Research of reagent-free waste water treatment methods of the chrome plating line for mineralizing the rod of hydraulic cylinders

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Abstract: The article is devoted to the analysis of the subject literature on the existing methods of non-reagent treatment of electroplating wastewater produced on the lines of deposition of chromium and nickel coatings, electrochemical methods of cleaning. The authors showed and determined the advantages and disadvantages of each of the considered methods. The authors determined the most effective wastewater treatment method based on the review.

One of the most important parts of the hydraulic cylinder is. A rod is a component that works at elevated loads, even in aggressive chemical environments. To increase the life of the rod, it is necessary to chrome. In the case of marine use, nickel-chrome plated rods are used. Chrome-plated or nickel-chrome rods are made from high-grade calibrated round steel by machining the surface of the bar and applying electroplating, followed by polishing. As a result of the use of water in the electroplating process, a huge amount of wastewater is formed, containing various harmful substances that must be removed before being discharged into the sewer system or water bodies. Industry accounts for 25% of the total discharge of polluted wastewater [1]. To solve the problems of wastewater treatment, various methods (mechanical, chemical, and physicochemical) are used with the use of modern water treatment equipment with high cleaning efficiency [23-33]. One of these areas are wastewater treatment methods using electrochemical processes.

Electrochemical methods are among the most effective methods of wastewater treatment from various types of pollution. The development of electrochemical methods of wastewater treatment, improvement and creation of new technical solutions will solve the problem of preventing high anthropogenic pressure on water bodies, create conditions for the use of substandard water in water circulation, and also ensure the environmental safety of water users.

Electrochemical methods make it possible to extract valuable products from wastewater with a relatively simple treatment scheme without the use of chemical reagents. Wastewater treatment by electrochemical methods can be carried out periodically or continuously.

Of the electrochemical methods of wastewater treatment, the electrocoagulation method has become the most widespread [2]. Electrochemical coagulation is the process of purifying water from colloidal and fine impurities using coagulants as metal hydroxides (aluminum, iron), carried out by passing a directed electric current through water.
The process of electrocoagulation occurs in the apparatus is called electrolyzers. The electrolyzer (figure 1) is a vessel (or several vessels) filled with electrolyte, with electrodes placed in it — the cathode and the anode [3]. In the electric field, which is created by electrodes, there is an orderly movement of ions in conductive liquids. Metal anodes under the action of direct current ionize and pass into the purified water. Hydroxides of aluminum or iron formed in water coagulate dispersed substances.

![Electrolytic process](image)

**Figure 1.** Electrolytic process.

It is also possible to use insoluble electrodes. When used, coagulation can occur as a result of electrophoretic processes and the discharge of charged particles on the electrodes, the formation in solution of substances that destroy the solvation shells on the surface of particles of pollution (chlorine, oxygen).

With an increase in the concentration of suspended substances more than 100 mg/l, the efficiency of electrocoagulation decreases. With a decrease in the distance between the electrodes, the energy consumption for anodic dissolution of the metal decreases. Electrocoagulation is recommended to be carried out in a neutral or slightly alkaline medium at a current density of not more than 10 A/m², the distance between the electrodes is not more than 20 mm and the speed of movement is not less than 0.5 m/s.

The main advantages of electrocoagulation are: no additional water pollution, no need to use chemical reagents, low sensitivity to abrupt changes in the conditions of the cleaning process, has a high bactericidal effect, waste has good structural and mechanical properties. The main disadvantages of this method are: high energy and metal intensity of the process, relatively low productivity.

In the process of electrochemical flotation, the main role is played by bubbles of hydrogen and oxygen, which are formed at the cathode and anode, respectively, during the electrolysis of water. Gas bubbles rise in water, collide with suspended solids, stick to them, and carry them to the surface. When using soluble electrodes, the coagulation process also occurs, this leads to an intensification of the electro-flotation process due to the aluminum or iron salts formed during this process. The size of hydrogen bubbles during electrocoagulation is much smaller than with other flotation methods. Their diameter varies from 20 to 100 microns. Small bubbles of hydrogen have a greater solubility than large ones, which contributes to their release on the surface of dirt particles, intensifying the flotation process.
Electrochemical flotation is often used to treat wastewater from refineries, food processing plants, as well as in the separation and compaction of activated sludge after aerotanks in biological sewage treatment plants. [4] The optimum value of current density is 200...260 A/m². The main advantage of the electrofloation method is the high degree of extraction of the treated wastewater from insoluble impurities. The disadvantages of electro-flotation are the insufficiently high productivity of electro-flotation units, the release of H2 bubbles, the cost of electrodes and maintenance, and the formation of sludge by volume.

One of the widely used methods of industrial wastewater treatment is the method of contact coagulation. The development of the method of contact coagulation is electrochemical filtration. The essence of the method of electrochemical filtration is as follows. The filter (figure 2) is loaded with at least three layers of granular materials. Layer 3 and 5 materials must be electrically conductive, have different values of standard potential. The material of layer 3 must be electronegative, capable of forming insoluble hydroxide, for example, aluminum. The material of layer 5 must be electropositive. Layers 3 and 5 are spatially separated by layer 4, consisting of a non-conducting granular filter material. When water is passed through the filter charge, an electromotive force arises between layers 3 and 5 and a galvanic current. Under the action of current, electronegative material 3 is dissolved, the ions of which form a coagulant on the loading grains 4. In layers 3 and 5, oxidative and reducing reactions occur, respectively, which significantly affect the effect of water purification in the presence of organic pollutants. In layer 5, activated carbon is used, which performs, in addition to those indicated, the function of a sorbent [5].

Figure 2. Electrochemical filter circuit: 1 – feed water supply; 2 – distribution system; 3 – granulated aluminum; 4 – filtering granular material; 5 – activated carbon; 6 – modular system; 7 – drainage of purified water; 8 – supply of wash water; 9 – flushing water outlet.

An important advantage of electrochemical filters is the lack of energy consumption for coagulation and redox processes, the simplicity of instrumentation. The only serious negative - the filter does not purify water from heavy metals and radioactive elements. To this it should be added that all beneficial mineral substances are preserved in water.

An important step in the development of electrocoagulation is galvanocoagulation [6]. The working area of the apparatus is loaded with a mixture of aluminum particles 20...70% and copper 80...30%. Upon contact of dissimilar particles, a short-circuited galvanic cell is formed, in which dissolution of
the more electronegative metal occurs, i.e. aluminum. This forms a colloidal hydroxide, which is the main water treatment tool. Minor distances between particles contribute to an increase in current density, which, along with the developed surface of the particles, contributes to the intensification of metal dissolution.

The choice of galvanic coupler material is determined by the specific task of cleaning solutions. Usually, coke-iron is used to remove toxic metals, aluminum is used as an anode to remove anions, aluminum is also used to remove sulfates in the form of aluminum oxysulfates, and copper is used to remove precious metals. The galvanic couples with activated carbon work most effectively, which can be explained by a higher intensity of oxidation processes and, accordingly, higher output values for iron or aluminum. Such galvanic couples made it possible to significantly expand the range of application of galvanocoagulation in the practice of wastewater treatment from heavy metals, as well as to remove hardness salts and sulfates from the treated fluids, extract valuable components from ash-slag dumps [7, 8].

Galvanocoagulation method is advisable to use in the treatment of wastewater from heavy metal ions, non-ferrous and noble metals, inorganic anions (sulfates, chlorides, etc.), flotation agents, oil products and various organic impurities [9, 11-17, 22]. Also, the process of water softening occurs due to the formation of complex salts with the participation of liquid salts [10]. The advantages of this method are: lack of reagents, lack of rectifying equipment, reduction of energy costs, metal granules are used instead of sheets, sediments occupy a small volume, high reliability, high unit productivity, has the property of automatic regulation, does not require pH correction [26, 26].

The main disadvantages of the galvanocoagulation method are: scaling, difficulty in servicing due to clogging, non-recyclable wastes (iron and chromium hydroxides) are formed. As a result of the review, it was found that a galvanocoagulation method of purifying wastewater from heavy metal ions, suspended solids and other pollutants has become widely used. It is worth noting that galvanocoagulation is included in the UNESCO Register as the recommended newest method of wastewater treatment.

This method allows reducing the cost of the cleaning process due to the absence of the need to use chemical reagents, reducing the cost of energy consumption, lower cost of loading. Also galvanocoagulation is a universal method of wastewater treatment, as it allows you to purify water from the main common types of pollution.

The method of galvanocoagulation in many technological characteristics is preferable to electrocoagulation. At the same time, the method cannot be rationally applied to purify large volumes of wastewater due to the significant size of the equipment and premises for its placement. It is also necessary to create innovative solutions to intensify the process of galvanocoagulation wastewater treatment, as it is becoming more and more difficult for modern galvanic-coagulation plants to clean up drains up to the established regulatory requirements.

In this paper, experimental studies of wastewater treatment using galvanocoagulation treatment were carried out. The task of the experimental studies was to determine the effectiveness of water purification from nickel under various operating conditions.

In the course of experimental studies, the most effective types of loading for the galvanocoagulation filter, the modes of mixing, the height of loading, the time of filtration were determined.

The results of the study showed that the effect of mixing on the galvanopair prevents passivation of the surface of its elements. The optimal load ratio for the most efficient cleaning of these heavy metal ions is, with constant load mixing, 3:1 (75% activated carbon, 25% granulated aluminum), without load mixing, the optimum load ratio is also 3:1. This load ratio was used further. Also it was determined the flow rate, which was changed in the range from 0.7 to 5.0 m/h. The initial concentration of nickel is 0.538 mg/l. The results are shown in table 1.

The results in table 1 showed that with increasing filtration rate, the efficiency of purification from nickel ions decreases. Optimal results were achieved at a filtration rate of 0.5…1.5 m/h. Under these conditions, it was possible to lower the concentration of heavy metals in water with an efficiency of over 80%.
Table 1. Results of water purification from nickel ions with constant stirring filter loading and different filtration rates.

| Stock concentration NiC₀, mg/l | Residual concentration Ni, mg/l | Effect purification of Ni, % | Time purification, min | Filtration rate v, m/h |
|--------------------------------|---------------------------------|-------------------------------|------------------------|------------------------|
| 0.538                          | 0.500                           | 7.063                         | 5                      | 5.00                   |
|                                | 0.398                           | 26.022                        | 10                     | 2.40                   |
|                                | 0.365                           | 32.156                        | 15                     | 1.60                   |
|                                | 0.212                           | 60.594                        | 20                     | 1.20                   |
|                                | 0.111                           | 79.368                        | 25                     | 0.96                   |
|                                | 0.087                           | 83.829                        | 30                     | 0.68                   |

The loading height is important; in this connection, the filtration capacity of the galvanocoagulation unit was investigated at different loading thicknesses (galvanic couples) in the galvanocoagulation chamber. Filtration was carried out at speeds of 0.7…5 m/h, the filter column was loaded with electroplating (aluminum and AG-3 coal in a ratio of 3:1, respectively), mass: 10, 20, 30 and 40 g. With these mass values, the height of the filter loading amounted to 0.07 m, 0.14 m, 0.21 and 0.28 m, respectively. The research results are showed in table 2.

Table 2. Water purification from heavy metal (nickel) at different heights of the filtering load.

| Stock concentration NiC₀, mg/l | Residual concentration Ni, mg/l, to loading height h, m | Filtration rate v, m/h |
|--------------------------------|-------------------------------------------------------|------------------------|
| 0.538                          | 0.500 0.481 0.460 0.437                               | 5.00                   |
|                                | 0.398 0.358 0.333 0.301                               | 2.40                   |
|                                | 0.365 0.345 0.325 0.300                               | 1.60                   |
|                                | 0.212 0.200 0.286 0.259                               | 1.20                   |
|                                | 0.111 0.092 0.077 0.057                               | 0.96                   |
|                                | 0.087 0.077 0.057 0.057                               | 0.68                   |

The results presented in table 2 show that increasing the height of the layer of filter material in the galvanocoagulation chamber enhances the coagulation of pollutants in the water. Summarizing, it is to note the following:

1. The effect of mixing on the galvanopair prevents passivation of the loading surface. The effect of mixing also increases the rate of dissolution of the oxide film, while the resulting flakes of formed aluminum hydroxide begin to move more actively during the filtration process, while encountering a large amount of pollutants, thereby accelerating the process of their coagulation.

2. The efficiency of cleaning from heavy metals with increasing filtration process increases.

3. With increasing filtration rate, wastewater treatment efficiency decreases. Optimum filtration rate for high cleaning efficiency is 0.5…1.5 m/h.

4. It was established experimentally that with an increase in the height of the layer of filter material, the cleaning efficiency increases.

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