Efficient treatment of wastewater from galvanic plants

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Abstract. The article discusses a promising method for the purification of chromium-containing wastewater from galvanic plants. A review and comparative analysis of existing methods and technologies for treatment of industrial waste from various organochromium compounds, such as reagent-based, biological, ion-exchange and others, are presented. The advantages of using the combined method of chromium-containing wastewater treatment based on electroflotation with preliminary electrocoagulation are shown. The effectiveness of the proposed combined method is evaluated and the design of electroflotocoagulator is developed.

1. Introduction
Recently, in our country and abroad, the development of environmental safety ideas is one of the important tasks of environmental control, which is also necessary to increase production capacity [1-10]. One of the important factors of economic efficiency of technological processes is a closed water use system with water condition monitoring devices [11-21]. This reduces emissions of harmful and toxic substances into the environment. At present, many methods and instruments have been developed to control emissions of various toxic substances into the environment as well as into the water [3-6, 8, 19, 22-29]. New methods of water treatment and control using optical and electromagnetic radiation have been proposed [27, 30-37]. But the development of industry poses more complex problems to scientists [38-41]. This requires research to find new solutions to these problems.

One of the problems of water treatment is the neutralization of chromemulsion wastewater of galvanic production. The chromium-containing wastewater flow of such productions is a complex system, including acids, alkalis, hard-to-oxidize organic compounds, and various mechanical impurities. The neutralization of this category of effluents is a complex and urgent problem today, especially in small towns where such production facilities are located [42, 43]. This problem is of particular importance for the adoption by the world economy of the principles of sustainable development, which ensure a balance between solving socio-economic problems and preserving the natural environment.

2. Analysis of the effectiveness of methods and schemes for the treatment of chromium-containing wastewater
Chromium-containing wastewater from manufacturing enterprises has a complex composition, so the treatment method should be chosen based on the composition and nature of the contamination.
In practice, when the initial concentration of chromium in wastewater is high, it is recommended to remove it in two stages. At the first stage (coarse treatment) the main mass of chromium compounds is removed from the wastewater, at the second stage (deep treatment) the treated liquid is brought up to standard. The first stage of treatment of such wastewater also consists of two stages:
- conversion of Cr(VI) to less toxic Cr(III)
- precipitation of Cr(III) as a hydroxide

Sodium salts of sulfuric acid are most widely used as reducing agents. Namely sulfite (Na₂SO₃), hydrosulfite (NaHSO₃), pyrosulfite (sodium pyrosulfite), sodium metabisulfite (Na₂S₂O₅), and sodium thiosulfate (Na₂S₂O₃) [44].

Deep treatment (post-treatment) can be carried out by treating the liquid with a mixture of reagents, as well as by electrodialysis, reverse osmosis and/or sorption materials. Reagent methods of chromium-containing wastewater treatment involve the reduction of Cr(VI) compounds to Cr(III) and the precipitation of the latter in the form of insoluble compounds (usually Cr(III) hydroxide).

The reduction of Cr(VI) to Cr(III) in an acidic environment occurs as follows:
- reduction with sodium sulfite
  \[ \text{Cr}_2\text{O}_7^{2-} + 3\text{SO}_3^{2-} + 8\text{H}^+ = 2\text{Cr}^{3+} + 3\text{SO}_4^{2-} + 4\text{H}_2\text{O}; \]  
- reduction with sodium bisulfite
  \[ \text{Cr}_2\text{O}_7^{2-} + \text{HSO}_3^- + 5\text{H}^+ = 2\text{Cr}^{3+} + 3\text{SO}_4^{2-} + 4\text{H}_2\text{O}; \]  
- reduction with sodium pyrosulfate
  \[ \text{Cr}_2\text{O}_7^{2-} + 3\text{S}_2\text{O}_5^- + 10\text{H}^+ = 4\text{Cr}^{3+} + 6\text{SO}_4^{2-} + 5\text{H}_2\text{O}; \]  
- reduction with sodium thiosulfate
  \[ \text{Cr}_2\text{O}_7^{2-} + \text{S}_2\text{O}_3 + 4\text{H}^+ = 2\text{Cr}^{3+} + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O}. \]

The theoretical amounts of reducing agents are usually 3.63 for sulfite, 3.0 for bisulfite, 2.88 for pyrosulfate, 1.67 for sodium dithionite. All values are given in terms of mg / 1 mg Cr⁶⁺.

Sulfurous acid salts are introduced into wastewater in the form of 10% aqueous solutions. The amount of reducing agent depends on the initial concentration of Cr⁶⁺ in the wastewater and the pH value. The rate and completeness of the reduction reactions of Cr⁶⁺ to Cr³⁺ also depend to a large extent on the pH value of the reaction mixture. The optimal rate of reduction reactions is achieved in an acidic environment at pH = 2.0-2.5. For this purpose, wastewater is additionally acidified with 10-15% sulfuric acid solution. It should be noted that it is possible to use solutions of other mineral acids.

The disadvantages of this method include:
- easy oxidizability of the reducing agent during storage, which complicates the correct dosage and leads to its increased consumption
- reduction in acidic media, which requires additional consumption of acid for acidification.

Biological, ion-exchange and other methods of wastewater treatment from chromium-containing compounds can be carried out using biological, electrochemical, and ion-exchange processes, as well as electrodialysis and reverse osmosis. The high accumulative capacity of microalgae in relation to heavy metals creates the prospects for their use in wastewater treatment. Existing experience in biotechnology shows that the accumulation efficiency reaches 95%. Bacteria capable of transforming highly toxic hexavalent chromium into low toxic chromium include bacteria of the genera Pseudomonas, Aeromonas, and Escherichia. They can tolerate the concentration of Cr⁶⁺ ions above 200 mg/l, with a purification time of 1 to 3 days. When the concentration of chromates is increased to 350 and 500 mg/l, the purification time increases to 20 and 60 days, respectively.

Electroflotation refers to electrochemical treatment methods. The process is based on the formation of gas bubbles during electrolysis. Oxygen bubbles occur at the anode and hydrogen bubbles at the cathode. The gas bubbles obtained in this way float into the liquid and interact with contaminant
particles, resulting in their mutual adhesion due to a decrease in surface energy of the flotated particle and the gas bubble at the gas-liquid interface.

Electrocoagulation is one of the methods of transferring impurities from the colloidal dispersions to the coarse dispersed state. This method is based on a variety of physical and chemical processes occurring in a liquid under the influence of an electric current. In the process of electrocoagulation, aluminum or iron anodes are dissolved, leading to the formation of metal hydroxides, which act as coagulants. When chromium-containing waste passes through the interelectrode space, electrolysis occurs. As a result of electrolysis, the electrolyte components are reduced or oxidized at the electrodes.

The electrocoagulation process is influenced by the material of the electrodes, the distance between them, the speed, temperature and composition of the wastewater, voltage and density of the current. As the concentration of suspended solids increases above 100 mg/l, the efficiency of electrocoagulation decreases. Reducing the distance between the electrodes results in lower energy consumption for the anodic dissolution of the metal. The theoretical energy consumption for dissolving 1 g of iron is 2.9 Wh, for 1 g of aluminum is 12 Wh. It is recommended to carry out the process in neutral or slightly alkaline environment at a current density of no more than 10 A/m² and a distance between the electrodes of no more than 20 mm.

Advantages of the method:

- compliance of wastewater treatment from \( \text{Cr}^{6+} \) compounds with the requirements of maximum permissible concentration
- high performance
- ease of operation and automation
- small footprint
- low sensitivity to changes in process parameters
- obtaining sludge with good structural and mechanical properties
- exclusion of reagent facilities
- high bactericidal effect of electric current and, as a result, reduced consumption of reagents for water disinfection.

Disadvantages of the method:

- significant power consumption
- significant consumption of metal of soluble anodes and their passivation.

3. Rationale for application of electrocoagulation method and increase of its efficiency

Coagulation of particles in electrolysis with soluble electrodes (anodes) is due to the introduction of positive metal ions that are hydrolyzed in water to form hydroxides and other intermediate compounds.

In accordance with the theoretical foundations of electrolytic coagulation and the above methodology, a possible general design of electrocoagulation wastewater treatment is shown in figure 1.

Electrocoagulation is the most versatile and effective method of decontamination of wastewater with such a complex multicomponent composition of contaminants. It allows sufficiently deep purification of chromium-containing wastewater and has a high level of flexibility and reliability (especially compared to reagent methods).

The highest degree of wastewater treatment is achieved in electrocoagulation devices, which have an electrofloation chamber along with an electrocoagulation chamber. In this case, the wastewater is preliminarily exposed to both the electric field and the metal oxides formed in the process of electrocoagulation, which are the products of dissolution of the anode electrode plates. When separating suspensions or cleaning waste liquids from chromium compounds, the most effective is the sequential execution of coagulation and flotation. In practice, both processes can be carried out in one electrolyzer, which is a container with flat steel electrodes located in it.
Based on the results of studies carried out on laboratory and pilot plants, the main parameters of the "electrocoagulation–flotation" process were determined: electrocoagulation time takes 3-5 minutes; flotation time takes 8–10 minutes; current density in both processes is 10–20 A/dm².

![Diagram of wastewater treatment using the electrocoagulation method.](image)

**Figure 1.** Scheme of wastewater treatment using the electrocoagulation method. It consists of storage S1, pumps P1 and P2, electrocoagulator EC, storages S2 and S3, dosing pumps DP1 and DP2, sump S, mechanical filter F, power source PS, filter press FP.

The results of studying the effectiveness of the electrocoagulation method of cleaning and the combined method are shown in table 1.

**Table 1.** Comparative analysis of the effectiveness of methods for the treatment of the chromium-containing wastewater.

| Parameter                              | Electrocoagulation | Electroflotocoagulation |
|----------------------------------------|--------------------|-------------------------|
| Chromium removal degree, %             | 80–95              | 95.0–99.5               |
| Secondary water pollution              | Fe, 1 mg/l         | Absent                  |
| Operating mode                         | Periodic           | Continuous              |
| Consumption of materials and reagents  | Iron anode in 5–10 days | Iron anode in 10–15 days |
|                                        | Titanium anode in 5–10 years | Titanium anode in 5–10 years |
| Performance, m³/h                      | Up to 10           | 1–90                    |
| Galvanic sludge                        | Pulp, 99% moisture | Foam product, 90% moisture |
| Energy consumption, kWh/m³             | 1.2–1.5            | 1.3–2.0                  |

Purification of chromium-containing wastewater by the combined method has significant advantages over purification using only the electrocoagulation method:

1) Lower consumption of electricity and metal electrodes compared to electrocoagulation.
2) The sumps are replaced by a smaller flotation chamber.
3) There is no need to introduce reagents into the waste. The foam produced by electroflotocoagulation has a high stability. It is destroyed after 24 hours of sedimentation.
4) Electroflotocoagulation allows returning up to 40% of water to the cycle.
4. Conclusion

When using the combined method, chromium removal is 95.0–99.5%. Removal of organic matter is 60–80%. The pH value during treatment increases by 2.5-3.5 units.

Thus, the combination of electrocoagulation and electroflotation methods makes it possible to create energy- and resource-saving industrial technologies for treatment of chromium-containing wastewater of galvanic plants.

The study of wastewater by various methods [22, 23, 28, 29, 45] showed that the degree of purification has improved several times in comparison with existing methods.

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