Methods for removing reduced sulfur compounds from groundwater

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Abstract. Reduced sulfur compounds contained in natural waters adversely affect human health in wastewater, cause corrosion of collector materials and structures, and inhibit biological treatment processes. The methods to reduce the reduced sulfur compounds concentration in natural and waste waters are quite well known, however, in each case, in accordance with the requirements for the quality of treatment and the initial concentration of reduced sulfur compounds, it is necessary to adapt the methods used. This article presents the results of studies on the removal of reduced sulfur compounds from groundwater. The results of the reduced sulfur compounds oxidation method with hydrogen peroxide to sulfates with aeration and without aeration of the treated water are presented, as well as the results of studies on colloidal sulfur coagulation resulting from the incomplete oxidation of the reduced sulfur compounds. The expediency of using the reduced sulfur compounds of hydrogen peroxide with simultaneous aeration of the treated water as an oxidizing agent is shown. It was established that the contact duration of the treated water containing the reduced sulfur compound with hydrogen peroxide, both with and without simultaneous aeration, should be at least 30 minutes. The results of experiments on the colloidal sulfur coagulation are also presented, indicating that the use of sodium hydro-aluminate in proportion to aluminum sulfate, which ensures the ratio $[\text{OH}^{-}]:[\text{Al}^{3+}] = 0.5$, allows not only to achieve results in water purification with bringing the quality to the standards for drinking water, but also to reduce the coagulant dose in its active part by 30%, compared to other options. It has been analytically established that when using aluminum oxy sulfates or oxy chlorides for coagulation of colloidal sulfur, it is advisable to use the low-base coagulants.

Introduction
The presence of the reduced sulfur compounds in the treated water largely determines the technology of water preparation or water treatment, which is associated with the need to remove these compounds from the treated wastewater or natural water. In accordance with the requirements of the World Health Organization (WHO), the permissible content of hydrogen sulfide in drinking water is 0.05 mg/dm$^3$. Hydrogen sulfide is toxic to humans, as it inhibits cellular redox processes. The effect of the reduced sulfur compounds on wastewater systems is associated with their toxicity to microorganisms; the recommended sulfide concentrations in wastewater are no more than 1 mg / dm$^3$; at higher concentrations, biological treatment processes are disrupted up to their cessation. The reduced sulfur compounds have high corrosivity to concrete and metals, which leads to the structures and materials destruction of the systems transporting waste water. An analysis of literature indicates that various
technological methods for preventing the negative consequences of the hydrogen sulfide presence in wastewater or natural waters start even at the stage of wastewater transportation, as well as in the development of technological methods for treating natural or wastewater, both domestic and industrial [1]. It is also advisable to use the data on the hydrogen sulfide system and the forms redox potential dependence to select the purification methods [2].

Reduced sulfur compounds in natural or wastewater may be in the form of undissociated molecules H₂S, HS⁻, hydrosulfide ions and sulfide ions S²⁻. The ratio between the concentrations of these forms is determined by the values pH water. So, with the values pH 4 to 6, predominantly present in water H₂S, at pH values from 7.5 to 9.0, the form HS⁻ dominates and at pH values above 10, the form S²⁻ dominates [3, p. 13]. For most natural and domestic wastewater, the pH value is in the range of 6 - 8, therefore, reduced sulfur compounds are present, as in the form H₂S (at pH =6 – 91.8% and at pH = 8 –10,1%), and in the form HS⁻ (at pH= 6 – 8,2% and at pH = 8 – 89.9 %).

The main technological methods for the reduced sulfur compounds removal include:
- aeration with pre-acidification of the system to pH value less than 5;
- electrooxidation. The process is carried out in electrolysers with and without a diaphragm. In addition to the main processes of electrooxidation and reduction, electro-flotation, electrophoresis and electrocoagulation can occur simultaneously;
- chemical oxidation. Chlorine, calcium and sodium hypo chlorites, bleach, ozone, hydrogen peroxide, potassium permanganate can be used as chemical oxidizing agents. The amount of reagent affects the chemical reactions products after their interaction with hydrogen sulfide. So, at a specific consumption of chlorine of 2.1 mg, hydrogen sulfide is oxidized to sulfur, and at a specific consumption of 8.4 mg - to sulfates. With a specific consumption of 0.5 mg ozone, hydrogen sulfide is oxidized to sulfur, with a specific consumption of 1.87 mg ozone to sulfates. Recently, the studies have been carried out and the method of oxidizing reduced sulfur compounds with hydrogen peroxide was put into practice, which is a selective oxidizing agent with respect to hydrogen sulfide and sulfides. It has a chemical inertness with respect to ammonium and organic compounds, which will not increase the reagent dose when treating the waters containing high concentrations of reducing agents. Hydrogen peroxide also has several advantages: it is highly soluble in water, stable in solution in a wide range of pH and temperature, stable compared to other oxidizing agents, non-toxic;
- coagulation. When a suspension of iron oxide hydrate is added to hydrogen sulfide water, hydrogen sulfide and hydrosulfide ions are bound to form iron sulfide. The precipitate of iron sulfide is separated from the water by settling, after which it can be regenerated by blowing air; iron or aluminum salts coagulation with a sulfur hydrosol formed during the reduced sulfur compounds oxidation;
- oxidation by microorganisms. During biochemical purification of water from hydrogen sulfide, its oxidation occurs as a result of the activated sludge and biofilm sulfur bacteria activity.

Depending on the content and specificity of pollutants, methods for their removal from water, and also on the concentration of the reduced sulfur compounds, the possibility and necessity of hydrogen sulfide and hydrosulfide complete oxidation to sulfates or the expediency of their oxidation to elemental sulfur with subsequent precipitation during coagulation are considered.

Thus, the studies aimed at determining the optimal solutions when choosing a method of purification from the reduced sulfur compounds are relevant. This article presents the studies’ results on the reduced compounds removal from groundwater, but this experience can be used both in the treatment of surface water including industrial wastewater.

**Research methods**

This article presents the results of the studies on the reduced sulfur compounds oxidation with hydrogen peroxide to sulfates with aeration and without aeration of the treated water, as well as the results of the studies on the coagulation of a sulfur hydrosol formed during the reduced sulfur compounds’ incomplete oxidation.
The purpose of this research is to study the specifics of the reduced groundwater sulfur compounds oxidation with hydrogen peroxide and determine the optimal doses and type of coagulant used to coagulate colloidal sulfur.

To achieve this goal, the following tasks were solved:
1. Empirical studies were performed to determine the effect of aeration, the dose of hydrogen peroxide and the duration of the process on the reduced sulfur compounds oxidation efficiency;
2. Empirical studies have been performed to optimize the process of coagulation of a sulfur hydrosol with aluminum-containing coagulants.

The research results were evaluated by the following criteria: residual concentration of the reduced sulfur compounds (in terms of hydrogen sulfide), residual turbidity of water, pH, concentration of residual aluminum. Standard parameters were used to determine the parameters.

The pH of the system was determined using a standard ionomer EV-74. The concentration of the reduced sulfur compounds was determined according to the method RD 52.24.450-2010 “Mass concentration of hydrogen sulfide and sulfides in water. Measurement procedure by photometric method with N, N-Dimethyl -n- phenylenediamine”. The residual aluminum concentration determination in the samples was carried out in accordance with the method according to GOST 18165-2014 “Water. Methods for determination of aluminum content”. The residual filtrate turbidity was determined according to the method of GOST R 57164-2016 “Drinking water. Methods for the determination of smell, taste and turbidity”. The optimal dose of coagulants was determined empirically by coagulation in free volume in accordance with the method of GOST R51642-2000 “Coagulants for drinking water supply. General requirements and method for determining effectiveness”.

Oxidation of the reduced sulfur compounds with hydrogen peroxide proceeds according to the following reaction equations:

\[2HS^- + 3H_2O_2 => 2H_2SO_4 + 2H_2O + 2H_2O \ \text{(specific coefficient} = 2.57)\]
\[2HS^- + H_2O_2 => 2H_2O + 2H_2O \ \text{(specific coefficient} = 0.51)\]
\[H_2S + 4H_2O_2 => H_2SO_4 + 4H_2O \ \text{(specific coefficient} = 4.0)\]

To solve the tasks, the results of preliminary studies were used, so the equation for determining the optimal dose \(H_2O_2\) when treating groundwater from reduced sulfur compounds, looks like [4]:

\[D_{H2O2} = 1.35 \cdot (2.57 \cdot C_{HS^-} \cdot 4 \cdot C_{H2S}).\]

For further research, underground water from a well located in the territory of Kushchevskaya village of the Krasnodar Territory. In the source water, the reduced sulfur compounds concentration is 13.6 mg/l dm³, \(pH=7.35\). Taking \(pH\), \(C_{H2S}\) is 26%, \(C_{H2S} = 3.5 \text{ mg/dm}^3\) into consideration, the concentration is \(C_{HS^-} = 10.1 \text{ mg/dm}^3\) accordingly (sulfide ion at this \(pH\) value is absent). The calculated dose of hydrogen peroxide in this case will be 55.9 mg/l dm³. The studies were carried out as follows: in a beaker with a volume of 1000 cm³ initial water, which was exposed in accordance with the experimental design was placed; during the next 30 minutes, \(pH\) changes and the reduced sulfur compounds concentration were recorded. Four series of experiments were performed.

The first series of experiments determined the control variant; changes in the reduced sulfur compounds concentration occurred spontaneously, without introducing an oxidizing agent into the sample and without aeration; the second series of experiments made it possible to determine the aeration effect on oxidation processes. The third series of experiments determined the effectiveness of hydrogen peroxide, and the fourth series of experiments determined the effectiveness of reducing the reduced sulfur compounds concentration during their oxidation with hydrogen peroxide with simultaneous aeration. Data on the average test results are presented in Table. 1.

| t, min | Concentration of reduced sulfur compounds, C (HS^- + H_2S), mg/dm³/pH |
|-------|---------------------------------------------------------------|
| Control (without reagent input and without aeration) | with aeration | with input \(H_2O_2\), \(D = 53.9 \text{ mg/dm}^3\) no aeration | with input \(H_2O_2\), \(D = 53.9 \text{ mg/dm}^3\) and with aeration |
The results’ analysis indicates the advisability of aerating water during the reduced sulfur compounds oxidation with hydrogen peroxide. Contact duration should be no less than 30 minutes.

If in water, in addition to the reduced sulfur compounds, there are other impurities that are well removed by coagulation, for example, suspended solids, compounds containing iron, including organo-mineral complexes, etc., it is advisable to carry out the purification in two stages, in the first stage, carry out oxidation with hydrogen peroxide with simultaneous aeration of the reduced sulfur compounds to elemental sulfur, coagulate the hydrosol in the second stage. This method will significantly reduce the dose of hydrogen peroxide and remove all impurities of colloidal degree of dispersion from the purified water. The effectiveness of coagulants in the removal of colloidal sulfur corresponds to the following formula:

\[ \text{Na}_2\text{Al}_2\text{O}(\text{OH})_6 + \text{H}_2\text{O} = 2\text{Al} (\text{OH})_3 + 2\text{NaOH} \]

It is known that in water, in addition to elemental sulfur, there are other impurities that are well removed by coagulation, for example, suspended solids, compounds containing iron, including organo-mineral complexes, etc., it is advisable to carry out the purification in two stages, in the first stage, carry out oxidation with hydrogen peroxide with simultaneous aeration of the reduced sulfur compounds to elemental sulfur, coagulate the hydrosol in the second stage. This method will significantly reduce the dose of hydrogen peroxide and remove all impurities of colloidal degree of dispersion from the purified water. The effectiveness of coagulants in the removal of colloidal sulfur corresponds to the following formula:

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When oxidizing the reduced sulfur compounds with hydrogen peroxide to colloidal sulfur, the concentration of the latter was 12.6 mg/dm³, the turbidity was 25.6 mg/dm³.

The coagulant dose was determined by the trial coagulation. Eight series of studies were performed with four repetitions. The average results for each series are presented in Table 2.

**Table 2.** The results of a study on the sulfur hydrosol coagulation effectiveness

| Dose Al₂O₃, mg/dm³ | Dose Na₂CO₃, mg/dm³ | Dose SHA Al₂O₃, mg/dm³ | AS: SHA Al₂O₃, (OH⁻)/[Al³⁺] | Filtrate Turbidity, M, mg/dm³ | pH | Residual concentration Al³⁺, mg/dm³ |
|-------------------|--------------------|------------------------|-----------------------------|-----------------------------|----|-------------------------------|
| 59.63             | 227.9              | -                      | (3.67)                      | 2.0                         | 7.10 | 0.74                          |
| 29.05             |                    | 30.58                  | 0.95:1 (2.05)               | 2.1                         | 7.15 | 0.67                          |
| 29.82             | 69.43              | -                      | (2.26)                      | 2.3                         | 7.40 | 0.89                          |
| 14.91             |                    | 14.91                  | 1:1 (2)                     | 1.8                         | 7.90 | 0.85                          |
| 14.90             |                    |                        |                             | 4.70                        | 6.5  | 1.40                          |
| 13.80             |                    | 16.02                  | 1:1.16 (2.08)               | 1.10                        | 7.9  | 0.82                          |
| 11.92             |                    | 2.98                   | 4:1 (0.79)                  | 2.60                        | 7.5  | 0.45                          |
| 13.03             |                    | 1.86                   | 7:1 (0.5)                   | 2.60                        | 7.6  | 0.58                          |
| 26.00             |                    | 3.71                   | 7:1 (0.5)                   | 1.20                        | 7.9  | 0.23                          |

According to the research results analysis, it is possible to say that the best result was achieved when the dose ratio of AS: SHA for alumina was 1: 7, which corresponds to the ratio [OH⁻]/[Al³⁺] = 0.5, at the total dose of the active part is Al₂O₃= 29.7 mg/dm³. With the same ratio [OH⁻]/[Al³⁺] = 0.5, but the total dose for Al₂O₃= 14.9 and the turbidity of the filtrate and the concentration of residual aluminum in the filtrate exceeded the permissible values. At a total dose Al₂O₃=29.82, but the ratio [OH⁻]/[Al³⁺] = 2, the filtrate quality also does not meet the requirements for drinking water.

Thus, it can be argued that the sulfur hydrosol coagulation is effective in the case of a sufficient dose of the coagulant in the active part, and the use of SA and SHA in ratios at which [OH⁻]/[Al³⁺] = 0.5.

The above can be explained by composing the formulas for the sulfur hydrosol micelles formation and the formulas for the aluminum hydroxide hydrosol micelles formation when only aluminum sulfate is used for coagulation and when aluminum sulfate and sodium hydro-aluminate are used together.

The colloidal sulfur micelle formula has the form:

\[
\{m[S]\cdot nSO_4^{2-}\cdot (n-x)\cdot Cd^{2+}\}_{x}\cdot xCa^{2+}
\]

The equation for the aluminum sulfate hydrolysis:

\[
Al_2(SO_4)3+6H2O =2Al(OH)3+ 3H2SO4;
\]

The micelle formula has the form:

\[
\{m[Al (OH)3]\cdot 2nH^+\cdot((n-x) \cdot SO_4^{2-})_{2x}\cdot xSO_4^{2-};
\]

The aluminum sulfate and sodium hydro aluminate joint hydrolysis equation:

\[
Al_2(SO_4)3+3 Na2Al2O(OH)6 + 9H2O =8Al(OH)3+ 6NaOH+ 3H2SO4
\]

In this case, the micelle structure will have the following form:

\[
\{m [Al (OH)3]\cdot 2nH^+\cdot((n-x) \cdot OH^- + (n-y) \cdot SO_4^{2-})^{2+n+x}\cdot (xOH^-\cdot ySO_4^{2-}).
\]

The effectiveness of the combined use of AS and SHA is apparently due to a significant decrease in the sulfate ion concentration, since sulfate ion is a stabilizing ion for sulfur hydrolysis, as well as a change in the structural formula of the hydrosol Al(OH)₃ in the double electric layer and in the diffuse layer, which is associated with a predominance of ion concentration OH⁻ over ion concentration SO₄²⁻ and with greater ion mobility OH⁻ compared with SO₄²⁻.
Currently, a significant amount of aluminum-containing coagulants with different basicity moduli B is produced:

\[ B = \left( \frac{[OH^-]}{3[Al^{3+}]} \right) \cdot 100\%, \]

where basically the ratio of the hydroxyl and aluminum molar contents, expressed as a percentage; \([OH^-]\) is the hydroxyl content, mol; \([Al^{3+}]\) is the aluminum content, mol; 3 is the aluminum valency.

For a different ratio \([OH^-]: [Al^{3+}]\) when using AS and SHA, it is possible to determine the indicator B. So, for \([OH^-]: [Al^{3+}] = 0.43, B = 14\%; \) for \([OH^-]: [Al^{3+}] = 0.54, B = 18\%; \) for \([OH^-]: [Al^{3+}] = 0.98, B = 33\%; \) for \([OH^-]: [Al^{3+}] = 2.05, B = 68\%.

Based on the above shown calculations, it is possible to say that when using the coagulants available on the market, the coagulants with a low degree of basicity should be used for sulfur hydrosol coagulation, for example, it is inappropriate to use Aqua-Aurat 10 with a basicity of 67\%, brand coagulant Epoche™ with a basicity of 40 to 83\%. GranEKOTM, with a basicity of 65 to 83\%, Aqua-Aurat 30 with a basicity of 33\%.

It is advisable to use aluminum sulfate together with sodium hydro-aluminate, which will allow not only to achieve the standard values for the treatment quality, but also to reduce the coagulant dose in the active part by more than 30\%.

**Summary**

1. In the process of performing the work, the expediency of using the reduced hydrogen peroxide sulfur compounds with simultaneous aeration of the treated water was shown as an oxidizing agent.
2. The contact duration of the treated water containing the reduced sulfur compound with hydrogen peroxide both with simultaneous aeration and without aeration should be at least 30 minutes.
3. The SHA use makes it possible to improve the colloidal sulfur coagulation process while reducing the coagulant consumption for alumina by 30\%.
4. The doses of aluminum sulfate and sodium hydro-aluminate in the active part (aluminum oxide) should be determined by the trial coagulation results and be based on ensuring the ratio \([OH^-]: [Al^{3+}] = 0.5\).
5. When using aluminum oxy-sulfates or oxychlorides for coagulation of colloidal sulfur, it is advisable to use the low-base coagulants.

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