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MODELING OF CHROMIUM(III) AND CHROMIUM(VI) RETENTION COEFFICIENT IN POLYELECTROLYTE ENHANCED ULTRAFILTRATION

MODELOWANIE WSPÓŁCZYNNIKA RETENCJI CHROMU(III) I CHROMU(VI) W ULTRAFILTRACJI WSPOMAGANEJ POLIELEKTROLITEM

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 the model analytical 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 non-linear dependencies 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)

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 ultrafiltration 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]. Relying 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.

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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 accurate prediction of the effectiveness of Cr(III) and Cr(VI) separation (expressed by chromium retention coefficient, R) in diverse process conditions (environment's pH, polymer : metal concentration ratio, initial Cr concentration and its chemical form).

Materials and methods

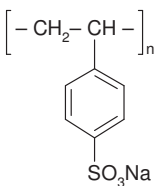
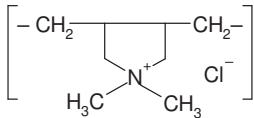
Model solutions of Cr(III) and Cr(VI) ions, of concentrations 5 and 50 mg dm⁻³, were prepared using analytical grade chromium(III) nitrate Cr(NO₃)₃·9H₂O and potassium dichromate K₂Cr₂O₇ (POCh S.A., Gliwice, Poland).

Water soluble polyelectrolytes: poly(sodium 4-styrenesulfonate) - PSSS ($M_w = 70$ kDa, 30% solution) and poly(diallyldimethylammonium chloride) - PDDAC ($M_w = 100\div 200$ kDa, 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 polyelectrolytes with the proper chromium species. Process environment's pH adjustment to the required level, within the 1-10 range, was done with the use of 1 mol dm⁻³ NaOH and HNO₃ solutions (POCh S.A.). More detailed characteristic of the solutions is presented in Table 1.

Table 1

Characteristic of the solutions used in ultrafiltration tests

Chromium ion	Cr(III)		Cr(VI)	
Polyelectrolyte	 <p>PSSS poly(sodium 4-styrene-sulfonate)</p>		 <p>PDDAC poly(diallyldimethylammonium chloride)</p>	
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, <i>Pol.:Met.</i>	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

Prepared solutions were a subject of ultrafiltration tests in AMICON 8400 membrane cell, equipped with magnetic stirrer. Ultrafiltration membrane HZ20 (GE Osmonics), made of polysulfone, was used in the separation processes. Water permeability coefficient of the membrane, determined experimentally, was 2.1·10⁻¹⁰ m³m⁻²s⁻¹Pa⁻¹. Transmembrane

pressure of 1 bar was applied in the ultrafiltration tests. The 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 (pseudoinversion, sub-sample, conjugate gradient and backpropagation error), both independently and/or in various sequences. Two optimal net structures were identified using 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 by 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 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). These two 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 process parameters on chromium forms retention effectiveness.

Results and discussion

Figures 1 and 2 present the neural network simulation results with respect to both chromium species, their initial concentrations and the appropriate polymers used.

The $R = f(Pol.:Met., pH)_{C_{met}}$ response surfaces, based on neural network predictions for selected data matrixes representing the assumed 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. The steep increase in $R = f(pH)_{Pol.:Met., C_{met}}$ function values with the increase in alkalinity of solution, compatible

with the experimental data results, is demonstrated clearly, especially within the pH 1÷4 (Cr(III)) and 1÷6 (Cr(VI)) ranges at small polyelectrolyte doses.

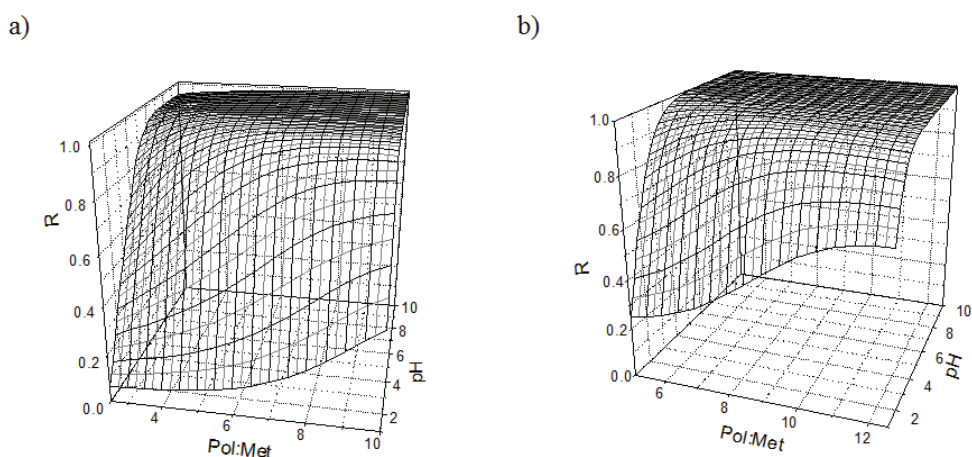


Fig. 1. Neural network model predictions - dependence of Cr(III) retention coefficient (R) on polymer : metal concentration ratio ($Pol.:Met.$) and process environment's pH. Initial Cr(III) concentrations: 5 mg dm^{-3} (a) and 50 mg dm^{-3} (b), polyelectrolyte - PSSS

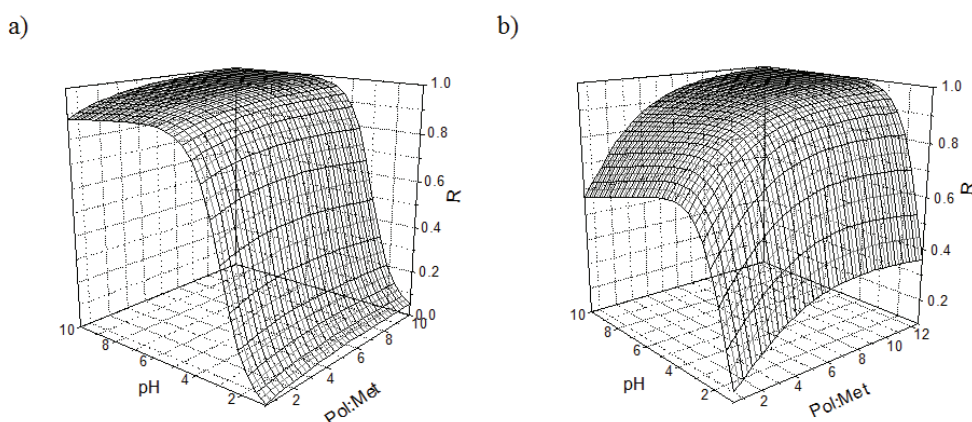


Fig. 2. Neural network model predictions - dependence of Cr(VI) retention coefficient (R) on polymer : metal concentration ratio ($Pol.:Met.$) and the process environment's pH. Initial Cr(VI) concentrations: 5 mg dm^{-3} (a) and 50 mg dm^{-3} (b), polyelectrolyte - PDDAC

Similar $R = f(Pol.:Met.)_{pH, C_{met}}$ 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 mg dm^{-3} corresponds to $Pol.:Met. > 5$, whereas in case of Cr(III) solutions it is attained at various $Pol.:Met.$ values, depending in a complex way also on pH value and

concentration of metal in initial solution. In case of Cr(VI) solution of concentration 50 mg dm^{-3} , the $R = f(\text{pH})_{\text{Pol.:Met.}, C_{\text{met}}}$ function for $\text{Pol.:Met.} < 5$ reaches clear maximum, corresponding to pH approx. 5-6. In a more alkaline environment visible decrease of R value is observed. For $\text{Pol.:Met.} > 6$ this extreme becomes more and more diffuse and after reaching the maximum small decline in R is only reported. 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 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 $\text{Pol.:Met.} < 2.5$ and < 5 , for 5 and $50 \text{ mg Cr(III) dm}^{-3}$, respectively.

Conclusions

Essential 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.

The numerical $R = f(\text{Pol.:Met.}, \text{pH})_{C_{\text{met}}}$ 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 Figs. 1 and 2).

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.

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MODELOWANIE WSPÓŁCZYNNIKA RETENCJI Cr(III) I Cr(VI) W ULTRAFILTRACJI WSPOMAGANEJ POLIELEKTROLITEM

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Abstrakt: Przedstawiono możliwości prognozowania efektywności separacji chromu z roztworów wodnych w procesie ultrafiltracji wspomaganej działaniem polielektrolitu, korzystając ze sztucznej sieci neuronowej. 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 wybranego 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 za pomocą sztucznej sieci neuronowej.

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