Resource-saving dialysis technology for electroplating wastewater treatment

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Abstract. In this work, the separation process of components of electroplating effluent containing sulfuric acid and nickel sulfate by dialysis through various ion-exchange membranes was carried out. Kinetic curves of changes in the concentration of sulfuric acid and nickel sulfate in chambers with permeate and retentate were obtained. The flux densities, nickel losses, the degree of sulfuric acid recovery and the separation factor were calculated. It was shown that the use of cation-exchange membranes does not allow to separate nickel sulfate and sulfuric acid. The use of commercial anion exchange membranes allows 90% sulfuric acid to be recovered with a nickel loss of 8%. The profiling of the anion exchange membranes significantly intensifies the process, but leads to an increase leakage of nickel sulfate through the membranes. The prospects of dialysis wastewater treatment from galvanic production for return of valuable components to production are shown.

1. Introduction

As a result of the operation of mining and metalworking enterprises, wastewater is generated containing acids and heavy metal ions. The most common acid in wastewater is the sulfuric acid, and among the salts is nickel sulfate, which appears in wastewater as a result of electroplating, metalworking, mining and other technological processes.

These substances are toxic to humans and the environment. Nickel sulfate is a highly toxic mutagen and carcinogenic [1,2]. Nickel sulfate in wastewater mixes with water bodies and can spread in nature, including in the soil. NiSO₄ has a detrimental effect on plant growth and is a root growth inhibitor. It was shown in [3] that when the content of nickel sulfate in the soil with a concentration of more than 80 µM in plants, point necrosis of leaves is observed. Nickel sulfate is also very toxic to aquatic life with long lasting effects as shown in the International Chemical Safety Card.

Sulfuric acid is also a hazardous substance that can be damaging and corrosive. Thus, these substances must not be allowed to enter the environment. Also, the recovered sulfuric acid and nickel can be recycled back into the process to create resource-saving technologies. In addition, due to the growth in the production of stainless steel, batteries for electric vehicles, nickel cast iron, experts predict an increase in global demand for nickel. Thus, the treatment of wastewater from electroplating enterprises is important not only from an environmental point of view, but can also bring significant economic benefits.

There are various methods of wastewater treatment from heavy metals: sorption [4-7], reagent method [8], ion exchange [9-11], flotation [12,13], and other methods [14]. These technologies have disadvantages, such as high consumption of reagents, loss of valuable substances (acids), high con-
sumption of electricity, re-pollution of waters during the regeneration of the sorbent and ion-exchange resins.

Therefore, it is especially important to improve old and develop new treatment systems that would not only allow cleaning wastewater, but also return valuable components back to the production cycle. Dialysis with ion exchange membranes is promising in this regard. It has proven itself well in water treatment for the removal of nitrates [15, 16], borates [17], arsenates [18] from drinking water, as well as in the creation of resource-saving technologies and purification systems [19, 20]. Therefore, the purpose of this work is to evaluate the effectiveness of dialysis for separating a solution containing nickel sulfate and sulfuric acid and recovering valuable components with the possibility of their reuse.

2. Materials and Methods

Dialysis separation of the solution components was performed on a dialyzer (figure 1), alternately formed by 10 ion exchange membranes with separators with the size of the working area of the membranes 5x20 cm$^2$, the distance between the membranes is 0.1 cm.

![Figure 1. Principal scheme of the dialyzer: 1 – permeate chamber; 2 – retentate chamber; A – anion exchange membrane.](image)

During the experiments, Ralex AM-PP, Ralex CM-PP membranes were used. Ralex AM-PP and Ralex CM-PP membranes made by "MEGA" a.s., Czech Republic are sheets of ion-exchange heterogeneous film with fixed quaternary amino and sulfo groups, respectively. Polyethylene acts as an inert binder. To give the membranes mechanical rigidity, they are reinforced with a polypropylene fabric that is resistant to acids and alkalis. These membranes are intended for use in electrodialysis, deionization and membrane electrolysis.

In the course of the work, the Ralex AM-PP anion-exchange membranes were modified for use in dialysis of the processed solution. Hereinafter, these membranes were referred to as Ralex AM-PP_Prof. The modification was carried out according to the method [21], and consists of pressing pre-swollen membranes by 15 MPa at a temperature of 90 °C and a holding time under a load of 30 seconds.

Modification by profiling increases the microporosity and diffusion permeability of the membrane [22], which should have a positive effect on the dialysis rate of the test solution. Such profiled membranes made it possible to significantly intensify the process of separation of phenylalanine and sodium chloride by diffusion dialysis [23].
For separation (retentate chamber), a 1 liter of electroplating waste solution was used containing approximately 0.3 M nickel sulfate and 2.5 M sulfuric acid. Distilled water was fed into the permeate chamber. The volume of the permeate chamber was 1 liter. The distilled water in the permeate chamber was changed occasionally. Samples for determining the concentration of nickel and sulfuric acid were taken at the inlet to the chambers with permeate and retentate, at fixed intervals. The concentration of sulfuric acid was determined using acid-base titration, nickel – by photometry at a wavelength 394 nm.

3. Results and discussion

To evaluate the applicability of dialysis for separating a solution consisting of sulfuric acid and nickel sulfate, some experiments were carried out on the dialysis processing of a solution of 2.5 M sulfuric acid and 0.3 M nickel sulfate using various membranes: Ralex AM-PP, Ralex CM-PP, Ralex AM-PP Prof. Experimental data on dialysis using Ralex AM-PP membranes are presented in figure 2.

Analysis of the data obtained shows that as the dialysis process is carried out, the difference in acid concentration in the retentate and dialyze decreases and the process slows down (Figure 2 a). After changing the dialysate to a fresh portion of distilled water (shown with vertical dashed lines in Figure 2), the process intensifies.

At the initial stage, the nickel concentration slightly decreased, and then remained approximately constant. At the same time, the concentration of nickel sulfate in the dialysate almost always did not exceed 1 g/L (which corresponds to the concentration of an acid solution acceptable for acid reuse in production). Figure 2 c is an enlarged fragment of figure 2 b.

![Figure 2](image_url)

Figure 2. Kinetic curves of changes in the concentration of sulfuric acid and nickel sulfate during dialysis using membranes Ralex AM-PP.

1 - data for the camera with retentate;
2 - data for the chamber with permeate;
3 - lines showing the change of water in the retentate chamber;
4 - limit of nickel content (1 g/L)

a – concentration of sulfuric acid;
b, c – concentration nickel sulfate.
In the course of the experiments, kinetic curves of changes in the concentration of sulfuric acid and nickel sulfate in chambers with retentate and permeate were obtained, on the basis of which the average flux density was calculated according to equation (1):

\[ J = \frac{n_0 - n}{St}, \]  

where:

\( J \) is the flux density, (mol/(m\(^2\)∙h));
\( n_0 \) – the amount of substance at the beginning of the experiment, (mol); \( n \) is the amount of substance at the end of the experiment, (mol);
\( S \) is the area of membranes, (m\(^2\)); \( t \) - time, (h).

The average specific flux of sulfuric acid through the membranes was 0.195 mol/(m\(^2\) h). In this experiment, despite the high degree of separation of nickel and sulfuric acid, the dialysis rate was periodically slowed down due to a decrease in the concentration gradient between the chambers.

An attempt has also been made to use cation exchange membranes for dialysis. For this, an experiment was carried out on dialysis of the initial solution using Ralex CM-PP membranes. The kinetic curves of changes in the concentration of nickel sulfate and sulfuric acid are shown in Figure 3.

Analysis of the data obtained shows that the concentration of nickel sulfate and sulfuric acid in the retentate chamber decreases, while the concentration in the permeate chamber increases insignificantly. In this case, a high increase in the volume of the solution was observed in the chamber with the retentate. This is due to the osmotic flow of water from the tract with the permeate to the tract with the treated solution, while a decrease in the concentration of the initial substances due to dilution is formally observed, while the total amount of the substance in the chamber remains unchanged. The intense osmotic flow of water through the cation-exchange membranes significantly reduces the diffusion rate, thus dialysis with cation-exchange membranes is not applicable for the separation of nickel sulfate and sulfuric acid.

**Figure 3.** Kinetic curves of changes in the concentration of sulfuric acid and nickel sulfate during dialysis using membranes Ralex CM-PP.
1 - data for the camera with retentate;
2 - data for the chamber with permeate;
3 - lines showing the change of water in the retentate chamber;
4 - limit of nickel content (1 g/L)

\( a \) - concentration of sulfuric acid;
\( b, c \) - concentration nickel sulfate.
To increase the dialysis rate, profiled anion exchange membranes Ralex AM PP_Prof were used (figure 4).

The average ratio of the concentration of sulfuric acid to the concentration of nickel sulfate in the dialysate was 30 times, while in the initial solution the concentration ratio was 3.7, and in the treated solution it decreased to 0.49. In this case, the average flux density of sulfuric acid for profiled membranes Ralex AM-PP_Prof is 0.61 mol/(m²·h), which is higher than in the experiment with commercially available anion-exchange membranes.

Thus, the profiling of anion-exchange membranes makes it possible to increase the rate of acid transfer through the membrane by about 3 times with a slight decrease in the selectivity for nickel sulfate.

To assess the selectivity of the dialysis process to nickel sulfate, the average losses of nickel sulfate from the initial content per hour were calculated by equation (2):

$$\omega = \left( \frac{100 \Delta n}{n_0} \right) \frac{1}{t},$$

where:
- \(\omega\) – loss of nickel sulfate per hour, (%/h);
- \(\Delta n\) – the amount of nickel sulfate transferred through the membranes during the experiment, (mol);
- \(n_0\) – the amount of nickel in the chamber with the initial solution, (mol);
- \(t\) – time of experiment, (h).

The separation factor (SF) was calculated by (3):
\[ SF = \frac{C_{H_2SO_4}^0}{C_{NiSO_4}^0} \cdot \frac{C_{NiSO_4}}{C_{H_2SO_4}} \]  

(3)

where:

\[ C_{H_2SO_4}, C_{NiSO_4} \] – concentrations of sulfuric acid and nickel sulfate in diluate (mol/L);

\[ C_{H_2SO_4}^0, C_{NiSO_4}^0 \] – concentrations of sulfuric acid and nickel sulfate in initial solution, (mol/L);

Summary characteristics of the dialysis process are presented in Table 1.

| Membrane          | Average acid flux through the membrane, mol/(m²·h) | Loss rate of Ni₂SO₄ with acid, %/h | Separation factor (SF) of sulfuric acid and nickel | Nickel loss during 90% sulfuric acid recovery |
|-------------------|----------------------------------------------------|-----------------------------------|-------------------------------------------------|---------------------------------------------|
| Ralex AM-PP       | 0.195                                              | 0.06                              | 11.3                                            | 8.0                                         |
| Ralex CM-PP       | 0.027                                              | –                                 | –                                               | –                                           |
| Ralex AM-PP_Prof  | 0.630                                              | 0.44                              | 6.3                                             | 14.4                                        |

Table 1. Summary characteristics of the dialysis process.

Analysis of the data in Table 1 shows that the maximum losses of nickel sulfate correspond to the use of Ralex AM-PP_Prof membranes. However, the use of profiled membranes makes it possible to process the solution 3 times faster than the original membranes.

Thus, dialysis can successfully separate sulfuric acid and nickel sulfate with a high separation factor. At the same time, 85-92% of nickel remains in the initial solution at a sulfuric acid recovery rate of 90%. This solution can be used for nickel recovery, for example, for the manufacture of batteries. The disadvantages of the dialysis method include a large amount of dilute sulfuric acid containing a small amount of nickel sulfate, which must be additionally concentrated using electromembrane methods such as electrodialysis and electrodialysis concentration to return to galvanic production.

4. Conclusion
A study of the dialysis processing of galvanic production waste containing 2.5 mol/L sulfuric acid and 0.3 mol/L nickel sulfate using various ion-exchange membranes was carried out. The use of cation exchange membranes for dialysis does not solve the problem of separating sulfuric acid and nickel sulfate. When carrying out dialysis through commercially available anion-exchange membranes, it is possible to successfully separate sulfuric acid and nickel sulfate with a separation factor of more than 11. The use of profiled membranes reduces the separation factor to 6.3 and increases nickel losses from 8 to 14.4%, but allows to increase the acid flow through the membranes by 3 times.

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