Removal of sulfides from tannery-sourced wastewaters

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Abstract. The paper presents the study results for the treatment of sulfide wastewater generated by tanneries. Wastewater treatment was carried out by electrolysis with a sacrificial ferrous anode. It is shown that during the treatment process, the ferrous anode dissolves and deposition of iron sulfide is formed. The process of effluent treatment is determined by the anode current density. The most efficient effluent treatment is carried out at a current density of 133 A/m². In this case, the purification efficiency reaches 99.2%, and the cost per unit of electricity makes 169.2 kW·h/kg.

1. Introduction
Sulfide wastewater treatment is relevant, especially for the tanning industry. The process solution used for leather liming includes sodium sulfide. After the operation of liming, the concentration of sodium sulfide reaches 8-10 g/l and, as a rule, the spent solution is discharged into the effluent. Lowering the concentration of sulfides in the effluent occurs mainly due to dilution when combining wastewater from various technological shop floors. In this case, quite often the concentration of sulfides in wastewater exceeds its maximum permissible value, which is equal to 0.003 mg/l [1].

From the literature, it is known that there are a number of methods to purify the wastewater from sulfide-containing compounds. The method of oxidation of sulfide ions by various oxidizing agents is the most widely applied, where ozone, chlorine, oxygen, hydrogen peroxide, and ammonium persulfate are used [2-6]. All of these methods involve the use of chemical reagents.

The oxidation of sulfides to sulfates by electrochemistry with anodes from PbOₓ, TiO₂, IrOₓ, Pt is possible [7, 8].

As is known, sulfides of many metals are sparingly soluble compounds [9]. It is attractive for its use in the sulfide-containing effluents treatment. In particular, iron can be used for this purpose by setting iron ions in solution by anodic dissolution [10]. The iron sulfide deposition formed during the process can be recycled at metallurgical plants.

The purpose of this work was to study the regularities of sulfides extraction from a solution by treating in an electrolyzer with a ferrous anode.

2. Materials and research methods
The experiments were carried out both with model solutions of sulfide effluent, containing from 30 mg/l to 200 mg/l of sodium sulfide, and with the wastewater of the Sterlitamak leather and footwear work. The electrolyzer was a reservoir with iron electrodes.

Power was supplied from a controlled rectifier, which allows varying the current load. The volume of the treated solution in all experiments remained constant and was of 300 ml.
3. Experimental results and discussion

The operation of the electrolysis plant was investigated at electrode current densities of 67, 133, 200 and 267 A/m². The dependence of sulfide concentration in the effluent on the time of its treatment in the electrolyzer is shown in Figure 1. It can be seen that when the effluent treatment time in the electrolyzer increases, the concentration of sulfides in it decreases. Moreover, the rate of extraction of sulfides from wastewater in the form of iron sulfide deposits is different at different electrode current densities. An increase in current load on the apparatus from 67 A/m² to 133 A/m² leads to an increase in the extraction rate. A further increase in the current load leads to a decrease in the rate of extraction of sulfides from the effluent.

Figure 1 shows the dependence of sulfide concentration in the effluent on the processing time.

Figure 2 shows the dependence of sulfide concentration in the effluent on the quantity of electricity passed through the solution. It should be noted that the experiment results were divided into two areas. So, to achieve the same concentration of sulfides in the waste water with a current density of 133 A/m², is needed less electricity than with other current densities.

The dependence of the extraction ratio of sulfides from wastewater on the electrode current density is shown in Figure 3. The effluent treatment time in the electrolyzer in these experiments was the same and made 40 minutes. It is evident that a change in the electrode current density leads to a change in the extraction ratio of sulfides from the effluent. The maximum value of the extraction ratio of 99.2% is achieved at a current density of 133 A/m².
Figure 2. Dependence of sulfide concentration in the effluent on the quantity of electricity

Figure 3. The dependence of the sulfides extraction ratio on the current density

Obviously, such behavior of the sulfide recovery process is associated with the following. The bivalent iron ions entering the solution due to an anodic dissolution react with sulfide ions, forming a deposition of iron sulfide, the main mass of which precipitates on the anode surface. Consequently, two processes will determine the rate of iron sulfide formation: the process of iron anodic dissolution, and the transport of iron ions and sulfide into the zone of iron sulfide formation. The rate of mass transfer of ions in the electrolyte volume, determined by convective currents, is rather high. Therefore, the anodic dissolution of iron and the diffusion of iron ions and sulfide through the layer of iron sulfide deposit
covering the anode will be limiting. The course of the curves shown in Figures 1-3 indicates that at a current density of 67 A/m², the iron dissolution from the anode will be the limit, and at current densities of 200 A/m² and higher, the diffusion of ions through the deposit layer of iron sulfide. This is also indicated by the formation of an iron hydroxide deposition, observed as yellow-brown inclusions in the mass of black iron sulfide deposition. Obviously, at a current density of 133 A/m², the rate of iron dissolution from the anode and the rate of diffusion of ions through the layer of iron sulfide deposition will be fairly close.

Figure 4 shows the dependence of the concentration of sulfides in the treated effluent on its concentration in the waste water before treatment. The electrode current density in these experiments was 133 A/m², and the treatment time in the electrolyzer makes 40 minutes. It can be seen that this dependence is linear. Moreover, a change in the sulfides concentration in the effluent from 30 to 200 mg/l corresponds to a change in the sulfides concentration in the purified water from 0.08 to 1.97 mg/l.

![Figure 4. Dependence of sulfide concentration after purification on initial concentration](image)

Since the economic indicators play an important role in the implementation of any process, it was investigated the dependence of the electricity expenditures in the process of extraction of sulfides from wastewater on the technological parameters. The data are shown in the table 1.

**Table 1. Dependence of energy consumption at removal of 1 kg of sulfides on current density**

| Current density, A/m² | Energy expenditures, kW⋅h/kg |
|-----------------------|------------------------------|
| 67                    | 75.8                         |
| 133                   | 169.2                        |
| 200                   | 379.2                        |
| 267                   | 653.3                        |

As it should be expected, when in the current load on the electrolyzer is increased, the power consumption for the sulfide extraction also increases. Thus, with a volume of wastewater containing sulfides at the Sterlitamak leather and footwear works of 45 m³/day and containing up to 30 mg/l of sulfides, the power consumption during the treatment process in an electrolyzer with an electrode current density of 133 A/m² will be 228 kW⋅h/day.
4. Conclusion
From the results presented in the paper, it follows that in the electrolyzer with a sacrificial iron anode, the sulfides are removed from the solution as an iron hydroxide deposition. The treatment process is determined by the anode current density. The optimum current density makes 133 A/m$^2$. Obviously, in this case, the process of iron dissolution of and the process of sulfides diffusion through the layer of FeS sediment covering the surface of the anode are in equilibrium. The purification efficiency under these conditions reaches 99.2%.

5. Acknowledgements
This scientific paper was prepared on basis of research work within the government work No. 5.12863.2018 / 8.9 of the Russian Federation.

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