APPLICATION OF ANN FOR PREDICTION OF Co^{2+}, Cd^{2+} AND Zn^{2+} IONS UPTAKE BY *R. squarrosus* BIOMASS IN SINGLE AND BINARY MIXTURES

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Abstract: Discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. The search for new technologies involving the removal of toxic metals from wastewaters has directed the attention to biosorption, based on metal binding capacities of various biological materials.
Degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases and this behavior can be described by adsorption isotherm models (Freundlich and Langmuir isotherm models) representing the classical approach. In this study, an artificial neural network (ANN) was proposed to predict the sorption efficiency in single and binary component solutions of Cd^{2+}, Zn^{2+} and Co^{2+} ions by biosorbent prepared from biomass of moss *Rhytidiadelphus squarrosus*. Calculated non-linear ANN models presented in this paper are advantageous for its capability of successful prediction, which can be problematic in the case of classical isotherm approach. Quality of prediction was proved by strong agreement between calculated and measured data, expressed by the coefficient of determination in both, single and binary metal systems (R^2= 0.996 and R^2= 0.987, respectively). Another important benefit of these models is necessity of significantly smaller amount of data (about 50%) for the model calculation. Also, it is possible to calculate *Qeq* for all studied metals by one combined ANN model, which totally overcomes a classical isotherm approach.

Key words: heavy metal, biosorption, metal uptake, prediction, ANN

1. Introduction

Past two decades has witnessed a drastic increase in the quality and quantity of metal pollutants discharged into aqueous environmental sink. Heavy metals are toxic to aquatic flora and fauna even in relatively low concentrations. Some of these are capable of being assimilated, stored and concentrated by organisms. A special care needs to be taken in order to prevent the cumulative accumulation in the wastewater (MOHAN and SINGH, 2002).

Various treatment technologies have been developed for the purification of water and wastewater contaminated by heavy metals. The most commonly used methods for the removal of metal ions from industrial effluents include: chemical precipitation, solvent extraction, oxidation, reduction, dialysis, reverse osmosis, ion-exchange, etc. Among these, adsorption has evolved as the front line of defense and especially for those, which cannot be removed by other techniques. Selective adsorption utilizing biological materials, mineral oxides, activated carbon, or polymer resins, has

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generated much excitement among researchers, environmental engineers and scientists (MOHAPATRA and GUPTA, 2005).

A lot of works have been focused on the application of various adsorbents for the metal removal from the aqueous media, but only a few of manuscripts are dedicated to the competitive uptake from the binary or multiple aqueous solutions (see e.g. BAYO, 2012; SEO *et al*., 2008). As a matter of fact, it is more important to evaluate the simultaneous adsorption behavior and interactions involving two or more metal species since sole toxic metal species rarely exist in wastewater (LI *et al*., 2011). So, it is necessary to extensively investigate the competitive binding of the heavy metal ions such as Co^{2+}, Cd^{2+} and Zn^{2+} onto a biosorbent thoroughly. In this research, *R. squarrosus* moss biomass has been used as a powerful biosorbent for the biosorption of metal ions. In the application of adsorption for purification of wastewater the solution will normally be a mixture of many compounds rather than a single one. The interactions of these compounds may mutually enhance or mutually inhibit adsorption capacity (HO and McKAY, 1999).

Industrial effluents, however, far from being single-component, are complex solutions containing several metals simultaneously. In the biosorption of complex solutions, different metal ions may compete for the active sites present on the cell wall of the biomass. Consequently, the preference of the biomass for some metals is an important issue, which is affected by the type of biomass, its physicochemical characteristics, its preparation or previous conditioning, and the nature of the metallic solution (RINCÓN *et al*., 2005).

In previous studies (REMENÁROVÁ *et al.*, 2010; PIPÍŠKA *et al.*, 2010; PIPÍŠKA *et al.*, 2009) the effect of multisolute interactions on the capacity of *R. squarrosus* biomass was investigated using binary and ternary mixtures of Co^{2+}, Cd^{2+} and Zn^{2+} having pre-fixed ratios. The Freundlich and Langmuir isotherm models were applied to the equilibrium data. Parameters of these isotherm models provided an insight into the sorption process, reflected the nature of the sorbent, surface properties as well as the degree of the affinity of the sorbents and could be used to compare biosorption performance (KAFSHGARI *et al.*, 2013).

In addition to common approach, artificial neural networks (ANN) were studied as a suitable method for estimating complex functions in order to evaluate the equilibrium data. GHOSH *et al*. (2014) used ANN and response surface methodology to develop predictive models for simulation and optimization of the biosorption process. TOVAR-GÓMEZ *et al*. (2013) applied the ANN for prediction of biosorption in fixed-bed column. Similarly, OGUZ and ERSOY (2014) used ANN modeling to investigate the cause-effect relationship in the bed studies of cobalt (II) biosorption onto sunflower biomass. FAGUNDES-KLEN *et al*. (2007) predicted biosorption equilibrium of the binary mixture of cadmium-zinc ions by the *Sargassum filipendula* species. PRAKASH *et al.* (2008) predicted biosorption efficiency of copper (II) removal from single aqueous solution by taking into account the effect of initial copper concentration, pH and temperature and particle size of the adsorbent using ANN.

ANNs are computational systems, which mimic the computational abilities of biological systems by using a number of interconnected artificial neurons (FAZLALI

et al., 2013). Considering the inherent ability of the ANNs to learn and recognize nonlinear and complex relations, they can be used in various fields of chemistry. The ANNs consist of a number of interconnected nodes arranged in layers corresponding to input layer, hidden layer and output layer. The hidden layers encode and arrange the information received from the input layer and deliver them to the output layer. Each neuron of the network is connected with an associated weight, to the others via direct communication links, which finally provides a logical relationship between input and output parameters. The number of neurons for the input and output layers is usually determined by the number of input and target variables, but the number of neurons in the hidden layers is variable significant for optimization of the network.

This work presents an ANN model, trained by the back propagation algorithm, to predict the metal uptake (Q_{eq}) of Co^{2+}, Cd^{2+} and Zn^{2+} by moss *R. squarrosus* in different mixtures. The main goal of this work was to test the capability of ANN as a promising tool for modeling of biosorption behavior in single and binary metal solutions. Study was divided into two parts: (1) first part was focused on development of an ANN model capable to predict sorption behavior in single metal solutions; (2) second part was focused on the modeling of competitive sorption behavior in binary metal solutions. Suitability of ANN models was proved by comparison of calculated results with a classical approach of Langmuir adsorption isotherms.

2. Materials and methods

2.1 Biosorbent preparation

A biomass of moss *R. squarrosus* used in present study was collected from the forests of High Tatras Mountains, Slovak Republic. To remove the impurities, the biomass was washed twice in deionised water, oven-dried for 72 h at a maximal temperature 45°C to avoid the degradation of binding sites. After drying the biomass was milled and sieved. Particle size 300 - 600 μm was used in biosorption experiments.

2.2 Batch biosorption experiments in single and multi-metal systems

Batch biosorption experiments in single-metal systems were carried out in aqueous solutions containing $CdCl_2$, $CoCl_2$ or $ZnCl_2$ in concentration range 100 to 4000 μM and spiked with $^{109}CdCl_2$, $^{65}ZnCl_2$ or $^{60}CoCl_2$. Biosorption experiments in binary metal systems were carried out in series of solutions (Cd-Zn, Co-Zn or Cd-Co) containing each metal in concentrations varying from 100 to 4000 μM and in various molar ratios 2:1, 1:1, 1:2. The pH was adjusted to 6.0 with 0.1 M NaOH. Biosorbent (2.5 g/L, d.w.) was added, and the content in Erlenmeyer flasks was agitated on a reciprocal shaker (120 rpm) for 4 h at 20°C. At the end of each experiment biosorbent was filtered out, washed twice with deionised water and radioactivity of both moss biomass and liquid phase was measured. The metal uptake was calculated as

$$Q_{eq} = \left(C_0 - C_{eq}\right)\frac{V}{M} \tag{1}$$

where Q is the uptake (μmol/g, d.w.), C_0 and C_{eq} is the initial and the final metal concentrations in solution (μmol/L) and M is the amount of dried biosorbent (given in grams). Each experiment was repeated only twice due to total number of experiments (replication of all measurements is very time consuming). If two values of same experiment were significantly different from each other ($\alpha = 0.05$), both were excluded from further data processing.

2.3 Radiometric analysis

For radiometric determination of ^{109}Cd, ^{60}Co and ^{65}Zn in liquid phase and moss biomass, gamma spectrometric scintillation detector 54BP54/2-X and 76BP76/3 with well type crystal NaI(Tl) (Scionix, Netherlands) and data processing software Scintivision32 (Ortec, USA) were used. Standardized $^{109}CdCl_2$ solution (3.857 MBq/ml, $CdCl_2$ 50 mg/L in 3 g/L HCl), $^{65}ZnCl_2$ solution (0.8767 MBq/ml; 50 mg $ZnCl_2$/L in 3 g/L HCl) and $^{60}CoCl_2$ solution (5.181 MBq/mL, $CoCl_2$ 20 mg/L in 3 g/L HCl) were obtained from the Czech Institute of Metrology, Prague (Czech Republic).

2.4 Experimental data analysis and isotherms calculations

Details about measured biosorption data have been already published in previous papers (e.g. REMENÁROVÁ *et al.,* 2010).

The Langmuir (Eq. 2) and Fruendlich (Eq. 3) adsorption models were used for describing equilibrium data in single metal systems. Langmuir sorption isotherm models the monolayer coverage of the sorption surfaces and assumes that sorption occurs on a structurally homogeneous adsorbent and all the sorption sites are energetically identical. The linearized form of the Langmuir equation is given by:

$$Q_{eq} = \frac{bQ_{\max}C_{eq}}{1 + bC_{eq}} \tag{2}$$

where Q_{eq} is the amount of metal ion sorbed per unit weight of sorbent (μmol/g), C_{eq} the equilibrium concentration of the metal ion in the equilibrium solution (μmol/L), Q_{max} is the maximum sorption capacity of the sorbent (μmol/g) and b is the affinity parameter.

Freundlich equation is derived to model for the multilayer sorption and for the sorption on heterogeneous surfaces. The logarithmic form of Freundlich equation may be written as:

$$Q_{eq} = KC_{eq}^{(1/n)} \tag{3}$$

where K is constant indicative of the relative sorption capacity of sorbent (μmol/g) and $1/n$ is the constant indicative of the intensity of the sorption process.

Sorption equilibrium in binary systems Cd^{2+}-Co^{2+}, Zn^{2+}-Cd^{2+} and Co^{2+}- Zn^{2+} was described by the competitive Langmuir model developed under the concept of original Langmuir isotherm for single systems for description of binary equilibrium data. The final expression of competitive Langmuir model is as follows:

$$Q_{eq}[Me_1] = \frac{b_{Me_1} Q_{\max Me_1} C_{eq}[Me_1]}{1 + b_{Me_1} C_{eq}[Me_1] + b_{Me_2} C_{eq}[Me_2]} \quad (4)$$

$$Q_{eq}[Me_2] = \frac{b_{Me_2} Q_{\max Me_2} C_{eq}[Me_2]}{1 + b_{Me_1} C_{eq}[Me_1] + b_{Me_2} C_{eq}[Me_2]} \quad (5)$$

$$b_{Me_1} = \frac{1}{K_{Me_1}} \text{ and } b_{Me_2} = \frac{1}{K_{Me_2}}$$

The total metal uptake in binary systems can be expressed as follows:

$$Q_{eq}[Me_1 + Me_2] = Q_{eq}[Me_1] + Q_{eq}[Me_2] = \frac{b_{Me_1} C_{eq}[Me_1] + b_{Me_2} C_{eq}[Me_2]}{1 + b_{Me_1} C_{eq}[Me_1] + b_{Me_2} C_{eq}[Me_2]} \quad (6)$$

where $Q_{eq}[Me_1]$ and $Q_{eq}[Me_2]$ represent equilibrium sorption capacities of metals Me_1 and Me_2, $Q_{eq}[Me_1+Me_2]$ is the sum of uptakes of the two metals, $C_{eq}[Me_1]$ and $C_{eq}[Me_2]$ represent equilibrium concentrations of metals remaining in solution and Q_{max} is the maximum sorption capacity of metals in the binary component systems. Parameters b_{Me1} and b_{Me2} represent affinity constants of Langmuir model for the first and second metal ions (APIRATIKUL and PAVASANT, 2006).

To calculate the maximum sorption capacities Q_{max} values and the corresponding parameters of adsorption isotherms non-linear regression analysis was performed by the software ORIGIN 8.5 Professional (OriginLab Corporation, Northampton, USA).

2.5 Data description and processing

The initial step in the ANN modelling is compiling an adequate database to train the network and to evaluate its capacity for generalization. Experimental and theoretical values were organized in the basic data matrix into the lines with respect to the metal and its metal uptake (Q_{eq}). The basic set of independent variables (columns) contained: type of metal (*M*) - categorical variable with 3 levels Zn, Co and Cd, its maximum sorption capacity (Q_{max}) and its physico-chemical parameters: ratio of charge squared to ionic radius (*IonInd*), covalent index (*KInd*), ionization energy (*IonEng*), ionic radius (*IonR*), electronegativity (*ElNeg*). Another group of variables were indicator variables of metals presented in analyzed solution (*MZn, MCd, MCo*). The last group was oriented on the initial concentrations of the metals in the system (*ZnC0*, *CdC0*, *CoC0*), initial concentration of metal with supplemented Q_{eq} value (*C0*), total concentration of all presented metals in solution (*sumC0*), ratio (*wM*) between the initial metal concentration (*C0*) and total concentration of all metals presented in the system (*sumC0*). In the case of the last group, all concentrations were adjusted by the speciation of the metal and pH values. In addition the "concentration variables" were transformed into the logarithmic form with the effort of better fitting the sorption behaviour. This provided a basic data matrix with 118 lines (cases) and 22 columns (variables).

The basic data matrix was reduced to contain data belonging to only single metal systems. This reduced data matrix contained only 21 cases (7 concentrations for 3 studied metals) and 22 original variables was used in modelling of single metal solutions by ANN and the basic data matrix was used for binary metal systems.

2.6 ANN model development

ANNs with different architectures provide different outputs, so there is more chance to reach the optimal model with more developed and evaluated models. In this study, various numbers of neurons were used for the hidden layer as well as the activation functions of the hidden and output layer, and the optimal settings were evaluated. In order to prevent overfitting in ANNs training process, the data set was randomly separated into three parts, the training set, the test set and the validation set, with the population ratio 2:1:1. The best ANN model was assessed by the calculation performances of these three sets, especially the validation set as the measure of model generalization (MAY *et al.,* 2011).

High number of variables at the ANNs input compared to the number of cases adversely influences the ANN performance and generalization. Thus very important step is reduction of the number of ANN inputs. In presented research, the variables considered as the inputs of the network were selected according to the sensitivity analysis of the best developed models. Sensitivity analysis, is a supplement of the ANNs output in software STATISTICA 10, which provides sensitivity ratio for each input variable of selected model. By referring to sensitivity ratio value, the input variables can be ranked for their contribution to the output. The results with a value more than 1 represent major variables and the value less than 1 represents minor variables (MONTANO *et al*., 2003). Sensitivity analysis approach was successfully used to select an optimal set of input variables for ANN calculation as well as their suitable representation (logarithmic form etc.).

All presented ANN outputs and developed models were performed by the STATISTICA 10 (Statsoft, Tulsa, USA).

3. Results and discussion

3.1 ANN modeling of biosorption in single metal systems

The first aim of the presented study was development of an ANN model with multilayer perceptron architecture capable to predict metal uptake (Q_{eq}) in single metal system and compare obtained results with a classical approach – Langmuir equilibrium isotherm. Reduced data matrix was used for the ANN calculations.

The best neural network (Fig. 1) configuration had five input neurons, namely *C0*, *IonInd and M* (with 3 levels Zn, Co and Cd), two hidden neurons and one output neuron (Q_{eq}). Best ANN model was trained using only eleven cases (training set) and five cases for internal validation (test set). Excellent results were obtained by the regression analysis (Tab. 1) of the training and test sets with the determination coefficients (0.986 and 0.999) and slopes (0.987 and 1.024) close to one and intercepts

(1.753 and 0.525) close to zero, respectively. The coefficient of determination (R^2), slope and intercept values of the validation set (five cases) for the prediction of the Q_{eq} were 0.996; 1.053 and 3.942, respectively. Fig. 2 shows fitting of the predicted values with the experimental results for each studied metal. Figures were made as an addition to the classical isotherm approach. This was the main reason, why graphs were not constructed by the common ANN principle (by training, test and validation subsets), but by the individual metals.

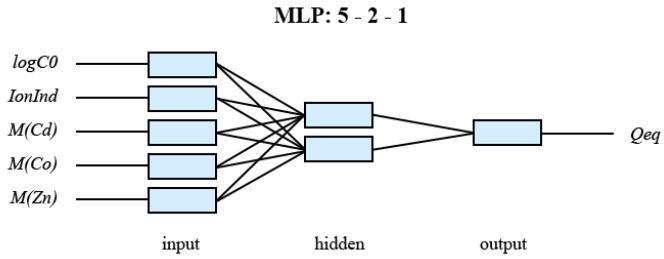

Fig. 1. Scheme of three-layer perceptron built for Q_{eq} prediction of single metal systems. In the case of categorical variable *M,* three sublevels are present in the brackets.

Results obtained by Langmuir isotherms for each metal were very similar to those calculated by the ANN model. The strong correlations between the calculated and experimental metal uptakes were proved for all studied metals. Coefficients of determination for Langmuir isotherm and ANN model were very close to one for cobalt 0.914 vs. 0.997, for cadmium 0.994 vs. 0.992 and zinc 0.995 vs. 0.980, respectively. The resulting ANN model was able to replace along three isotherms (for each of the studied metal). Compared with a traditional approach of isotherm modelling was able not only to describe the sorption behavior, but in addition it could also predict the sorption efficiency what was confirmed by an independent validation.

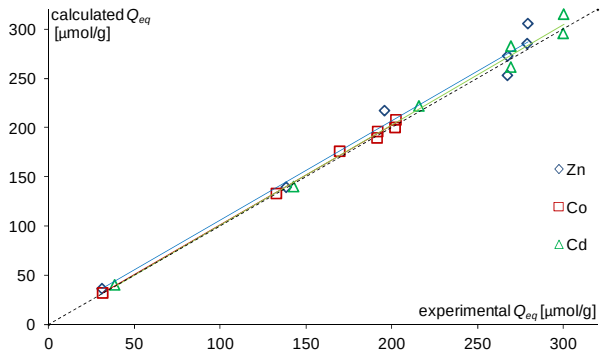

Fig. 2. Q_{eq} values calculated by the ANN model compared with the experimental data for each metal that offers an alternative view on prediction performance of biosorption. Straight-line indicates the ideal scenario, where the calculated values are identical with the experimentally measured data.

Achieved ANN performance is also comparable with other authors. MASOOD *et al*. (2012) used artificial neural network for prediction of biosorption of total chromium by *Bacillus* sp. Developed model used pH, time and initial metal concentration on the input. Regression analysis of the results proved strong correlation between the calculated and the experimental values, R^2= 0.971. For determination of the degree of effectiveness of a variable the sensitivity analysis was conducted using the proposal ANN model. Findings of the sensitivity analysis showed that initial pH was the most significant parameter for the prediction of removal efficiency.

Similarly, RAJ *et al*. (2013) highlighted the possibility of the prediction of sorption efficiency for the arsenic species from water bodies using *Leucaena Leucocephala* seed powder (LLSP) in the range at which lab experiments have not been conducted.They have developed a single layer ANN model (using biosorbent dosage, arsenic ion concentration, contact time and volume on the input) for the predicition of sorption efficiency of arsenic species using LLSP.

YETILMEZSOY and DEMIREL (2008) utilized ANN for more complex tasks, which included also kinetic studies of Pb^{2+} sorption on *Pistacia Vera L.* shells. Developed model used sorbent dosage, initial concentration of Pb^{2+}, pH, temperature and contact time on the input. Regression analysis of sorption efficiency results proved strong correlation between the calculated and the experimental values, R^2= 0.936, slope b_1= 0.896 and intercept b_0= 8.46.

In spite of the results are promising, the application of the complex nonlinear algorithm is not necessary. Classical isotherm model approach is more than sufficient for description of the sorption behaviour in single component systems. In this phase of the research, the development of the ANN model was more about methodical than practical importance.

Tab. 1. Table shows the results of ANN validation expressed by the regression analysis for each system and subset, where *n* represents the number of objects in subset, R^2 is the coefficient of determination, b_1 and b_0 are the slope and intercept, respectively.

System type	Subset	*n*	R^2	b_1	b_0
single metal systems	training	11	0.998	1.024	0.525
	testing	5	0.986	0.987	1.753
	validation	5	0.996	1.053	3.942
binary metal systems	training	49	0.987	1.030	-2.532
	testing	24	0.987	1.018	-2.889
	validation	45	0.987	1.007	-0.881

3.2 ANN modeling of biosorption in binary metal systems

The second part of this study was oriented to the modeling of a competitive sorption behavior in binary metal systems (Zn-Cd, Cd-Co, Co-Zn). The basic data matrix was used containing the sorption data of studied metals in single systems as well as their combinations in binary metal systems. Again, the ANNs results were

compared with the classical approach represented by competitive Langmuir isotherm for binary systems.

The best ANN model has fourteen input neurons, five neurons in the hidden layer and one output neuron (Fig. 3). The most important variables ordered by the sensitivity analysis were: metal indicator variables *MCo, MCd*, *MZn* (each with two levels Y-present and N-not present), followed by the concentration variables in logarithmic form, initial concentrations of the metals *C0Co*, *C0Cd*, *C0Zn* and the total concentration of all metals in the system *sumC0*, type of the predicted metal *M* (with 3 levels Zn, Co and Cd), and ratio of charge squared to ionic radius *IonInd*. Distribution of the cases was 40% used in the training process, 20% in the test set for internal validation and 40% of data was in the validation set. Regression analysis (Fig. 4) confirmed the calculation accuracy of the final ANN model, where the coefficients of determination were 0.997; 0.985 and 0.994 in the order training, test and validation set. Slopes and intercepts were reasonably close to one and zero, respectively; detailed results for the training data 0.993 and 0.497; test data 0.983 and 1.651 and validation data 1.056 and -5.638 (Tab. 1).

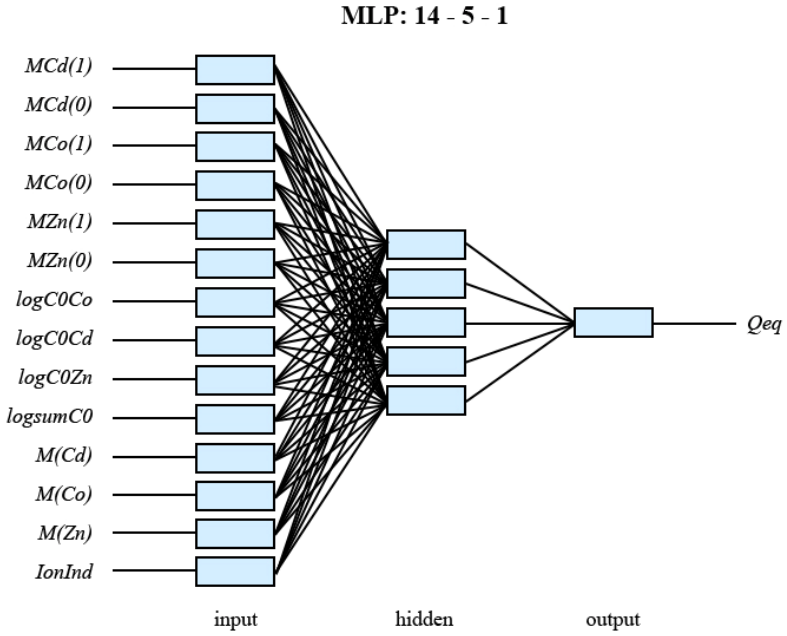

Fig. 3. Scheme of three-layer perceptron built for Q_{eq} prediction of binary metal systems. This figure contains input categorical variables *M, MCd, MCo* and *MZn*, which sublevels are shown in brackets.

The Langmuir isotherms for binary systems were used to compare the results of the classical approach with the obtained ANN output. Also in this case were evaluated the calculated metal uptakes with the experimental data by coefficients of determination for each binary system. For the system zinc-cobalt were obtained high values of the coefficients of determination in both cases; 0.992 for Langmuir isotherms and 0.990

for ANN model. Other two systems Co-Cd and Zn-Cd for both approaches had values a little smaller, but still very good. Classical approach had 0.938 and 0.901 while ANN model provided 0.938 and 0.946, in previously given order.

CHU and KIM (2006) studied the competitive sorption of copper and cadmium on the microbial biosorbent. Feed-forward ANN model was developed for the description of the competitive sorption behavior in the binary metal system. The ANN topology composed from the initial metal concentrations (Cu and Cd) and pH used as the inputs, ten hidden neurons and two output neurons (one neuron for each metal). Developed model achieved the mean absolute relative errors 3.3% for Cu and 3.5% for Cd sorption prediction, which is a very good performance considering the simplicity of the model - just 3 input neurons.

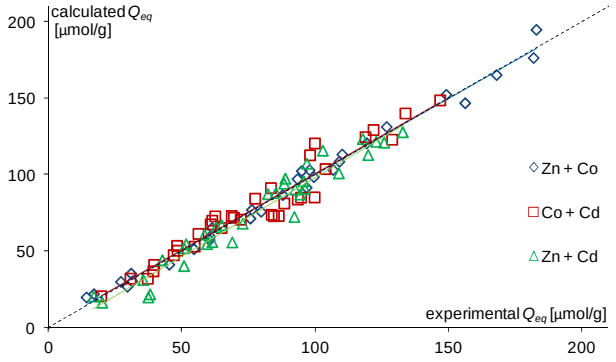

Fig. 4. Regression analysis of Q_{eq} values calculated from ANN model, compared with the experimental data separately for each binary system. This graphical output offers an alternative view on prediction performance of biosorption. Straight-line indicates ideal scenario, where the calculated values are identical with the experimental data.

Similarly, KABUBA *et al*. (2012) used a neural network for prediction of the sorption of binary mixture of copper-cobalt ions. They found that experimental data of the single-component system and the binary mixture were well described by several isotherm models. However, these isotherm models were not able to predict the adsorption in binary mixture accurately. On the contrary, application of neural network showed that this technique is more efficient with the one using the adsorption isotherms.

4. Conclusions

It can be concluded that the approach of ANN is efficient in modeling of complex biological phenomenon such as biosorption. The preliminary study on single systems proves high potential of ANNs in the modeling of experimental data of biosorption processes. Developed models provide also several advantages compare to the classical isotherm approach: (1) one ANN model can successfully describe the behavior of several metals (in this study three) while isotherm can always describe sorption behavior of only one metal; (2) in general, the ANN model development requires

approximately 50% of original cases in contrast to isotherm approaches requiring most of the data; (3) Q_{eq} calculation for new (not measured) initial concentrations (in studied range) was proved as very accurate according to the validation set results; (4) ANNs allow to study different input variables and their influence on the target metal uptake using the sensitivity analysis.

ANN models presented in this paper are advantageous for its capability of successful prediction, which can be problematic in the case of classical isotherm approach. Quality of prediction was proved by coefficient of determination between calculated and measured data in single (R^2= 0.996) and binary metal systems (R^2= 0.987). Slightly lower R^2-value for binary system was expected due to the effect of metal competition.

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