Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1077741

57 (2016) 15999–16007
July

Taylor & Francis
Taylor & Francis Group

Removal of ammonia by high-frequency ultrasound wave (1.7 MHz) combined with TiO_2 photocatalyst under UV radiation

Masoud Rahimi*, Negin Moradi, Mahboubeh Faryadi, Sahar Safari

CFD Research Center, Chemical Engineering Department, Razi University, TagheBostan, Kermanshah, Iran, Tel. +98 8314274530; Fax: +98 8314274542; emails: m.rahimi@razi.ac.ir, masoudrahimi@yahoo.com (M. Rahimi), Negin.moradi724@yahoo.com (N. Moradi), Mahbube.faryadi@yahoo.com (M. Faryadi), Shr.safari@yahoo.com (S. Safari)

Received 15 October 2014; Accepted 24 July 2015

ABSTRACT

This study aims to use high-frequency ultrasound wave combined with ultraviolet radiation and titanium dioxide as a photocatalyst for ammonia removal. The performances of several treatment methods including aeration, ultraviolet, ultrasound, ultrasound–aeration, ultrasound–ultraviolet, ultraviolet–titanium dioxide–aeration, and finally ultrasound–ultraviolet–titanium dioxide were compared. The results clearly indicated the superiority of ultrasound–ultraviolet–titanium dioxide (US/UV/TiO_2) system over other treatment processes. The effect of various variables including initial ammonia concentration, pH, TiO_2 dosage, liquid height, UV intensity, and ultrasound frequency were investigated in the US/UV/TiO_2 system. The results show that the removal efficiency of ammonia reduced as the initial ammonia concentration and liquid height increased. However, increase in TiO_2 dosage caused an increase in removal efficiency. In addition, the optimum removal efficiency of US/UV/TiO_2 system for ammonia was obtained at pH 11. After 120-min sonication by high-frequency ultrasonic wave and UV radiation in conjunction with TiO_2, almost 100% ammonia removal was achieved. In addition, the results demonstrated that the UV intensity has significant influence on the removal efficiency of ammonia in the US/UV/TiO_2 system. The presented results show that high-frequency ultrasound plays the main role in the US/UV/TiO_2 system owing to its ability to generate atomization and acoustic streaming.

Keywords: Ultrasound (US); High frequency; Ultraviolet (UV); TiO_2; Ammonia removal

1. Introduction

Over the past decade, ammonia has become common and undesirable contamination in wastewater due to its extensive use in household, agriculture, and industrial processes. It is well known that ammonia released into environment has adversely affected water supply, aquatic life, and human health [1,2]. Subsequently, the presence of ammonia in wastewater has led to a search for suitable and effective treatment methods to minimize the risk of contamination. In recent years, a variety of biological, physical, and chemical processes have been widely used for ammonia removal [3–7]. Advanced oxidation processes (AOPs) as an innovative technique are extremely promising, owing to their unique potential for production of hydroxyl radicals ($OH^{\cdot}$) that are highly reactive in chemical solutions. AOPs include numerous combinations of ultrasound (US) irradiation, ultraviolet

---

*Corresponding author.

(UV) radiation, photocatalyst, and strong oxidants, e.g. hydrogen peroxide and ozone [8,9]. Recently, there has been an increasing interest in the use of TiO_2 as a photocatalyst in different treatment methods due to some of its extraordinary advantages including low cost, commercial availability, stability, harmlessness, non-toxic, and high efficiency [10,11]. The main mechanism of a UV/TiO_2 system is the photodegradation of organics. In photocatalysis with UV/TiO_2, hydroxyl radicals are mainly formed from water by UV light, and OH radical as an extremely powerful oxidizing agent is responsible for destroying organics species. Nevertheless, some catalysts are able to the screen out the UV wave and cause the reduction of the utilization efficiency of UV radiation. Combining high-frequency ultrasound in the range of MHz with UV/TiO_2 can be capable to overcome this limitation and enhance photocatalysis efficiency [12,13].

Ultrasound (US) irradiation is one of the most effective treatment methods in AOPs. The principal advantages of using ultrasound for wastewater treatment are: easy to apply compared with conventional treatment methods and unlike some technologies is quite cheap from economical point of view [14,15]. Up to now, different types of combining ultrasound irradiation with other techniques such as UV [16], TiO_2 [17], H_2O_2 [18], UV/TiO_2 [12], and UV/H_2O_2 [19] have been reported. Among these combination methods, using ultrasound (US) in the presence of titanium dioxide (TiO_2) under UV irradiation (US/UV/TiO_2) leads to significant synergies in degradation of different organic pollutant and has attracted considerable attention as an effective method.

Ultrasound propagation through the liquid causes a high local temperature (5,000˚C) and pressure (1,000 atm) as a consequence of acoustic cavitation phenomenon that is consisting of formation, growth, and collapse of the bubble. Under such extreme conditions, organic pollutants may undergo pyrolytic decomposition. Hot spots lead to breakdown of compounds present inside cavitation bubbles, including water and produce highly reactive radicals ($H^\cdot$, $HO_2^\cdot$, and $OH^\cdot$). Alternatively, hydroxyl radicals from sonolysis of water can recombine to generate hydrogen peroxide [20–23]. Moreover, ultrasound waves in the range of MHz are able to generate convective flows through liquid which is called acoustic streaming. Acoustic cavitation and acoustic streaming improve micro and macro agitation, which has been realized as a main reason of uniform distribution of ultrasound energy and enhancement of mass transfer of chemical species between the solution phase and the catalyst surface. Therefore, using high-frequency waves leads to good mixing in the systems and promotes the oxygen transfer on the liquid phase because of establishing acoustic streaming. Oxygen, as an efficient electron trap, prevents recombination of electrons and holes in TiO_2 and thereby increases the photocatalytic reactions significantly [12,24–26]. In addition, acoustic streaming generated by high-frequency ultrasound promotes photocatalytic degradation of pollutant because of keeping particle in floating condition and increasing dispersion of TiO_2. Another mechanical effect of ultrasound irradiation in US/UV/TiO_2 system is increasing the catalyst surface due to reducing particle size and surface cleaning that lead to acceleration of photocatalytic reactions [9]. Furthermore, generated H_2O_2 by ultrasound wave is an efficient electron acceptor, which decreases the charge recombination and enhances the production of additional hydroxyl radical [27]. Also, ultrasound wave in the range of MHz contributes to the photocatalytic degradation by atomization phenomenon and producing of ultrasonic mist. TiO_2 photocatalyst particles and ammonia molecules are enclosed in ultrasonic mist and the photocatalytic reaction occurred on the mist surface under UV irradiation [28,29]. In addition, the high-frequency ultrasound is suitable from the energy consumption point of view [24,25].

Nowadays, the environmental application of US/UV/TiO_2 has been increased remarkably and numerous studies have been conducted by this method [9,10,12].

The main difference of the present study with mentioned references is using ultrasound waves in the range of MHz (1.7 MHz) combined with UV/TiO_2 system for decomposition and removal of ammonia. Generally, the novelty of this paper is improving photocatalytic degradation of ammonia by acoustic streaming and atomization phenomena from high-frequency ultrasound waves. The phenomena produced by high-frequency ultrasound waves improve agitation, oxygen transfer and trapping ammonia, and TiO_2 particles in the ultrasonic mist which results in photocatalytic reaction on the mist surface. Regarding the authors literature survey there are not any studies concerning the effects of convective flows and ultrasonic mist for ammonia removal in the US/UV/TiO_2 system. In this work, the removal efficiencies of ammonia in the solution by various methods were compared. Then, the effect of operational conditions such as initial ammonia concentration, pH, TiO_2 dosage, liquid height, UV intensity, and ultrasound frequency on the rate of ammonia removal in the US/UV/TiO_2 system was examined.

2. Experimental work

2.1. Apparatus

A Pyrex glass separable beaker with a diameter of 12 cm and a height of 30 cm was used as a reservoir for ammonia degradation by the US/UV/TiO_2 processes. Two piezoelectric transducers with a frequency of 1.7 MHz with an input power of 9.5 W (Model ANN-2517GRL, Annon Piezo Technology Co. Ltd, China) were installed at the reservoir's bottom in a way that the examined solution was in direct contact with them. Fig. 1 shows a schematic view from the experimental rig. Ultra-violet (UV) light irradiation sources were four LT 15 W/009 UV lamps (NARVA Co., Germany) having the radiation peak at 355 nm (total power = 60 W). Lamps were located around the reservoir and externally irradiated the solution. Each of the lamps was vertically located on four sides of the reservoir. A pH meter probe (827 pH Lab Metrohm) was immersed into liquid solution inside the reservoir to measure the solution pH. The temperature of the solution was measured using a thermometer (Lutron, BTM-4208SD) during the experiment. Air for aeration was supplied by an air compressor (Model BS-410 SHENGZHE). In order to generate the low frequency ultrasound wave in the reservoir, a wave transducer manufactured by UP400S with a frequency of 24 kHz and the horn tip diameter of 20 mm was placed at top of the reservoir. In order to ensure the accuracy of test results, the tests were done at least three times.

2.2. Materials and methods

Ammonia solution with a purity of 25% and Nessler's reagent were provided by Merck Inc. In order to prepare solutions containing 400, 800 and 1,200 mg/L of ammonia, a high purity ammonia was diluted with deionized water to reach the desired initial concentrations. In each experiment, a certain volume of ammonia solution (400, 600, and 800 ml which are exactly equivalent to 4, 6, and 8 cm height) with different initial concentrations of ammonia was poured into the reservoir and desired concentrations of TiO_2 were added to the solution to prepare the reaction mixture. TiO_2 (P-25) photocatalyst was supplied from Degussa Co. Ltd, Germany (anatase 75%, rutile 25%, BET specific surface area 48 m^2/g, and mean particle size 25 nm). Reaction temperature was kept at 21 ± 1°C using a water bath. The concentrations of ammonia were evaluated using Nessler reagent. In this method, the ammonia reacts with Nessler reagent to form a colored complex that can change from yellow to deep amber. Absorbance of ammonia (at 440 nm) was measured by a UV-spectrophotometer manufactured by UNIC Company at 440 nm [30]. Changes in ammonia solution concentrations were determined by the above-mentioned method during two hours.

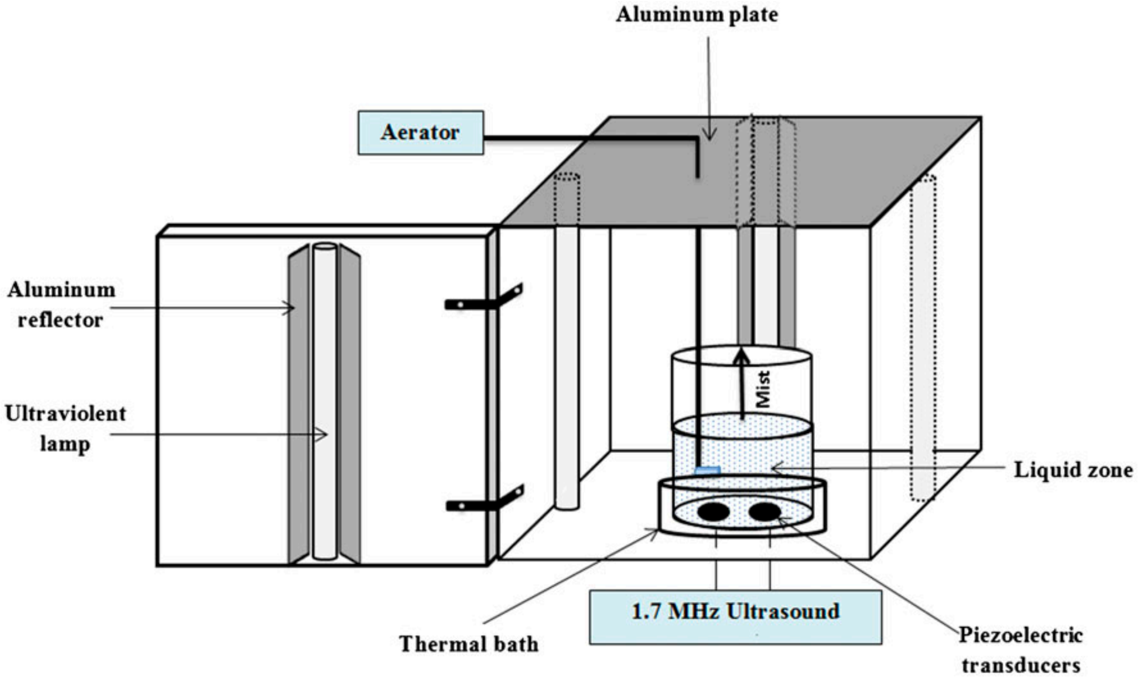

Fig. 1. A schematic view of the experimental setup.

3. Results and discussion

3.1. Screening of various treatment methods

In order to remove ammonia, various treatment methods, namely, aeration, ultraviolet (UV), ultrasound (US), ultrasound–aeration (US/aeration), ultrasound–ultraviolet (US/UV), ultraviolet–titanium dioxide–aeration (UV/TiO_2/aeration), and finally ultrasound–ultraviolet–titanium dioxide (US/UV/TiO_2) were examined. The operational parameters for each approach are listed in Table 1. Fig. 2 shows the removal efficiency by the various schemes. Results indicate that only aeration or UV had low removal efficiencies of less than 20%. Moderate removal efficiencies of 53.5, 60.1, 65.2, and 71% were observed in the US, US/UV, US/aeration, and UV/TiO_2/aeration, respectively. The highest removal efficiency of 91.5% was obtained by combining high-frequency ultrasound, ultraviolet, and titanium dioxide at 1 g/L of TiO_2 and UV intensity of 60 W. Generally, the following order in removal efficiency was observed: US/UV/TiO_2 > UV/TiO_2/aeration > US/aeration > US/UV > US > aeration > UV.

The above obtained result can be attributed to the capability of high-frequency ultrasound to generate convective flows besides micro-streams and improve micro and macromixing with lower electrical power consumptions. The induced acoustic streams by the ultrasound wave in the range of MHz are capable to prevent particle coagulation; thus the TiO_2 particles dispersed in the whole volume of the solution. The collapse of cavities enhances the reaction of $OH^\cdot$ radicals with ammonia by greatly accelerating the mass transfer rates. Furthermore, ultrasound wave in the range of MHz causes producing mist by ultrasonic atomization phenomenon [9,24,25]. TiO_2 particles and ammonia molecules are captured in the ultrasonic mist and irradiated with UV light. Ultrasonic mist photocatalyst induces photocatalytic degradation on its surface and contribute to ammonia decomposition effectively [28,29]. The main effects of ultrasound wave on ammonia decomposition under US/UV/TiO_2 conditions can be summarized as follows:

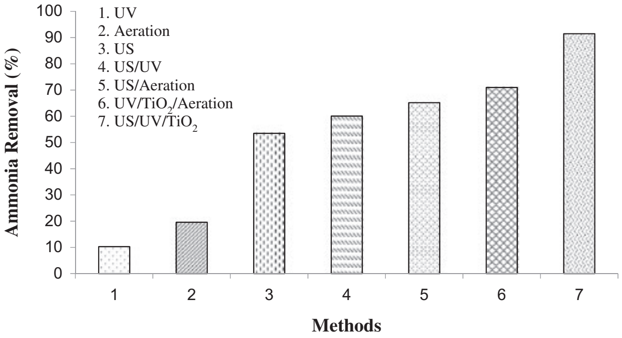

Fig. 2. Ammonia removal by various methods. Experimental conditions: $[NH_3]_0$ = 400 mg/L, $[TiO_2]_0$ = 1 g/L, initial pH 11, initial volume = 400 ml (liquid height = 4 cm), US frequency = 1.7 MHz, UV intensity = 60 W, and reaction time = 120 min.

(1) The mechanical effects of ultrasound such as enhancing mass transfer to the TiO_2 surface, preventing the TiO_2 particles sticking, increasing the catalyst surface area and keeping a clean TiO_2 surface [12].

(2) The effects of atomization phenomenon and trapping ammonia molecule and TiO_2 particles in the ultrasonic mist. The mentioned phenomenon can be leading to improvement of photocatalytic decomposition of ammonia in the ultrasonic mist region according to high UV light permeability compared with liquid phase [28,29].

Table 1

The summary of the operational parameters optimized for each treatment schedule

	Experimental conditions							
Treatment schedule	$[NH_3]_0$ (mg/L)	$[TiO_2]_0$ (g/L)	Initial pH	Initial solution volume (ml)	Time (min)	US frequency (MHz)	UV intensity (W)	Temperature (℃)
Aeration	400	–	11	400	120	–	–	21
UV	400	–	11	400	120	–	60	21
US	400	–	11	400	120	1.7	–	21
US/aeration	400	–	11	400	120	–	–	21
US/UV	400	–	11	400	120	1.7	60	21
UV/TiO_2/ aeration	400	1	11	400	120	–	60	21
US/UV/TiO_2	400	1	11	400	120	1.7	60	21

(3) Finally, the effects of acoustic streaming and convective flows which lead to improving agitation and oxygen transfer as an appropriate electron acceptor. And thereby minimize the recombination of electrons and holes [12,24–26].

The results clearly demonstrate the superiority of the US/UV/TiO_2 combination over other treatment processes studied in this study. Therefore, further studies were focused on the US/UV/TiO_2 treatment method.

3.2. Effect of initial concentration

In order to investigate the influence of initial concentration on removal efficiency for ammonia, experiments were carried out for three different initial concentrations of ammonia solution, including 400, 800, and 1,200 mg/L. Amount of TiO_2 in all of these experiments was 1 g/L and the measurements were done during 150 min. The pH values of these ammonia solutions with different initial concentrations were all about 11.

The removal ratio is defined as follows:

$$\text{Removal } (\%) = \frac{C_{A0} - C_{Af}}{C_{A0}} \times 100 \tag{1}$$

In which, C_{A0} is the initial concentration of ammonia (mg/L) and C_{Af} is the final concentration of ammonia (mg/L) after applying ultrasound wave combined with UV/TiO_2. Fig. 3 reveals the effect of various initial concentrations on ammonia removal in a US/UV/TiO_2 system. After 150 min, the removal percentages of 400, 800, and 1,200 mg/L of ammonia were 93.3, 77.2, and 58.8%, respectively. The results presented in this figure demonstrate that using high-frequency ultrasound wave combined with UV/TiO_2 had a significant effect on ammonia removal at various concentrations. It is clear that the concentration reduces with time, which means that the removal rate of ammonia is proportional to time. Also, this figure shows that the initial concentration of ammonia is an effective parameter on the removal efficiency. As shown in Fig. 3, with increase in initial concentration of ammonia the removal efficiency of ammonia reduced. According to this figure, it can be seen that the maximum percentage of ammonia removal after 150 min occurred when initial concentration was 400 mg/L. Reduction in ammonia degradation rate with increase in solution concentration may relate to a competition for reaction with hydroxyl radicals at high concentrations. Meanwhile, the removal ratio of ammonia depends on the adsorption and photocatalysis capability of TiO_2. When the initial concentration of ammonia is increased the adsorption and photocatalysis capability of TiO_2 will be shortened [13,31]. Therefore, the efficiency of photocatalytic reaction and removal efficiency of ammonia will be reduced. Also, with increase in initial concentration, the number of ammonia molecules in the solution rise so that the number of ammonia molecules entering cavitation bubbles increases and leads to diminish the transient high temperature inside the cavitation bubble [32]. Thus, the removal efficiency of ammonia is decreased as the initial concentration of ammonia increases. Also, regarding to the constant cavitation density, higher initial concentration of ammonia reduces the chance of the ammonia molecules to be atomized.

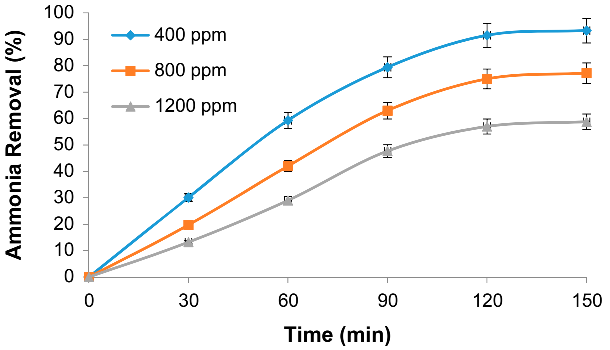

Fig. 3. Effect of initial ammonia concentration in US/UV/TiO_2 system. Experimental conditions: $[TiO_2]_0$ = 1 g/L, initial pH 11, initial volume = 400 ml (liquid height = 4 cm), US frequency = 1.7 MHz, UV intensity = 60 W, and reaction time = 150 min.

3.3. Effect of pH

In order to survey the effect of pH, the removal of ammonia at initial concentration of 400 mg/L was measured in US/UV/TiO_2 system. The experiments were carried out for 0.4 L liquid solution (liquid height = 4 cm) and five pH values of 3, 7, 9, 11, and 12. Fig. 4 shows the ammonia degradation profile for these pH conditions. The ammonia degradation rates have been found to be significantly influenced by pH as shown in Fig. 4. The removal efficiencies of US/UV/TiO_2 system at pHs of 3, 7, 9, 11, and 12 after 120 min were 16.2, 23, 49.8, 91.5, and 68.2%, respectively. Accordingly, the removal ratio of US/UV/TiO_2 system followed the order pH 11 > pH 12 > pH 7 > pH 9 > pH 3. This behavior can be attributed to the influence of pH on surface properties of TiO_2, ammonia adsorption and hydroxyl radical formation.

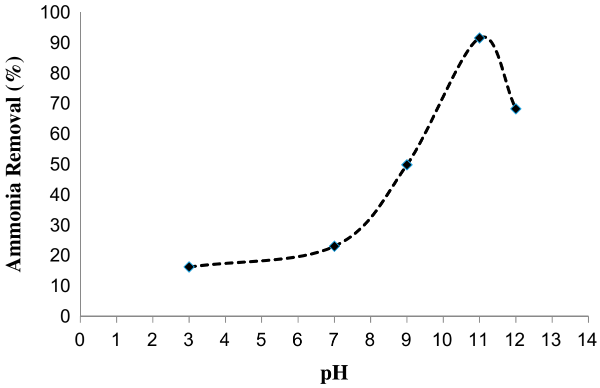

Fig. 4. Effect of pH in US/UV/TiO_2. Experimental conditions: $[NH_3]_0 = 400$ mg/L, $[TiO_2]_0 = 1$ g/L, initial volume = 400 ml (liquid height = 4 cm), US frequency = 1.7 MHz, UV intensity = 60 W, and reaction time = 120 min.

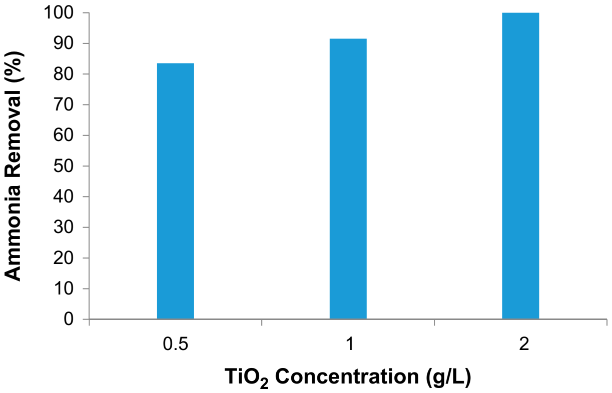

Fig. 5. Effect of TiO_2 dosage in US/UV/TiO_2 system. Experimental conditions: $[NH_3]_0 = 400$ mg/L, initial pH 11, initial volume = 400 ml (liquid height = 4 cm), US frequency = 1.7 MHz, UV intensity = 60 W, and reaction time = 120 min.

In acidic condition, the TiO_2 surface is positively charged and becomes protonated (TiO_2H^+) while in alkaline condition the TiO_2 surface becomes hydroxylated ($TiOH^-$) and remains negatively charged. On the other hand, at pH < 11, the ammonium ion concentration in solution increases when pH reduced and consequently the attraction between NH_4^+ ions and TiO_2 surface becomes weak. Therefore, pH changes enable to modify the adsorption of ammonia molecules upon the TiO_2 surface. Moreover, presence of a large quantity of OH^- in alkaline pH facilitates the generation of hydroxyl radical and leads to enhancement of removal ratio compared with acidic condition [12]. The reason of removal efficiency reduction at pH 12 may be related to conversion of NH_4^+ to NH_3 specious or deactivation of some of the active sites of TiO_2 surface [13]. Therefore, the optimal US/UV/TiO_2 activity for the ammonia reduction can be at pH between 10 and 11.

3.4. Effect of TiO_2 dosage

In another part of the experimental work, the effects of TiO_2 dosage on ammonia removal were examined. For this purpose, 0.4 L liquid solution (liquid height = 4 cm) with an initial ammonia concentration of 400 mg/L and TiO_2 concentration in the range between 0.5 and 2 g/L were used. The percent of ammonia removal at various TiO_2 concentrations is shown in Fig. 5. As clearly shown in this figure, increase in TiO_2 dose from 0.5 to 1 and finally to 2 g/L had a significant effect on ammonia removal ratio. Results show a complete ammonia removal (100%) at 2 g/L TiO_2 after 120 min. Increase in TiO_2 dose can raise the number of active sites and strengthens its photocatalysis capability [27]. Therefore, by increasing the amount of TiO_2 in the suspension, the fraction of incident absorbed light enhanced. However, aggregation of TiO_2 particles due to increasing of TiO_2 dose from 0.5 to 2 g/L may causes light scattering and screening [12]. High-frequency ultrasound irradiation combined with UV/TiO_2 system diminishes the fraction of drawback and contributes to penetrate UV light by generation of convective flows and micro-streams, which can improve micro and macromixing. In other words, ultrasound enhances the catalyst surface area by degradation action and improving mass transfer due to acoustic streaming and leads to promote in the performance of the photocatalytical system. Therefore, removal ratio enhanced continually as the concentration of TiO_2 increased, which is in agreement with previous studies in literature [9,24,25].

3.5. Effect of liquid height

In another part of this work, an investigation related to the effect of liquid height was performed. Three different liquid volumes, including 400, 600, and 800 ml, which related to 4, 6, and 8 cm liquid height, were used. The maximum volume of ammonia solution was fixed at 800 ml and the pH value adjusted to 11. When liquid height was more than 8 cm, no mist was observed and no significant atomization was occurred. The differences in ammonia removal efficiency for three above-mentioned liquid height are given in Fig. 6. It was found that the removal efficiency of ammonia strongly depends on liquid height. The obtained results in this figure demonstrate that as the liquid height increases, the

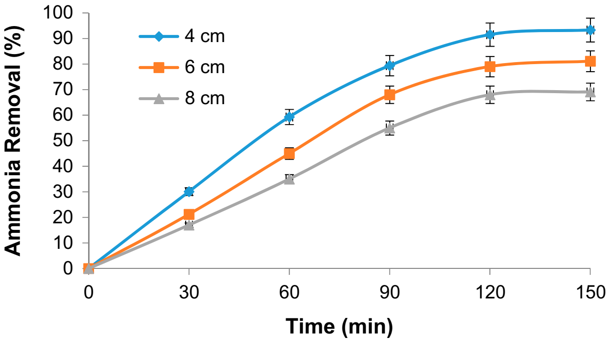

Fig. 6. Effect of liquid height in US/UV/TiO_2 system. Experimental conditions: $[NH_3]_0 = 400$ mg/L, $[TiO_2]_0 = 1$ g/L, initial pH 11, US frequency = 1.7 MHz, UV intensity = 60 W, and reaction time = 150 min.

removal ratio decreases and the maximum removal of ammonia was obtained when liquid height was 4 cm. This may be due to the fact that there is a strong relationship between liquid height and power of the transducer for atomizing ammonia and producing mist. When the solution height is higher, the capacity of the transducer for atomizing ammonia will be less and subsequently production of ultrasonic mist will be diminished. Therefore, a lower number of ammonia molecules have a chance to be in the mist region, which is a suitable zone for photocatalytic ammonia decomposition. In this region, the UV light can penetrate more easily; thus, the decomposition reactions occur more efficiently [28,29]. A similar observation was previously reported in the literature [33].

3.6. Effect of UV intensity

In the present study, the influence of the UV light intensity, as a crucial operating parameter in US/UV/TiO_2 system, was examined. Various UV source lamps with powers of 15, 18, and 30 W were used. As four lamps were employed in the setup, the total powers of 60, 72, and 120 W were used in the experiments. All experiments were carried out in the same experimental condition in presence of ultrasound waves. Fig. 7 shows the removal efficiency of ammonia under various radiation intensities. The figure shows an increase in removal efficiency of ammonia with increase in light intensity for a certain initial ammonia and TiO_2 contents, namely 400 mg/L and 1 g/L, respectively. As can be seen in this figure, increasing UV intensity to 120 W led to 100% removal of ammonia after 90 min reaction time. Increasing in light intensity causes an increase in reaction rate of photocatalytic degradation of ammonia. Increasing in UV intensity will provide higher energy for more TiO_2 to produce electron–hole pairs and thus promote catalyst activation. In addition, an enhancement in the rate constant occurred by increase in the light intensity. This observation was in good agreement with other studies [13,34].

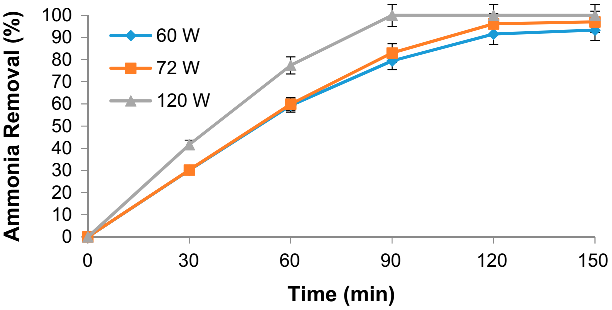

Fig. 7. Effect of UV intensity in US/UV/TiO_2 system. Experimental conditions: $[NH_3]_0 = 400$ mg/L, $[TiO_2]_0 = 1$ g/L, initial pH 11, initial volume = 400 ml (liquid height = 4 cm), US frequency = 1.7 MHz, and reaction time = 150 min.

3.7. Effect of ultrasound frequency

The influence of ultrasound frequency on photocatalytic efficiency was investigated in US/UV/TiO_2 system, and the results are illustrated in Fig. 8. In order to study the effect of ultrasound frequency, a high frequency 1.7 MHz ultrasound transducer and a low frequency one, generating 24 kHz waves, were used. All the other operating parameters were kept constant as follows: the initial ammonia concentration of 400 mg/L, TiO_2 dosage of 1 g/L, the initial solution pH 11, and initial solution volume of 400 ml. As shown in this figure, when the frequency of ultrasound decreases from 1.7 MHz to 24 kHz, the ammonia removal also decreases.

Two reasons can be cited to explain this behavior: atomization and acoustic streaming. As previously mentioned, when the ultrasound wave in the range of MHz propagates through the liquid, it can generate small droplets such a fog or mist in the gas phase which is called atomization phenomenon. Atomization phenomenon causes the ammonia molecules and TiO_2 particles are trapped in ultrasonic mist. Therefore, photocatalytic reaction occurs on the mist surface under UV irradiation. It should be noted that penetration of UV light in ultrasonic mist is more easily compared with liquid phase [28,29]. Furthermore, high-frequency ultrasound is capable of producing convective flows and acoustic streaming which

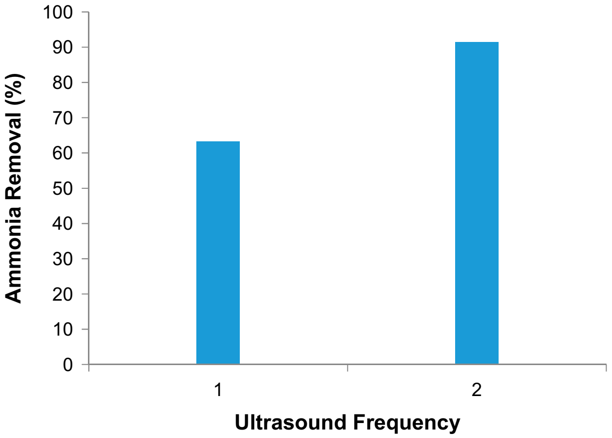

Fig. 8. Effect of ultrasound frequency in US/UV/TiO_2 system. Experimental conditions: $[NH_3]_0 = 400$ mg/L, $[TiO_2]_0 = 1$ g/L, initial pH 11, initial solution volume = 400 ml (liquid height = 4 cm), UV intensity = 60 W, and reaction time = 120 min.

improve micro- and macro-agitation and create sufficient mixing. The establishing of acoustic streaming and improve of the agitation can promote the oxygen transfer on the liquid phase. Oxygen as an electron trap eliminates the chance of recombination of electrons and holes in TiO_2 and thereby enhances significantly the photocatalytic reactions [10,24–26].

4. Conclusions

In this study, the performances of several treatment methods, namely, aeration, ultraviolet, ultrasound, ultrasound–aeration, ultrasound–ultraviolet, ultraviolet–titanium dioxide–aeration, and finally ultrasound–ultraviolet–titanium dioxide for ammonia removal were compared. The results reveal that US/UV/TiO_2 process was the best among all examined methods. The effects of various operational parameters including initial ammonia concentration, pH, TiO_2 dosage, liquid height, UV intensity, and ultrasound frequency on the ammonia removal were studied. Experimental results indicate that the removal efficiency of ammonia decreases in the UV/US/TiO_2 system when the initial concentration of ammonia increases. An enhancement in the pH value raised the removal efficiency of ammonia by increasing the catalyst activity. Increasing TiO_2 dosage in the range between 0.1 and 2 g/L caused an increase in the removal efficiency of ammonia. In addition, the experimental results demonstrated that as the liquid height increases, the transducer capability to atomize ammonia and producing ultrasonic mist reduces. This caused a decrease in the removal efficiency of ammonia. The results also show that the UV intensity is an effective factor on ammonia removal efficiency. In the combined system using a 120-W lamp as UV source, the ammonia removal efficiency of approximately 100% was obtained. The presented results indicate that high-frequency ultrasound plays an important role because of its ability to generate atomization and acoustic streaming. From this study, it can be concluded that using high-frequency ultrasound waves in the range of MHz in the presence of UV/TiO_2 can be a suitable way to remove ammonia from wastewaters.

References

[1] N. Değermenci, O.N. Ata, E. Yildiz, Ammonia removal by air stripping in a semi-batch jet loop reactor, J. Ind. Eng. Chem. 18 (2012) 399–404.

[2] Y. Shavisi, S. Sharifnia, M. Zendehzaban, M.L. Mirghavami, S. Kakehazar, Application of solar light for degradation of ammonia in petrochemical wastewater by a floating TiO_2/LECA photocatalyst, J. Ind. Eng. Chem. 20 (2014) 2806–2813.

[3] D.C. Rodríguez, O. Ramírez, G.P. Mesa, Behavior of nitrifying and denitrifying bacteria in a sequencing batch reactor for the removal of ammoniacal nitrogen and organic matter, Desalination 273 (2011) 447–452.

[4] Y. Deng, C.M. Ezyske, Sulfate radical-advanced oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate, Water Res. 45 (2011) 6189–6194.

[5] N. Widiastuti, H. Wu, H. Ang, D. Zhang, Removal of ammonium from greywater using natural zeolite, Desalination 277 (2011) 15–23.

[6] T. Zhang, L. Ding, H. Ren, Pretreatment of ammonium removal from landfill leachate by chemical precipitation, J. Hazard. Mater. 166 (2009) 911–915.

[7] D. Qu, D. Sun, H. Wang, Y. Yun, Experimental study of ammonia removal from water by modified direct contact membrane distillation, Desalination 326 (2013) 135–140.

[8] Y. Li, W. Hsieh, R. Mahmudov, X. Wei, C.P. Huang, Combined ultrasound and Fenton (US-Fenton) process for the treatment of ammunition wastewater, J. Hazard. Mater. 244–245 (2013) 403–411.

[9] K. Sekiguchi, C. Sasaki, K. Sakamoto, Synergistic effects of high-frequency ultrasound on photocatalytic degradation of aldehydes and their intermediates using TiO_2 suspension in water, Ultrason. Sonochem. 18 (2011) 158–163.

[10] J. Yano, Complete mineralization of propyzamide in aqueous solution containing TiO_2 particles and H_2O_2 by the simultaneous irradiation of light and ultrasonic waves, Ultrason. Sonochem. 12 (2005) 197–203.

[11] S. Lee, S. Park, TiO_2 photocatalyst for water treatment applications, J. Ind. Eng. Chem. 19 (2013) 1761–1769.

[12] C.H. Wu, C.H. Yu, Effects of TiO_2 dosage, pH and temperature on decolorization of C.I. Reactive Red 2 in a UV/US/TiO_2 system, J. Hazard. Mater. 169 (2009) 1179–1183.

[13] Y. Shavisi, S. Sharifnia, S.N. Hosseini, M.a. Khadivi, Application of TiO_2/perlite photocatalysis for degradation of ammonia in wastewater, J. Ind. Eng. Chem. 20 (2014) 278–283.

[14] D.T. Sponza, R. Oztekin, Removals of some hydrophobic poly aromatic hydrocarbons (PAHs) and Daphnia magna acute toxicity in a petrochemical industry wastewater with ultrasound in Izmir-Turkey, Sep. Purif. Technol. 77 (2011) 301–311.

[15] X. Ning, W. Wenxiang, H. Pingfang, L. Xiaoping, Effects of ultrasound on oily sludge deoiling, J. Hazard. Mater. 171 (2009) 914–917.

[16] V. Naddeo, M. Landi, V. Belgiorno, R.M.A. Napoli, Wastewater disinfection by combination of ultrasound and ultraviolet irradiation, J. Hazard. Mater. 168 (2009) 925–929.

[17] J. Wang, Z. Pan, Z. Zhang, X. Zhang, F. Wen, T. Ma, Y. Jiang, L. Wang, L. Xu, P. Kang, Sonocatalytic degradation of methyl parathion in the presence of nanometer and ordinary anatase titanium dioxide catalysts and comparison of their sonocatalytic abilities, Ultrason. Sonochem. 13 (2006) 493–500.

[18] C.H. Wu, Sonocatalytic degradation of C.I. Reactive Red 198 in H_2O_2-based systems, React. Kinet. Catal. Lett. 92 (2007) 377–384.

[19] C.S. Poon, Q. Huang, P.C. Fung, S. Engineering, H. Horn, H. Kong, Degradation kinetics of cuprophenyl yellow RL by UV/H_2O_2/ultrasonication (US) process in aqueous solution, Chemosphere 38 (1999) 1005–1014.

[20] J. Xu, J. Jia, J. Wang, Ultrasonic decomposition of ammonia-nitrogen and organic compounds in coke plant wastewater, J. Chin. Chem. Soc. 52 (2005) 59–65.

[21] A. Hayyan, M. Ali, M.E.S. Mirghani, M. Hayyan, I.M. Alnashef, Treatment of industrial low grade palm oil via esterification reaction using sonoreactor, J. Ind. Eng. Chem. 20 (2014) 2066–2070.

[22] S. Aljbour, H. Yamada, T. Tagawa, Ultrasound-assisted phase transfer catalysis in a capillary microreactor, Chem. Eng. Process. 48 (2009) 1167–1172.

[23] S. Serkan, COD and color removal from synthetic textile wastewater by ultrasound assisted electro-Fenton oxidation process, J. Ind. Eng. Chem. 19 (2013) 601–605.

[24] M. Rahimi, N. Azimi, F. Parvizian, Using microparticles to enhance micromixing in a high frequency continuous flow sonoreactor, Chem. Eng. Process. 70 (2013) 250–258.

[25] F. Parvizian, M. Rahimi, M. Faryadi, A.A. Alsairafi, Comparison between mixing in novel high frequency sonoreactor and stirred tank teactor, Eng. Appl. Comput. Fluid 6 (2012) 295–306.

[26] S. Merabet, A. Bouzaza, D. Wolbert, Photocatalytic degradation of indole in a circulating upflow reactor by UV/TiO_2 process—Influence of some operating parameters, J. Hazard. Mater. 166 (2009) 1244–1249.

[27] R.A. Torres, J.I. Nieto, E. Combet, C. Pétrier, C. Pulgarin, Influence of TiO_2 concentration on the synergistic effect between photocatalysis and high- frequency ultrasound for organic pollutant mineralization in water, Appl. Catal. B Environ. 80 (2008) 168–175.

[28] K. Sekiguchi, D. Noshiroya, M. Handa, K. Yamamoto, K. Sakamoto, Degradation of organic gases using ultrasonic mist generated from TiO_2 suspension, Chemosphere 81 (2010) 33–38.

[29] K. Sekiguchi, K. Yamamoto, K. Sakamoto, Photocatalytic degradation of gaseous toluene in an ultrasonic mist containing TiO_2 particles, Catal. Commun. 9 (2008) 281–285.

[30] Betz Laboratories, Inc., Betz Handbook of Industrial Water Conditioning, nineth ed., 1991, Betz Laboratories Inc., Trevose, PA.

[31] J. Li, C. Mi, J. Li, Y. Xu, Z. Jia, M. Li, The removal of MO molecules from aqueous solution by the combination of ultrasound/adsorption/photocatalysis, Ultrason. Sonochem. 15 (2008) 949–954.

[32] H. Monnier, A.M. Wilhelm, H. Delmas, Effects of ultrasound on micromixing in flow cell, Chem. Eng. Sci. 55 (2000) 4009–4020.

[33] M.A.D. Matouq, Z.A. Al-Anber, The application of high frequency ultrasound waves to remove ammonia from simulated industrial wastewater, Ultrason. Sonochem. 14 (2007) 393–397.

[34] Y. Li, S. Sun, M. Ma, Y. Ouyang, W. Yan, Kinetic study and model of the photocatalytic degradation of rhodamine B (RhB) by a TiO_2-coated activated carbon catalyst: Effects of initial RhB content, light intensity and TiO_2 content in the catalyst, Chem. Eng. J. 142 (2008) 147–155.