EFFECTIVENESS OF NANOFILTRATION DURING WATER PURIFICATION FROM HEAVY METAL IONS

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ABSTRACT

Nowadays the problem of pollution of natural waters with heavy metals is extremely acute and urgent. The effective and accurate methods for the determination of concentration of heavy metal ions have been developed to improve the accuracy of their analytical control. The processes of membrane water purification from the heavy metal ions in highly diluted solutions were studied in this work. It was shown that the productivity of the nanofiltration membrane of OPMN-P during the filtration of highly diluted solutions of cadmium sulfate mostly depends on the operating pressure and is close to the values obtained with the use of the distilled water. For example, during the separation of copper, cadmium and lead ions at concentrations of ~ 0.1 mg dm$^{-3}$ the membrane selectivity was very low and did not exceed 10 %. In some cases when using chelators, the selectivity of the membrane reached 100 % with a decrease in the initial concentration of metal ions to $10^{-8}$ mg dm$^{-3}$. In this case, metal ions accumulated in concentrates in equivalent amounts, which is important when concentrating metal ion solutions in the analysis of super-dilute solutions.

Keywords: nanofiltration, membranes, heavy metals, permeate, concentrated product, water purification.

INTRODUCTION

The problem of pollution of natural waters with heavy metals is extremely important and urgent today and its solution requires the organization of measures to improve the quality of natural waters. The study of the state of metal ions in natural waters is rather difficult [1 - 3]. This can be explained by low concentrations of metals in natural waters, the presence of mineral salts and organic compounds and a wide range of pH values of natural waters [4 - 6].

Pollution of water resources by heavy metals ions, which are toxic for living organisms, is a consequence of technological and industrial achievements of modern society [7 - 9]. Components of heavy metals have the ability to bioaccumulate and biomagnify at the high level due to their significant solubility in the aquatic environment [10 - 12]. In many cases while monitoring water bodies, insufficiently accurate methods and monitoring devices are used to assess the real state of water bodies. In addition, almost no increase in the concentration of heavy metals in water during the eutrophication of water bodies is taken into account [13, 14]. The concentration of heavy metal ions in natural reservoirs of Ukraine in a number of cases exceeds the permissible concentration for fishery water reservoirs. In some reservoirs the concentration of heavy metals at a level of ~ 5 mg dm$^{-3}$ is determined [15, 16]. This is due to the accumulation of heavy metals in bottom sediments, their concentration in hydrobionts and the reverse transition to water after the decomposition of dying plants, algae, phytoplankton and zooplankton due to eutrophication of water bodies [17, 18]. Nuclear power plants have a significant influence on the level of heavy metals in water bodies as well [19, 21]. The most important criteria for choosing the appropriate method for determining heavy metals are sensitivity, accuracy, reproducibility and selectivity of the analysis.
We made a combination of preliminary concentration of elements and their further determination to reduce the detection limits and increase the selectivity of the determination.

The aim of the investigation was to create efficient, high-precision methods for the concentration of heavy metal ions to improve the accuracy of their analytical control as well as to determine the efficiency of nanofiltration in the purification of diluted solutions of heavy metal ions.

EXPERIMENTAL

In the research a cell for baromembrane water purification with a volume of 1 dm$^3$, designed to operate at a pressure of up to 5 atm was used. A 12 cm diameter OPMN-P membrane was put in the cell. The pressure was created by a compressor, monitored with a pressure gauge and adjusted using a tap to relieve excess pressure [22].

Copper sulfate, cadmium sulfate and lead nitrate were dissolved in distilled water with a concentration of 1 to 1·10$^{-8}$ mg dm$^{-3}$ for metal ions and were used as model solutions. The concentration of heavy metal ions was determined by inversion chronopotentiometry [23]. As chelators we applied nitrilotrimethylenephosphonic acid (NTMPA), oxyethylidenediphosphonic acid (OEDPA), their sodium salts, Trilon B, sodium diethyl dithiocarbamate (SDDT) and polyhexamethylenepolyguanidine hydrochloride (Aquaton).

The distilled water and metal solutions were placed in a cell samples with a volume of 1 dm$^3$ to determine the productivity of the membrane. After that the pressure was raised to 0.15 MPa - 0.4 MPa and the membrane productivity dependence on the degree of permeate selection was defined, and the permeative volumes and filtration time were determined. In addition, when studying the dependence of the membrane selectivity on the degree of permeate extraction and filtering metal salt solutions, the permeate samples were taken, fixing the filtration time and determining metal concentrations in the permeate [22].

To determine the random error, the arithmetic mean of the measurements and the standard deviation of the measurements were determined. The calculation of the arithmetic mean of the value was performed using the formula:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$$

The standard deviation of the true or mean value was calculated as:

$$s_n = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n}$$

When $n=5$ correction factors were based on the Student’s distribution. Random error was calculated using

$$\vartheta(x_i) = \xi \sqrt{\frac{1}{n(n-1)} \sum_{i=1}^{n} (\bar{x} - x_i)^2}$$

where $\xi$ is the Student’s ratio.

When performing calculations, the values of $P = 0.95$ were set.

Uncertain error occurs due to imperfect accuracy of the equipment ($\delta_e$), instruments and sensors ($\delta_s$), when rounding constants and reference data ($\delta_r$), so the experimental-instrumental error was determined using the formula:

$$\delta_{ux} = \sqrt{\delta_{ex}^2 + \delta_{ep}^2 + \delta_{erp}^2}$$

The total absolute error of the experiment was determined taking into account the measurements of random and instrumental error:

$$\delta(x) = \sqrt{\theta^2(x_i) + \delta(ux)}$$

The relative error was determined using the formula:

$$\varepsilon(x) = \frac{\delta(x)}{\bar{x}} \cdot 100\%$$

RESULTS AND DISCUSSION

One of the simplest and most common methods of concentrating inorganic compounds in aqueous solutions is the distillation method. However, at very low concentrations of metal ions it becomes necessary to evaporate very large volumes of water which makes the method cumbersome and impractical. In addition, during evaporation process, metals partially fly away with water vapor which at low metal concentrations leads to a significant increase in the experimental error.
When the reverse osmosis is used, a large part of the concentrate is in the installation communications, some of the metals are sorbed by the membrane which makes it difficult to establish quantitative ratios of metals in solutions, concentrates and permiates. In addition, osmotic concentration of metals involves the use of pressure > 5 bar - 10 bar. The simplest and most reliable method is nanofiltration, where the initial solution for permeate and concentrate is simply separated in the cell [24, 25]. It was shown on the example of hardness ions that the selectivity of the nanofiltration membrane OPMN-P is low and varies from 50 % to 87 % depending on the pH of the medium. In the weakly acidic solutions the membrane selectivity is lower [22]. However, the use of chelators makes it possible to substantially improve the efficiency of the isolation of metals from aqueous solutions even in the ultrafiltration processes [26].

When the concentrations of metal ions such as copper, cadmium and lead were at 0.100 mg dm$^{-3}$; 0.125 mg dm$^{-3}$; 0.080 mg dm$^{-3}$ and 0.082 mg dm$^{-3}$ the efficiency of water purification from heavy metal ions on the nanofiltration membrane was very low; this can be explained by the high level of dilution of the solutions (Figs. 1(a), 1(b), 2). The selectivity of the membrane reached 4.8 % for cadmium ions, 6.0 % for copper and 6.1 % for lead. At pH = 2.66 the selectivity to the lead ions dropped to 2.26 %.

The selectivity of the membrane increases significantly when the complexants are used. Thus, when Trilon B is used at a concentration of 0.005 N the selectivity to copper ions increases to 69 % - 77 % in the first stages of filtration and decreases to 47.9 % - 47.5 % with an increase in the degree of selection of the permeate to 90 % (Fig. 3). When OEDPA is used at a concentration of 50 mg dm$^{-3}$, the selectivity reaches 100 % during the entire filtration with initial copper ion concentrations of 1.85·10$^{-3}$ mg dm$^{-3}$ and 1.00·10$^{-3}$ mg dm$^{-3}$. At a copper concentration of 1.85·10$^{-3}$ mg dm$^{-3}$ at 90 % of copper permeate removal the copper in the filtrate was completely absent and its concentration in the concentrate reached 1.55·10$^{-2}$ mg dm$^{-3}$ with an estimated amount of 1.85·10$^{-2}$ mg dm$^{-3}$. The absolute error was 0.3·10$^{-2}$ mg dm$^{-3}$ and the relative error was 16.2 %.

At an initial concentration of Cu$^{2+}$, which was 1.00·10$^{-3}$ mg dm$^{-3}$, the copper content in the concentrate...
was 1.07·10^{-4} mg dm^{-3} at a calculated value of 1.00·10^{-4} mg dm^{-3}. The absolute error was only 7·10^{-5} mg dm^{-3}, and the relative error was 7 %.

When NTMPA was used as a chelator at concentrations from 10 to 50 mg dm^{-3} in the solution of copper at concentrations of 10^{-3} mg dm^{-3} - 10^{-7} mg dm^{-3}, a complete separation of copper from water was achieved at concentrations of NTMPA 25 mg dm^{-3} - 50 mg dm^{-3}. With a 10 mg dm^{-3} content of NTMPA the selectivity for copper reached 26 % (Fig. 4).

For the copper concentration of 1.5·10^{-3}, 1.16·10^{-3} the copper content in the concentrate was 0.0150 mg dm^{-3}, 0.0115 mg dm^{-3} and 0.0039 mg dm^{-3}, respectively (curves 1 - 3). The absolute (Δx) and relative (δ) errors were 0.002 mg and 13 %; 0.0001 mg and 0.9 %. The third value of the measured concentration coincided with the calculated value. For a concentration of 1.5·10^{-5} mg dm^{-3} Δx = 1·10^{-6} mg, δ = 0.99 % and for a concentration of 1·10^{-7} mg dm^{-3} Δx = 9·10^{-8} mg, δ = 1.0 %.

The information about the efficiency of water purification from cadmium ions is given in Table 1. Less effective was the use of the composition of Aquaton and SDDT and zero selectivity was provided by NTMPA. At the same time, the OEDPA provided complete cadmium retention.

It is obvious that the structure of the NTMPA molecule ensured the formation of mononuclear complexes that are highly soluble in water what led to a decrease in membrane selectivity. The structure of the OEDPA molecule ensured the formation of polynuclear complexes which were well retained by the membrane during filtration of the solution.

At cadmium concentration of 0.1 mg dm^{-3}, the concentration of cadmium in the concentrate reaches 1.98 mg dm^{-3}. When compared with the calculated value (2.00 mg dm^{-3}), Δx = 0.02 mg dm^{-3}, δ = 1 %. When a cadmium concentration is 1.5·10^{-5} mg dm^{-3} Δx = 0.01 mg dm^{-3}, δ = 3.3 %, and at a concentration of 3.8·10^{-6} mg dm^{-3} Δx = 2·10^{-4} mg dm^{-3}, δ = 3.45 %.

It is interesting to notice that the use of the previously discussed chelators was ineffective in isolating lead ions Pb^{2+} from water while using the OPMN-P membrane. This is due to the fact that lead ions do not form stable complexes with the reagents that were used. However, they easily become insoluble when co-precipitated with calcium carbonate.

At a lead concentration of 0.1 mg dm^{-3} its concentration in the sediment reaches 0.096 mg dm^{-3}. When it was compared with the calculated value (0.1 mg dm^{-3}), Δx = 0.004 mg dm^{-3}, δ = 4 %. At a lead concentration of 1·10^{-5} mg dm^{-3} Δx = 1.7·10^{-5} mg dm^{-3}, δ = 17 % and at a concentration of 1·10^{-6} mg dm^{-3} Δx = 0.1·10^{-4} mg dm^{-3}, δ = 10 %.

It can be concluded that while filtering calcium carbonate slurries together with a lead carbonate, it is released from the water quantitatively what makes it quite easy to solve the problem of the concentration of lead.
Nanofiltration methods using complexones allow one to effectively remove copper ions from the distilled and tap water. However, these methods have certain limitations; for example, cadmium ions are effectively removed only from the distilled water when using complexes. In tap water, Ca$^{2+}$ and Mg$^{2+}$ ions interfere with the extraction of cadmium ions. Therefore, in the presence of hardness ions in the water the filtration using the membrane OPMN-P using complexones is appropriate for purification of water from copper ions. When purifying water from cadmium ions, it is necessary to pre-soften the water. With the development of this area of research, it is planned to develop new methods for pre-cleaning solutions to improve the efficiency of heavy metal extraction.

**CONCLUSIONS**

It is shown that the nanofiltration membrane OPMN-P has high productivity and low selectivity in the filtration of highly diluted solutions of heavy metals. The productivity of the membrane is enhanced by the degree of selection of the permeate when the operating pressure is increased from 1.5 to 4 atm.

With the use of chelators the membrane selectivity increases to 100 % even when very dilute solutions were used. OEDPA and NTMPA provide quantitative separation of copper from water within the concentration range from 1 mg dm$^{-3}$ to $1\times10^{-8}$ mg dm$^{-3}$. Cadmium ions are completely released from water only when using OEDPA.

The used chelators of OEDPA, NTMPA, Aquaton, Trilon B, SDDT do not affect the selectivity of the membrane when Pb$^{2+}$ lead ions are released. When lead carbonate is co-precipitated with calcium carbonate, lead ions are released from water using the OPMN-P membrane quantitatively.

### Table 1. Dependence of the degree of water purification of cadmium ions using the OPMN-P membrane based on the initial concentration of cadmium ions with the type and dose of the chelators (pH $\approx$ 6.7).

<table>
<thead>
<tr>
<th>Chelator</th>
<th>Concentration, mg dm$^{-3}$ (g-equiv dm$^{-3}$)</th>
<th>Concentration of cadmium, mg dm$^{-3}$</th>
<th>R, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>In the permeate</td>
<td>In concentrate</td>
</tr>
<tr>
<td>NTMPA</td>
<td>50</td>
<td>0.125</td>
<td>0.122</td>
</tr>
<tr>
<td>Aquaton + SDDT</td>
<td>50 + 20</td>
<td>0.010</td>
<td>0.148</td>
</tr>
<tr>
<td>Trilon B</td>
<td>0.005N</td>
<td>0.100</td>
<td>0.044</td>
</tr>
<tr>
<td>OEDFA</td>
<td>50</td>
<td>0.100</td>
<td>1.980</td>
</tr>
</tbody>
</table>

**REFERENCES**

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