Ammonium nitrogen content regulation in sewage water at the transportation stage

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Abstract. Practical observations of the ammonium nitrogen content at the existing wastewater treatment plant show its excess over the calculated concentration by 30–60%, which occurs due to the atmospheric nitrogen fixation and its transition to ammonium. Hydrogen peroxide has been shown theoretically and experimentally to be an environmentally friendly oxidizer in the wastewater pretreatment technology in order to prevent and regulate corrosion processes in the systems and structures transporting wastewater, as well as nitrogen fixation, and can be recommended for practical use.

Introduction
It is known [1] that the majority of wastewater contains bacteria capable of carrying out the decay processes, and also contains organic substances and sulfate ions, so the conditions for the hydrogen sulfide formation in the sewer pipelines will always be objectively present.

Literary studies and the authors’ own experience indicate that nitrogen fixation is observed at normal atmospheric pressure and ambient temperature in reducing liquid media [2, 3]. This effect allows to explain the increase in the ammonium nitrogen concentration in the process of transporting wastewater through the collector to the treatment plant from 18-30 to 45-80 mg / dm³.

The nitrogen fixation process explanation, apart from the water disposal process, was given in 1964 by M.E. Volpin and V.B. Shur [4]. They obtained nitrogen-fixing systems in which nitrogen was fixed by transition metal compounds under “mild” conditions (at room temperature and normal pressure).

Based on these works’ results, it can be assumed that the electrons presence in the donor system in the strong competitive oxidizing agents absence, that is, in the reducing environment characteristic of wastewater transported through the collector, without the participation of microorganisms, the reaction is carried out according to the scheme: \( N_2 + 6e^- + 6H^+ = 2NH_3 \).

In accordance with the principle of Le Chatelier, when the concentration of dissolved nitrogen changes, as a result of its transition to ammonia (ammonium), in order to comply with the system equilibrium conditions, the processes aimed at compensating for external exposure are enhanced, that is, the dissolution of nitrogen from the gaseous medium is intensified. Considering the fact that ammonia is very soluble in water (one volume of water at room temperature dissolves about seven hundred volumes of ammonia), the process of nitrogen fixation under these conditions is practically not limited by this factor.
In [2], the control experiments series results, which confirmed the assumptions about the possibility of a medium with reducing conditions to fix nitrogen were presented. It is shown (Table 1) that media with an indicator of oxidation-reduction properties ($rH_2$) from 17.0 and less - have a pronounced ability to fix nitrogen-fixing, which is typical for the reducing conditions [2].

**Table 1.** The chemical nitrogen fixation indicators in model solutions on ammonia-free water when air is reaerated through an open surface.

| No. | Terms of experience                  | pH   | ORP, [mV] | $T_1$, [$^\circ C$] | $\tau_{\text{contact}}$, [min] | $C_{\text{NH}_4^+}$, [mg /dm$^3$] | $rH_2$ |
|-----|-------------------------------------|------|-----------|-------------------|-------------------------------|---------------------------------|--------|
| 1   | Ammonia-free solution (AFS)         | 6.40 | 285       | 14.3              | 2                             | 0.98                            | 22.46  |
| 2   | AFS                                 | 6.45 | 246       | 14.5              | 10                            | 0.86                            | 21.51  |
| 3   | AFS + organ substances solution     | 4.15 | -130      | 14.2              | 2                             | 13.77                           | 3.74   |
| 4   | AFS + organ substances solution     | 4.05 | -120      | 14.5              | 10                            | 9.83                            | 3.90   |
| 5   | AFS + solution Na$_2$S              | 9.14 | -160      | 14.5              | 2                             | 8.85                            | 12.67  |
| 6   | AFS + solution Na$_2$S              | 9.18 | -146      | 14.2              | 10                            | 7.75                            | 13.24  |

Notes: 1) the results are average of 3 measurements; 2) the concentration of model water by COD in a mixture of fatty acid (glycerin), amino acids (lysine) and carbohydrate (glucose) was 320 mg / dm$^3$; 3) the concentration of model water for hydrogen sulfide is 5.3 mg / dm$^3$.

In the ammonia-free solution itself, in the electron donors’ absence, regardless of the re-aeration time duration, the increase in ammonium nitrogen concentration is insignificant. The conjugate reactions $O_2^- - 2e \rightarrow O_2$ and $N_2O^+ + 3e \rightarrow N^3$ do not fully follow, since there are no electron donors and free H$^+$ and OH$^-$ ions in deionized water with which oxygen and nitrogen would react.

Under oxidative conditions ($eH > 100$ mV and $rH_2 > 20$), nitrogen fixation is practically absent, regardless of aeration or re-aeration time. In reducing conditions, the lower the ORP of the medium, the higher the ammonium nitrogen concentration, while it should be noted that the reduced medium aeration does not lead to the nitrogen fixation process termination. That is, in a reducing environment, nitrogen fixation practically does not depend on the way the air enters the wastewater, but depends mainly on electron donors and acceptors.

**Main part**

Based on the results of these works, it can be assumed that the electrons presence in the donor system in the absence of strong competitive oxidizing agents occurs, that is, transported through the collector in the reducing environment wastewater characteristic, without the microorganisms participation, the reaction is carried out according to the scheme: $N_2 + 6e^- + 6H^+ = 2NH_3$.

In accordance with the principle of Le Chatelier, when the concentration of dissolved nitrogen changes, as a result of its transition to ammonia (ammonium), in order to comply with the equilibrium system conditions, the processes aimed at compensating for external exposure are enhanced, that is, the dissolution of nitrogen from the gaseous medium is intensified. Considering the fact that ammonia is very soluble in water (one volume of water at room temperature dissolves about seven hundred volumes of ammonia), the process of nitrogen fixation under these conditions is practically not limited by this factor.

In [2], the results of a series of control experiments which confirmed the assumptions about the possibility of a medium with reducing conditions to fix nitrogen were presented. It is shown (Table 1) that media with an indicator of oxidation-reduction properties ($rH_2$) - from 17.0 and less - have a pronounced ability to fix nitrogen-fixing, which is typical of reducing conditions [2].

**Table 2.** The chemical nitrogen fixation indicators in model solutions on ammonia-free water when air is reaerated through the open surface.
### Experimental conditions

| № | Conditions                          | pH  | ORP, [mV] | T, [ºC] | Tcont, [min] | $C_{NH4^+}$, [mg /dm$^3$] | rH$_2$ |
|---|------------------------------------|-----|-----------|---------|-------------|---------------------------|--------|
| 1 | Ammonia-free solution (AF)         | 6.40| 285       | 14.3    | 2           | 0.98                      | 22.46  |
| 2 | Ammonia-free solution              | 6.45| 246       | 14.5    | 10          | 0.86                      | 21.51  |
| 3 | AF + organic solution              | 4.15| -130      | 14.2    | 2           | 13.77                     | 3.74   |
| 4 | AF + organic solution              | 4.05| -120      | 14.5    | 10          | 9.83                      | 3.90   |
| 5 | AF + solution Na$_2$S              | 9.14| -160      | 14.5    | 2           | 8.85                      | 12.67  |
| 6 | AF + solution Na$_2$S              | 9.18| -146      | 14.2    | 10          | 7.75                      | 13.24  |

Notes: 1) the results are the 3 measurements average; 2) the concentration of model water by COD in a mixture of fatty acid (glycerin), amino acids (lysine) and carbohydrate (glucose) was 320 mg / dm$^3$; 3) the concentration of model water for hydrogen sulfide is 5.3 mg / dm$^3$.

In the ammonia-free solution itself, in the electron donors’ absence, regardless of the re-aeration time duration, the increase in ammonium nitrogen concentration is insignificant. The conjugate reactions $O^2_2 + 2 e \rightarrow O^2_2$ and $N_2^0 + 3e \rightarrow N^3$ do not fully follow, since there are no electron donors and free H$^+$ and OH$^-$ ions in deionized water with which oxygen and nitrogen would react.

Under oxidative conditions ($eH> 100$ mV and $rH_2> 20$), nitrogen fixation is practically absent, regardless of aeration or re-aeration time. In reducing conditions, the lower the ORP medium, the higher the ammonium nitrogen concentration, while it should be noted that the aeration of the reduced medium does not lead to the nitrogen fixation process termination. That is, in a reducing environment, nitrogen fixation practically does not depend on the way air enters the wastewater, but depends mainly on electron donors and acceptors.

### Main part

The wastewater nitrogen fixation during transportation process intensification occurs due to sulfur-containing substances microbiological transformation. This is due to the fact that chemical nitrogen fixation occurs under conditions of an oxidizing agents shortage, and the reduced sulfur accumulation compounds causes a decrease in the medium ORP. Figure 1 shows the characteristic values dependences: ORP — sulfide concentration — ammonium nitrogen concentration.

![Graph](image)

**Figure 1.** The nitrogen fixation process indicators dependence on the concentration of sulfides [5]: 1 - rH$_2$; 2 - ORP; 3 - ammonium nitrogen concentration.

It can be seen that the higher the concentration of hydrogen sulfide, the lower the ORP of the medium and the more intense the nitrogen fixation. The ORP change range in wastewater in wastewater systems...
covers the ORP values for which nitrogen fixation is characteristic, therefore, secondary contamination with ammonium nitrogen is in principle possible.

An increase in the ammonium nitrogen concentration and reduced sulfur compounds in wastewater entering biological treatment requires a change in the operating mode of the facilities and, above all, will require additional oxygen consumption in order to implement the nitrification processes, in addition, additional volumes of facilities in which nitrification and denitrification processes are carried out.

As an example, we determined the necessary additional air flow for the aeration process for the nitrification implementation under nitrogen fixation conditions. In the wastewater of village Kushchevskaya in winter, at a temperature of initial wastewater of 7–10 °C, the content of reduced sulfur compounds was 3-5 mg / dm³, the concentration of ammonium nitrogen — 25 mg / dm³. In spring, during the period of rising groundwater levels and increasing infiltration, the temperature of the source wastewater increased to 16-20 °C, the content of reduced sulfur compounds in the wastewater increased to 30-40 mg / dm³, the concentration of ammonium nitrogen was 110.0 mg / dm³ [5].

The ammonium nitrogen concentration in the biological treatment process is reduced due to its assimilation by microorganisms. If we use the ratio of 100 BOD - 5N(NH₄) and if the BOD value in purified water is 10 mgO₂ / dm³, then for the considered example, as a result of assimilation in the first case, the concentration of ammonium nitrogen will decrease to 13.5 mg / dm³, and in the second to 89.5 mg / dm³ Then, in addition, 76 mg / dm³ of ammonium nitrogen should be nitrified. It is known [5] that oxygen consumption during nitrification is 4.57 gO₂ / gN, and during the process "nitrification + denitrification" - 1.71 gO₂ / gN. Consequently, in the considered example, the additional oxygen requirement will amount to 347.32 mg / dm³ for nitrification, and for the nitrification implementation + denitrification processes - 130 mg / dm³. Then the additional specific air consumption for ammonium water purification will be, respectively, 10.7 and 4 m³ / m³.

An additional oxygen amount will also be required for the group of thionic bacteria, the development of which in biological treatment facilities is associated with a high concentration of reduced sulfur compounds in the initial wastewater. It should also be noted that there are critical reduced sulfur compounds concentration values in the wastewater, at which the nitrification process is impossible, since the reduced sulfur compounds are toxic for many groups of bacteria (and above all for nitrifying agents), other than thione, which metabolism is aimed at using data compounds as a substrate.

Regulation of changes in the composition of wastewater in the course of their transportation is practically the only technologically feasible way to ensure the wastewater treatment plants reliability and stability and increase the service life of the collector while reducing the costs and volume of treatment facilities. In England, for example, technical oxygen is pumped into the sewage discharge pipeline for over 30 years, which leads not only to the suppression of sulfate reduction, but also to chemical purification of water from organic pollutants and nitrogen by 65 - 75% [6].

The oxidizers choice principle used for introduction into the reservoir is based on the absence of their toxicity to microorganisms in the wastewater, and, accordingly, on the bacterial mass of activated sludge from epy sewage treatment plants. Hydrogen peroxide corresponds to these conditions as an oxidizing agent; in addition, it is a selective oxidizing agent for the reduced sulfur compounds.

**Discussion**

The studies determining the hydrogen peroxide low doses effect on the change in the ORP values characteristic of wastewater entering the treatment plant without prior treatment in the collector have been conducted. In the initial wastewater, the ORP value was determined, after which 5 mg / l 30% hydrogen peroxide was injected. Then for a long time, the ORP value change was determined, preventing the air oxygen access to the wastewater (Table 2).

| Settling-vat DW | Research duration, hour |
|----------------|------------------------|

**Table 3.** Process parameters in the system “raw drainage water without treatment” + hydrogen peroxide, dose 5 mg / dm³.
The results of the study show that the dose (5 mg / dm³) of hydrogen peroxide makes it possible to keep the initial ORP value (-291: -285 mV) along the sewage flow in the collector for a long time (27 hours), much longer than their transportation to the sewage treatment plant duration.

The purpose of further research was to determine the sulfur using oxidation reduced forms removal effectiveness with hydrogen peroxide to prevent and regulate nitrogen fixation during the wastewater movement to sewage treatment plants. The reduced sulfur compounds concentration determination in water was carried out according to the standard technique: pH adjustment to 4 and titration.

The minimum dose of H₂O₂ was determined by the stoichiometric ratio of the coefficients of the corresponding reaction equations given below:

\[ 2\text{HS}^- + 5\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} + 2\text{H}^+ \] (specific coefficient - 2.57);

\[ 2\text{HS}^- + \text{H}_2\text{O}_2 \rightarrow 2\text{S}_\text{\downarrow} + 2\text{H}_2\text{O} \] (specific coefficient - 0.27);

\[ \text{H}_2\text{S} + 4\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 + 4\text{H}_2\text{O} \] (specific coefficient - 4.0).

Thus, the estimated dose of hydrogen peroxide for wastewater can be determined by the expression:

\[ D_{\text{H}_2\text{O}_2} = K_p \cdot (K_{\text{HS}^-} \cdot C_{\text{HS}^-} + K_{\text{H}_2\text{S}} \cdot C_{\text{H}_2\text{S}}), \]

where \( K_{\text{HS}^-} \) and \( K_{\text{H}_2\text{S}} \) are the stoichiometric coefficients equal to 2.57 and 4.0, respectively; \( C_{\text{HS}^-} \) and \( C_{\text{H}_2\text{S}} \) is the hydrogen sulfide derivatives concentration of in the HS⁻ and H₂S forms; \( C_f \) - correction factor taking into account the increase in the actual dose of hydrogen peroxide relative to the calculated.

\( C_f \) value was determined empirically. For research, wastewater with a concentration of reduced sulfur compounds of 9.35 mg / dm³ was used. Based on the hydrogen sulfide derivatives forms ratio, depending on the pH of the water, with the initial concentration (HS⁻ + H₂S) - 9.35 mg / dm³, and taking into account the fact that when the pH value of water is 7, about 47.65% of the reduced sulfur compounds accounts for hydrosulfide (HS⁻) and 52.35% - for H₂S, then the calculated dose of H₂O₂ will be equal to:

\[ D_{\text{H}_2\text{O}_2} = 2.57 \cdot 4.455 + 4 \cdot 4.895 = 31.03 \text{ mg / dm}^3. \]

The following doses were taken in the experiment, mg / dm³: 15; 20; 30; 40, the contact time was chosen 0 and 30 minutes. The results of the research are presented in Table. 3

**Table 4.** The results of studies on the purification of water from reduced sulfur compounds

| Initial concentration of hydrogen sulfide, [mg / dm³] | Dose H₂O₂, [mg/dm³] | Contact time, [min] | H₂S concentration in treated water, [mg / dm³] |
|-----------------------------------------------------|----------------------|---------------------|-------------------------------------------|
| -                                                   | -                    | -                   | 9.35                                      |
| 9.35                                                | 15                   | 0                   | 9.16                                      |
|                                                     |                      | 30                  | 4.21                                      |
|                                                     | 20                   | 0                   | 9.13                                      |
|                                                     |                      | 30                  | 2.48                                      |
|                                                     | 30                   | 0                   | 9.30                                      |
Thus, for purifying water with an initial concentration of reduced sulfur compounds (HS\(^-\) + H_2S) - 9.35 mg / dm\(^3\), pH = 7.0, the optimal dose is 35 mg / dm\(^3\). Consequently, the correction factor, C\(_f\), is 1.3. Then the expression for determining the optimal dose of H\(_2\)O\(_2\) in the oxidation of reduced sulfur compounds in wastewater will take the form: 
\[ D_{H_2O_2} = 1.3 \cdot (2.57 \cdot C_{HS^-} + 4 \cdot C_{H_2S}), \text{ mg / dm}^3 \]

Hydrogen peroxide is an oxidizing agent, and, despite the fact that its action is selectively aimed at the reduced sulfur compounds oxidation, it is advisable to assess the effect on the process of organic matter content (COD, mgO / l (chemical oxygen demand), because in real wastewater hydrogen sulfide organic and nitrogen pollution is presented and oxidized simultaneously (Table 4).

Content in the initial wastewater: (HS\(^-\) + H\(_2\)S) - 14.14 mg / dm\(^3\); COD = 299.4 mgO / dm\(^3\). Exposure is 15 min.

| Hydrogen peroxide dose, [mg / dm\(^3\)] | HS\(^-\) + H\(_2\)S in drainage water after treatment, [mgO/dm\(^3\)] | Drainage water COD after treatment, [mgO / dm\(^3\)] |
|----------------------------------------|-------------------------------------------------|---------------------------------------------------|
| 30                                     | 2.7                                            | 254.5                                             |
| 56                                     | 2.41                                           | 216.2                                             |
| 70                                     | 2.12                                           | 199.6                                             |
| 90                                     | 1.89                                           | 166.3                                             |

The research results confirm the simultaneous oxidation of the reduced sulfur compounds and the reduction in COD by an average of 15–45%, depending on the hydrogen peroxide dose.

Figure 2. The nitrogen fixation dependence in wastewater from the hydrogen sulfide content
The generalized dependence of nitrogen fixation, i.e., ammonium nitrogen content on the amount of reduced sulfur compounds (Figure 2) has a high event probability value \( P = \sqrt{R^2} = 0.83 \) - 0.91, which characterizes the reliability of ratios. At the developing technical solutions stage, using the obtained dependence, it is possible to estimate the wastewater nitrogen fixation during transportation regulation economic component from preventing sulfate reduction by treatment with hydrogen peroxide.

**Summary**

Hydrogen peroxide has been shown theoretically and experimentally to be an environmentally friendly oxidizer in the wastewater pretreatment technology in order to prevent and regulate corrosion processes in the systems and structures transporting wastewater, as well as nitrogen fixation and can be recommended for practical use.

**References**

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