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Mathematical Modeling and Software for Calculating Regimes of Galvanic Wastewater Purification from Heavy and Nonferrous Metals in Devices with Flow-Through Three-Dimensional Electrodes

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Abstract. The paper briefly discusses progressive technologies of wastewater treatment from ions of heavy and nonferrous metals of industrial and small enterprises of urban agglomerations. An analysis of the efficiency of three-dimensional flow-through electrodes for wastewater treatment of harmful reagents is given. The mathematical models of electrochemical processes in three-dimensional flow-through electrodes as applied to extract metals from the solutions of galvanochemical industries are presented. The description of the set of programs developed in the programming language Object Pascal for computational experiments according to the obtained mathematical models is given. Numerical solution of scientific problem of practical importance has been obtained by using the program complex. A good correspondence between the results of calculations and experiments is shown.

Keywords: mathematical modeling; software package; Object Pascal programming language; three-dimensional flow electrode; extraction of metals from galvanochemical solutions.

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Математическое моделирование и программное обеспечение для расчета режимов очистки гальванических стоков от тяжелых и цветных металлов в аппаратах с проточными трехмерными электродами

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Аннотация. В работе кратко обсуждаются прогрессивные технологии очистки сточных вод от ионов тяжелых и цветных металлов промышленных и малых предприятий городских агломераций. Приводится анализ эффективности применения проточных трехмерных электродов для очистки сточных вод от вредных реагентов. Приводятся математические модели электрохимических процессов в трехмерных проточных электродах применительно к извлечению металлов из растворов гальванохимических производств. Приводится описание комплекса программ, разработанных для проведения вычислительных экспериментов по полученным математическим моделям. При использовании программного комплекса получено численное решение научной задачи, имеющей практическое значение. Показано хорошее соответствие результатов расчетов и экспериментов.

Ключевые слова: математическое моделирование; комплекс программ; язык программирования Object Pascal; проточный трехмерный электрод; извлечение металлов из растворов гальванохимических производств.

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1. Introduction

A new approach to the study of electrochemical processes in three-dimensional flowing electrodes as applied to the extraction of metals from solutions of galvanochemical production is to conduct computational experiments based on mathematical modeling and software package.

Galvanochemical productions, with all their advantages, have a sufficient environmental hazard, which is mainly determined by the harmful impact of galvanochemical effluents containing components of technological solutions on surface and ground water bodies, including in urban agglomerations. The exceeding of the maximum permissible concentrations (MPC) of metals in wastewater is caused by salvo discharges of electrolytes in electroplating plants. The problem of salvo discharges is caused by so-called "technical fatigue" of solutions. Such discharges lead to high water consumption, disruption of treatment facilities, a sharp increase in MPC in wastewater. The causes of deterioration of 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, and their reuse is one of the possible ways to solve the problems of creating closed technological processes.

Until recently, in the treatment of galvanic and other wastewater the dominant direction was the treatment of the total effluent of galvanochemical production [1]. However, there are a number of publications showing that the creation of local solution processing systems gets the greatest application, as local cycles along with the solution of environmental problems provide the return of reagents and water, allowing the creation of low- and waste-free production [2, 3].

2. Methodology

Among the known methods of creating local treatment systems for galvanic solutions a special place should be given to electrochemical methods of extraction of valuable components to return them into industrial cycles. Electrochemical methods satisfy the basic requirements to the processes developed for extraction of metals from solutions of galvanochemical productions: 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 process automation is easily realized, water consumption is reduced [4–7], etc.

One of the promising methods for solving this problem seems to be the use of apparatuses with flow-through three-dimensional electrodes (FTE) for extracting metals from solutions with low concentrations. The development of original technologies of electrodeposition of various metals based on the use of FTE is necessary for the intensification of electrochemical processes, especially in solutions with low concentrations of electroactive components, which is achieved primarily through the use of cathode materials with a high reaction surface and the possibility of intense mass transfer in the electrode volume [4–7]. The solution of this problem is obviously promoted by the development of methods of mathematical modeling of processes in FTE and application of computational experiment. 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 control parameters [4–6, 8].

Let's assume that the flux of charged particles of the i-th grade N_i (i = 1, ..., n) in the electrolyte volume is determined by migration and convective components, which is realized in most electrochemical systems [9]:

$$N_i = z_i u_i F C_i \nabla E + C_i V. \tag{1}$$

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; ∇E is the electric field potential gradient; V is the velocity vector of the convective transfer of the solution.

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

$$j = F\,\Sigma(z_i N_i). \tag{2}$$

Material balance condition in the absence of a homogeneous electrochemical reaction:

$$\partial C_i / \partial t = -\nabla \bullet N_i. \tag{3}$$

Here $\nabla \bullet N_i$ is the divergence of the N_i flow.

Conversion of equations (1) – (3) using known rules of differential calculus, as well as the equation of the relationship between the change in concentration of the extractable component C_k with the partial current density j_{Sk} [10]

$$\partial C_k / \partial r = -\,S\, j_{Sk} / (|V| z_k F) \tag{4}$$

eventually leads to the following system of differential equations:

$$F\,\partial \Sigma(z_k C_k)/\partial t = \nabla \bullet[-\kappa_s \kappa_l \nabla E / (\kappa_s + \kappa_l)] + S\,\Sigma(j_{Sk}). \tag{5}$$

Here S is the reaction surface; j_{Sk} is the polarizing current density by k-component, κ_s, κ_l – conductivities of solid and liquid phases of the system. Together with natural boundary conditions:

$$[\partial E(t)/\partial n]_{\sigma c} = j\,(t)\rho_s,\ \ [\partial E(t)/\partial n]_{\sigma a} = j\,(t)\rho_l \tag{6}$$

$$[\partial E(t)/\partial n]_{\sigma i} = 0,\ \ [\partial E(t)/\partial n]_{\sigma e} = C_0. \tag{7}$$

Here *n* is the direction of the normal to the boundary of the reaction region, consisting of the surfaces of the cathode, anode, insulators and the electrolyte supply zone: $\sigma = \sigma_c + \sigma_a\ \sigma_i + \sigma_e$; ρ_s, ρ_l are the specific resistance of the solid and liquid medium, respectively.

The system (5) – (7) makes it possible to calculate the distribution of potential, current density, and concentration of the electroactive substance in the volume of the porous electrode.

The mathematical models given in [4-7] are based on the development of earlier modeling results obtained both by the authors of the present paper and by other authors, for example, in [11], but the generalized dynamic models proposed by the authors of the present paper are not found in the literature.

The study and criticism of the mathematical models of the authors of this publication and other authors are given in detail, for example, in [12].

Mathematical aspects of the implementation of the proposed mathematical models of electrodeposition in three-dimensional flow electrodes are discussed, for example, in [13].

To carry out computational experiments, a set of programs has been developed to simulate electrochemical processes in PTE [14]. The software package is designed to calculate and analyze the parameters of the electrochemical process when extracting metals from electrolyte solutions onto the flowing carbon-fiber electrode. The main structural elements of the program complex are modules: *general.pas* is the main form that allows opening the forms for entering basic process parameters – the *parametr.pas* module, for selecting electrochemical constants from available files – the *vybor.pas* module, for editing data – the *redact.pas* module, modules for calculating process parameters, optimization, plotting dependencies, etc. Program modules can be executed in parallel that allows increasing speed of computer calculations.

The program complex is implemented in the Object Pascal programming language [15-17]. Used libraries are the following: Windows, Messages, SysUtils, Variants, Classes, Graphics, Controls, Forms, Dialogs, Menus, StdCtrls, etc. An IBM PC-compatible PC with Windows XP/Vista/7/8/10 operating systems was used for the computational experiments.

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

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

One of the most recent works on the use of the software package developed by the authors is, for example, the article [18].

3. Results and discussion

The original approach consisting in the representation of the carbon-graphite cathode in the electrochemical reactor with the flowing three-dimensional electrode made of fibrous carbon materials in the form of pseudo-homogeneous medium has allowed to construct the dynamic mathematical models of the process of metals extraction from electroplating waste water and regeneration of spent electrolytes. Based on the models a set of programs in the Object Pascal programming language was developed that allows conducting theoretical research of regularities of the electrodeposition process and determining optimal parameters of the process and the electrolyzer to solve various technological problems. One of the program complex variants is published, for example, in [14].

To illustrate the efficiency of the methods let us calculate co-deposition of gold and silver from thiourea sulfate solution with the following composition: $H_2 SO_4$ – 0.5 mol/l, thiourea – 50 g/l, gold – 22.4 mg/l, silver – 141 mg/l (*Fig. 1*).

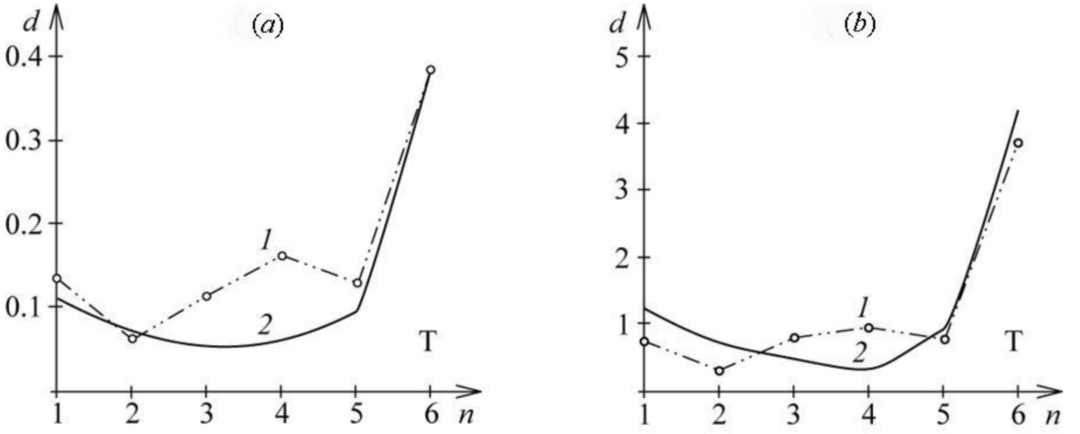

Fig. 1. Distribution of metal sludge over the thickness of the electrode: (a) – gold; (b) – silver; d – metal mass to CFM mass ratio; 1 – experiment; 2 – calculation; n – layer number; T – electrode back side; electrode thickness – 1 cm; current density – 0.2 A/m^2 , the solution flowrate – 0.56 cm/s.

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

The experimental and calculated dependences presented in *Fig. 1*, as well as the consistency of the results of calculations of electrochemical functions of classical electrochemical theory allow us to conclude that the mathematical models and calculation algorithms described in this communication and in our other works [4–6] are effective for numerical studies and optimization of the control parameters of processes of metal ions extraction from industrial waste water to flowing threeedimensional electrodes for the purpose of decontaminating waste water. It should be noted that FTEs could be effectively used simultaneously for cathodic metal extraction and anodic oxidation of toxic electrolyte compounds in one electrolyser [4–7].

4. Conclusions

The application of mathematical modeling for the study of electrochemical processes in three-dimensional flowing electrodes in order to solve the problem of metal extraction from solutions of galvanochemical industries allows us 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. The use of the developed program complex allowed to obtain a numerical solution of the scientific problem of practical importance. A good correspondence of calculation and experimental results is shown. The possibility of parallel execution of software modules allows increasing the speed of computer calculations.

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