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NEURAL NETWORK MODEL PREDICTION OF CHROMIUM SEPARATION IN POLYELECTROLYTE-ENHANCED ULTRAFILTRATION

MODELOWANIE EFEKTYWNOŚCI SEPARACJI CHROMU W ULTRAFILTRACJI WSPOMAGANEJ POLIELEKTROLITAMI

Abstract: Effectiveness of polyelectrolyte-enhanced ultrafiltration in chromium recovery from its aqueous solutions was tested experimentally. Two chromium species, Cr(III) and Cr(VI) ions, were the subject of ultrafiltration processes enhanced with two water-soluble, ion-exchanging polyelectrolytes. These were: poly(sodium 4-styrenesulfonate) – PSSS (for Cr(III) ions recovery) and poly(diallyldimethylammonium chloride) – PDDAC (for Cr(VI) ions recovery). Experimental ultrafiltration tests with two different membranes and model solutions of appropriate chromium ions (5 and 50 mg · dm^{-3}), at different pH and with various polyelectrolyte doses, provided numerical data for the artificial neural networks training procedure. Numerical neural network models made prediction of chromium retention coefficient (*R*) under different process conditions (pH, polymer dose, concentration of selected Cr form) possible. Strongly nonlinear dependences of retention coefficient (*R*) on pH and polymer : metal concentration ratio for both chromium species, represented by experimental data, were identified and modeled by neural networks correctly. Good compatibility between experimental data and neural network predictions was observed.

Keywords: polyelectrolyte-enhanced ultrafiltration (PEUF); Cr(III); Cr(VI); poly(sodium 4-styrenesulfonate); poly(diallyldimethylammonium chloride)

Introduction

Over the last years, the polymer-enhanced ultrafiltration (PEUF), used to separate heavy metal ions from their water solutions, has been gaining in popularity. The process is based on binding the metal ions by water-soluble chelating polymers or polyelectrolytes containing ion-exchange groups, followed by their retention on an ultra-

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filtration membrane. Normally, the ultrafiltration separation of metals is enhanced by macromolecules containing amino (chitosan, polyethyleneimine), carboxyl (poly(acrylic acid), its salts and copolymers) or hydroxyl (poly(vinyl alcohol)) groups [1–3]. Polymer-enhanced ultrafiltration has been successfully applied to the separation of chromium from aqueous solutions, both Cr(III) and Cr(VI) [4–9]. Promising effects corresponded to binding Cr(III) with poly(acrylic acid) or its copolymer with maleic acid [5, 6], chitosan, pectin, polyethyleneimine and ethoxylated polyethyleneimine [4, 6, 7]. Polyethyleneimine appeared also to be an effective agent in enhancing the ultrafiltration separation of Cr(VI), due to the anion-exchange nature of the primary, secondary and tertiary amino groups present in its structure [5, 6]. Similar effect was achieved in ultrafiltration of Cr(VI) with addition of modified starch having cationic functional groups, capable of reacting with contaminants of anionic nature [8]. Based on literature reports and own research [5], the authors suggested ultrafiltration removal of Cr(III) and Cr(VI) ions enhanced with polyelectrolytes which contain functional groups of strong ion-exchange properties. Poly(sodium 4-styrenesulfonate) – PSSS, a water-soluble polymer which contains sulfonic groups capable of binding metal cations (Cr(III)) and poly(diallyldimethylammonium chloride) – PDDAC, whose quaternary ammonium groups exhibit anion-exchange properties (Cr(VI)) were selected for the process [9].

The work demonstrates possibility of application of artificial neural networks trained on experimental data sets for prediction of the effectiveness of Cr(III) and Cr(VI) separation (expressed by chromium retention coefficient, *R*) in diversified process conditions (environment's pH, polymer : metal concentration ratio, initial Cr concentration and its chemical form).

Materials and methods

Model solutions of Cr(III) and Cr(VI) ions, of concentrations 5 and 50 mg $\cdot$ dm^{-3}, were prepared using analytical grade chromium nitrate $Cr(NO_3)_3 \cdot 9H_2O$ and potassium dichromate $K_2Cr_2O_7$ (POCh S.A., Gliwice, Poland).

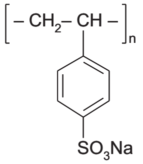
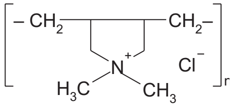
Water soluble polyelectrolytes: poly(sodium 4-styrenesulfonate) – PSSS (M_w 70000, 30 % solution) and – PDDAC (M_w 100000–200000, 20 % solution), Sigma-Aldrich, were used as Cr(III) and Cr(VI) binding agents. In order to remove small molecules, polyelectrolytes were preliminarily diafiltrated using UF membrane.

The set of polymer–chromium solutions of different molar concentration ratios (mol of mer unit per mol of metal) were prepared by mixing the appropriate doses of suitable polyelectrolyte with the proper chromium species. Process environment's pH adjustments to the required level, within the 1–10 range, were done with the use of 1 mol $\cdot$ dm^{-3} NaOH and HNO_3 solutions (POCh S.A.), respectively. More detailed characteristic of the model solutions used is presented in Table 1.

Prepared model solutions were a subject of ultrafiltration tests in AMICON 8400 membrane cell, equipped with magnetic stirrer. Two ultrafiltration membranes of different transport and separation characteristics were used in the PEUF process. A polysulfone membrane HZ20 (cut-off 50 kDa) and a modified polyacrylonitrile membrane

Table 1

Characteristic of the model solutions used in ultrafiltration tests

Chromium ion type	Cr(III)		Cr(VI)	
Polyelectrolyte	 PSSS poly(sodium 4- -styrenesulfonate)		 PDDAC poly(diallyldimethylammonium chloride)	
pH	1; 2; 4; 6; 8; 10		1; 2; 4; 6; 8; 10	
Chromium concentration	5 mg · dm^{-3}	50 mg · dm^{-3}	5 mg · dm^{-3}	50 mg · dm^{-3}
Polymer : metal molar concentration ratio, *Pol.:Met.*	2.5; 5; 7.5; 10	5; 7.5; 10; 12.5	0.5; 1; 2.5; 5; 7.5; 10	1; 2.5; 5; 7.5; 10; 12.5

MX50 (cut-off 100 kDa) were provided by GE Osmonics. Water permeability coefficients, determined experimentally, were 2.1 · 10^{-10} and 6.4 · 10^{-10} m^3 · m^{-2} · s^{-1} · Pa^{-1}, respectively. Transmembrane pressure of 1 bar was applied in the ultrafiltration tests. Effectiveness of polymer enhanced ultrafiltration was evaluated by measurement of chromium concentrations in the permeate and in the feed (Atomic Absorption Spectrometer SpectrAA 880, Varian) followed by calculation of chromium retention coefficient (R) according to the formula: $R = 1 - C_P/C_F$, where: C_P, C_F – chromium concentrations in the permeate and in the feed, respectively. Detection limit for chromium ions analysis was 0.005 mg · dm^{-3}.

Calculations

Raw experimental data matrixes collected, matching chromium separation efficiencies (R) with various combinations of Cr initial concentrations, *Pol.:Met*. molar ratios and ultrafiltration process environment's pH provided basis for the artificial neural networks creation, followed by their training, validating and testing procedures. Computations were done with the use of *STATISTICA Neural Networks software*. Various network types were preliminary tested, including radial basis function (RBF) networks, general regression neural networks (GRNN), multilayer perceptrons (MLP) and linear ones. Each net structure was trained with appropriate algorithms (pseudo-inversion, sub-sample, conjugate gradient and backpropagation error), both independently or in various sequences. Four optimal net structures were identified using appropriate statistical indicators.

For the network modeling ultrafiltration process on HZ20 membrane with PSSS polymer in a form of $R = f(C_{met}, Pol.:Met., pH)$ it was MLP type network of 3-9-8-1 structure (three inputs representing: C_{met}, *Pol.:Met.*, *pH*, one output neuron (R), with two hidden neuron layers with 9 neurons in the first and 8 in the second one), trained 100 iterations with backpropagation error algorithm (BP) followed by additional training covering 59 cycles with the conjugate gradient (CG) algorithm (resulting mean deviation MD = –0.0085, root mean square deviation RMSD = 0.0552). In case of artificial neural network modeling ultrafiltration behavior of HZ20 – PDDAC – Cr(VI) system, the best model structure proved to be a multilayer perceptron of 3-3-1 structure (3 inputs, one hidden layer with 3 neurons and one output neuron), trained with 100 backpropagation error iterations followed by 61 conjugate gradient cycles (resulting MD = 0.0074, RMSD = 0.0654).

In case of network modeling ultrafiltration behaviour of MX50 – PSSS – Cr(III) system, the optimal net configuration proved to be 3-6-1 configuration, trained with 100 iterations of backpropagation error algorithm with adjustment of the net's weight matrix using additional training with 20 iterations of conjugate gradient algorithm (MD = = 0.0273, RMSD = 0.1028). On the other hand it was identified that the MX50 – PDDAC – Cr(VI) system performance in various process conditions was the best described using multilayer perceptron of 3-5-4-1 topology trained with 100 initial iterations of backpropagation error algorithm supplemented with 63 cycles of conjugate gradient training (MD = –0.0029, RMSD = 0.0553).

These four optimal neural network configurations were then used for numerical simulation of the polyelectrolyte enhanced ultrafiltration process, especially for the identification of complex influence of various combinations of PEUF parameters on chromium forms retention effectiveness, R.

Results and discussion

Fig. 1 presents neural network simulation results for the two membranes used (MX50, HZ20) with respect to Cr(III) ultrafiltration enhanced by PSSS. Fig. 2 depicts the same simulation schedule for the Cr(VI) – PDDAC system.

The $R = f(Pol.:Met., pH)_{\mathrm{Cmet.}}$ response surfaces, based on neural network predictions for selected matrixes of assumed PEUF process conditions, demonstrate essential, strongly nonlinear influence of both parameters under study (pH, polymer dose), as well as concentration, chemical form of chromium in its initial solution and the added polyelectrolyte type on the ultrafiltration process effectiveness. Observed steep increase in $R = f(\mathrm{pH})_{\mathrm{Pol:Met,Cmet}}$ dependency values with the increase of the solution alkalinity, compatible with the trends within the experimental data, is demonstrated clearly, especially within the pH 1–4 (Cr(III)) and 1–6 (Cr(VI)) ranges at small polyelectrolyte doses.

Similar $R = f(Pol.:Met.)_{\mathrm{pH,Cmet}}$ function dependency can be observed, especially for all Cr(III) solutions and for higher Cr(VI) concentrations. As a result, systematic increase in R is observed, corresponding to the increase in polyelectrolyte dose, up till attaining the maximal, stable metal retention effect, which for Cr(VI) solutions of concentration 50 $\mathrm{mg \cdot dm^{-3}}$ corresponds to $Pol.:Met. > 5$ and pH value > 4, whereas in case of Cr(III) solutions it is attained at various $Pol.:Met.$ values, depending in

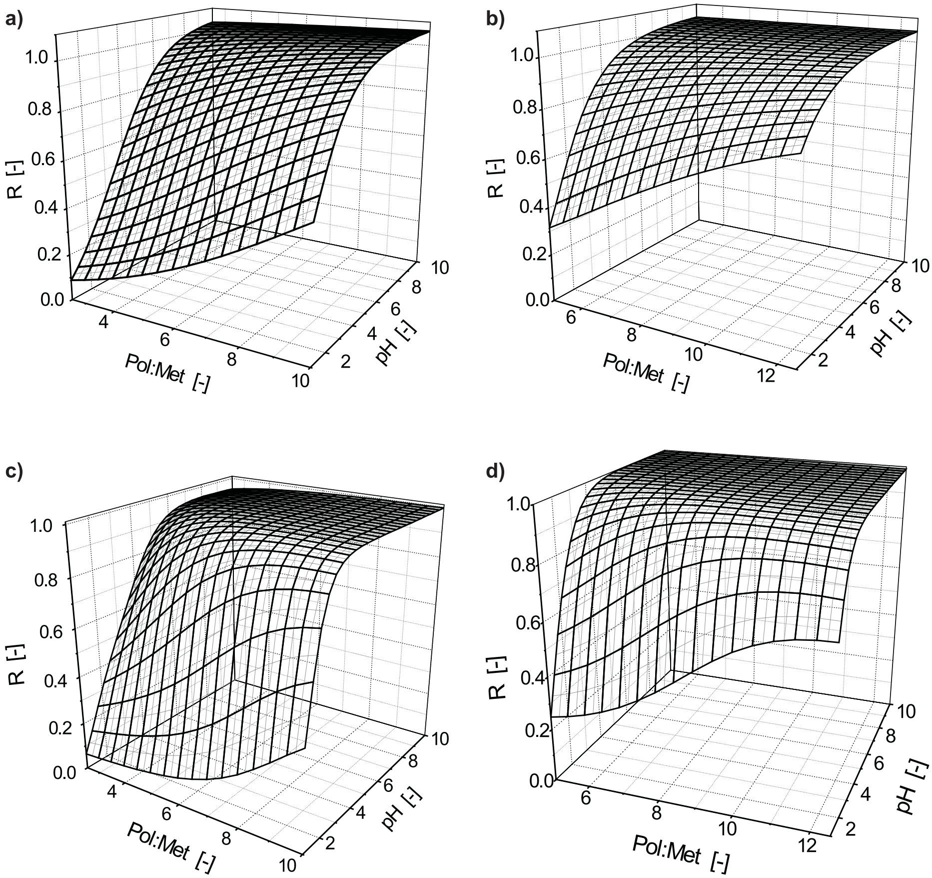


Fig. 1. Neural network model predictions – dependence of Cr(III) retention coefficient (*R*) on polymer: metal concentration ratio (*Pol.:Met.*) and process environment's pH. Membrane MX50, Cr(III) concentrations: 5 mg · dm^{-3} (a) and 50 mg · dm^{-3} (b); membrane HZ20, Cr(III) concentrations: 5 mg · dm^{-3} (c) and 50 mg · dm^{-3} (d); polyelectrolyte – PSSS

a complex way also on pH value, concentration of metal ions in initial solution and the membrane type used.

In case of Cr(VI) solution of concentration 50 mg · dm^{-3}, the $R = f(\text{pH})_{\text{Pol:Met}}$ dependency for *Pol.:Met.* < 5 reaches clear maximum, corresponding to pH approx. 5–6 range. In a more alkaline environment some slight decrease in *R* value is observed, particularly visible for MX50 membrane (Fig. 2b). For *Pol.:Met.* > 6 this extreme becomes more and more diffuse and after reaching the maximum only small decline in *R* is reported (Fig. 2a) – more stronger effect is visible in Fig. 2b. Comparing both neural network response surfaces, attributed to two concentrations (5 and 50 mg · dm^{-3}) and corresponding to some selected chromium form, in solutions of higher Cr concentrations within the low pH values (*ca.* 1–2) – for a constant *Pol.:Met.* ratio – one can notice also higher values of metal retention coefficient, *R*. On the other hand it

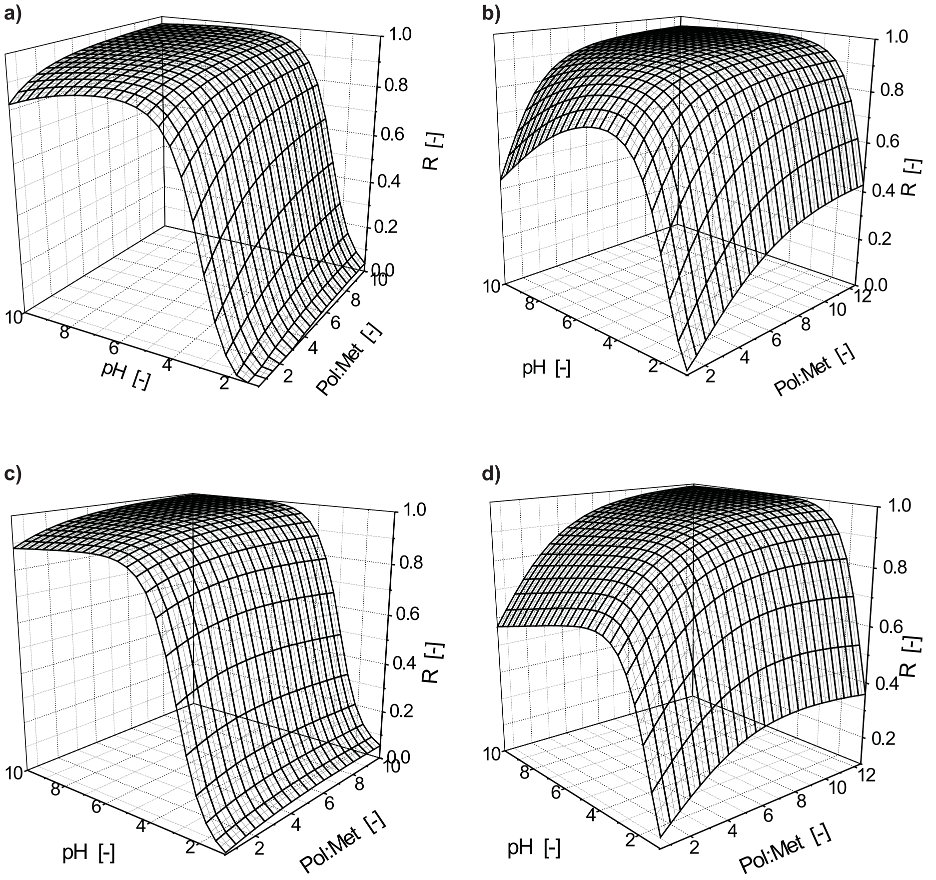


Fig. 2. Neural network model predictions – dependence of Cr(VI) retention coefficient (*R*) on polymer : metal concentration ratio (*Pol.:Met.*) and the process environment's pH. Membrane MX50, Cr(VI) concentrations: 5 mg · dm^{-3} (a) and 50 mg · dm^{-3} (b); membrane HZ20, Cr(VI) concentrations: 5 mg · dm^{-3} (c) and 50 mg · dm^{-3} (d); polyelectrolyte – PDDAC

should be noted, that Cr(III) solutions of concentration 50 mg · dm^{-3} required application of larger polyelectrolyte doses than Cr(III) solutions of concentration 5 mg · dm^{-3}, resulting from formation of precipitates, observed within the range of *Pol.:Met.* < 2.5 and < 5, for 5 and 50 mgCr(III) · dm^{-3}, respectively.

In general, spatial courses of the object's response surfaces (neural networks simulation results), attributed to MX50 and HZ20 membranes, were considered similar within all pH and *Pol.:Met.* ranges tested experimentally, for both chemical chromium forms and both metal concentrations (compare Fig. 1a–d and 2a–d). Insignificant differences between the model-predicted *R* values for MX50 and HZ20 membrane were observed in solutions of higher Cr(III) and Cr(VI) concentrations, within the lowest pH and *Pol.:Met.* ratio values tested, demonstrated thus a little better efficiency of chromium separation on HZ20 membrane.

Fig. 3 demonstrates comparison of retention coefficients *R* predicted by artificial neural network model for the Cr(III)-PSSS and Cr(VI)-PDDAC systems, respectively, and the corresponding original experimental values (model target values).

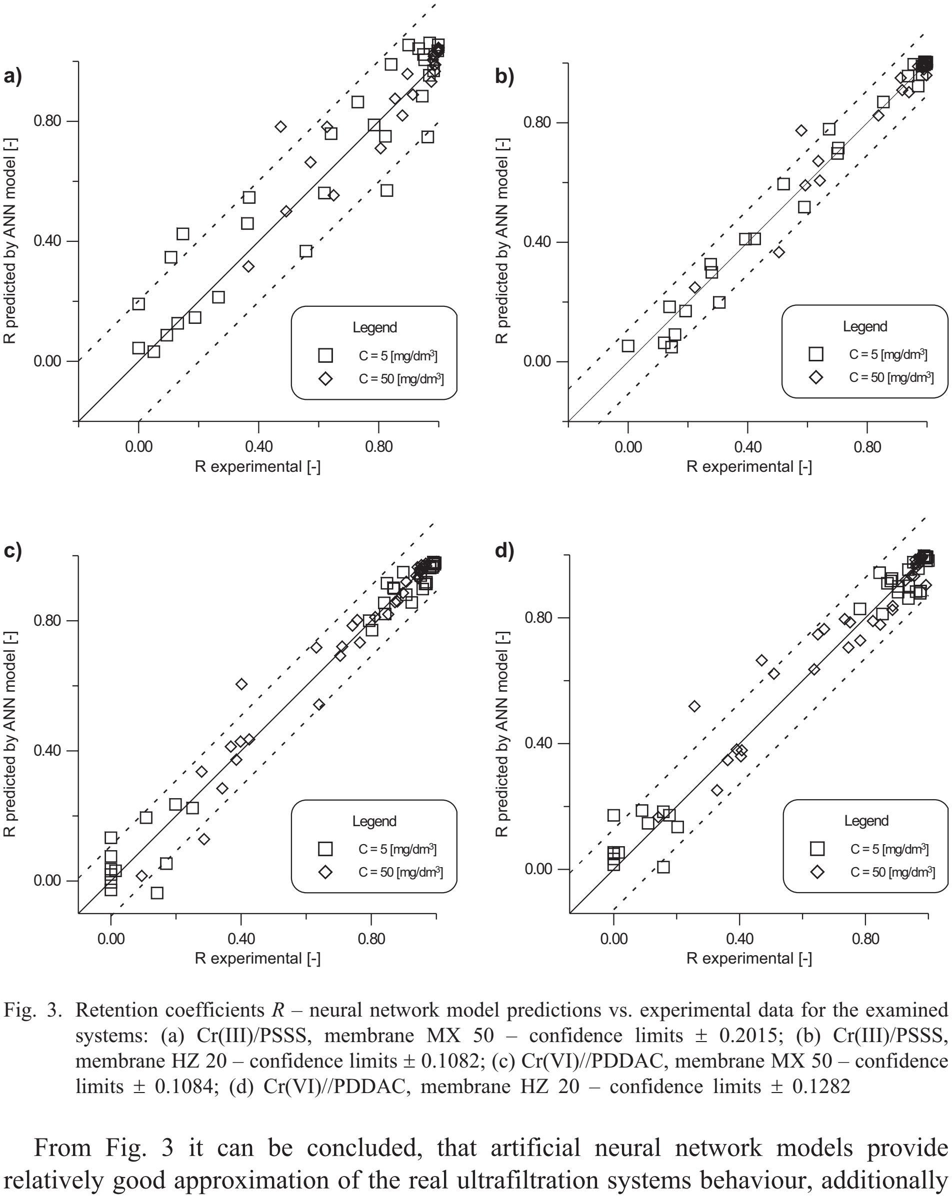


Fig. 3. Retention coefficients *R* – neural network model predictions vs. experimental data for the examined systems: (a) Cr(III)/PSSS, membrane MX 50 – confidence limits ± 0.2015; (b) Cr(III)/PSSS, membrane HZ 20 – confidence limits ± 0.1082; (c) Cr(VI)//PDDAC, membrane MX 50 – confidence limits ± 0.1084; (d) Cr(VI)//PDDAC, membrane HZ 20 – confidence limits ± 0.1282

From Fig. 3 it can be concluded, that artificial neural network models provide relatively good approximation of the real ultrafiltration systems behaviour, additionally confirmed by MD and RMSD values. The observed differences between experimental and predicted *R* values can be attributed to the unavoidable experimental procedure/analytical apparatus errors resulting in scattering of the laboratory output values. However, it should be noted that main, strongly nonlinear trends within the experimental data, with some experimentally proved extremes, were identified by ANN models properly.

Conclusions

Significant influence of polymer dose and environment's pH on Cr(III) and Cr(VI) separation efficiency in the ultrafiltration process enhanced by polyelectrolytes of strong ion-exchange properties was demonstrated.

Numerical $R = f(Pol.:Met., pH)_{\mathrm{Cmet}}$ function response surfaces, elaborated on the basis of neural network models simulation results, identified clearly (for both chromium forms and their concentrations used) the existence of some pH – *Pol.:Met.* regions, within which metal retention processes can run with very high efficiency, $R \approx 1$ (corresponding to plateau ranges noticeable in Fig. 1 and 2).

In the case of both membrane types used, within the Cr(III) and Cr(VI) concentrations tested, artificial neural network model provided good compatibility between the predicted values of chromium retention coefficient (*R*) and the corresponding experimental values for the defined PEUF process conditions.

Numerical artificial neural network models presented can be regarded as a helpful tool in design works, especially concerning optimization of metals removal in polyelectrolyte enhanced ultrafiltration processes in various environment protection applications. It should be, however, noted that the elaborated neural models can be effectively used for modeling only the systems represented by experimental data used for the neural nets training, validating and testing.

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MODELOWANIE EFEKTYWNOŚCI SEPARACJI CHROMU W ULTRAFILTRACJI WSPOMAGANEJ POLIELEKTROLITAMI

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Abstrakt: Przedstawiono możliwości prognozowania efektywności separacji chromu z roztworów wodnych w procesie ultrafiltracji wspomaganej działaniem polielektrolitu w oparciu o sztuczną sieć neuronową. Badaniom poddano układy zawierające dwie różne formy chromu – Cr(III) i Cr(VI). Do wspomagania ultrafiltracyjnej separacji metalu wykorzystano dwa rozpuszczalne w wodzie polimery o właściwościach jonowymiennych – poli(4-styrenosulfonian sodu), PSSS (separacja Cr(III)) oraz poli(chlorek diallilodimetyloamoniowy), PDDAC (separacja Cr(VI)). Wyniki testów ultrafiltracji przeprowadzonej dla wodnych roztworów modelowych obu form chromu o stężeniach 5 i 50 mg · dm^{-3}, przy różnych wartościach pH środowiska oraz zróżnicowanych dawkach właściwych polielektrolitów, stanowiły podstawę uczenia i testowania struktur obliczeniowych sztucznych sieci neuronowych, umożliwiających predykcję współczynnika retencji (*R*) danej formy chromu dla różnych warunków procesowych (pH, dawka wybranego polimeru, stężenie odpowiedniego jonu Cr). Na podstawie wyników doświadczalnych oraz opracowanych sieciowych modeli numerycznych zidentyfikowano istotny, mocno nieliniowy wpływ pH oraz stosunku stężeń polimer : metal na wartości współczynników retencji (*R*) obu form chromu. Uzyskano dobrą zgodność danych eksperymentalnych z wartościami wyznaczonymi przy pomocy sztucznej sieci neuronowej.

Słowa kluczowe: ultrafiltracja wspomagana polielektrolitem (PEUF); Cr(III); Cr(VI); poli(4-styrenosulfonian sodu), poli(chlorek diallilodimetyloamoniowy)