Electrochemical treatment of waste water from nickel in galvanic production

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Abstract. In the production of metal coating by electroplating, wastewater containing the metal ions is used. The paper presents the study results of cleaning waste water of nickel after electroplating. Wastewater treatment was implemented in an electrodialysis plant. The initial wastewater contained from 20 to 80 mg/l of nickel II. Experimental results obtained by studying the electrodialysis extraction of nickel from wastewater of electroplating plants, indicate that the cleaning process is influenced by such factors as the effluent treatment time, the current load on the electrodialyzer, the initial metal concentration in the effluent. The increase in voltage in the electrodialysis plant leads to an increase in the treatment efficiency. So after six hours of processing, the processing rate during nickel extraction increases from 39 to 66.5% with an increase in voltage from 40 to 100V. Along with cleaning wastewater of nickel electrolyte, the electrodialysis method allows obtaining concentrates of this electrolyte containing from 260 to 1230 mg/dm³ of nickel and suitable for use in the electroplating process.

1. Introduction
Electrochemical deposition of metal coatings on various products are widely used in various areas of production: mechanical engineering, automotive, electronics, precision instruments, and so on. It is enough to note that about 70% of machine building enterprises have galvanizing plant or bays in its structure.

The application of electroplated coatings in mechanical engineering is one of the most common methods to protect the products against corrosion. In addition, the electroplating significantly increases the wear resistance of parts, improves its electrical conductivity and other important properties. Most often for these purposes the material surfaces are coated by the chromium, nickel, copper, cadmium and other metals [1].

As a result of the electroplating plants operation, some wastewaters are produced containing non-ferrous metals and other chemicals, the release of which into the natural environment can lead to significant damage. In addition, with the wastewater of electroplating, plant facilities lose quite expensive non-ferrous metals.

In this regard, the treatment of electroplating plants wastewater and extraction of non-ferrous metals from it are of great environmental and economic importance.

The wastewater containing nickel (II) was monitored generated at the Sterlitamak Lenin Machine-Tool Factory, where electroplating is carried out in a hardening plant for hardening parts, and in the consumer goods plant (TKBN) to impart decorative properties to products. The nickel content in the wastewater of the galvanic section of the thermal workshop and the TKBN workshop on average...
exceeds the maximum permissible concentration from 1 to 30 times (MPC of nickel (II) 0.1 mg/dm$^3$ [2]). There are one-time jumps in nickel concentration exceeding the MPC from 100 to 450 times. Obviously, this occurs at the time of discharge of the electrolyte from the bath.

Thus, the problem of wastewater treatment from nickel (II) in machine-tool plants is acute. There are a number of methods to treat such wastewater. The most common of them is the method of nickel (II) deposition [3, 4].

Electrodialysis treatment allows not only purifying waste water, but also obtaining a concentrate suitable for the preparation of electrolyte solutions. As a result, expensive metals are returned to the production cycle [5-10].

2. Material and research methods
To study the process of electrodialysis extraction of nickel from the galvanic section wastewater, a plant was used, schematically shown in Figure 1. The electrodialysis plant is an assembly of cells separated by alternating cationic and anion-exchange membranes. The entire assembly is in a DC electric field created between the electrodes.

Under electric field, directed motion of ions occurs. In this case, the cations move in the direction of the lines of the electric field strength, and the anions in the opposite direction. If pumping the runoff through the plant is organized as shown in Figure 1, the cations and anions migrate through the cation-exchange and anion-exchange membranes, respectively, and from the desalting cells will fall into the concentration cells, where ion-exchange membranes with opposite exchange properties will impede their further promotion. Thus, in the concentration cells of the electrodialysis plant the solutions of the same composition will be generated as in the desalting cells, but with a higher concentration.

The hull frames made of PVC sheets, 2 mm thick, form cells for pumping effluent and collecting the resulting concentrate. For the sell separation it is applied the cation-exchange membrane of the mark MK-40 and anion-exchange membrane of the mark MA-40.

To turbulize the solutions and to prevent the contact of the membranes, a mesh of stretched calendered vinyl plastic was placed in each cell. The plexiglass plates were used to tie the whole structure. Electrode cells were also made in plates. Titanium plates coated with ruthenium oxide were used as electrodes. The distribution and collection of solutions flowing through the plant was carried out using supply manifold and gathering main made in the dialyser core. The experimental
electrodialyzer contained 17 cells, in eight of which the effluent was desalted, and in nine the extractable salt was concentrated. The working surface of the membranes was \(115 \text{ cm}^2\).

The waste water was pumped through the desalting cells of the electrodialysis plant. The concentrate as it accumulated in the corresponding cells flowed out of the electrodialysis unit by gravity. A 0.1 N solution of sulfuric acid was circulated in the electrode cells. The power of the electrodialyzer was carried out from a controlled rectifier.

3. **Experimental results and discussion**

Laboratory studies were performed with model solutions of effluent containing from 20 to 80 mg/dm\(^3\) of chromium per metal. The volume of wastewater exposed to desalting in all experiments remained constant and amounted to 61 liters.

During the operation of the electrodialysis plant, samples of the treated effluent and concentrates generated in the electrodialysis concentration cells were periodically collected and analyzed for nickel content. The concentration of nickel was determined by the colorimetric method with dimethylglyoxime.

The dependence of nickel concentration in the effluent on the time of its electrodialysis treatment is shown in Figure 2.

![Figure 2](image)

**Figure 2.** Dependence of nickel (II) concentration in wastewater on the treatment time in the plant

It may be seen that after the first hour of operation of the experimental installation, the dependence of nickel concentration in the effluent on the processing time is linear. With increasing voltage on the device, the degree of nickel extraction from the effluent increases. So after 6 hours of operation, the degree of extraction of nickel from the effluent varies from 39.0\% at a voltage of 40V to 66.2\% at a voltage of 100V.

Table 1 presents the values of the rate of nickel extraction from the effluent at different voltages on the electrodialyzer.

The data presented in the table show that with increasing voltage on the plant, the rate of nickel extraction increases also.
The dependence of nickel concentration in the electrodialysis plant concentration cells on the run-off treatment time with its initial concentration of 20 mg/dm$^3$ is presented in Figure 3.

Table 1. Nickel extraction rate from effluent

| Voltage on plant, V | Nickel extraction rate, mg/dm$^3$·h$^{-1}$ |
|---------------------|---------------------------------------------|
| 40                  | 1.01                                        |
| 60                  | 1.39                                        |
| 80                  | 1.59                                        |
| 100                 | 1.80                                        |

Analysis of the presented results shows that the maximum rate of increase in the concentration of nickel in the concentration cells of the electrodialysis plant is observed in the first hour of its operation.

Thus, the rate of change of nickel concentration in the concentration cells during the first hour of operation of the plant is 91 mg/dm$^3$·h for a voltage of 40 V and 413 mg/dm$^3$·h for a voltage of 100 V. And during the sixth hour of work at a voltage on the plant equal to 40 V the rate of change of nickel concentration in the concentration cells is 5 mg/dm$^3$·h and 47 mg/dm$^3$·h at a voltage of 100 V.

It should be noted that with voltage increasing on the electrodialyzer, the concentration of nickel in a concentrate increases as well. So after six hours of the process, the concentration of nickel in the concentration cells reaches 260 mg/dm$^3$ at a voltage of 40 V and 961 mg/dm$^3$ at a voltage of 100 V.

Figure 3 shows the dependence of nickel concentration in wastewater on the treatment time.

Figure 4 shows the dependence of nickel concentration in the concentrate on its initial concentration in an effluent after 6 hours of the plant operation.

It is seen that with an increase in the initial concentration of nickel in effluent, its concentration in the concentrate also increases. The greatest increase in concentration is observed at low initial nickel concentrations in the effluent. Indeed, when the concentration of nickel in the effluent changes from 0 to 20 mg/dm$^3$, its content in the concentrate changes from 510 to 840 mg/dm$^3$, depending on the voltage on the plant. An increase in the initial nickel concentration in the effluent to 80 mg/dm$^3$ leads to an increase in its concentration in concentrate from 755 to 1230 mg/dm$^3$. 
4. Conclusion
Analysis of the above results shows that to treat the wastewater generated during the electrochemical deposition of nickel coatings, the electrodialysis method is the most suited. It allows creating a closed cycle in water and producing concentrates suitable to use in the process.

Experimental results obtained at study of processes of nickel electrodialysis extraction from wastewater of electroplating plants, indicate that the treatment process is influenced by such factors as the treatment time of the effluent, the current load on the electrodialyzer, the initial concentration of the metal in the effluent.

The voltage increasing on the electrodialysis plant leads to an increase in the treatment efficiency. So after six hours of operation, the purification efficiency during nickel extraction increases from 39 to 66.5% with a voltage increase from 40 to 100V.

Along with wastewater treatment from nickel electrolyte, the electrodialysis method allows obtaining concentrates of this electrolyte containing from 260 to 1230 mg/dm$^3$ of nickel and suitable for using in the electroplating process.

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

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