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# ОСОБЛИВОСТІ ОЧИЩЕННЯ СТІЧНИХ ВОД ГАЛЬВАНІЧНИХ ВИРОБНИЦТВ ВІД ВАЖКИХ МЕТАЛІВ НА ПРИКЛАДІ ШЕСТИВАЛЕНТНОГО ХРОМУ. ЕКОЛОГІЧНІ АСПЕКТИ

*Гальваніка – галузь промисловості, яка займається нанесенням захисних і декоративних покриттів на металеві та неметалеві вироби. Гальваніка – електрохімічний процес. Електричний ланцюг містить електроліт, два аноди, підключені до джерела струму, і заготовку, що обробляється, яка виступає в ролі катода. Коли через нього проходить електричний струм, іони металу відновлюються на катоді в електроліті, утворюючи тонку плівку при осадженні на поверхні виробу.*

*Процес гальваніки відбувається в спеціалізованих ваннах (електролізерах). У ванну завантажують електроліт, до складу якого входять солі металу, що осідає на поверхні катода. Для очищення промислових стічних вод використовуються лужні та кислі промивні води. Концентрованими стічними водами, витрата яких визначається об'ємом ванни і складом розчину, є відпрацьований технологічний розчин у ванні або промивні води з іншої технологічної операції. 90–95% гальванічної води використовується на промивні операції. При цьому близько 80% маси всіх шкідливих речовин у стічних водах надходить зі стічними водами і розчинами електролітів.*

*Різні процеси, пов'язані з гальванікою, призводять до утворення стічних вод різного складу. Загалом, для кожної групи забруднювачів існують свої методи очищення.*

*Значної шкоди довкіллю завдають виробництва, які продукують стічні води, що містять хром. Якщо забруднені промислові стічні води скидати у водойму без попереднього очищення, це може призвести до серйозних порушень біологічного режиму водойми. Сполуки хрому є канцерогенними і мають шкідливий вплив на живі організми. У гальванічній промисловості стічні води, забруднені сполуками хрому, утворюються під час хромування, травлення та очищення виробів після пасивації поверхонь деталей. Через використання шестивалентного хрому ці стічні води необхідно відокремлювати і попередньо очищати в окремій системі.*

*Перевагою реагентного очищення стічних вод є його економічність і простота. Однак цей метод вимагає споживання великої кількості реагентів, громіздкого обладнання та утилізації великої кількості шламу.*

***Ключові слова:*** *гальванічний процес, електролізер, іони важких металів, хром, стічні води.*

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# PECULIARITIES OF WASTEWATER TREATMENT OF ELECTROPLATING INDUSTRIES FROM HEAVY METALS ON THE EXAMPLE OF HEXAVALENT CHROMIUM. ENVIRONMENTAL ASPECTS

*Electroplating is an industrial sector that applies protective and decorative coatings to metal and non-metal products. Electroplating is an electrochemical process. An electrical circuit contains an electrolyte, two anodes connected to a current source, and the workpiece to be processed, which acts as a cathode. When an electric current is passed through, metal ions are reduced on the cathode in the electrolyte, forming a thin film when deposited on the surface of the product.*

*The electroplating process takes place in specialized baths (electrolyzers). An electrolyte is loaded into the bath, which includes salts of the metal deposited on the cathode surface. Alkaline and acidic wash water is used to treat industrial wastewater. Concentrated wastewater, the consumption of which is determined by the volume of the bath and the composition of the solution, is the spent process solution in the bath or rinsing water from another process operation. 90–95% of electroplating water is used for rinsing operations. At the same time, about 80% of the mass of all harmful substances in wastewater comes from wastewater and electrolyte solutions.*

*Various processes related to electroplating produce wastewater of different composition. In general, each group of pollutants has its own treatment methods.*

*Industries that produce chromium-containing wastewater cause significant environmental damage. If contaminated industrial wastewater is discharged into a water body without prior treatment, it can lead to serious disruption of the biological regime of the water body. Chromium compounds are carcinogenic and have a harmful effect on living organisms. In the electroplating industry, wastewater contaminated with chromium compounds is generated during chrome plating, pickling, and cleaning of products after passivation of component surfaces. Due to the use of hexavalent chromium, this wastewater must be separated and pretreated in a separate system.*

*The advantage of reagent wastewater treatment is its cost-effectiveness and simplicity. However, this method requires the consumption of large quantities of reagents, bulky equipment, and the disposal of large amounts of sludge.*

***Key words:*** *electroplating process, electrolyzer, heavy metal ions, chromium, wastewater.*

## Introduction

Electroplating is an industrial sector that applies protective and decorative coatings to metal and non-metal products.

Electroplating is an electrochemical process. An electrical circuit contains an electrolyte, two anodes connected to a current source, and the workpiece to be processed, which acts as a cathode. When an electric current is passed through the electrolyte, metal ions are reduced at the cathode, forming a thin film when deposited on the surface of the product [1–3].

Electroplating is used to improve the protective properties and decorative characteristics of products. It is used if it is impossible to make a whole product from metal or if the cost of the product is too high. A good example is chrome. The production of parts and objects from chrome is impossible because this metal is hard, but also has a brittle property. Nevertheless, when chrome is applied to steel, it makes it harder and more resistant to corrosion. The most common processes are galvanizing, nickel plating, chrome plating, copper plating, silver plating, and gilding [4–7].

The electroplating process takes place in specialized baths (electrolyzers). An electrolyte is loaded into the bath, which includes salts of the metal that is deposited on the cathode surface. Electrodes are connected to the bath and the product to allow electric current to flow. The positive charge is connected to the anodes, and the negative charge is connected to the workpiece. When the galvanic system is started, an electric current pass through the electrolyte. The metal contained in the electrolyte is deposited on the workpiece in a uniform layer. Two anodes in the electrolysis tank are used to treat both surfaces simultaneously [8].

Each galvanic process consists of various operations that can be divided into three groups:

- Preparatory work. Before starting the main electroplating process, the components must be cleaned. At this stage, the parts are processed, degreased, etched, and polished.
- The main process is the application of a suitable metal coating using electroplating techniques.
- Finishing processes are necessary to maintain and improve the appearance of galvanic coatings. For this purpose, painting, polishing, and varnishing are commonly used [9–12].

The purpose of degreasing is to remove organic oils, mineral oils, and various solids retained in the oil film from the surface of the film components. Alkaline degreasing agents should contain substances that neutralize fatty acids and emulsifiers. They should also not cause corrosion of metals and should be easily removed with water. These conditions are best met by silicates and phosphates of alkali metals. Surfactants with good emulsifying properties are also added. After degreasing, the solution is sent for refining [13].

Before painting, metal surfaces must be cleaned of scale, rust, and oxide films by pickling. The pickling process usually follows the degreasing process, and the quality of cleaning directly depends on the quality of the previous degreasing process. Pickling is carried out with solutions based on sulfuric, nitric, chloric, and phosphoric acids. Chloric acid mainly dissolves and removes oxides on the surface of the part. When sulfuric acid is used, oxides are removed mainly by etching the metal and mechanically removing a loose oxide film with the help of hydrogen released. The solution after pickling should be aimed at removing harmful contaminants [14].

Therefore, alkaline, and acidic wash water is used to treat industrial wastewater. Concentrated wastewater, the consumption of which is determined by the volume of the bath and the composition of the solution, is the spent process solution in the bath or rinsing water from another process operation. 90–95 % of electroplating water is used for rinsing operations. At the same time, about 80 % of the mass of all harmful substances in wastewater comes from wastewater and electrolyte solutions [15, 16].

The quantity, quantitative and qualitative composition of wastewater depends on the water consumption for washing, the cleaning method, and the composition of the technical solution.

For example, consider a galvanic line with a capacity of 26 m$^2$/h of nickel and 2 m$^2$/h of chromium with a decorative nickel-chromium coating and a stationary hand bath for one-stage purification (Fig. 1).

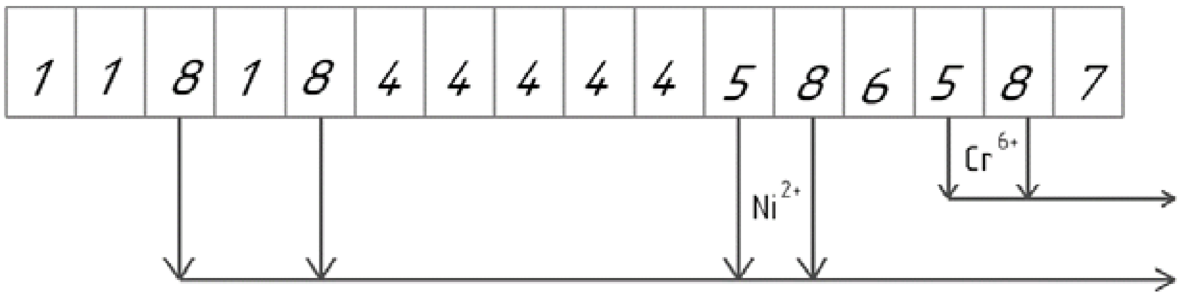


**Fig. 1. Galvanic lines for applying decorative coatings (nickel and chrome) with a nickel-plating capacity of 26 m$^2$/h and a chrome plating capacity of 2 m$^2$/h: 1 – degreasing, 4 – nickel plating, 5 – metal recovery, 6 – chrome plating, 7 – drying of components, 8 – cold rinsing**

In this method, the acid-base drainage consists of alkaline rinse water after degreasing 1, acid rinse water after nickel plating 4, and process fluids. Concentrate wastewater is represented by rinsing water and wastewater after chrome plating 6. The volume and composition of the wastewater of such a galvanic line are shown in Table 1 [17–19].

Table 1

**Composition of wastewater from the electroplating line [19]**

| Component | Max. concentration of the component in the bath, g/L | Max. component outreach, g/h | Maximum concentration of components in wastewater, mg/L |
|---|---|---|---|
| NaOH | 36 | 263 | 15 |
| $Na_3PO_4 \cdot 12H_2O$ | 35 | 263 | 15 |
| $Na_2CO_3$ | 35 | 263 | 15 |
| HCl | 100 | 500 | 28 |
| $NiSO_4 \cdot 7H_2O$ | 320 | 1600 | 89 |
| $NiCl_2 \cdot 6H_2O$ | 60 | 300 | 17 |
| $H_3BO_4$ | 40 | 200 | 11 |
| Formalin | 1.2 | 6 | 0.3 |
| Chloramine B | 2.5 | 13 | 0.7 |
| $CrO_3$ | 250 | 225 | 49 |
| $H_2SO_4$ | 2.5 | 2.3 | 0.5 |
| Chromoxane | 0.2 | 0.2 | 0.04 |

The choice of equipment and flushing method determines the quantitative and qualitative composition of flushing and wastewater, which in turn determines the composition and efficiency of the treatment plant [20].

**Methods of wastewater treatment of electroplating production**

The various processes involved in electroplating produce wastewater of varying composition. Depending on the phase state of the substances in solution, all pollutants in wastewater can be divided into the following groups:

- Fine suspensions, emulsions.
- Polymeric compounds, colloids.
- Organic substances dissolved in water.
- Salts, acids, and alkalis dissolved in water.

In general, each of these groups of pollutants has its own treatment methods. For example, gravity, flotation, and adhesion are the most effective methods for treating water from fine suspensions and emulsions. For colloidal systems, coagulation methods are used. Dissolved organic substances are most effectively removed from water by adsorption methods of purification, while salts, acids and alkalis dissolved in electrolytes are most effectively removed from water by reactive methods or desalination methods by converting ions into insoluble compounds [21].

If we classify purification methods by the dominant process (or main equipment), they can be divided into seven groups: mechanical, chemical, flocculation-suspension, electrochemical, sorption, membrane, and biological.

However, these methods alone cannot fully satisfy modern requirements, treatment in accordance with MPC standards (especially heavy metal ions), 90–95 % of water returns to the circulation cycle, lower treatment costs, and utilization of valuable resources (acids, alkalis, metals) [21].

**Treatment of hexavalent chromium waste with reagents**

Industries that produce chromium-containing wastewater cause significant environmental damage. If contaminated industrial wastewater is discharged into a water body without prior treatment, it can lead to serious disruption of the biological regime of the water body. Chromium compounds are carcinogenic and have a harmful effect on living organisms.

In the electroplating industry, wastewater contaminated with chromium compounds is generated during chrome plating, pickling, and cleaning of products after passivation of component surfaces. Due to the use of hexavalent chromium, this wastewater must be separated and pretreated in a separate system [22].

This wastewater is subjected to a two-stage hexavalent chromium recovery process:

- Conversion of hexavalent chromium to trivalent chromium.
- Precipitation as trivalent chromium hydroxide.

Waste metallic iron (iron powder) or iron (II) sulfate can be used as reducing agents. In the first case, the wastewater is acidified to pH 2 and filtered through a foam layer of iron powder with a continuous supply of air. In the second case, a solution of ferrous (II) sulfate (in the form of a 10 % aqueous solution) is added to the reactor receiving the wastewater. The reduction of $Cr^{6+}$ to $Cr^{3+}$ by iron salts occurs at a very high rate.

The advantage of this method is its cost-effectiveness: only a small amount of ferrous (II) sulfate is required to reduce $Cr^{6+}$ to $Cr^{3+}$, regardless of the initial $Cr^{6+}$ concentration and pH value in the wastewater. The disadvantage of using ferrous (II) sulfate and ferrous metal as reducing agents is that a large amount of precipitate is generated during the neutralization process. In addition, when stored in unfavorable conditions, iron (II) is easily oxidized to iron (III), which makes it difficult to properly dose the salt solution into the wastewater [23].

The salts are added to the wastewater in the form of a 10% aqueous solution; the speed and completeness of the $Cr^{6+}$ to $Cr^{3+}$ reduction reaction strongly depends on the pH of the reaction mixture. The highest rate of the reduction reaction is achieved in an acidic environment with a pH of 2–2.5 and usually requires further acidification of the wastewater with a 10–15% sulfuric acid solution (solutions of other mineral acids can also be used). An overdose of the reagent, even at the level of 10%, is unacceptable, as complex salts of chromium (III) and sulfuric acid are formed, which are destroyed during further neutralization of the wastewater.

After the reduction of $Cr^{6+}$ in an acidic environment is completed, the wastewater is sent for neutralization, and the reaction results in the precipitation of $Cr^{3+}$ in the form of hydroxides.

The wastewater containing $Cr^{3+}$ is pre-mixed with acidic and basic wastewater from electroplating production and neutralized.

Table 2 shows the theoretical reagent consumption required to remove 1 kg of $CrO_3$ from wastewater. [23].

Thus, it can be concluded that the usage of $NaHSO_3$ as a reducing agent is the most suitable method for removing harmful $Cr^{6+}$. The amount of precipitate formed after neutralization is almost the same in all cases, but the consumption of reagents is the lowest for the chosen method.

Table 2

**Stoichiometric flow rate of the reagent and mass of the precipitate formed during the neutralization of 1 kg of CrO3**

| Reductant | Consumption of the reductant, kg | Consumption of $H_2SO_4$, kg | Consumption of NaOH, kg | Mass of sludge, kg |
|---|---|---|---|---|
| $FeSO_4$ | 8.340 | 2.940 | 4.800 | 4.230 |
| $NaHSO_3$ | 1.561 | 0.735 | 1.200 | 4.414 |
| $Na_2SO_3$ | 1.891 | 1.470 | 1.200 | 5.576 |

The strong point of reagent wastewater treatment is its cost-effectiveness and simplicity. However, this method requires the consumption of large amounts of reagents, bulky equipment, and the disposal of large amounts of sludge. In addition, after the reactive removal of heavy metals in the form of hydroxides, small residual concentrations of these metals remain in the wastewater. The final treatment can be carried out by various methods, such as ion exchange, electrolocation, electrodialysis, reverse osmosis, and ultrafiltration [24].

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