INVESTIGATION OF ELECTRIC DISCHARGE TREATMENT OF WATER FOR AMMONIUM NITROGEN REMOVAL

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The possibility of water purification from ammonium nitrogen using pulsed electric discharge in water-air mixtures was investigated. The model solution of chlorous ammonium was used in experiments. The concentration of ions ammonium was about 300 mg/l. Achieved reduction of ammonium concentration was about 35%. In this paper the mechanism of this process is discussed. The ways to increasing efficiency of this method are proposed.
Keywords: *water, ammonium, pulsed electric discharge*

INTRODUCTION

Extensive water pollution has become one of the greatest problems all the humanity. The pollution leads to the loss of both water quality and resources of pure water on the planet. The problem of water quality is one of the most actual problems in the world.

Ammonium compounds are one of the components of industrial and domestic sewages. Use of the well-known methods of the ammonium removal from water often is not enough efficient, complicated, and requires the greater costs. That is why development of new methods of purification is an actual problem. Use of the new physical-chemical methods such as electronic-beam processing, use of low-temperature plasma of the barrier discharge for purification of sewages has shown the good results [1, 2], but such studies are experimental.

One of the most perspective directions in water purification is use of electric discharge. Today water treatment technologies based on the use of electric discharge attract attention of scientists all over the world. A realization of electric discharge directly in cleaned water is the simplest way of water treatment. Electromagnetic radiation, shock waves, products of ionizing the material influence on the processing water in conditions of electric discharge The disadvantages of such method are a small volume of the processing water, contraction of discharge channels, and great energy consumption. The largest efficiency of water purification is reached at electric discharge treatment of the water-air mixtures. The electric discharge in the two-phase ambience is an efficient source of O_3 and ultraviolet radiation, as well as of active particles – radical OH, atomic oxygen, excited particles, which have reactivity much higher, than O_3. The results of studying possibility of water treatment by electric pulsed discharge for removal of ammonium compounds are presented in this paper.

EXPERIMENTAL TECHNIQUE

The study of water treatment, containing chlorous ammonium NH_4Cl by pulsed electric discharge in water-air mixtures, ozonization and coprocessing by the electric discharge and ozone was carried out. The concentration of ions ammonium was about 300 mg/l. The model solution was processed during 20–30 minutes; sampling for analysis was made in 5 minutes. The quantitative determination of admixtures was made on standard methods. The

concentration of ammonium was determined by photometrical method; also pH of solution was controlled.

The functional scheme of installation is shown on fig. 1. The treatment of the model solution NH_4Cl by electric discharge was carried out in closed cycle according this scheme. It was turned on the pump, the compressor, the high voltage pulsed generator IG1. The solution from the chamber was given by the pump in the injector, where was crushed on small drops with diameter 0.1–1 mm. The flow of drops with velocity 10 m/s absorbed the atmospheric air, then the mixtures of drops and air entered in the discharge gap of reactor. In the reactor this mixture was processed by pulsed electric discharge. Then the drops of the solution fell on bottom of the chamber. The mixture of air and water vapor with products of reactions was removing into the air.

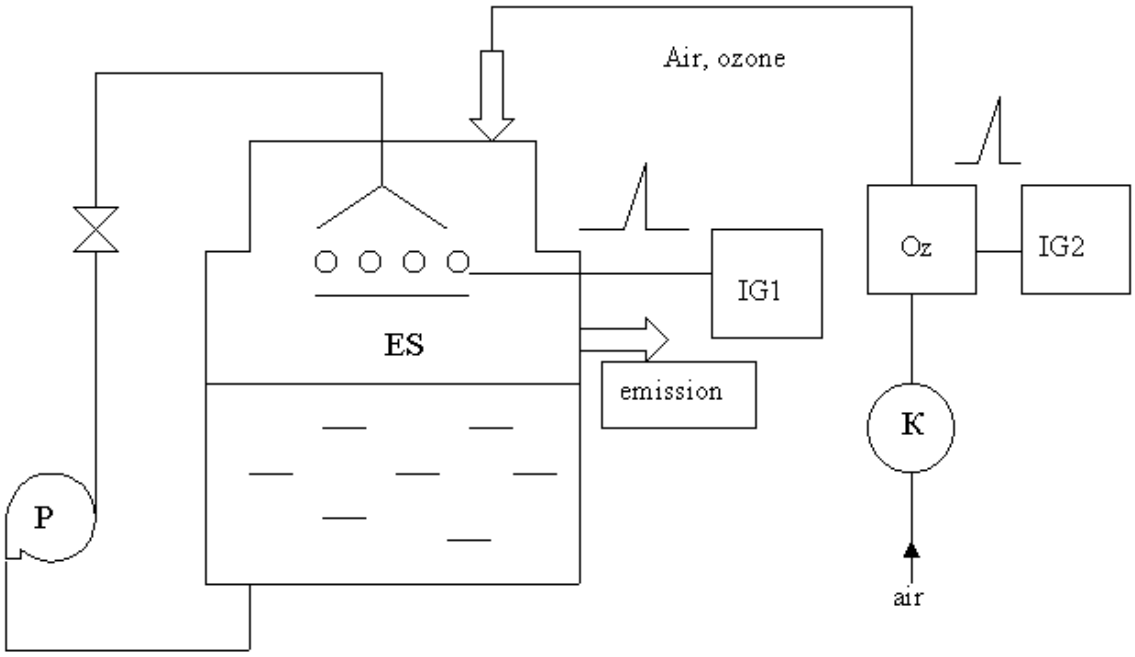

Figure 1. Functional scheme of installation for water treatment: IG1, IG2 – high voltage pulsed generator, Oz – ozonizer, ES – electrodes system, P – pump, K – compressor

Under the action of high voltage pulses in the discharge gap a quasi-volume discharge appears, factors of influence of which on water-air mixture are a flow of electrons, ultraviolet radiation, O_3, H_2O_2, positive gas ions, radicals OH, etc. Under the action of complex of these factors, besides, it was supposed the destruction of ammonium occurs.

In case of the treatment of model solution by ozone the experiment was carried out in that way: it was turned on the pump, the compressor, the high voltage generator IG2. The pulse high voltage was input on the ozonizer. The air-ozone mixture was input at chamber.

The high voltage pulsed generator had such characteristics:

- Pulse amplitude of voltage – 30-40 kV;
- Pulse width – 200 ns;
- Pulse frequency – 1000 s^{-1};
- Pulse energy – 0.25 J;
- Power of generator – 250 W.

The velocity of water flow through the injector was 100–400 l/h or 0.1–0.06 l/s. The velocity of the airflow was 1–4 м^3/h or 0.1–1 l/s. Time of processing water-air mixture in the discharge gap was defined on formula $t_c = S \cdot l/v$, where S – area of section of electrodes system, l – distance between electrodes, v - velocity of flow. Time of contact of the processed solution with zone of electric discharge in experiments was 1–5 ms.

EXPERIMENTAL RESULTS AND DISCUSSION

Ozonization

It is known [3, 4], the positive ion of ammonium NH_4^+ is resistance to action of ozone. However, on the one hand, in the alkaline medium, under pH > 9, chemical equilibrium in system $NH_4Cl – H_2O$ shifts aside separations of ammonia, which interacts with ozone to nitric acid and water:

$$NH_3 + O_3 + OH^- \rightarrow NO_3^- + O_2 + H_2O + H^+.$$

On the other hand, in the alkaline medium ozone destroys. That is why there are the adverse conditions in alkaline medium for reaction of ozonization. At the same time the destruction of ozone causes the forming the free radicals OH^-, being strong oxidants and which are capable to oxidize free NH_3, but not NH_4^+ [4]. The using ozonization for purification of water containing ammonia [5] has shown that ammonia (240 mg/l) completely oxidizes during ~8 hours in next conditions: pH 10,5 and the temperature ~55 ºC.

In our experiments the treatment of the model solution NH_4Cl by ozone for 30 minutes did not bring the visible results. Considering duration of the process ozonization [5], there was decided to use the electric discharge for water treatment.

Electric discharge

The analysis of remaining concentration ammonium after processing has shown that the best results are received when time of contact of processed solution with zone of the electric discharge was 5 ms. In this case in 20 minutes from the beginning process a concentration of ammonium fell from 390 mg/l to 260 mg/l. The dependence of the remaining concentration of ammonium with duration of processing t_{pr} is shown in figure 2.

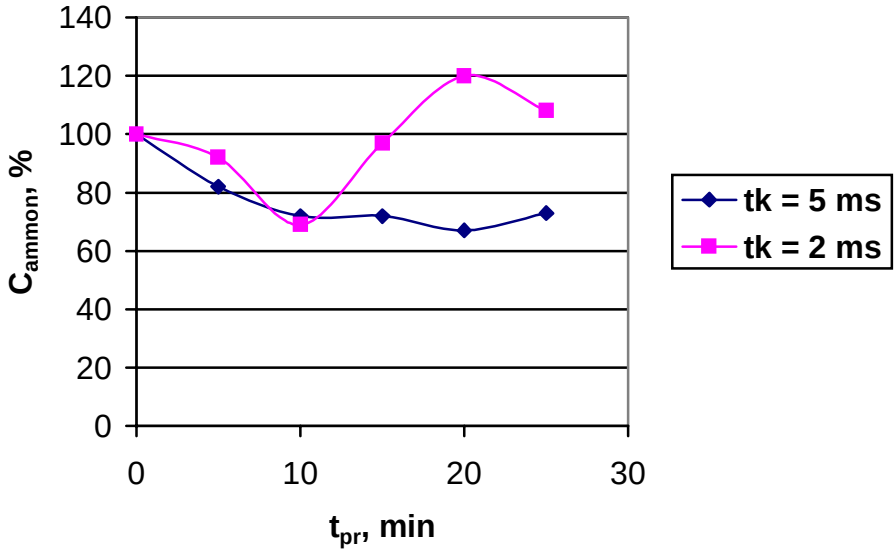

Figure 2. Remaining concentration of ammonium with duration of processing t_{pr} and time of processing water-air mixture in the discharge gap t_k

The lesser duration of contact of processed solution with zone of the electric discharge has resulted in the growing concentration of ammonium in water (fig 2). In case of the coprocessing by the electric discharge and ozone the same results were got. A conclusion was made that the product of chemical reactions under the action of the electric discharge in the water-air mixture is a nitrate ammonium.

MECHANISM OF CHEMICAL TRANSFORMATIONS

The results of experiments show that processes that occur in conditions of the high voltage processing of water are complex and have many stages. The principal chemical reactions in system $NH_4Cl – H_2O$ leading to removal of ammonia from water can be grouped in the next scheme:

1. The primary formation of the ions and radicals through the collision of the molecules with electrons like $NH4^+$, NH_3, H^+, Cl^-, H, OH, H_2, O^-, H^-, H_2O^+, O^-, O, N_2^*.

2. The conversion of primary ions in ions of secondary sorts and formation of neutral particles in the result of the collision of the molecules, ions, and electrons: NH_2, NH, H, H_2, N_2, OH, O, OH^-, H_3O^+, O_2^-, O_3^-.

3. The final products of ammonia destruction are N_2, H_2O, Cl_2, HNO_3. Probably, in the conditions of experiments the transformation of NO_x in acids HNO_3 and HNO_2 and the neutralization of the formed acids by remaining ammonia NH_3 took place.

Later the analysis for determination of nitrates-ions and nitrites-ions was carried out. According the results of this analysis the decrease of nitrates-ions and nitrites-ions takes place in the initial stage of the treatment of raw water (table 1). After treatment of model solution the concentration of nitrites-ions decreases, and the concentration of nitrates-ions increases slightly (table 2).

Table 1. Concentration of NO_2^- and NO_3^- after treatment of raw water

Duration of processing	0 min	5 min	10 min	15 min
NO_2^-,mg/l	0.1	0.088	0.088	0.089
NO_3^-,mg/l	1.1	0.96	0.97	0.98
pH	7.1	7.6	7.9	8.2

Table 2. Concentration of NO_2^- and NO_3^- after treatment of model solution

Duration of processing	0 min	5 min	10 min	15 min
NO_2^-, mg/l	0.2	0.1	0.06	0.04
NO_3^-, mg/l	2.0	2.8	3.0	3.1
pH	7.4	7.6	8.1	8.1

The reason of reduction of ammonium concentration during first 10–20 minutes of processing is, probably, formation of "active chlorine", which oxidizes ammonia, forming in process of the plazmochemical destruction, and, possible, oxidation of NH_3 by active atoms of oxygen and hydroxyl radicals [2, 6]. Later the interaction NH_3 with NO_3 in liquid phase occurs after absorption of nitrogen oxides by water. It is known [7], reaction of forming the acid anions have an induction period, connected with time of diffusion of products from gas phase in liquid and accumulations them in such amount that reaction between these products occurs with considerable velocity.

It should be noted that when processing of water by electric discharge with frequencies of pulse f = 200–400 s^{-1}, nitrites disappear, as shown in figure 3. This fact can be used in future development of electric discharge water treatment technology.

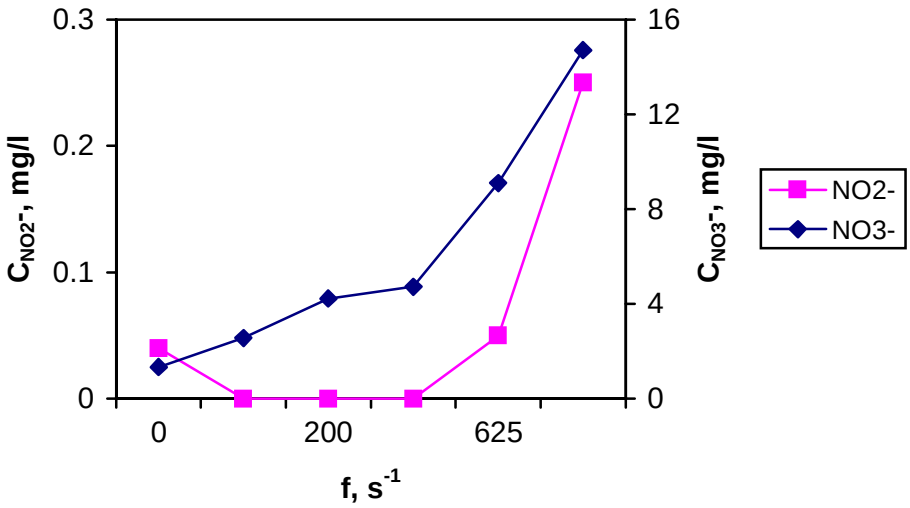

Figure 3. Dependency of NO_2^- and NO_3^- concentration from pulse frequency, t_{pr} = 20 min

Another reason of the slow removal of water from ammonium nitrogen can be chemical interaction of ammonium with water hardness salts (Ca^{2+}, Mg^{2+}) with obtaining insoluble substances that can introduce an error by photocolorimetric determination of admixtures.

The effect of electric discharge treatment was analysed in real conditions on working the complex "Pulse" and small concentrations ammonium and oxidized nitrogen in underground water of West Siberia. The reduction of their concentration exists after electric discharge processing was made.

In our opinion, one of the ways of carrying out the high voltage processing of system $NH_4Cl – H_2O$ to achieve as final products of ammonium destruction the nitrogen and nitrogen oxides in gas phase is the changing parameters of electric discharge.

CONCLUSION

It was shown a possibility of purification of water, containing ammonium compounds, by pulsed electric discharge. Achieved reduction of ammonium concentration was about 35%. The ways of increasing efficiency of this method are discussed.

The kinetics of processes depends on large number of different physical-chemical processes: chemical reactions in two-phase water-air mixture, processes of dissolution of components that participate in chemical reactions, dynamics of formation and destruction of active particles. A lot of high-energy elementary processes in plasma of the quasi-volume electric discharge cause the various physical-chemical conversions of materials, which can result in the differing results depending on conditions. For carrying out the high voltage processing water it is necessary to study the mechanisms accompanying physical-chemical processes and features of transformation of source compounds.

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