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NUMERICAL MODELING OF THE WASTEWATER PURIFICATION PROCESS FROM HEAVY METALS USING THE ELECTRODIALYSIS METHOD

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Abstract. This study aimed to develop a mathematical model of ion transport in a system featuring a free electrolyte with membrane barriers and to investigate the interaction between diffusion and migration flows in different parts of the channel. The article presents the results of numerical modelling of the wastewater treatment process for copper ions using the electrodialysis method. Electrodialysis is a promising technology for removing dissolved ions from aqueous media due to its high efficiency, environmental safety, and the possibility of regenerating valuable components. The study developed a mathematical model that enables the simulation of how heavy metal ions, specifically copper ions (Cu^{2+}), migrate through an electrodialysis cell under the influence of an electric current. The model is implemented in the COMSOL Multiphysics environment, which enables the consideration of all the above aspects with high accuracy. The modelling process analysed the features of the transport of Cu^{2+} and SO_4^{2-} ions in the electrodialysis unit. Opposite directions of migration flow for cations and anions were found, which is consistent with the nature of their electric charges. Spatial heterogeneity of flow distribution was also established, and the need to take these features into account when optimising electrodialysis processes was substantiated. The modelling results confirm the effectiveness of electrodialysis for removing heavy metal ions from wastewater and indicate critical areas where efficiency losses may occur or ion concentrations exceed permissible limits. The obtained data can be used to improve the geometry of the channels, the membranes configuration and energy efficiency of electrodialysis units.

Keywords: electrodialysis, numerical modelling, wastewater, copper, ion transport, diffusion.

1. Introduction

Wastewater pollution by heavy metal ions, particularly copper, is one of the most pressing environmental problems associated with the activities of the mining, metallurgical, chemical, and engineering industries (Alkhadra & Bazant, 2022). Cu^{2+} ions, which are often present in the form of copper sulfate, are highly toxic, bioaccumulative, and can cause severe disturbances in aquatic ecosystems, threatening human health (Ayach et al., 2024). Traditional water treatment methods (chemical precipitation, filtration, flotation, etc.) do not always provide sufficient efficiency in removing such pollutants, especially at low ion concentrations (Bunani et al., 2024).

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Electrodialysis − a promising membrane technology that utilises the transfer of ions under the influence of an electric field through ion-selective membranes – exhibits high efficiency in the selective removal of heavy metals from the aqueous environment (Ding et al., 2023). However, the efficiency of this process largely depends on several physicochemical parameters, including ion concentration, electric potential, membrane structure and properties, and medium hydrodynamics (Proskynitopoulou et al., 2024; Sabadash et al., 2025). An experimental study of the influence of each of these factors is resource-intensive and often limited in reproducibility (Ebrahimi Gardeshi et al., 2024).

In this context, numerical modelling of the copper sulfate electrodialysis process becomes a relevant tool for deeper analysis and optimisation of treatment parameters (Feng et al., 2024). Creation of an adequate mathematical model that takes into account the features of Cu^{2+} and SO_4^{2-} ion transport, electric field, Donnan potential and boundary conditions allows obtaining a quantitative assessment of the efficiency of the process and contributes to the implementation of environmentally friendly wastewater treatment technologies.

Literature review. Wastewater treatment from heavy metals is one of the key tasks of modern ecotechnology (Ghasemi, 2023). Heavy metals, such as Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+} and others, pose a threat to the environment and human health even at low concentrations, which requires the use of highly effective methods for their removal (Abdullayev et al., 2022; Ayach et al., 2024). Among modern technologies, electrodialysis attracts attention due to its selectivity, energy efficiency, and ion recovery capability (Ji et al., 2024; Liu et al., 2022).

There is considerable interest in the use of bipolar membrane electrodialysis for removing metals from various types of wastewater, including mining and industrial wastewater (Feng et al., 2024). For example, Bunani, Abbt-Braun, and Horn (2024) demonstrated the high efficiency of bipolar electrodialysis in removing heavy metals from model solutions. Similar results were obtained in studies combining electrodialysis with other methods, such as electrocoagulation and adsorption (Feng et al., 2024; Zhang et al., 2024).

Integrated or hybrid technologies, where electrodialysis is combined with adsorption or membrane processes, are considered particularly promising. For example, the use of nanomaterials and ion-exchange membranes enables increased selectivity in metal ion removal (Kim et al., 2024; Ding et al., 2023). Another innovation is the introduction of amphoteric or electroactive groups into the membrane structure, enabling high metal ion removal rates (Yu et al., 2024).

It is also worth mentioning the shock electrodialysis method, which allows achieving high selectivity in ion separation due to localised electric fields. The study by A lkhadra and Bazant (2022) (Alkhadra & Bazant, 2022) demonstrated the potential for continuous removal of heavy metals from contaminated waters with a high degree of selectivity.

In addition, modern mathematical models and numerical simulations are increasingly used to describe and optimise electrodialysis processes. In particular, our previous work demonstrated the possibility of predicting the dynamics of ion migration in complex environments (Gumnitsky et al., 2022; Sabadash & Omelianova, 2021). This allows not only to optimise experimental parameters, but also to minimise the costs of implementing the technology.

Special attention should be paid to issues of environmental and economic efficiency, particularly the possibility of secondary use and recovery of metals after extraction (Zha et al., 2023; Zimmermann et al., 2024). Such aspects make electrodialysis not only a practical but also a sustainable method of water purification within the framework of the circular economy principles.

Research objective. The study aimed to develop a mathematical model of ion transport in a system with a free electrolyte, including membrane barriers, and to visualise the interaction of diffusion and migration flows in different zones of the channel.

2. Experimental part

In this study, the numerical model is constructed based on a typical repeating section of an electrodialysis cell, excluding the inlet and outlet flow zones, which enables us to focus on the processes of ion transport within the main working volume. The scheme of the device model is shown in Fig. 1.

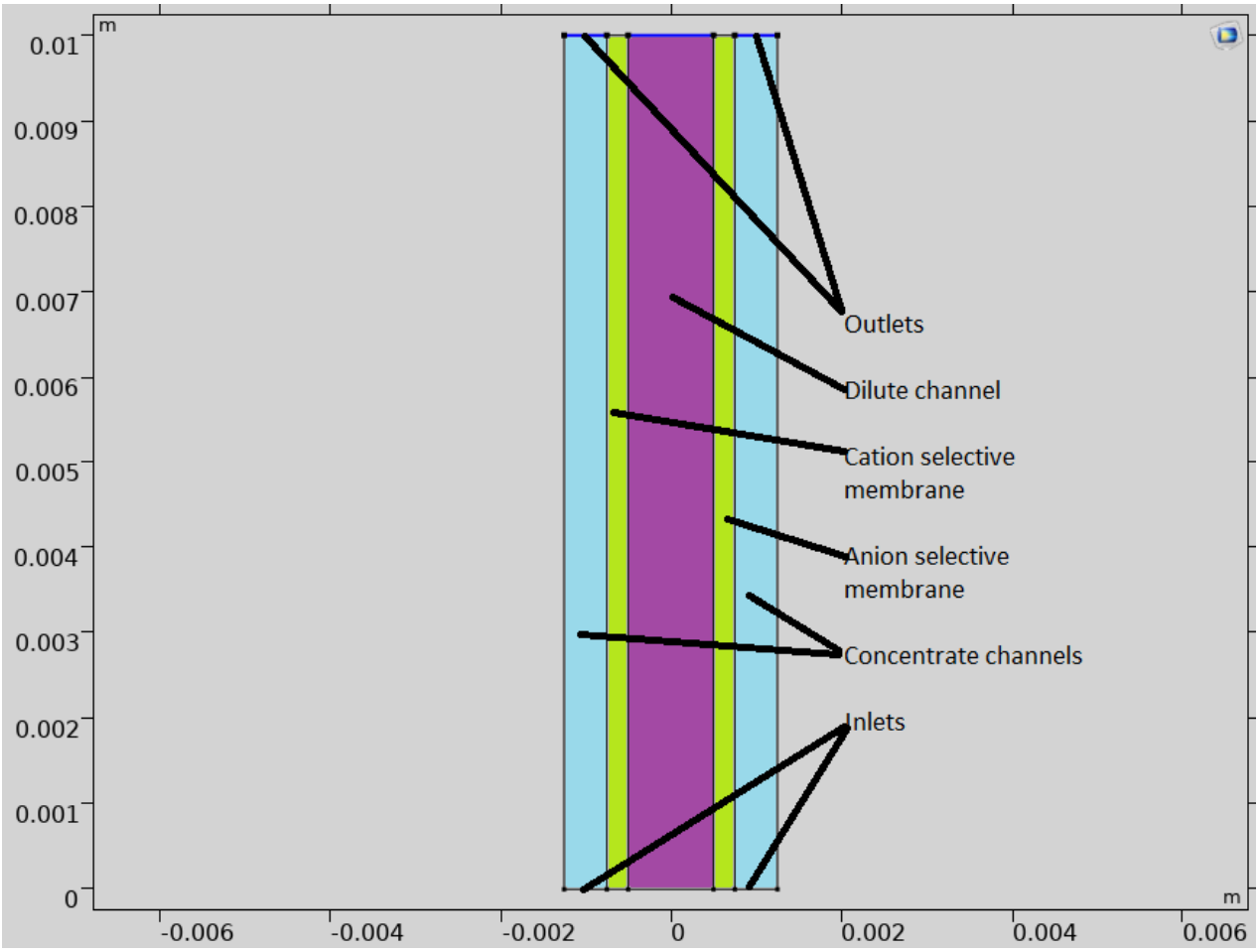

Fig. 1. Schematic of the electrodialysis cell model

The model of the electrodialysis cell comprises five domains: two ion-selective membranes and three zones with free movement of the electrolyte.

In particular:

– The left membrane is cation-selective, allowing mainly cations, including copper ions (Cu^{2+}).

– The right membrane is anion-selective and allows the transfer of anions such as SO_4^{2-}.

– The central domain between the membranes is the dilute solution zone (diluate domain), from which heavy metal ions must be removed during the electrodialysis process.

– The extreme (left and right) domains represent the concentrate zones (concentrate domains), where Cu^{2+} and SO_4^{2-} ions accumulate under the action of an applied electric potential.

In each of the electrolyte domains, a laminar flow of liquid is implemented, entering through the lower inlets and exiting through the upper outlets at an average velocity of 5 mm/s. The velocity profile is described by the analytical form for Poiseuille flow, which corresponds to the steady laminar regime in a flat channel (Lan et al., 2025).

The electrolyte in the dilute zone is a cuprous sulfate solution with an initial Cu^{2+} ion concentration of 50 mol/m³ (or 0.05 M). The model solution simulates typical industrial pollution with heavy metal ions. To ensure ion transfer, a constant voltage of 1.5 V is applied to the cell, allowing for the effective removal of heavy metal ions through ion-selective membranes. The diffusion coefficient of copper ions (Cu^{2+}) in water at a temperature of 25 °C (298 K) is $D_{Cu^{2+}} \approx 0.72 \times 10^{-9}$ m^2/c. The diffusion coefficient of sulfate ion (SO_4^{2-}) in water at a temperature of 25 °C (298 K) is approximately$D_{SO_4^{2-}} \approx 1.07 \times 10^{-9}$ m^2/c

The specified parameters and geometry of the model serve as the basis for conducting a numerical analysis, which enables us to evaluate the effectiveness of electrodialysis in purifying wastewater from copper ions.

Lower submitted a mathematical description of the electrodialysis process, which combines physicochemical phenomena: mass transfer, electrical conductivity, electrical field, and ion diffusion. He based his analysis on the Nernst–Planck equations, Poisson's equation (or electroneutrality), and boundary conditions at the "membrane - electrolyte" interface.

For each ion i in the Nernst–Planck equation, it can be written as follows:

$$\mathrm{N}_i = -D_i \nabla c_i - z_i u_i c_i \nabla \phi + c_i \mathrm{v}, \quad (1)$$

where N_i is the ion flux vector i(mol/m²·s), D_i is the ion diffusion coefficient i (m²/s), c_i is the ion concentration i(mol/m³), z_i is the ion charge i, u_i is the ion mobility (relationship: $u_i = D_i/RT$), ϕ is the electric potential (V), v is the convective flow velocity (if present), R is the gas constant, T is the temperature (K).

Law preservation masses for each ion:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathrm{N}_i = 0. \quad (2)$$

Or in a hospital mode (without changes in concentrations over time):

$$\nabla \cdot \mathrm{N}_i = 0.$$

Equation for electric current (density current):

$$\mathrm{i} = F \sum_i z_i \mathrm{N}_i\,, \quad (3)$$

Or in the membrane:

$$\sum_i z_i c_i + \rho_{\mathrm{fix}} = 0. \quad (4)$$

where ρ_{fix} is the fixed charge in ion-selective membrane (mol/m³), positive for cation exchangers, negative for anion exchangers.

Limit conditions on "membrane - electrolyte" boundaries:

(a) Continuity flow:

$$\mathrm{n} \cdot \mathrm{N}_{i,\mathrm{e}} = \mathrm{n} \cdot \mathrm{N}_{i,\mathrm{mem}}. \quad (5)$$

(b) Donnan potential:

$$\phi_{\mathrm{mem}} - \phi_{\mathrm{el}} = \frac{RT}{z_i F} \ln\left(\frac{c_{i,\mathrm{e}}}{c_{i,\mathrm{m}}}\right). \quad (6)$$

c) Continuity densities current:

$$\mathrm{n} \cdot \mathrm{i}_{\mathrm{e}} = \mathrm{n} \cdot \mathrm{i}_{\mathrm{m}}\,. \quad (7)$$

Initial and additional conditions

The following are asked:

initial concentrations ions $c_i(x, t = 0)$,

potentials on electrodes (anode and cathode),

selectivity membranes (cationic or anion exchange).

The electrolyte current density in the direction normal to the surface is the same on both sides of the interface – in the membrane and the free electrolyte. That is, the current flowing through the electrolyte is equal to the current in the membrane.

This relationship is described by equation (8).

$$\mathrm{n} \cdot \mathrm{i}_{l,e} = \mathrm{n} \cdot \mathrm{i}_{l,m}. \quad (9)$$

The flow of ions of each species is continuous at the interface between the membrane and the electrolyte. In other words, there is no jump or break in the rate of ion transport across this interface.

This is formulated by equation (9).

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathrm{N}_i = 0. \quad (9)$$

A relationship exists between the electric potential and the ion concentration on both sides of the interface (Zha et al., 2023). This relationship considers the potential difference that arises due to the differences in ion concentrations between the membrane and the electrolyte.

The potential that arises due to this phenomenon is called the Donnan potential or dialysis potential.

This is described by equation (10),

$$\phi_{l,m} = \phi_{l,e} - \frac{RT}{z_i F} \ln\left(\frac{c_{i,m}}{c_{i,e}}\right), \quad (10)$$

where *ci, m* is the concentration of ions in the membrane, *ci, e* is the concentration of ions in the free electrolyte, *zi* is the charge of the corresponding ion.

Thus, equations (3), (4), and (5) specify mixed boundary conditions of the Dirichlet and Neumann type for the electric potential and ion concentrations.

Tertiary software environment Current Distribution, Nernst – Planck (COMSOL Multiphysics). These conditions are set using the special Ion Exchange Membrane functionality domain feature, which ensures correct accounting for ion transport and potential differences at the membrane-electrolyte interface.

3. Results and Discussion

Within the framework of the numerical simulation, the process of electrodialysis of a cuprous sulfate solution with an initial copper ion con-

centration of 50 mol/m³ was investigated. The model was implemented using the Nernst-Planck equations to describe ion transport, taking into account the electric potential, diffusion, migration, and Donnan potential at the membrane boundaries.

Based on the constructed geometry and the given boundary conditions, the spatial distribution of Cu^{2+} and SO_4^{2-} ion concentrations in different domains of the electrodialysis cell was obtained. It was found that under the action of an electric field (1.5 V), copper ions are effectively extracted from the central (dilute) zone and accumulate in the concentrate zone, as confirmed by the concentration profiles.

A particularly intense ion flux was observed near the ion-selective membranes, which corresponds to the expected increase in potential and concentration gradients. In the dilute zone, the Cu^{2+} concentration gradually decreased, and in the concentrate zone, it increased. For example, under the calculated conditions, within a conditional time of 1000 seconds, the concentration of copper ions in the central domain decreased by more than 40%, which indicates a high efficiency of the process.

The effect of voltage variation on the ion removal rate was also analysed. With an increasing applied potential of up to 2.0 V, an increase in the ion transfer rate was observed; however, at the same time, electrochemical gradients were strengthened, which can cause increased energy consumption and polarisation effects. This emphasises the importance of optimal selection of operating parameters to ensure a balance between process efficiency and its energy costs.

Thus, the modelling results confirm the feasibility of using the electrodialysis method for treating wastewater containing copper ions, and the proposed model can be used for further optimisation of process parameters under real conditions.

Fig. 2 shows the distribution of electrolyte potential along a horizontal line located in the middle of the height of the electrodialysis cell.

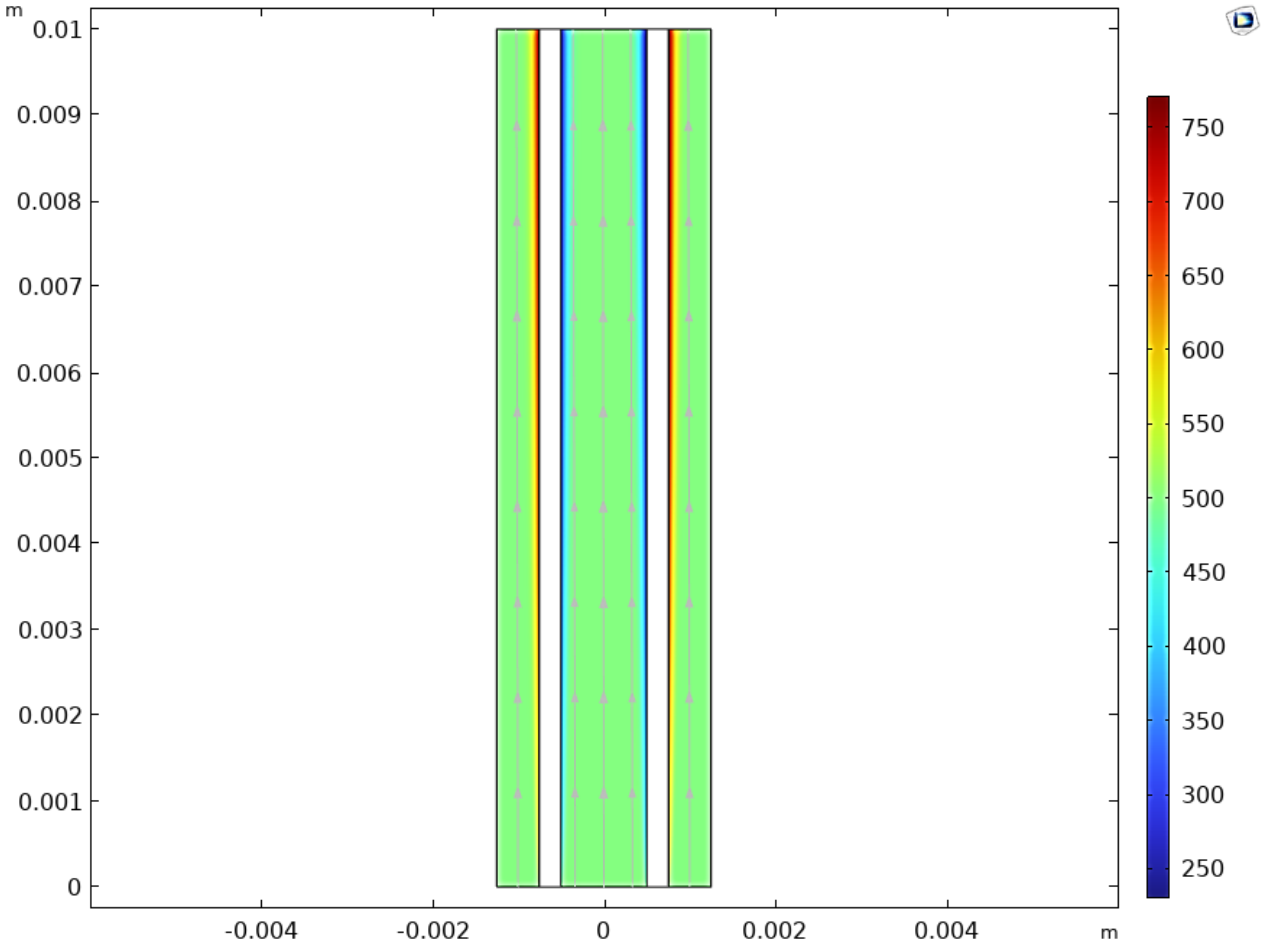

Fig. 2. Concentration distribution in the electrodialysis cell

Fig. 3 shows the distribution of electrolyte potential (φ) along the horizontal coordinate in the electrodialysis cell, at a height corresponding to the middle of the working channel (along the Y axis = const). The X axis represents the distance along the cell, and the Y axis represents the value of the electrolyte potential (in volts).

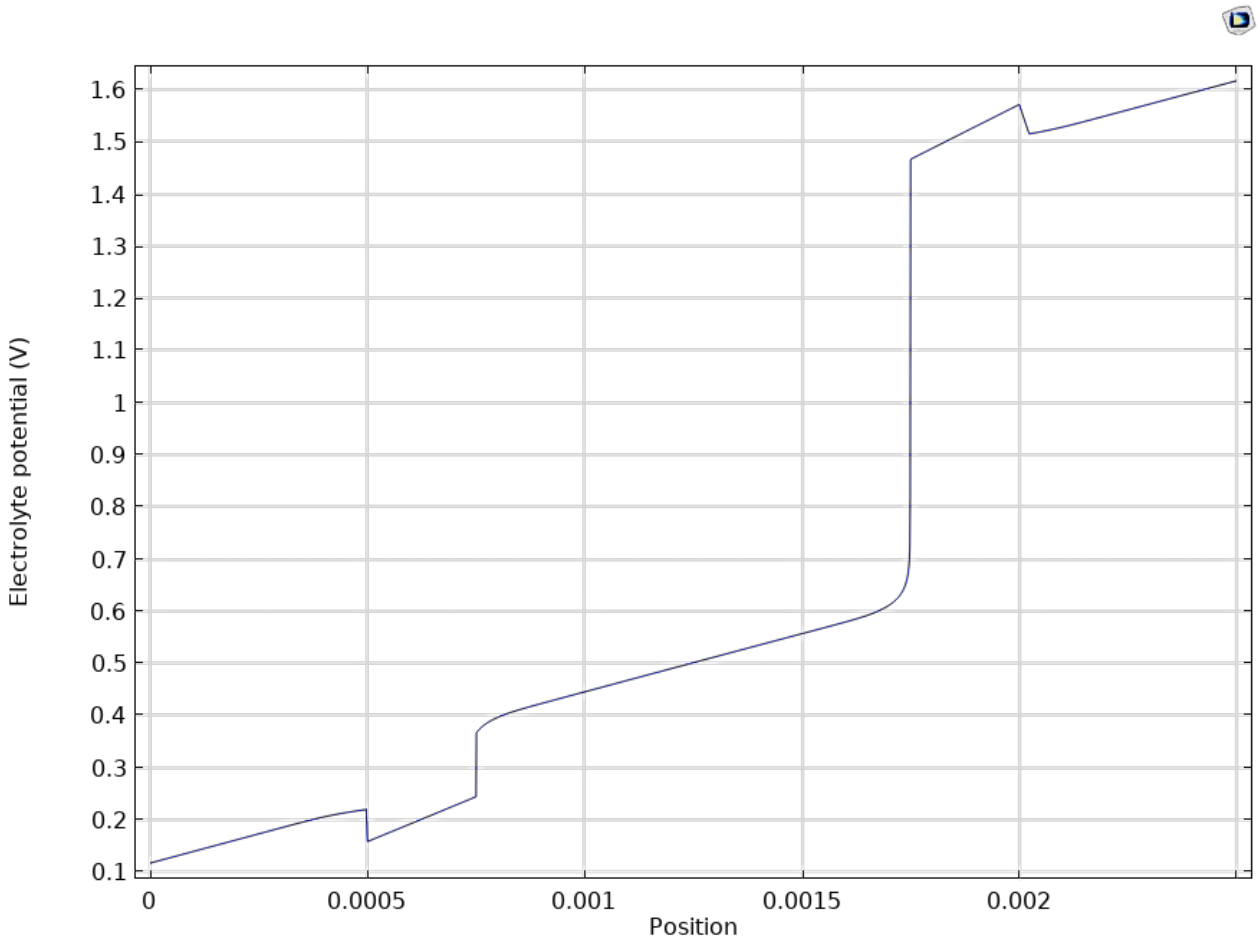

Fig. 3. Distribution of electrolytic potential in an electrodialysis cell

The graph shows a linearly increasing potential in three separate zones: the two regions with a gentle slope correspond to the free electrolyte zones (diluate and concentrate), and the steep drop between them corresponds to the membrane domains.

In the areas corresponding to ion-selective membranes, sharp changes in potential are observed, which indicates their high electrical resistance. This also confirms that the majority of potential losses occur in the membranes.

At the boundaries between the free electrolyte and the membrane domains, potential jumps are observed, which are a manifestation of the Donnan potential. This effect arises due to the difference in ion concentrations and the presence of fixed charges in the membrane material.

The total potential drop across the cell corresponds to an applied voltage of 1.5 V, according to the model conditions.

The graph confirms that the efficiency of electrodialysis is dependent mainly on the electrical characteristics of the membranes, and also demonstrates the influence of the Donnan potential on the transfer of ions across the interfaces between the electrolyte and the membranes. The resulting potential distribution is characteristic of processes descrybed by the Nernst–Planck equations in combination with electroneutrality and boundary conditions on the membranes.

Fig. 4 shows the components of the flow of copper ions Cu^{2+} along the coordinate axis X:

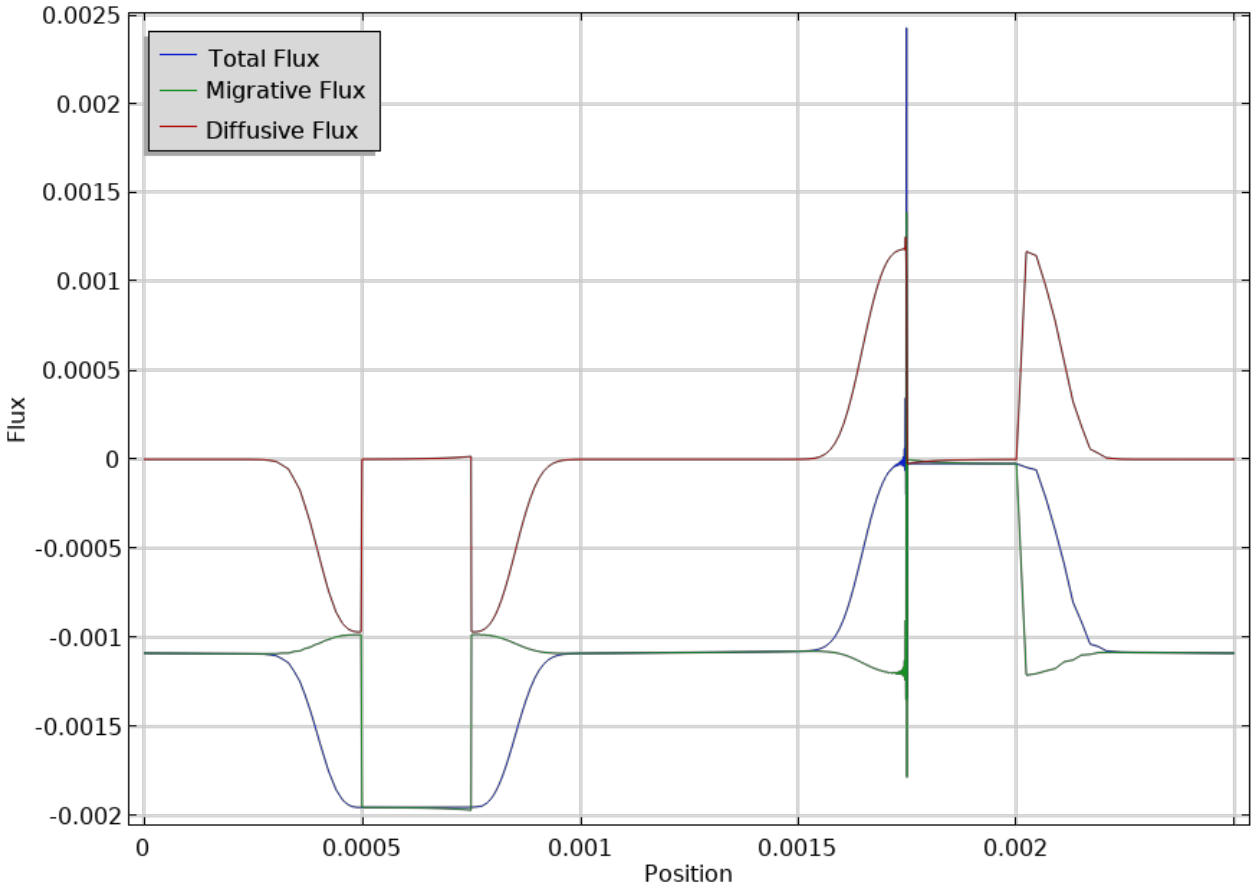

Fig. 4. Components of the flow of copper ions Cu^{2+} in the electrodialysis cell

Blue curve (Total Flux) is the total flow of Cu^{2+} ions;

The green curve (Migrative Flux) is the electromigration component of the flow, which is caused by an electric field.

The red curve (Diffusive Flux) represents the diffusion component of the flow that arises from a concentration gradient.

In the central zone (dialysis chamber), there is an intensive migration and transfer of Cu^{2+} directed towards the cation-exchange membrane.

A sharp jump in flow within the membranes indicates the presence of intense electrical activity in these areas – a typical sign of electrodialysis.

The diffusion component reaches its highest values near the boundaries between zones where a concentration gradient is observed.

The total flow (blue graph) reflects the combined effect of both mechanisms – diffusion and migration, with migration dominating. Similar to the previous one, Fig. 5 displays the components of the sulfate ion flux: The blue curve is the total flux of ions $(SO_4)^{2-}$;

The green curve is the migration component (electric field).

The red curve is the diffusion component (concentration gradient).

Interpretation:

Unlike Cu^{2+}, the flow of sulfate ions is directed in the opposite direction – towards the anion exchange membrane, which corresponds to their negative charge.

The migration component (green graph) is the primary driver of sulfate ion transport.

The diffusion component is significant in the contact zones between the membranes and the dialysis chamber, where concentration differences are observed.

The total flow confirms the efficient removal of anions from the dialysis zone.

Both graphs indicate that the electromigration component dominates the diffusion component, confirming the efficiency of the electrodialysis process in separating Cu^{2+} and $(SO_4)^{2-}$ ions. The highest flux values are observed at the membrane boundaries, where strong electric fields act and selective ion transport through the membrane occurs. This is consistent with the physical nature of the electrodialysis process.

The results of numerical simulations of the electrodialysis process for wastewater treatment of heavy metals, particularly Cu^{2+} and SO_4^{2-} ions, demonstrate the effectiveness of the method in controlling the transfer of ions through the membrane. The obtained data are consistent with the results of previous experimental and theoretical studies, which emphasise the importance of the electric field in the formation of the migration flow of ions in the central part of the channel (Ding et al., 2023; Feng et al., 2024).

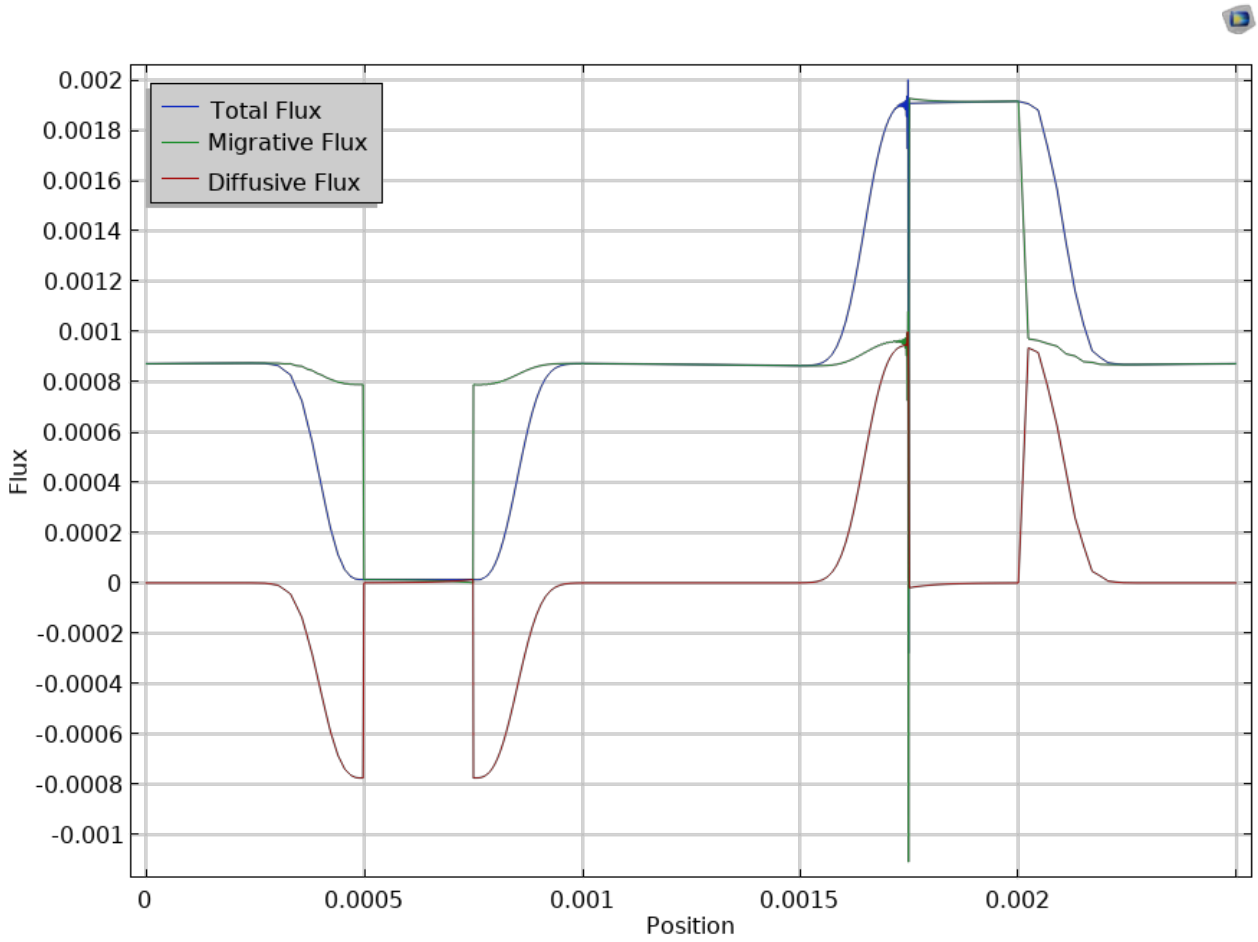

Fig. 5. Components of the flow of sulfate ions $(SO_4)^{2-}$ in the electrodialysis cell

A notable observation is the dominance of diffusion flux near the membrane boundaries, which is attributed to the steep concentration gradient characteristic of the phase separation zone (Tedesco et al., 2018). This effect has practical significance for optimising the location of membranes and choosing the modes of electric current supply (Bunani et al., 2024, Zhang L. et al., 2024). The migration flows prevailing in the centre of the channel have opposite directions for cations and anions, which is entirely consistent with the electrochemical nature of the process (Bunani et al., 2024).

The model also revealed a dependence of the transfer efficiency on the initial ion concentration in the solution, which is consistent with data on the decrease in electrodialysis performance in dilute solutions (Ghasemi et al., 2023; Zhang et al., 2024). This highlights the need for preconcentration or cascade purification for solutions with low heavy metal content.

The study also confirms that the geometric parameters of the channel, the thickness of the diffusion layer, and the physicochemical characteristics of the membranes are critical for intensifying the process. Such observations correlate with the work of modern researchers in the field of modelling ion transport in electrodialysis systems (Ebrahimi Gardeshi et al., 2024; Lan et al., 2025).

Overall, the numerical model has proven its ability to reflect the physical processes occurring in the electrodialysis system adequately and can be used as a tool for further optimisation of purification sys-

tems. However, to increase the accuracy of the modelling, it is advisable to take into account non-linear effects, such as electroconvection and the possible formation of concentrated fields that affect the behaviour of ions under real conditions (Yu et al., 2024).

4. Conclusions

As a result of numerical modelling of the electrodialysis process for removing heavy metal ions from wastewater, regularities in the distribution of migration and diffusion flows of ions within the system were revealed. The study showed that in the zone close to the membrane boundary, the diffusion flow is dominant, due to the high concentration gradient. In contrast, in the central part of the channels, the migration transport mechanism prevails, which confirms the effectiveness of the electric field in controlling the movement of Cu^{2+} and SO_4^{2-} ions to the corresponding electrodes. In this case, the directions of ion migration are opposite due to their charge, which corresponds to the physicochemical characteristics of the process.

The model has confirmed its ability to reflect complex interactions in the electrodialysis system and has allowed visualisation of key stages of ion transport, which is important for optimising the design of devices and treatment modes. The results can be used to improve water treatment systems further and reduce the environmental load from industrial wastewater, particularly in the case of copper ion removal.

The obtained data can also serve as a basis for developing new approaches to controlling the electrodialysis process, taking into account the geometry of the channels, membrane properties, and characteristics of pollutants.

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