Mathematical Modelling of Processes in Apparatus with Flowing Three-Dimensional Electrodes for Calculation of Galvanic Waste Water Purification Modes

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Abstract. The ecology of the urban environment significantly depends on the intensity and toxicity of industrial and other wastewater discharges, both within the city limits and in the areas adjacent to the city. This paper discusses advanced technologies for wastewater treatment from heavy and non-ferrous metal ions in industrial and small enterprises of urban agglomerations. An analysis of the efficiency of using flow-through three-dimensional electrodes for wastewater treatment from harmful reagents is presented. The use of mathematical modeling allows calculating and predicting the results of the technological process, as well as optimizing the process by calculating the effective values of the control parameters, in particular, calculating the modes of treatment of galvanic wastewater from heavy and non-ferrous metals in devices with three-dimensional flow electrodes. The given mathematical models of electrochemical processes in three-dimensional flow electrodes in relation to the extraction of metals from solutions of galvanochemical production allow us to conduct computational experiments. For this purpose, a set of programs has been developed that allows calculating the parameters of the electrochemical process of metal deposition from heavy and non-ferrous metals in devices with three-dimensional flow electrodes. The input data for the calculation are the parameters of the deposited component (ion valence, diffusion coefficient), the ion concentration of the deposited component in the solution, the flow rate of the solution, the mass transfer coefficient, the electrical conductivity of the solid and liquid phases of the electrode – solution system, the overall current density, the electrode parameters (porosity, fiber radius, electrode thickness), the electrolysis time. The results of the calculation are: the concentration of metal ions (calculation can be carried out for one or two metal ions contained in the solution), the distribution through the thickness (volume) of the electrode, its conductivity, the mass of metals, the speed of flow of the electrolyte, the coefficients of mass transfer of metal ions, the mass transfer coefficient for oxygen, the potential profiles of the current metals, profile of the current oxygen profile of the current hydrogen, given the profile of the current metals. The solution of a scientific problem of practical importance for improving the ecological state of the urban environment is presented.

1. Introduction
Galvanochemical production, with all their advantages, have a sufficient environmental hazard. The harmful effects of galvanochemical effluents on surface and underground water bodies, including in urban agglomerations, are mainly determined by the components of technological solutions contained
in them. Salvo discharges of electrolytes in electroplating plants lead to exceeding the maximum permissible concentrations (MPC) of metals in wastewater. The so-called "technical fatigue" of solutions causes the problem of salvo discharges. Such discharges lead to high water consumption, disruption of treatment facilities, and a sharp increase in the MPC in wastewater. The reasons for the deterioration of the electrolytes are usually associated with the accumulation of inorganic and organic substances in them, including impurities introduced with reagents, products of electrode reactions. Conditioning of electrolytes, extraction of valuable components of electrolytes, their reuse is one of the possible ways to solve the problems of creating closed technological processes.

The direction that implements the treatment of the general runoff of galvanochemical production, until recently, was dominant in the treatment of galvanic and other wastewater [1]. However, there are a number of publications showing that the creation of local systems for processing solutions is most widely used, since local cycles, along with solving environmental problems, ensure the return of reagents and water, allowing for the creation of low- and non-waste production [2, 3].

A special place among the well-known methods for creating local systems for processing electroplating solutions should be given to electrochemical methods for extracting valuable components to return them to industrial cycles. Electrochemical methods meet the basic requirements for processes developed for the extraction of metals from solutions of electrochemical production: they do not require the use of reagents, the metal is obtained in the purest concentrated form and can in most cases be returned to production; the possibility of automating the process is easily realized, water consumption is reduced, etc. [4–6].

The use of devices with flow-through three-dimensional electrodes (PTE) for the extraction of metals from solutions with low concentrations is one of the promising methods for solving this problem. The development of original technologies for electrodeposition of various metals based on the use of PTE is necessary for the intensification of electrochemical processes, especially in solutions with low concentrations of electroactive components. This is achieved primarily due to the use of cathode materials with a high reaction surface and the possibility of intensive mass transfer in the electrode volume [4–6]. Obviously, the development of methods for mathematical modeling of processes in PTE and the use of computational experiments contribute to the solution of this problem. The use of mathematical modeling makes it possible to calculate and predict the results of the technological process, as well as to optimize the process by calculating the effective values of the control parameters [4, 5, 7].

2. Algorithm Description
We assume that the flow of charged particles of the i-th grade \( N_i (i = 1,..., n) \) in the volume of the electrolyte is determined by the migration and convective components, which is realized in most electrochemical systems [8]:

\[
N_i = z_i u_i F C_i \nabla E + C_i V.
\] (1)

Here \( z_i, C_i, u_i \) are, respectively, the charge, concentration, and mobility of the i-th electroactive component in a pseudo-homogeneous medium; \( \nabla E \) is the gradient of the electric field potential; \( V \) is the velocity vector of the convective transport of the solution.

The current in the electrode – electrolyte volume is expressed by the formula:

\[
j = F \sum z_i N_i.
\] (2)

The material balance condition in the absence of a homogeneous electrochemical reaction:
\[
\frac{\partial C_i}{\partial t} = -\nabla \cdot N_i,
\]

where \(\nabla \cdot N_i\) is the divergence of the \(N_i\) flow.

The transformation of equations (1) – (3) using the known rules of differential calculus, as well as the equation of the relationship between the change in the concentration of the extracted component \(C_k\) with the partial current density \(j_{S_k}\) [9]

\[
\frac{\partial C_k}{\partial r} = -\frac{S}{V'_{z_k} F} j_{S_k},
\]

eventually leads to the following system of differential equations:

\[
F \frac{\partial}{\partial t} \sum z_k C_k = \nabla \left[ -\frac{\kappa_s \kappa_l \nabla E}{\kappa_s + \kappa_l} \right] + S \sum j_{S_k}.
\]

Here \(S\) is the reaction surface; \(j_{S_k}\) – the density of the polarizing current by \(k\)-th component, \(\kappa_s, \kappa_l\) – the conductivity of the solid and liquid phases of the system.

Natural boundary conditions:

\[
\left. \frac{\partial E}{\partial n} \right|_{\sigma_e} = J(t) \rho_i; \quad \left. \frac{\partial E}{\partial n} \right|_{\sigma_s} = -J(t) \rho_i; \quad \left. \frac{\partial E}{\partial n} \right|_{\sigma_i} = 0; \quad C(t) \mid_{\sigma_{st}} = C_0.
\]

where \(n\) is the direction of the normal to the boundary of the reaction region \(\sigma = \sigma_e + \sigma_s + \sigma_i + \sigma_{st}\) consisting of the surfaces of the cathode, anode, insulators and the electrolyte supply zone.

The system (5) – (6) makes it possible to calculate the distribution of the potential, current density, and concentration of the electroactive substance in the volume of the porous electrode.

3. The results of numerical experiments

For conducting computational experiments, a set of programs has been developed that allows calculating the parameters of the electrochemical process of metal deposition from electrolyte solutions on flow-through three-dimensional electrodes.

The input data for the calculation are the parameters of the deposited component (ion valence, diffusion coefficient), the ion concentration of the deposited component in the solution, the flow rate of the solution, the mass transfer coefficient, the electrical conductivity of the solid and liquid phases of the electrode – solution system, the overall current density, the electrode parameters (porosity, fiber radius, electrode thickness), the electrolysis time.

The results of the calculation are: the concentration of metal ions (the calculation can be carried out for one or two metal ions contained in the solution), the distribution of the thickness (volume) of the electrode of its electrical conductivity, the mass of metals, the flow rate of the electrolyte, the mass transfer coefficients of metal ions, the mass transfer
coefficient for oxygen, the potential, the current profiles for metals, the current profile for oxygen, the current profile for hydrogen, the reduced current profile for metals.

As an illustration of the efficiency of the methods, we present calculations of the processes of joint electrodeposition of gold and silver from a sulfuric acid thiourea solution of the composition: H$_2$SO$_4$ – 0.5 mol/l, thiourea – 50 g/l, gold – 22.4 mg/l, silver – 141 mg/l (Figure 1).

![Figure 1](image)

**Figure 1.** The distribution of sediment metal on the thickness of the electrode: a – gold; b – silver; d – the ratio of the mass of metal to the mass of the CFM; 1 – experiment; 2 – calculation; n is the layer number; T – the back side of the electrode; thickness electrode – 1 cm; the current density of 0.2 A/m$^2$, flow rate solution of 0.56 cm/s

The studies were carried out with a frontal (from the side of the counterelectrode) supply of the solution to the electrode. In the first case, the electrode was composed of 12 layers of carbon fiber material (CFM) and 6 layers – in the second. Characteristics of CFM (VVP-66-95): specific surface area – 255 cm$^2$/cm$^3$, specific electrical conductivity – 0.03 Cm/cm, porosity – 0.95 [4-6]. The specific electrical conductivity of the solution is 0.1 Cm/cm, the electrolysis time is 60 minutes.

4. Conclusions
The experimental and calculated dependences presented in Figure 1, as well as the consistency of the results of calculations of the electrochemical functions of the classical electrochemical theory, allow us to conclude that the mathematical models and calculation algorithms described in this report and in our other works [4, 5] are effective for conducting numerical studies and optimizing the control parameters of the processes of extracting metal ions from industrial wastewater to flow three-dimensional electrodes for the purpose of neutralization of industrial wastewater and regeneration of electrolytes.

It should be noted that PTE can be effectively used simultaneously for the cathodic extraction of metals and the anodic oxidation of toxic electrolyte compounds in a single cell [4 – 6].

References
[1] S. V. Sverguzova “Complex neutralization of waste water, utilization of water treatment sludge and secondary use of gypsum and metal-containing industrial waste”. Diss. D., Kazan: KSTU, 2008.
[2] D. M. Harutyunyan, A. Yu. Tregubov “A method for cleaning washing waters and spent electrolytes”. In the proceedings of the conference, Volgograd: VSTU, pp. 81–83, 2017.
[3] A. A. Sineltsev “Sorption treatment of wastewater from heavy metal ions using modified
granular glauconite”. Diss. Ph. D., Kazan: KNRTU, 2016.

[4] V. K. Varentsov, A. N. Koshev, V. I. Varentsova “Modern problems of electrolysis and problems of optimization of processes in reactors with three-dimensional carbon electrodes”: monogr. Penza: PSUAC, 288 p., 2015.

[5] V. K. Varentsov, A. N. Koshev, V. I. Varentsova, V. V. Kuzina “Redox processes on flow-through three-dimensional electrodes. Mathematical modeling. Theory. Experiment”, Penza: PSUAC, 172 p., 2020.

[6] V. K. Varentsov ‘Electrolysis with three-dimensional electrodes in the regeneration processes of metals from leaching solutions in electroplating”. Izvestiya of USSR Academy of Sciences. Ser. chemical Sciences, vol. 3, pp. 124-138, 1988.

[7] V. F. Skorokhodov, A. S. Kitaeva, V. V. Biryukov, M. R. Nikitin, A. V. Artemyev “Computer simulation of processes in industrial wastewater treatment to their optimal settings”. In the proceedings of the conference "Theory and Practice of System Dynamics". Kola Research Center of the Russian Academy of Sciences (Apatity), 2019.

[8] J. Newman “Electrochemical systems”. M.: Mir, pp. 463, 1977.

[9] R.E. Siota “Flow through electrodes composed of parallel screens”. J. Electrochem Acta, vol. 22, no 4, pp. 439–443, 1977.