

Applying Artificial Neural Networks in the Modelling of Copper Recovery Process by Ionic Exchange in Aqueous Solutions

LEONARD MIHALY COZMUTA^{1*}, CAMELIA VARGA¹, MONICA MARIAN¹, ANCA MIHALY COZMUTA¹, TUTU HLANGANAN²

¹North University of Baia Mare, Faculty of Science, 76 Victoriei Str., 430122, Baia Mare, Romania

²School of Chemistry, University of the Witwatersrand, P. Bag X 3, WITS 2050, Johannesburg, South Africa

Artificial neuronal networks are widely used in different fields such as finance, medicine, engineering, geology, chemistry, physics in order to predict, classify and control the development of different processes.

The paper presents experimental data on the adsorption process of copper from aqueous solutions and compares it with theoretical data obtained by mathematical modeling using artificial neural networks (ANN). The aim of the paper is to demonstrate that ANN ensure a high accuracy in the mathematical modeling of the process. We have collected experimental data by using synthetic solutions with different pH and copper ions concentrations, which were retained on a PUROLITE S930 cationic resin. Both experimental and theoretical data obtained using ANN show the correlation between factors which influence the ionic exchange process (pH, temperature, initial copper concentration, activation energy).

Keywords: neural networks, copper recovery, mathematic modelling

The pollution of the environment continues to be one of the global contemporary issues that portray the new millennium. By affecting the quality of air, of water sources and of soil, pollution negatively impacts the quality of life. The application of efficient sewerage methods and the development of new, non-pollutant technologies become prerequisites for such phenomenon to decline.

Extraction activities in mines together with the preparation of useful minerals stand as one of the pollution sources with extremely damaging impact on the environment. The ecologic crisis triggered by such activity can be spotted, for instance, around the mining zone in Maramures. The outcomes of pollution are obvious in this area in economic, social and biologic terms, and depend on an array of local factors, meteorologic or geographic in nature. The depression that hosts the city of Baia Mare bordered by hills on its northern side is part of the factors that determine the stagnation of polluted air for a considerable annual length, particularly in the early hours of the day. The Săsar River, crossing the city, never freezes because of the concentration of pollutants generated during mining extraction and preparation activities. The river's biocenose is fully compromised, as any form of life, except some bacteria, has disappeared. Around the city's neighborhoods lichens, bees or swallows, sure bio-indicators of environmentally - healthy environments, have simply disappeared.

Acidic waters from mines stand for one of the major components of pollution generated through mining. Their aggressiveness and nocivity on the environment stems from their acidity and content of heavy metals.

This paper aims to make inroads about possibilities to recover some of the useful elements that such waters contain based on an ionic exchange procedure, which proves to be an elegant and easy-to-use sewerage - recovery process in the cleaning of acidic waters from mining. In this respect we have performed a series of ionic exchange tests, by using an array of synthetic solutions and the Purolite S930 cationite, which is copper - selective.

The processing and modelling of experimental data took place by applying artificial neural networks (ANN). The goal

consisted in substantiating the high capabilities of ANN on spotting and shedding light on variations in trends, as well as on modelling the process with the aim to make predictions about the system under scrutiny.

The theory of artificial neural networks

Artificial neural networks (ANN) have developed starting from a simplified concept about human brain. This concept entails about 10 billion neurons interconnected through 60 trillion synapses. Three components mainly make up a neuron: the body of the cell, the dendrites and the axon with its terminal ramifications (fig. 1).

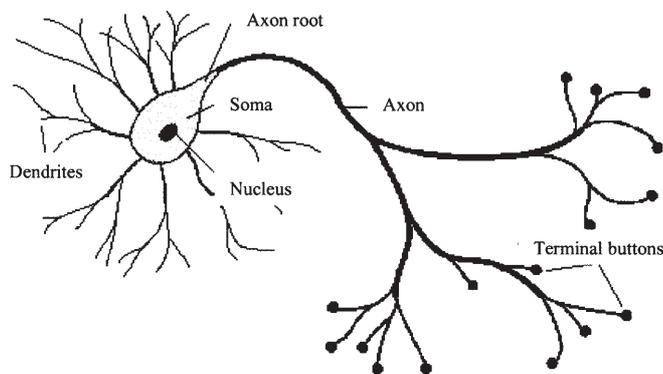


Fig. 1. Schematic diagram of the biologic model of the neuron

Dendrites have the role of signal input (excitation) while the axon and its terminal ramifications have the role of signal output. If the total of input signals reaching dendrites exceeds a certain threshold, the neuron is activated and will send an impuls to terminal buttons through the axon.

The perceptron's model based on which artificial neural networks were developed has similarities with the neuron [1-3] (fig. 2).

The dendrites stand as equivalent to input levels x_i , each having a certain synaptic weight w_i . The activation function f connects inputs to the output signal, depending on the input values, the synaptic weights and the threshold value θ that tigeers the activation of the neuron:

* email: mihaly1@yahoo.com; Tel.: 0742588575

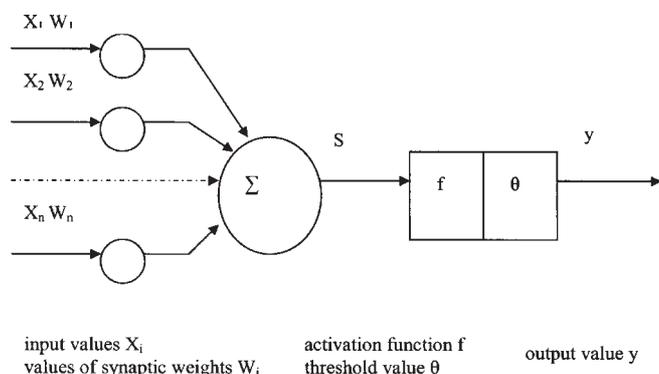


Fig. 2. Schematic representation of the perceptron based on the neural model

$$y = f\left(\sum_{i=1}^{i=n} w_i \cdot x_i - \theta\right) \quad (1)$$

During the first stage of the development of artificial neural networks (Rosenblatt 1958, Widrow 1960) threshold type linear inputs were used as activation function. Non-linear functions of sigmoid type were later introduced, as linear inputs allow only for solving some linearly - separable cases.

The simplest neural network consists in arranging a group of neurons on a single layer. The input vector will apply to all neurons while the output vector will be the result of applying the activation function of the scalar product between the matrix of input values and the matrix of synaptic weights. The use of multi - layers networks (fig. 3) that contain perceptrons with linear activation but also perceptrons with non - linear activation function generates the best performance.

Artificial neural networks display a certain learning capacity, depending on a certain training algorithm. A network is trained if by applying a vector as input the output consists in the desired value (with minimum deviation). This can be achieved by repeatedly applying input signals and by adjusting the synaptic weights on the algorithm applied. In this way synaptic weights become the storage place of capabilities, similar to the natural model in which not neurons but synapses warehouse knowledge.

Many training models for multi - layer artificial neural networks are available (Back Propagation, Conjugate Gradients, Levenberg - Marquardt, Quick Propagation, Delta - Bar - Delta), out of which the back - propagation algorithm enjoys the widest use (Werbos 1974, Parker 1985, Rumelhart, McClelland 1986, Fausett, Haykin 1994, Patterson 1996). This algorithm relies on the descent gradient method in order to minimise the gap between the desired output signal and the actual signal for the same

input vector, starting from an arbitrary point and applying successive iterations. This entails in determining the minimum of the error function, which depends on the values of synaptic weights.

As artificial neural networks stand as sophisticated modelling technique for the most diverse functions, they were successfully applied in a high variety of areas such as finance, medicine, engineering, geology, chemistry and physics [4]. In any sort of problem in which prediction, classification or control is an issue such modelling is fit to be applied.

In this paper the copper's adsorption process by ionic exchange in aqueous solutions is treated, by comparing experimental data with data generated by modelling based on artificial neural networks (ANN). The goal was to show that ANN display high capability in both extracting and formulating trends in variations and in process modelling.

Experimental data were processed and modelled using Statistica 6.0 (StatSoft, Inc., USA) and Trajan Neural Network Simulator 3.0 (Trajan Software Ltd, Durham, UK). Figure 3 displays the ANN network obtained by automatic design based on the software in use.

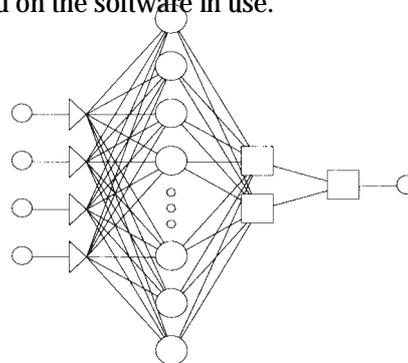


Fig. 3. ANN architecture used in the modelling of the recovery process of copper from aqueous solutions by ionic exchange

Methodology

In order to apply in practice the ionic exchange process for sewerage and recovery of copper content of residual waters and of acidic waters from mines, we have considered fit to clarify some physico - chemical aspects related to the process. In this respect, we have performed a series of experimental tests in order to determine: partial order of reaction related to the copper ions, the ionic exchange capacity and the way in which the concentration and the pH of the solution affects it (for low pH values, characteristic for dump waters), the apparent activation energy of the ionic exchange process and the way a pool

Table 1
LISTING OF SOLUTIONS USED FOR EXPERIMENTS

Crt. no.	Copper ion concentration in solutions	Solution pH						
		5,00	4,26	3,08	2,41	1,75	1,12	0,97
1	C=77,46 mg Cu/L	S1.1	S1.2	S1.3	S1.4	S1.5	S1.6	S1.7
2	C=104,53 mg Cu/L	S2.1	S2.2	S2.3	S2.4	S2.5	S2.6	S2.7
3	C=121,13 mg Cu/L	S3.1	S3.2	S3.3	S3.4	S3.5	S3.6	S3.7
4	C=170,55 mg Cu/L	S4.1	S4.2	S4.3	S4.4	S4.5	S4.6	S4.7
5	C=214,11 mg Cu/L	S5.1	S5.2	S5.3	S5.4	S5.5	S5.6	S5.7
6	C=232,60 mg Cu/L	S6.1	S6.2	S6.3	S6.4	S6.5	S6.6	S6.7
7	C=264,66 mg Cu/L	S7.1	S7.2	S7.3	S7.4	S7.5	S7.6	S7.7
8	C=279,66 mg Cu/L	S8.1	S8.2	S8.3	S8.4	S8.5	S8.6	S8.7

Table 2
PHYSICAL-MECHANICAL AND CHEMICAL CHARACTERISTICS OF THE
PUROLITE S-930 CATIONYTE

Crt. no.	Characteristic	
1	Nature and structure of the matrix of the polymer	Macroporous divinil-benzen
2	Form and appearance	Opaque, beige spheres
3	Particle dimension	+1,2mm <2% -0,3mm <1%
4	Active functional groups	Iminodiacetice
5	Ionic exchange capacity	Forma H 77 mgCu/g Forma Na 62 mgCu/g
6	Maximum operating temperature	70°C
7	Operational interval for pH	3-6 in H form 2-3 in Na form

of parameters [5-10] influence it. In this respect we have used synthetic solutions prepared out of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and H_2SO_4 (Merk, p.a.), with different copper concentrations and with different pH (table 1).

During experimentation we have put in contact, under continuous stirring, a volume of 400 mL of synthetic solution with 1 g of cationyte (activated in H^+ status). Periodically, at each 2 min, samples were collected in order to be analysed in terms of copper content, by atomic adsorbance spectroscopy by using an AAS3 Karl Zeiss Jena device. Also, after reaching equilibrium (in about 4 h) the contact solution was analysed. In order to continuously monitor the pH of the solution, we have used during experimentation an electronic pH-meter of the Consort P901 (Belgium) type while the apparent activation energy was established by conducting the experiments at 20°C and 50°C, in thermostatic conditions.

We have used during experiments the Purolite S-930 cationyte manufactured by Purolite International (U.K). This cationyte consists of a chelatic resin of macroporous

polystyrene, in which iminodiacetic groups allow for the removal of heavy metals from industrial effluents. The cationyte is used in the extraction and regeneration of metals from wastewaters generated in galvanotechnology, sometimes even in the presence of alkaline-earth metals (Ca and Mg). In practice, it can be used to reduce the concentration of residual toxic heavy metals, below the maximum acceptable concentration (0.1 mg/L). Table 2. shows the physical - mechanical and chemical properties of the resin.

The processing and modelling of the experimental data were performed by using Statistica 6.0 (StatSoft, Inc., USA) and the Trajan Neuronal Network Simulator 4.0 (Trajan Software Ltd, Durham, UK).

Experimental part

Figures 4-7 include the experimental data, for various concentrations of copper contact solutions depending on initial concentration and on time, for various values of the

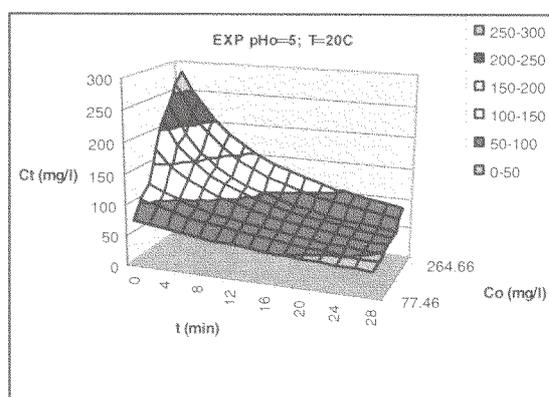


Fig. 4. Variation in time of the experimental concentration, for 5 as initial pH and 20°C

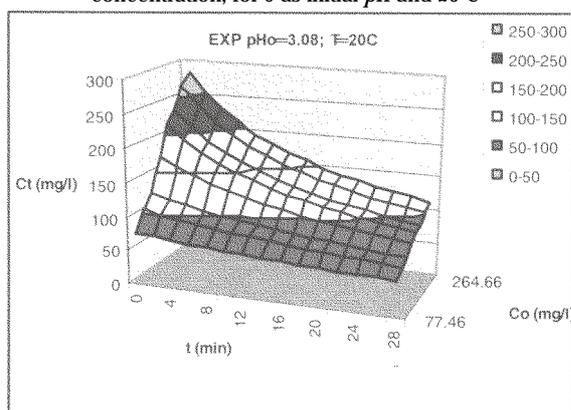


Fig. 5. Variation in time of the experimental concentration, for 3.08 as initial pH and 20°C

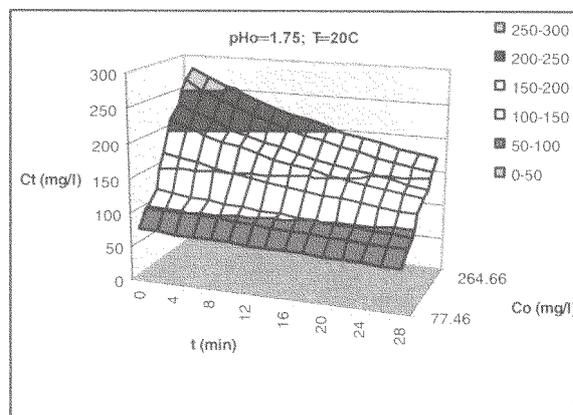


Fig. 6. Variation in time of the experimental concentration, for 1.75 as initial pH and 20°C

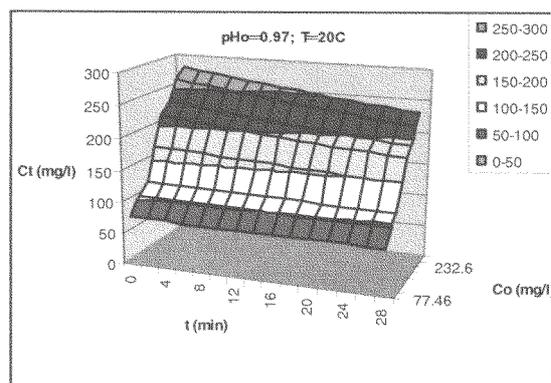


Fig. 7. Variation in time of the experimental concentration, for 0.97 as initial pH and 20°C

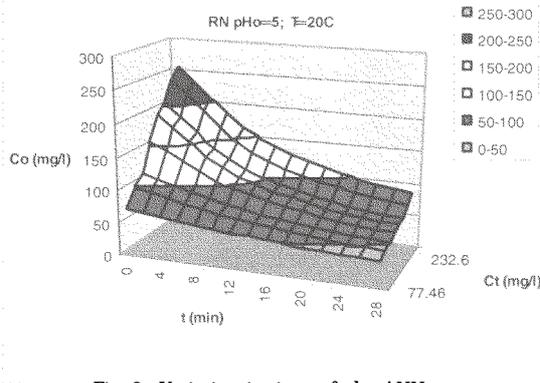


Fig. 8. Variation in time of the ANN concentration, for 05 as initial pH and 20°C

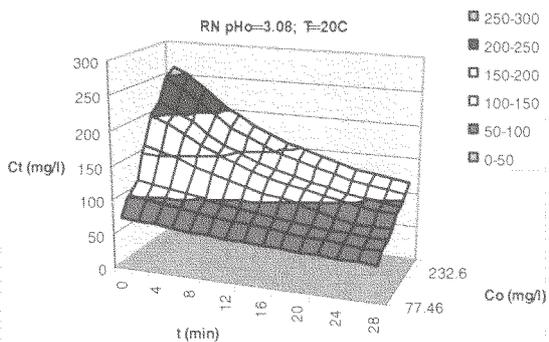


Fig. 9. Variation in time of the ANN concentration, for 3.08 as initial pH and 20°C

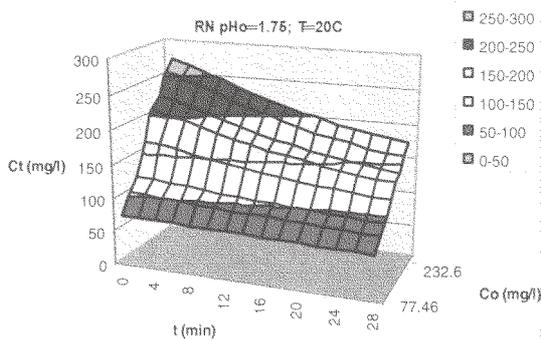


Fig. 10. Variation in time of the ANN concentration, for 1.75 as initial pH and 20°C

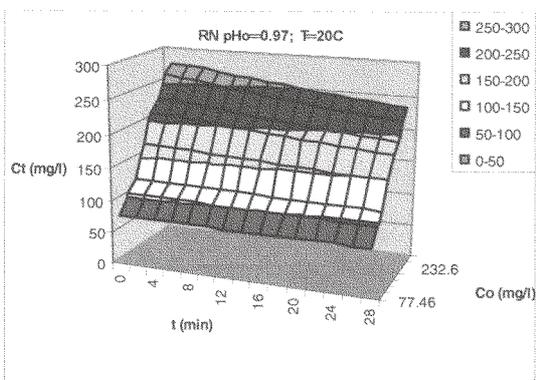


Fig. 11. Variation in time of the ANN concentration, for 0.97 as initial pH and 20°C

initial pH equal to 5; 3.08; 1.75; 0.97 (corresponding to a working temperature of 20 degrees). Figures 8–11 include the similar variations, build-up based on data collected by modelling with the neural network (ANN).

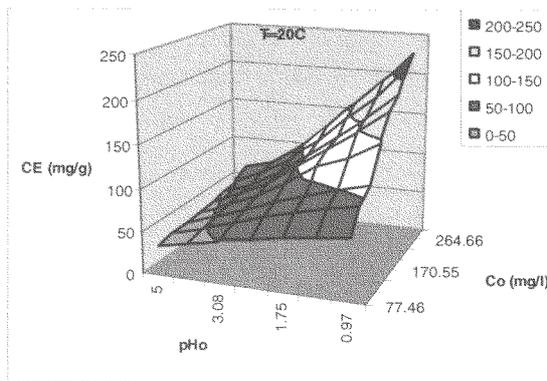


Fig. 12. Variation of the experimental equilibrium concentration depending on the pH and the initial concentration of the contact solution (20°C)

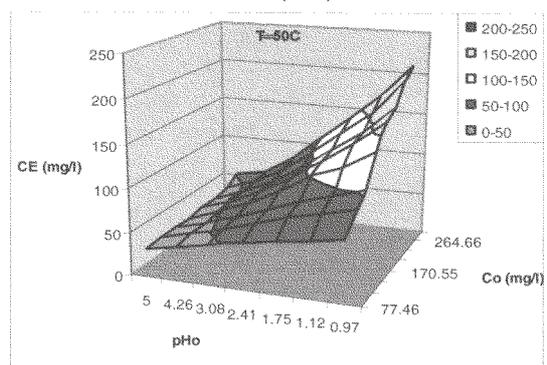


Fig. 13. Variation of the experimental equilibrium concentration depending on the pH and the initial concentration of the contact solution (50°C)

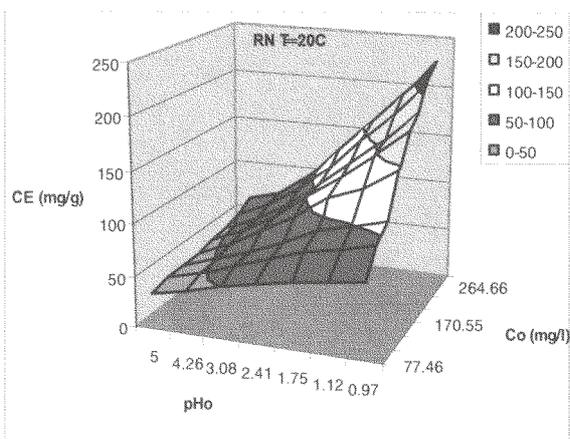


Fig. 14. Variation of ANN - based equilibrium concentration depending on the pH and the initial concentration of the contact solution (20°C)

As comes out from the two types of diagrams, there is a strong correlation between experimental data and data generated by modelling. We have quantified this correlation by means of the correlation coefficient, established based on all experimental data and data generated based on the neural network, for similar conditions. The value of this correlation coefficient is 0.9985.

Figures 12–13 and 14–15 display experimental variations, and variations established by modelling respectively, for equilibrium concentrations depending on pH and the initial concentration of the contact solution, at temperatures of

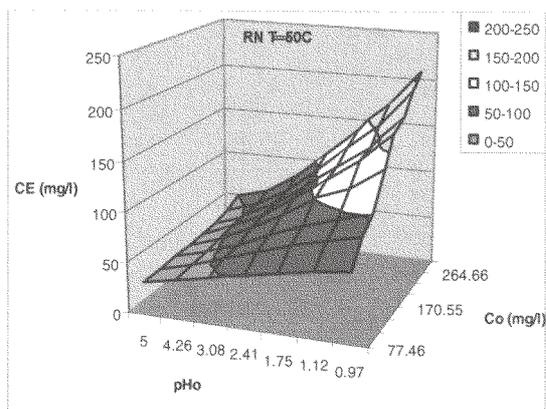


Fig. 15. Variation of ANN - based equilibrium concentration depending on the pH and the initial concentration of the contact solution (50°C)

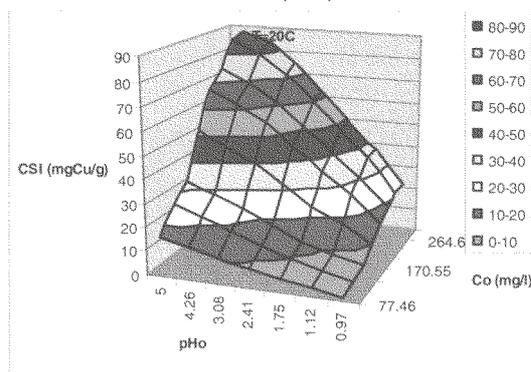


Fig. 16. Variation of the experimental ionic exchange capacity depending on the pH and the initial concentration of contact solution (20°C)

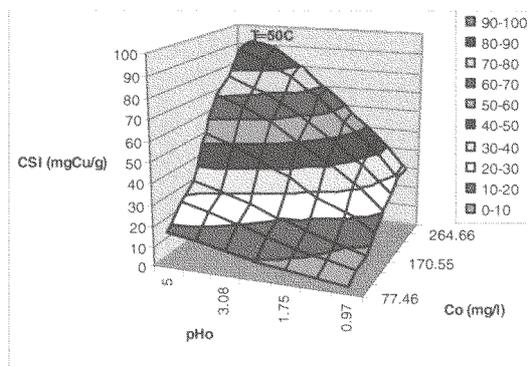


Fig. 17. Variation of the experimental ionic exchange capacity depending on the pH and the initial concentration of contact solution (50°C)

20 and 50°C. Based on these data, we have computed the corresponding ionic exchange capacities. Figures 16–17, and 18–19 respectively include those values.

Thus, the ionic exchange capacity of the cationyte used grows proportionally with the growth in initial concentration in copper of the solution, and with the growth in temperature and the growth of the initial pH. The correlation coefficient established between the ionic exchange capacities determined by experiment and based on data from modelling (by using neural networks) is of 0.9999.

For a kinetic approach of the copper adsorption process by ionic exchange, we have considered that the adsorption process of copper on the Purolite S-930 cationyte could be described by an heterogeneous chemical reaction (of ionic exchange):

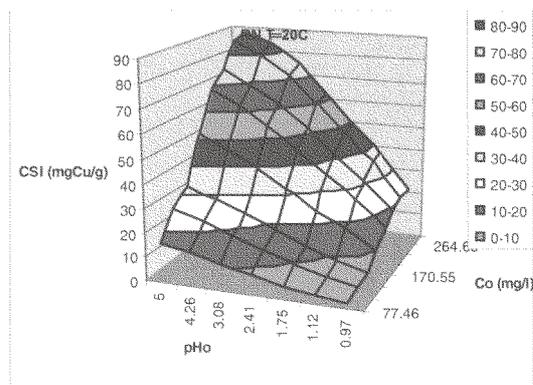


Fig. 18. Variation of ANN - based ionic exchange capacity depending on the pH and initial concentration of contact solution (20°C)

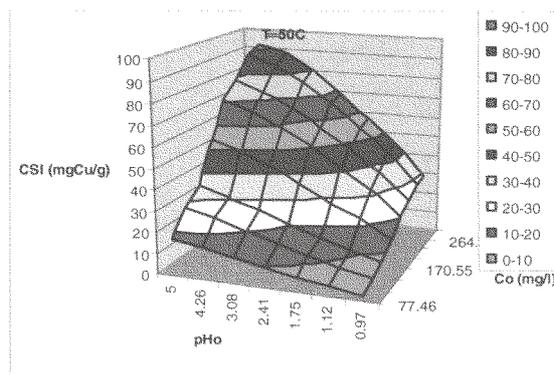
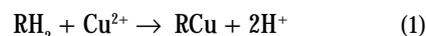


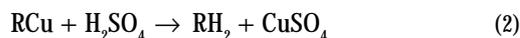
Fig. 19. Variation of ANN - based ionic exchange capacity depending on the pH and initial concentration of contact solution (50°C)



where RH_2 is the cationyte activated in H^+ form, while RCu is the cationyte after the retention of the copper ion from the solution.

The release of hydrogen ions because of the retention of copper ions will trigger the change in time of the pH of the solution.

In case the cationyte loaded will get in contact with acidic solutions, the reverse chemical reaction will occur, and will take place with the release of the copper ions:



Such reactions explain the fact that at a decline in the pH of the contact solution a decline in the ionic exchange capacity for copper occurs.

Under the condition of a constant concentration of cationyte in the reaction mix, this chemical process can be described by the general kinetic equation [11,12] of the type:

$$v = k \cdot C^n \quad (3)$$

where:

v = reaction speed, $mol \cdot L^{-1} \cdot s^{-1}$

C = copper ions concentration of the contact solution, $mol \cdot L^{-1}$

n = partial order of reaction related to the copper ion

k = apparent speed constant, that incorporates the constant contribution of the resin, $L^{n-1} \cdot s \cdot mol^{1-n}$

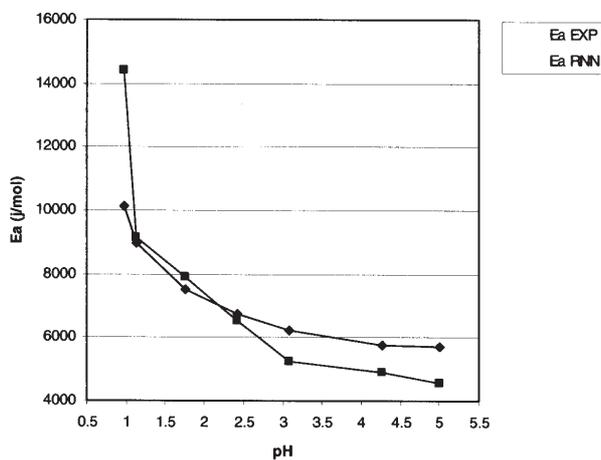


Fig. 20. Variation of the activation energy experimentally determined and by using ANN, with the initial pH of the contact solution

In order to interpret the $C(t)$ curves, we have designed in Turbo Pascal a program that includes the following algorithm:

- computes the values of the reaction speed v , as $\Delta C/\Delta t$;
- computes the corresponding values of $\log v$ and $\log C$;
- in order to display graphically $\log v$ as function of $\log c$ applies the smallest square method and establishes the equation of the linear curve;
- computes the partial order of reaction (n) depending on the ionic copper type;
- computes the speed constant for each of the temperatures of 20 and 50°C and the value of the apparent activation energy (based on the Arrhenius relationship).

In the computation algorithm of the program we have worked with values for concentrations expressed in mol/L (by converting the values in mg/L). Also, no rounding was applied to values, all data being preserved with many decimals. Partial order of reaction related to copper was determined as average of individual values. Based on experimental data a partial order of 2.1893 was established, with a standard deviation of 0.0097, while based on data collected from the neural network we have obtained the partial reaction order of 2.0425 with a standard deviation of 0.0641.

As regards the apparent activation energy, we have taken into consideration the fact that the pH of the solutions has major effect on it. We have established the average values of the apparent activation energies, corresponding to experiments in which initial contact solutions with the same pH were used, but having different initial copper concentrations. Figure 20 displays the variations of those average values of apparent activation energy, as determined based on experimental data, and determined based on the ANN respectively, depending on the initial pH of the contact solutions. We have established for these values, namely based on experiment and based on modelling, a correlation coefficient of 0.9665. The relationship between the values of apparent activation energies and the capacities for ionic exchange was established by means of the pH of the contact solution. Thus, as the pH of the contact solution goes up, the growth of the ionic exchange capacity occurs while the apparent activation energy declines, a fact that enables the chemical process by means of the reaction speed.

Conclusions

The adsorption process of copper by ionic exchange was comparatively studied, based on experimental data and based on data generated by modelling with artificial neural networks (ANN).

Following experimental tests to retain copper from various synthetic solutions with different copper content and different pH, out of the analysis of variations in the concentration of contact solutions we have subsequently concluded that the factors exerting an influence on the specific adsorption of the cationite for copper are:

- the initial concentration in copper of the contact solution and its pH: for the same initial pH of the contact solutions, the growth of the copper concentration generates a higher specific adsorption, such growth being the higher as the lower the pH of the solution is. Thus, for a pH of 0.97, the growth in copper content of the contact solution from 77.46 up to 279.66 mg/L has determined a growth of the specific adsorption from 2.128 up to 21.632 mg Cu/g (namely 10.16 times up), while for a pH of 5.00 the same growth in terms of concentration has determined a growth in specific adsorption from 16.544 up to 87.880 mg Cu/g (namely 5.31 times up).
- the initial pH of the contact solution, exerting major influence: a pH growth from 0.97 to 5.00 has generated the growth of specific adsorption from 2.128 up to 16.544 mg Cu/g (a 7.77 times growth) for a solution with 77.46 mg Cu/L in concentration, and from 21.632 to 87.88 mg Cu/g respectively (a 4.06 times growth) for a solution with 279.66 mg Cu/L in concentration;
- temperature, having a favorable influence on the ionic exchange process, the values of specific adsorption produced at 50°C being slightly superior to similar values at 20°C. This can be explained by a higher reaction speed as temperature goes up.

Partial order of reaction related to copper (in case the ionic exchange process is perceived as etherogenous reaction described by the kinetic equation $V=K \cdot C^n$) depends neither on the content and the initial pH of contact solutions, nor on the working temperature.

The apparent activation energy of the ionic exchange process depends only on the pH of the contact solutions and does not depend on the value of initial copper concentrations. Thus, for the growth of the initial content of contact solutions from 77.46 up to 279.66 mg Cu/L, while maintaining constant the pH of those solutions, the apparent activation energy displays a variation coefficient in the 3.54-9.86% range. The activation energy goes up as the pH of the contact solution goes down. While the pH goes from 5.00 down to 0.97 the activation energy goes up from 5.7155 to 10.1467 KJ/mol.

A large array of parameters influence the adsorption of copper by ionic exchange, such as: the ratio between the volume of solution and the quantity of cationite, time, pH and the initial concentration of the contact solution, temperature, ionic strength of the solution, the nature of the accompanying anion, the simultaneous presence of many cations, etc.

Using the neural networks (ANN) in modelling, describing and profiling the adsorption process of copper by ionic exchange allows for a realistic view of the phenomenon to be obtained with high precision. The accuracy with which it depicts reality is higher as the number of experimental data used in training the network gets larger. For the cases under analysis, a correlation coefficient between experimental data and the equivalent data obtained by ANN modelling of 0.9985 was established.

The advantage of such modelling consists in determining with high accuracy the ionic exchange capacity for any working conditions that are part of the range of experimental studies. In the case at hand, within the working conditions, using ANN allows for the determination of the ionic exchange capacity (namely of the copper concentration of the contact solution) for any time sequence between 0 and 240 min (established by experiment as maximum needed to reach exchange equilibrium), for temperatures in the 20 and 50°C range, for initial concentrations in the 77.46–279.66 mgCu/l range and for the initial pH in the 0.97–5.00 range. The correlation coefficient computed between the values of the ionic exchange capacities based on experimental data and based on modelling by ANN is 0.9999.

Evidence was produced that data generated by modelling can be taken into consideration in order to conduct selected kinetic studies on the process. All influence experimentally noted on the ionic exchange process was spotted and validated by data obtained through ANN modelling. The use of artificial neural networks is important background not only in terms of making predictions, in terms of spotting and describing variations that have influence on the phenomenon, but also for profiling the behaviour of cationites in dynamic regimes, for contexts of practical applicability in the sewerage and the recovery of useful metals out of various types of residual solutions and water sewerage with content of heavy metals.

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