted in more strongly strengthening effect at a lower pH.

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