

APPLICATION OF DIELECTRIC BARRIER DISCHARGE AND PLASMA-CHEMICAL REACTOR FOR WATER PURIFICATION FROM NH₄OH

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Water purification from ammonium hydroxide was carried out by using two methods of processing: treatment with ozone generated by a dielectric barrier discharge (DBD) as well as processing in plasma-chemical reactor equipped with a water electrode and a diaphragm, where the main oxidation factors were OH hydroxyl radicals. The volume of the treated aqueous solution was 300 ml and the NH₄OH concentration was 0.025 ml in both cases. The phenolphthalein test was used for visual analysis of the content of an aqueous solution of ammonia in water. The ozone concentration was about 5.8 mg/l in water with ozone injection from an ozone generator and 0.7 mg/l in a plasma-chemical reactor, respectively. The analysis of OH and NO radicals in the water-air gap of the plasma-chemical reactor was carried out using a spectrometer operated in the range of 200...800 nm.

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INTRODUCTION

Water purification from ammonia is an urgent problem at various industrial and agricultural facilities, in artificial reservoirs and pools. Ammonia can be present in water in two forms, either ammonium hydroxide (NH₃·H₂O or more common NH₄OH) or as the ammonium ion (NH₄). The total sum of the concentrations of ammonium and ammonia is called total ammonia nitrogen (TAN). The source of ammonia in water is salts and dissolved ammonia as well as nitrogen-containing substances resulting from the decomposition of protein compounds. Ammonia is a colorless gas, readily soluble in water, with a characteristic odor, has a toxic effect on the aquatic flora and fauna and can occur in an aqueous solution at a pH of less than 8 in the form of ammonia, at a pH of more than 11 in the form of ammonium, between pH 8...11 both ammonium and ammonia exist. Taking into consideration the environmental hazard of ammonia, a number of methods are aimed at its removal, both in air and in the aquatic environment.

Today, there are various methods which can significantly reduce the ammonia content in water. Known methods of chemical precipitation, purging, desorption and adsorption are usually used for the purification of ammonia-nitrogen wastewater with a low concentration.

The chemical precipitation method is designed to reduce the solubility of ammonia nitrogen in water by forming an insoluble salt. The purge method typically uses NaOH to adjust the pH to basic wastewater and ammonia nitrogen can exist in the form of free ammonia (NH₃). Then, ammonia nitrogen leaves the aqueous solution and exits into the atmosphere. The removal of ammonia by desorption is a process that is often considered as one of the possible ways of wastewater

treatment, but it does not find wide practical application. In addition, to remove nitrogen from water, which exists in the wastewater in the form of free ammonia, ammonium salts and nitrites, it is possible to use the reduction of nitrates to molecular nitrogen in a biological way (denitrification). First, it is necessary to oxidize ammonia nitrogen into nitrites and nitrates (nitrification) [1]. However, biological nitrification layers are subject to significant fluctuations in efficiency, since nitrifying bacteria in the biofilter layers are sensitive to environmental disturbances and changes in working conditions, which are often associated with color, smell and taste problems and, in addition, worsen the biofilter function [2]. When removing nitrogen in the ammonium form, it is advisable to use ion-exchange filters, in particular, filtering waste water through loading from natural zeolites [3]. Free chlorine (HOCl⁺OCl⁻) is usually used in water and wastewater treatment to disinfect and remove ammonia. However, in addition to the desired effects, residual free chlorine can also have a number of undesirable ones: for example, it is toxic to organisms existing in the water, lowers the palatability of drinking water, and is aggressive in the industrial use of water. Thus, free chlorine should be removed from water or at least reduced in its content.

Ozone (O₃) is a strong oxidizing agent, especially in the presence of OH⁻, H₂O₂/HO⁻, Fe₂, UV, and other activators or accelerators of free radicals [4, 5]. Under the influence of excited radicals and accelerators, ozone will cause a large number of hydroxyl radicals (OH) in the reaction system, which will lead to chain reactions and then more reactive radicals will be produced.

Studies by Hoigne J. and Bader H. [6] showed that ozone-induced oxidation of ammonia in water can be the result of a direct reaction of ozone with ammonia, as

well as reactions of hydroxyl radicals generated by the decomposition of ozone. The direct ozone reaction predominates at $\text{pH} < 9$, but in the presence of low concentrations of free ammonia this is a slow reaction. At $\text{pH} > 9$, the hydroxyl ionic and radical-catalyzed decomposition of ozone to a reactive intermediate hydroxyl radical determines the kinetics of ammonia oxidation. The reaction rate constant of the hydroxyl radical with ammonia is relatively small. Whenever the mechanism of hydroxyl radicals is activated, ammonia is easily protected by other dissolved substances, which also consume hydroxyl radicals.

According to De Pena and Olszyna [7, 8], NH_3 can react with O_3 to form ammonium nitrate (NH_4NO_3). In these reaction processes, NH_3 is first oxidized to nitric acid and then reacts with nitric acid to form NH_4NO_3 . Xianping Luo, Qun Yan et al. [9] studied the purification process using the two-stage method of ozone oxidation of wastewater with ammonia nitrogen content (about 100 mg/l). Also, the effect of the ozone flow rate and the initial pH on the removal of ammonia was investigated. It was determined that after the initial stage of ozone oxidation, the ammonia removal efficiency reached 59.32 %, and the pH decreased from 11 to 6.63 at an ozone flow rate of 1 l/min, and after the second stage, the removal efficiency was more than 85 %. In [10], when treating ammonia in air, it was shown that 1.8 mg of O_3 is necessary for the oxidation of 1 mg of NH_3 .

Considering the above mentioned, all methods have their own characteristics, but each of them has its own limitations or has different levels of investment in equipment, high operating costs, secondary pollution and other disadvantages [11-15]. Therefore, it is necessary to find effective, practical methods for removing ammonia. In so doing, considerable interest is given to non-equilibrium low-temperature plasma and, in particular, dielectric barrier discharge (DBD) used for ammonia removal from aqueous medium.

1. EXPERIMENTAL SETUP

1.1. OZONE REACTOR BASED ON DBD

A reactor based on a dielectric barrier discharge with air-cooled plane-parallel electrodes was used as an ozone generator (Fig. 1).

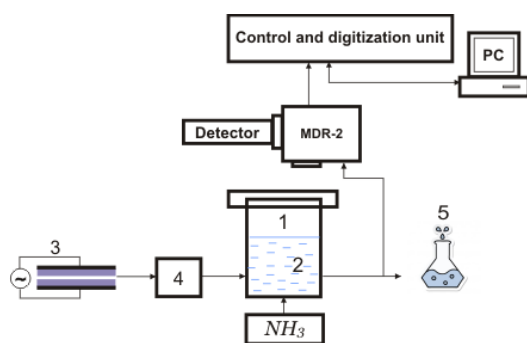


Fig. 1. Scheme of NH_4OH oxidation with ozone in DBD: 1 – stainless steel container with plexiglass cover; 2 – water; 3 – ozone reactor based on a dielectric barrier discharge; 4 – ozone concentration meter of M454 DIN type; 5 – system for obtaining a solution for analysis

Glass with $\epsilon = 6$ was used as a dielectric. The reactor is powered by a high-voltage pulse supply of 7 kV and power consumption comprised 10 W. The ozone concentration at the reactor outlet was 25 mg/l at a dry air flow rate of 0.2 mg/l. The concentration of NH_4OH was 0.025 ml. NH_4OH treatment was carried out in a stainless steel container with a volume of 0.5 l; the ozone concentration in water without ammonia was 5.8 mg/l at a water temperature of 20°C.

1.2. PLASMA-CHEMICAL REACTOR

A diaphragm discharge was used to generate ozone in a plasma-chemical reactor. The NH_4OH solution was processed inside the discharge chamber – a container made of a dielectric material with a separating dielectric diaphragm membrane having holes of 1 mm in diameter. A general view of the diaphragm reactor is shown in Fig. 2. The diaphragm reactor was described in more detail in [16]. The ozone concentration in water was determined by using an automated stand equipped with MDR-2 monochromator and a photomultiplier tube (PMT) and amounted to about 0.7 mg/l. The NH_4OH concentration was 0.025 ml.

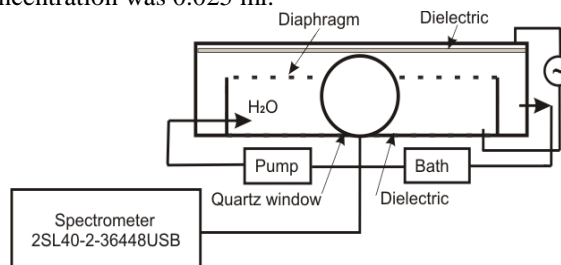


Fig. 2. Schematic view of plasma-chemical reactor and diaphragm discharge

1.3. DISCUSSION

Plasma in an oxygen-containing environment in contact with an aqueous solution is a source of such strong oxidants as O, OH, HO_2 , H_2O_2 , O_3 , which, penetrating into the solution, lead to the destruction of organic pollutants. Regardless of the type of discharge, the emission spectrum contains bands of N_2 , OH, and NO molecules and lines of O and H atoms during a discharge in air and oxygen [17].

The performed spectroscopic studies in the range of 200...800 nm in the water-air gap of the discharge revealed the presence of OH and NO lines in the water-air gap (Fig. 3).

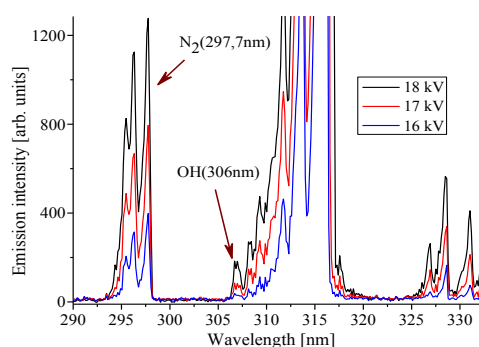


Fig. 3. The emission spectrum of the discharge in the air-water gap depending on the applied voltage

The change in the intensity of the OH and N₂ peaks in the discharge was also obtained depending on the applied voltage. We assume that the presence of hydroxyl radicals in the discharge has a significant effect on the treated impurities in water, because this ozone concentration may not be enough for NH₄OH oxidation.

To visually determine the oxidation of the NH₄OH solution, a phenolphthalein sample was used, which stains the solution in a raspberry color. When the NH₄OH solution was treated with a diaphragm discharge, coloration was not observed after 10 min of treatment, and when treated with ozone, which was generated by a dielectric barrier discharge after 20 min. The absence of coloration confirms the fact that the solution is not alkaline. Fig. 4 shows the change in the color of the NH₄OH solution when using a phenolphthalein sample (a – during oxidation in a diaphragm discharge; b – during oxidation with ozone generated by the DBD reactor).

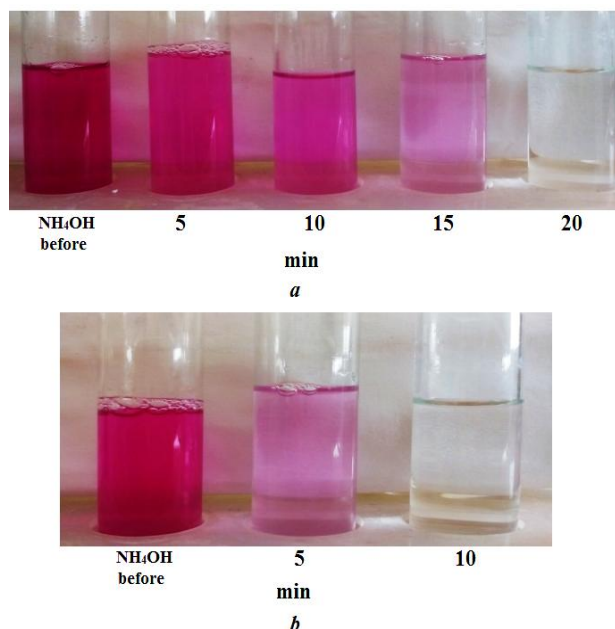


Fig. 4. Visual observation of NH₄OH removal by color change during oxidation in a – diaphragm discharge, b – DBD

For a more accurate determination of the oxidation state of NH₄OH in ozone, we used a method for determining the concentration of ozone in water on an automated stand using an MDR-2 monochromator (LOMO, Russia) and a photomultiplier tube (PMT). First, in the presence of NH₄OH in water, the device recorded the absence of ozone in the water. When the ozone concentration started to increase, this meant that ozone was present in the water and NH₄OH was oxidized. Ozone concentration was recorded every 5 min. With a diaphragm discharge, small values of the ozone concentration began to be recorded after 10 min of treatment, and with DBD – after 20 min. As a result it was calculated that 4 g of O₃ generated by DBD is sufficient for the oxidation of 1 ml of NH₄OH. For the oxidation of 1 ml of NH₄OH in a plasma-chemical reactor, this device must be in operation for at least 6 h.

CONCLUSIONS

Two methods of water purification from NH₄OH are proposed: treatment with ozone generated by DBD and plasma-chemical treatment. A comparison of the kinetics of their oxidative processes is also given. The phenolphthalein sample was used to visually observe the NH₄OH oxidation process. The change in the color of NH₄OH upon treatment with ozone indicated the oxidation process sequence. As a result of the work carried out, it was calculated that for the oxidation of 1 ml of NH₄OH, 4 g of O₃ is sufficient, which is generated by DBD or at least 6 h of operation of the plasma-chemical reactor.

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ПРИМЕНЕНИЕ ДИЭЛЕКТРИЧЕСКОГО БАРЬЕРНОГО РАЗРЯДА И ПЛАЗМОХИМИЧЕСКОГО РЕАКТОРА ДЛЯ ОЧИСТКИ ВОДЫ ОТ NH₄OH

В.С. Таран, И.Е. Гаркуша, В.В. Красный, А.В. Таран, А.С. Лозина, О.Г. Чечельницкий, И.Н. Болдырев, С.П. Романюк

Очистка воды от гидроксида аммония проводилась двумя способами: обработкой озоном, генерируемым диэлектрическим барьерным разрядом (ДБР), и обработкой в плазмохимическом реакторе, оборудованном водяным электродом и диафрагмой, в котором основным фактором окисления являлись гидроксильные радикалы OH. Объем обработанного водного раствора составлял 300 мл, а концентрация NH₄OH составляла 0,025 мл в обоих случаях. Фенолфталеиновый тест использовали для визуального анализа содержания водного раствора аммиака в воде. Концентрация озона составляла около 5,8 мг/л в воде при вводе озона из генератора озона и 0,7 мг/л в плазмохимическом реакторе соответственно. Анализ радикалов OH и NO в водно-воздушном зазоре плазмохимического реактора проводился на спектрометре, работающем в диапазоне 200...800 нм.

ЗАСТОСУВАННЯ ДИЕЛЕКТРИЧНОГО БАР'ЄРНОГО РОЗРЯДУ І ПЛАЗМОХІМІЧНОГО РЕАКТОРУ ДЛЯ ОЧИЩЕННЯ ВОДИ ВІД NH₄OH

В.С. Таран, І.Є. Гаркуша, В.В. Красний, А.В. Таран, А.С. Лозина, О.Г. Чечельницький, І.М. Болдырев, С.П. Романюк

Очищення води від гідроксиду амонію проводилося двома способами: обробкою озоном, що генерується діелектричним бар'єрним розрядом (ДБР), і обробкою в плазмохімічному реакторі, обладнаному водяним електродом і діафрагмою, в якому основним чинником окислення були гідроксильні радикали OH. Обсяг обробленого водного розчину становив 300 мл, а концентрація NH₄OH становила 0,025 мл в обох випадках. Фенолфталеїновий тест використовували для візуального аналізу змісту водного розчину аміаку у воді. Концентрація озону становила близько 5,8 мг/л у воді при введенні озону з генератора озону і 0,7 мг/л в плазмохімічному реакторі відповідно. Аналіз радикалів OH і NO в водно-повітряному проміжку плазмохімічного реактора проводився на спектрометрі, що працює в діапазоні 200...800 нм.