

Proton / Cu(II) and Proton / Ni(II) Ion Exchange Equilibria on Sulfonated Hypercrosslinked Resin Sorption and Surface Complexation Models

CORINA M. BOHDANA^{1*}, EUGEN PINCOVSCI², ANA-MARIA S. OANCEA³

¹Purolite SRL Romania, 11 Aleea Uzinei Str., 505700, Victoria, Braşov, Romania

²University Politehnica of Bucharest, Department of Environmental Protection, 1-3 Gh. Polizu Str., 011061, Bucharest, Romania

³University Politehnica of Bucharest, Department of Inorganic Chemistry, 1-3 Gh. Polizu Str., 011061, Bucharest, Romania

Proton/Cu(II) and Proton/Ni(II) ion exchange equilibria on a sulfonated hypercrosslinked styrene-divinylbenzene resin were investigated in order to assess the possibility of using this resin to eliminate heavy metal ions from industrial wastewaters. The ion exchange isotherms were measured at 298 K and 0.01 eq/L total concentration of aqueous external solution using atomic absorption spectrometry. The data were modeled with classical adsorption models and surface complexation model. The results show that both Langmuir isotherm and the surface complexation model describe well the selected systems. The ion exchange equilibrium constants are reported and compared with the corresponding constants of other binary systems given in literature revealing short selectivity series on the strong acid hypercrosslinked resin.

Keywords: ion exchange equilibrium; surface complexation model; sulfonated macronet resin; hypercrosslinked polymer

The sources of copper and nickel pollutants include mining/smelting, electronics and chemical industries as well as waste disposal in the form of leakages from landfills. Copper can be found in many wastewaters arising from agriculture, printed circuit board manufacturing, electroplating, wire drawing, copper polishing, paint manufacturing and wood preservatives. Nickel is found mainly in plating, metal pickling and metal cleaning wastewater [1].

Ion exchange is a highly effective method for separation of harmful metal ions from wastewaters of different industries in order to diminish their release into environment [2-4]. The properties of ion exchange systems at equilibrium determine the column performance in the separation process [5], justifying thorough studies of ion exchange equilibria both for binary and multicomponent systems.

Davankov and Tsyurupa developed a class of hypercrosslinked styrene-divinylbenzene polymers [6, 7] manufactured in the last years by Purolite International under the trade name "Macronet Hypersol" [8]. These resins were obtained from beads of styrene-divinylbenzene copolymers swelled in a solvent in excess and post-crosslinked with conformational rigid methylenic bridges [6-10]. This class of hypercrosslinked styrene-divinylbenzene resins was not enough investigated, even if their properties seem to be promising for industrial applications [10]. A few data on the ion exchange equilibria on the strong acid macronet MN500 resin were reported in literature for H⁺/NH₄⁺ [11], H⁺/Na⁺, K⁺ [12], H⁺/Cu²⁺, Zn²⁺, Cd²⁺ [13], H⁺/Mg²⁺ [14] together with data for ion exchange kinetics for H⁺/Cd²⁺ [15] and H⁺/Cs⁺, Sr²⁺ [16].

The objective of the present work was to investigate H⁺/Cu²⁺ and H⁺/Ni²⁺ ion exchange equilibria on the strong acid macronet ion exchanger Purolite MN500 in order to evaluate the selectivity of this resin for copper and nickel ions. This is important for wastewater depollution processes. The ion exchange isotherms were measured

at 298 K and the data were modeled using classical adsorption models together with the surface complexation model, determining the ion exchange equilibrium constants.

Sorption models

Some classical adsorption models were taken into account, namely the Langmuir equation for monolayer adsorption of a pure component from an ideal fluid media on uniform surface without lateral interactions [17, 18] and the equations of the isotherms of Freundlich, Sips and Tóth, together with the Unilan equation for non-ideal cases [17], for porous solids with energetically heterogeneous surfaces. These equations are:

$$\text{Langmuir: } q = q_m \cdot \frac{KC}{1+KC} \quad (1)$$

$$\text{Freundlich: } q = k C^{1/n}; n > 1 \quad (2)$$

$$\text{Sips: } q = q_m \cdot \frac{(KC)^{1/n}}{1+(KC)^{1/n}}; n \neq 1; \text{ usually } n > 1 \quad (3)$$

$$\text{Tóth: } q = q_m \cdot \frac{KC}{[1+(KC)^n]^{1/n}}; n \neq 1; \text{ usually } n < 1 \quad (4)$$

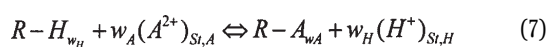
$$\text{Unilan: } q = \frac{q_m}{2s} \cdot \ln \left(\frac{1+\bar{K} \cdot C \cdot \exp(s)}{1+\bar{K} \cdot C \cdot \exp(-s)} \right); s = \frac{E_{\max} - E_{\min}}{2RT} \quad (5)$$

Jovanovich isotherm was derived from kinetic considerations and describes the sorption equilibrium on a solid with a homogenous surface as Langmuir isotherm, but with vertical interactions between the bulk and the surface phases [17]:

$$q = q_m \cdot (1 - \exp(-KC)) \quad (6)$$

Surface complexation model

The Surface Complexation Model (SCM) was proposed for ion exchange processes on polymeric ion exchangers by Höll and co-workers [19]. The model supposes that the fixed ionic groups of the ion exchanger are uniformly distributed on a plane surface, while each counterion is located in separately Stern layer parallel to the surface plane, at a characteristic definite distance from the plane. A small amount of counterions forms a diffuse layer, but in order to simplify the mathematical treatment they are neglected [19]. Between the counterions from their corresponding Stern layers and the fixed ionic groups on the resin surface arise physical and/or chemical interactions forming species called "surface complexes". The ion exchange process for a binary system is the process of replacement between two surface complexes. For H^+ / Cu^{2+} or H^+ / Ni^{2+} ion exchange on the ion exchanger the replacement can be represented by:



where w_H, w_A are the stoichiometric coefficients defined as the ratio between the resin valence $z(R)$ and the corresponding counterion valence, multiplied with -1 . For our system $z(R) = -2$, $w_H = +2$ and $w_A = +1$ [19].

The corresponding thermodynamic ion exchange constant for the ideal case (activity coefficients equal to unity) [19] is defined by:

$$K_H^A = \frac{C(R-A)[C(H^+)_{St,H}]^2}{C(R-H_2)C(A^{2+})_{St,A}} \quad (8)$$

Let suppose that the Stern layer of the divalent counterion A^{2+} is the first one next to the resin surface and the proton Stern layer is the second one. The two layers form an electric capacitor. Assuming a Boltzmann distribution [19] of ions in the electrical field, the concentrations of the free ions in the corresponding Stern layers in equation 8 are expressed as a function of the concentration in the liquid phase and the electrical potential of the layer. Taking into account the electric capacity of a capacitor formed by the two Stern layers, and replacing the ratio of the concentrations of the counterions in the resin phase with the ratio of the counterion loadings [19], the equation 8 becomes:

$$\begin{aligned} \log Q_H^A &= \log \frac{y_{A^{2+}} C_{H^+}^2}{y_{H^+} C_{A^{2+}}} = \log K_H^A + \frac{|z(R)|}{\ln 10} \frac{F^2 q_{\max}}{A_0 C(A, H) RT} y_{H^+} = \\ &= \log K_H^A + m(A, H) y_{H^+} \end{aligned} \quad (9)$$

where the ratio Q_H^A is called *the generalized separation factor*, and can be measured experimentally. The logarithm of the ion exchange constant ($\log K_H^A$) is the intercept of the linear regression $\log Q_H^A$ vs. y_{H^+} . The slope $m(A, H)$ of the linear regression is also a constant of SCM. The slope is positive, if the sequence of the two Stern layers were correctly assumed.

Experimental part

Materials

The ion exchanger was Purolite MN500 macronet resin with hypercrosslinked polystyrenic matrix and sulfonic acid functional groups. Details about the properties of this resin were described elsewhere [8, 10]. The resin was dried at

room temperature, screened by sieving and the size fraction between $[-710+600]$ was selected in order to have a more homogeneous material. The purification of the resin was done in three cycles of successive treatments with 1M HCl solution, demineralized water with specific conductivity of $0.055 \mu\text{S}/\text{cm}$, 1M NaOH solution, demineralized water. The final form of the resin was H^+ , and the final washing was done with demineralized water until the effluent had a specific conductivity less than $1 \mu\text{S}/\text{cm}$. After purification the resin was air-dried and kept in a desiccator on saturated NaCl solution in order to sorb water vapors and to reach a constant mass at room temperature. The total ion exchange capacity was $2.48 \text{ meq}/\text{g}$.

The external solutions were prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ p.a. Merck, using demineralized water ($0.055 \mu\text{S}/\text{cm}$). HCl 36% and NaOH p.a. Merck were used for the preparation of the other solutions.

Determination of the ion exchange isotherms

Known quantities of the resin in H^+ form saturated with water vapors ($0.01 - 1 \text{ g}$) were introduced in 100 mL solution of $0.01 \text{ eq}/\text{L}$ of copper and nickel nitrates, in glass bottles with lids, kept at 25°C in an acclimatized laboratory during one week and stirred from time to time. The concentrations of the copper and nickel ions in the initial solution and at equilibrium were analyzed using atomic absorption spectrophotometry, with an AA100 Perkin - Elmer spectrophotometer. The calibration stock solutions were p.a. Merck. The pH of the external solutions were measured at the equilibrium and ranges for Cu^{2+} between 2.03 and 3.78, while for Ni^{2+} between 2.2 and 3.76, as a function of the amount of resin introduced in the salt solution. The isotherms were obtained from three or four independent runs, namely from new prepared external solutions.

Speciation

Speciation of metallic ions in the aqueous solution at different pHs occurs and transforms a binary ion exchange system in a multicomponent one. The selected salts for preparing the external solutions containing copper(II) and nickel(II) were nitrates in order to diminish speciation, knowing that nitrate anion is a weak ligand. A study of the solutions composition versus pH was done to support that the investigated systems were binary ion exchange systems and the determined ion exchange constants correspond to the binary systems. Table 1 gives the equilibrium constants for different reactions occurring in an aqueous solution containing nitrates of copper and nickel divalent ions.

It can be observed from table 1 that the equilibrium constants of formation of the species $\text{Cu}(\text{OH})_2(\text{aq})$, $\text{Ni}(\text{OH})_2(\text{aq})$ and of the complexes $1:2 \text{ Cu}(\text{NO}_3)_2(\text{aq})$, $\text{Ni}(\text{NO}_3)_2(\text{aq})$ are extremely low and these reactions can be neglected. The reactions of formation of the hydroxo-aqua-species CuOH^+ , NiOH^+ and of the complexes CuNO_3^+ , NiNO_3^+ must be considered in the speciation analysis as correlated processes competing in the evolution of the system toward equilibrium. The molar concentrations at equilibrium of the free metallic ion (aquaion) $[\text{M}^{2+}]$, of the hydroxo-aqua-species $[\text{MOH}^+]$ and of the 1:1 complexes metallic ion-nitrate ligand $[\text{MNO}_3^+]$ where obtained at different pHs by solving the system of equations 10-13:

$$K_1 = \frac{[\text{MOH}^+][\text{H}^+]}{[\text{M}^{2+}]} \quad (10)$$

Equilibrium reaction	logK	Reference
$\text{Cu}^{2+} + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CuOH}^+ + \text{H}^+$	-7.497	20
$\text{Cu}^{2+} + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Cu}(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-16.194	20
$\text{Cu}^{2+} + \text{NO}_3^- \rightleftharpoons \text{CuNO}_3^+$	0.500	20
	0.44 ± 0.13	21
	0.54	22
$\text{Cu}^{2+} + 2\text{NO}_3^- \rightleftharpoons \text{Cu}(\text{NO}_3)_2$	-0.400	20
$\text{Ni}^{2+} + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NiOH}^+ + \text{H}^+$	-9.897	20
	-9.50 ± 0.36	23
$\text{Ni}^{2+} + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Ni}(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-18.994	20
	-18.0 ± 1.0	23
$\text{Ni}^{2+} + \text{NO}_3^- \rightleftharpoons \text{NiNO}_3^+$	0.400	20
	0.4	23
$\text{Ni}^{2+} + 2\text{NO}_3^- \rightleftharpoons \text{Ni}(\text{NO}_3)_2$	-0.6	23

Table 1
EQUILIBRIUM CONSTANTS FOR
REACTIONS INVOLVING COPPER(II) AND
NICKEL(II) IONS IN AQUEOUS SOLUTION
AT 25°C AND 1 atm

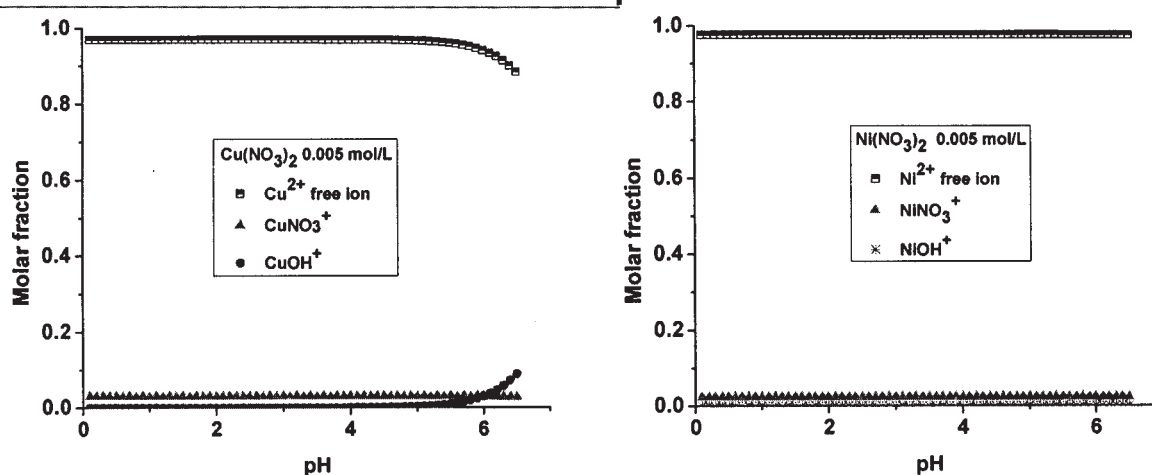


Fig. 1. The molar fraction of the species formed in $\text{Cu}(\text{NO}_3)_2/\text{Ni}(\text{NO}_3)_2$ solutions versus pH; 298 K; 0.01 eq/L total equivalent concentration

$$K_2 = \frac{[\text{MNO}_3^+]}{[\text{M}^{2+}][\text{NO}_3^-]} \quad (11)$$

$$[\text{M}^{2+}]_{\text{total}} = [\text{M}^{2+}] + [\text{MOH}^+] + [\text{MNO}_3^+] = a \quad (12)$$

$$[\text{NO}_3^-]_{\text{total}} = [\text{NO}_3^-] + [\text{MNO}_3^+] = 2a \quad (13)$$

where K_1 and K_2 are the equilibrium constants of aquaion and metal-nitrate complex formation, respectively, and a is the molar concentration of the copper/nickel nitrate solution. The computations were done for $K_1 = 10^{-7.497}$ and $K_2 = 10^{0.5}$ for copper, and for $K_1 = 10^{-9.50}$ and $K_2 = 10^{0.4}$ for nickel, for solutions of 0.005 mol/L $\text{Cu}(\text{NO}_3)_2/\text{Ni}(\text{NO}_3)_2$. In figure 1 are given the molar fractions of the considered species at different pHs in the range 0 - 6.5. It must be noted that the experimental pH range was 2 - 4 for external solutions at equilibrium of the studied ion exchange processes on the macronet strong acid resins. At pH = 2 the molar fractions of the species Cu^{2+} , CuOH^+ and CuNO_3^+ were: 0.9698, $3.1 \cdot 10^{-6}$, 0.0302, respectively, and at pH = 4

the corresponding values were: 0.9695, 0.000308, 0.03019. For the species Ni^{2+} , NiOH^+ and NiNO_3^+ the molar fractions at pH = 2 were: 0.97578, $3.1 \cdot 10^{-8}$, 0.02421, and at pH = 4 were: 0.97578, $3.1 \cdot 10^{-6}$, 0.2421. The dominant species in the studied cases were the free aquaion of divalent copper or nickel ions and we can assume with good accuracy that the investigated systems were binary ion exchange systems.

Results and discussions

Figures 2 and 3 give the experimental isotherms obtained for $\text{H}^+/\text{Cu}^{2+}$ and $\text{H}^+/\text{Ni}^{2+}$ ion exchange on MN500 strong acid macronet resin for different runs, namely for experiments done using initial solutions prepared independently.

The equations 1-6 of the adsorption isotherms were fitted to the experimental points. The obtained adsorption constants for the binary systems $\text{H}^+/\text{Cu}^{2+}$ and $\text{H}^+/\text{Ni}^{2+}$ on the hypercrosslinked strong acid resin are given in table 2 and table 3, respectively.

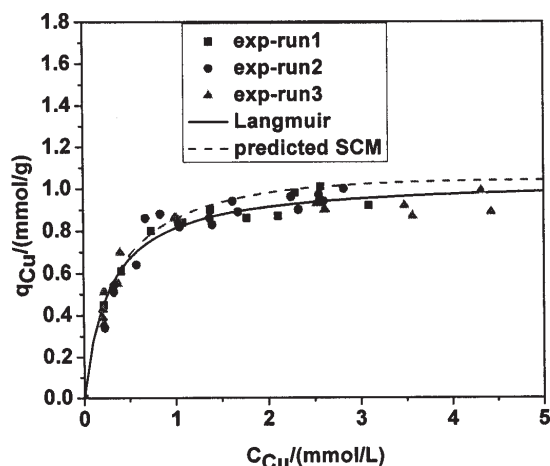


Fig. 2. Experimental, fitted Langmuir and predicted SCM isotherms for H^+/Cu^{2+} ion exchange on the sulfonated hypercrosslinked resin MN500; 298 K; 0.01 total equivalent concentration

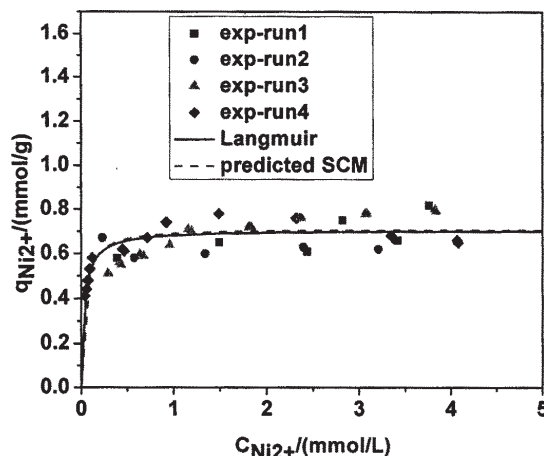


Fig. 3. Experimental, fitted Langmuir and predicted SCM isotherms for H^+/Ni^{2+} ion exchange on the sulfonated hypercrosslinked resin MN500; 298 K; 0.01 total equivalent concentration

Isotherm	r^2	F-statistic	$q_m \times 10^3 / (\text{mol/g})$	$K \times 10^{-3}$	n
Langmuir	0.942	765	1.04 ± 0.04	3.5 ± 0.5	
Freundlich	0.854	276	$3.89 \pm 0.95^*$		4.2 ± 0.7
Jovanovich	0.951	909	0.92 ± 0.02	2.8 ± 0.2	
Sips	0.953	465	0.96 ± 0.04	3.9 ± 0.4	0.7 ± 0.2
Tóth	0.953	468	0.95 ± 0.04	2.4 ± 0.4	1.7 ± 0.5
Unilan	0.932	318	0.99 ± 0.07	4.2 ± 0.7	$0.01 \pm 130^{**}$

* "k" in the Freundlich's equation; ** "s" in Unilan equation

Isotherm	r^2	F-statistic	$q_m \times 10^3 / (\text{mol/g})$	$K \times 10^{-3}$	n
Langmuir	0.790	196	0.71 ± 0.02	27.6 ± 8.1	
Freundlich	0.814	228	$1.3 \pm 0.2^*$		9.5 ± 1.9
Sips	0.828	123	0.85 ± 0.2	26 ± 29	2.5 ± 1.9
Tóth	0.828	122	0.88 ± 0.3	153 ± 10315	0.32 ± 0.34
Unilan	0.822	123	0.77 ± 0.09	42 ± 30	$4.7 \pm 2.6^{**}$
Jovanovich	0.711	128	0.68 ± 0.02	17.8 ± 4.0	

* "k" in the Freundlich's equation; ** "s" in Unilan equation

Table 2

FITTED ADSORPTION ISOTHERMS FOR H^+/Cu^{2+} ION EXCHANGE ON THE MACRONET STRONG ACID RESIN MN500 AT 298K AND 0.01 N TOTAL EQUIVALENT CONCENTRATION; PARAMETERS OF GOODNESS OF FIT; COEFFICIENT OF DETERMINATION r^2 AND F STATISTIC; 95% CONFIDENCE LIMITS; 48 EXPERIMENTAL POINTS

Table 3

FITTED ADSORPTION ISOTHERMS FOR H^+/Ni^{2+} ION EXCHANGE ON THE MACRONET STRONG ACID RESINS MN500 AT 298K AND 0.01 N TOTAL EQUIVALENT CONCENTRATION; PARAMETERS OF GOODNESS OF FIT; COEFFICIENT OF DETERMINATION r^2 AND F STATISTIC; 95% CONFIDENCE LIMITS; 53 EXPERIMENTAL POINTS

The results presented in tables 2 and 3 show that all investigated adsorption isotherms are significant from statistical point of view with comparable parameters of goodness of fit, taking into account the large number of experimental points. The parameter "s" from Unilan equation for H^+/Cu^{2+} and the sorption constants obtained for H^+/Ni^{2+} with Sips and Tóth equations have negative values of the lower confidence limit for 95% probability. These equations were discarded for the corresponding cases, even if the parameters of goodness of fit were significant. The fitting method does not permit a sharp discrimination between these isotherms. In other words, it is difficult to understand if the resin surface is energetically homogeneous or heterogeneous from the above results. Consequently the Langmuir equation can be considered to describe with good accuracy the ion exchange equilibria investigated in the present work. The fitted Langmuir isotherms are also given in figures 2 and 3, and are in good agreement with the experimental data for both systems.

The surface complexation model was evaluated for the H^+/Cu^{2+} and H^+/Ni^{2+} binary ion exchange equilibria on the sulfonated polystyrenic resin type macronet. The generalized separation factor was obtained from both experimental isotherms and the fitted Langmuir isotherm [12, 13]. The results are presented in figures 4 and 5.

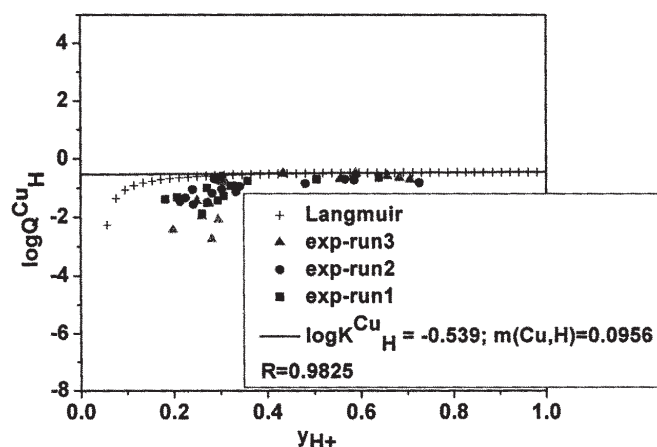


Fig. 4. The logarithm of the generalized separation factor versus the proton ionic fraction in the resin phase for H^+/Cu^{2+} ion exchange equilibrium on MN500 resin; 298 K; 0.01 eq/L total equivalent concentration

The SCM constants were obtained from the linear regression $\log Q_H^A$ vs. y_{H^+} ($A^{2+} = Cu^{2+}, Ni^{2+}$). Deviations from the linear behaviour for low values of y_{H^+} can be observed, namely when most of the amount of H^+ initially in the resin phase was replaced by the divalent ion. This

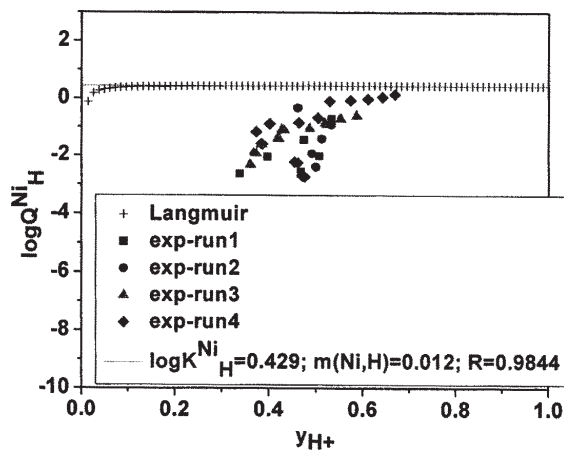


Fig. 5. The logarithm of the generalized separation factor versus the proton ionic fraction in the resin phase for H^+/Ni^{2+} ion exchange equilibrium on MN500 resin; 298 K; 0.01 eq/L total equivalent concentration

Table 4
COMPARISON OF THE SCM CONSTANTS FOR PROTON/DIVALENT ION EXCHANGE SYSTEMS ON MACRONET STRONG ACID RESIN MN500

Counterions	$\log K_H^A$	K_H^A	$m(A,H)$	Ref.
H^+/Cu^{2+}	-0.539	0.289	0.0956	this work
	-1.04	0.0912	0.164	[13]
H^+/Ni^{2+}	0.429	2.68	0.0120	this work
H^+/Cd^{2+}	-0.341	0.456	0.183	[13]
H^+/Mg^{2+}	-1.10	0.079	2.24	[14]
H^+/Zn^{2+}	-0.739	0.182	0.132	[13]

behaviour was recognized for many systems reported in literature [12-14, 19] due to model simplifying assumptions, and these regions were neglected. The SCM constants $\log K_H^A$ and $m(A,H)$ for the investigated systems were obtained and reported in figures 4 and 5. The observed positive slope supports a correct assessment of the order of the Stern layers, namely the proton Stern layer being the second one. The obtained SCM constants were used to predict the ion exchange isotherm by SCM. A computer program was developed by Höll and co-workers [19] for the prediction of the ion exchange isotherm for binary systems based on the experimental values of SCM constants and equation 9. Using this program, the ion exchange isotherms for H^+/Cu^{2+} and H^+/Ni^{2+} on MN500 were obtained. The results are given in figures 2 and 3 in comparison with the experimental isotherms and the fitted Langmuir isotherm. A good agreement between these isotherms for each investigated binary system can be observed from figures 2 and 3, showing that both Langmuir and surface complexation models describe well the H^+/Cu^{2+} and H^+/Ni^{2+} ion exchange equilibria on the macronet strong acid resin.

The SCM constants for binary proton/divalent ion exchange systems on the hyper-crosslinked sulfonated ion exchanger obtained in this work are compared in table 3 with the data reported previously in literature [13, 14].

The increasing selectivity series resulting from table 4 is: $Mg^{2+} < Zn^{2+} < Cu^{2+} < Cd^{2+} < Ni^{2+}$, if the ion exchange equilibrium constant obtained in this work for H^+/Cu^{2+} is considered. The same selectivity sequence was given for the gel and macroporous strong acid cation exchangers [5].

Conclusions

The H^+/Cu^{2+} and H^+/Ni^{2+} ion exchange equilibria on a polystyrenic resin with sulfonic functional groups and a

hypercrosslinked matrix, Purolite MN500, were investigated in order to assess the possibility of using this resin in wastewater purification. The H^+/Cu^{2+} and H^+/Ni^{2+} ion exchange isotherms on the selected resin were measured at 298 K and 0.01 eq/L total equivalent concentration, using atomic absorption spectrometry. The equations of the adsorption isotherms Langmuir, Freundlich, Sips, Toth, Jovanovich and Unilan were fitted to the experimental data. The results show that for the investigated cases it is difficult to discriminate between the ideal adsorption model and those corresponding to solid surfaces energetically heterogeneous. The Langmuir equation describes with good accuracy the experimental data. Besides the adsorption models, the surface complexation model (SCM) was also evaluated for the investigated systems. This model also fits the experimental ion exchange isotherms of the selected binary systems. The ion exchange constants were determined, and subsequently the model was used to predict the ion exchange isotherms. The results showed that the Langmuir and predicted SCM isotherms are in good agreement with the experimental isotherms. The comparison of the obtained ion exchange constants with data previously published in literature for binary ion exchange equilibria on the same macronet strong acid resin revealed the following selectivity series: $Mg^{2+} < Zn^{2+} < Cu^{2+} < Cd^{2+} < Ni^{2+}$, in accordance with the selectivity series for the classical gel and macroporous sulfonated polystyrenic ion exchangers.

Acknowledgements: In the memory of professor Wolfgang H. Höll (Technology Center for Water, Karlsruhe, Germany) who offered us the computer program used to simulate the isotherms in surface complexation model. The authors acknowledge Purolite International Ltd. for supplying the resin.

Symbols

A_0 – specific surface area of the fictitious plane surface representing the ion exchanger in SCM

(m^2/g)

a – concentration of the divalent ion nitrate solution (M)

C – concentration of the adsorbed species in the liquid phase at equilibrium (M)

$C_{A^{2+}}, C_{H^+}$ – concentration of corresponding ions in the external solution at equilibrium (M)

$C(A^{2+})_{St,A}, C(H^+)_{St,H}$ – concentration of corresponding free ions in the Stern layer formed by these ions (M)

$C(A,H)$ – specific electric capacitance of the capacitor formed by the Stern layer of metallic counterions A^{2+} and the Stern layer of protons (F/m^2)

$C(R-A)$ – equilibrium concentration of the surface complex formed by one divalent metallic ion from the Stern layer of these ions and two monovalent functional groups from the resin surface (M)

$C(R-H_2)$ – equilibrium concentration of the surface complex formed by two protons from the proton Stern layer with two monovalent functional groups bent on the resin surface (M)

F – Faraday constant (96500 C/mol)

k – parameter of Freundlich equation

K – thermodynamic adsorption/sorption constant, adsorption/sorption affinity (dimensionless)

K_1 – thermodynamic equilibrium constant of the reaction of hydrolysis of the metallic aquaion (dimensionless)

K_2 – thermodynamic equilibrium constant of the formation reaction of metal- nitrate 1:1 complex (dimensionless)

K_H^A – ion exchange equilibrium constant defined in SCM (dimensionless)

$m(A,H)$ – SCM constant; the slope of the linear regression $\log Q_H^A$ vs. y_{H^+}

$[M^{2+}], [MOH^+], [MNO_3^+], [H^+], [NO_3^-]$ – concentration of the corresponding species (free metallic aquaion, hydroxo aquaion, metal-nitrate complex, proton, nitrate anion) in the aqueous solution (M)

n – parameter of adsorption isotherm characterizing the system heterogeneity (dimensionless)

$q; q_m$ – quantity of sorbed ion at equilibrium; quantity of ions sorbed in Langmuir monolayer (mol/g)

q_{\max} – maximum resin loading in given condition (mol/g)

Q_H^A – generalized separation factor defined in SCM (dimensionless)

R – universal gas constant (8.314 J/mol K)

T – temperature (K)

$y_{A^{2+}}, y_{H^+}$ – equivalent ionic fraction of the metallic ion and the proton in the resin phase at equilibrium, respectively (dimensionless)

$z(R)$ – resin valence in SCM; in the investigated case $z(R) = -2$

w_A, w_H – stoichiometric factor of the corresponding ion defined in SCM

References

- 1.ALLOWAY, B.J., AYRES, D.C., Chemical Principles of Environmental Pollution, Blackie Academic and Professional, London, 1993
- 2.KEANE, M.A., Colloids and Surfaces, **138**, 1998, p.11
- 3.LIN, L.C., JUANG, R.S., Chemical Engineering Journal **112**, (2005), p 211
- 4.UNTEA, I., ORBECCI, C., TUDORACHE, E., TURTOI, D., NEAGU, V., Rev. Chim. (Bucharest), **55**, no. 6, 2004, p. 439
- 5.HELFFERICH, F., Ion Exchange, Dover Publications, New York, 1995, p.421
- 6.TSYURUPA, M.P., DAVANKOV, V.A., React. Funct. Polym., **53**, 2002, p 193
- 7.TSYURUPA, M.P., DAVANKOV, V.A., React. Funct. Polym., **66**, 2006, p 768
- 8.The Purolite Company, Purolite Technical Bulletin, Hypersol-Macronet Sorbent Resins, The Purolite Company, Bala Cynwyd, PA, 1999
- 9.DORFNER, K., Synthetic Ion Exchange Resins, in Ion Exchnagers, ed: Dorfner K., Walter de Gruyter, Berlin, (1991) , p. 189 – 396
- 10.BOHDANA, C.M., CANTEA, D.S., DALE, J.A., PINCOVSCHI, E., OANCEA, A.M.S., Recent Advences in Ion Exchange Theory & Practice, Proceedings of IEX2008, Editor M. Cox, SCI, Cambridge, 2008, p. 427
- 11.JORGENSEN, T.C., WEATHERLEY, L.R., Water Res., **37**, 2003, p 1723
- 12.OANCEA, A.M.S., DRINKAL, C., HÖLL, W.H., J. Ion Exchange (Japan), **18**, nr. 4, 2007, p.162
- 13.OANCEA, A.M.S., DRINKAL, C., HÖLL, W.H., React. Funct. Polym., **68**, (2008), p 492
- 14.BOHDANA, C.M., CANTEA, D.S., PINCOVSCHI, E., OANCEA, A.M.S., Rev. Chim. (Bucharest), **62**, no.2, 2011, p 233
- 15.OANCEA, A.M.S., RADULESCU, M., OANCEA, D., PINCOVSCHI, E., Ind. Eng. Chem. Res., **45**, 2006, p. 9096
- 16.OANCEA, A.M.S., POPESCU, A.R., RADULESCU, M., WEBER, V., PINCOVSCHI, E., COX, M., Solvent Extr. Ion Exch., **26**, 2008, p. 217
- 17.DO DUONG, D., Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London, (1998), Chapters 2, 3, 4, 6.
- 18.OANCEA, D., Modelarea Cinetică a Reacțiilor Catalitice, Editura All, Bucuresti, 1998, p. 222
- 19.HÖLL, W.H., FRANZREB, M., HORST, J., EBERLE, S.H., Description of Ion-Exchange Equilibria by Means of the Surface Complexation Theory, in: J. A. Marinsky, Y. Marcus (Eds.) Ion Exchange and Solvent Extraction, A Series of Advances, Marcel Dekker, Inc., New York, 1993, Vol. **11**, p. 151
- 20.ALLISON, J.D., BROWN, D.S., NOVO-GRADAC, K.J., (1999) *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 4.0 User's Manual*. United States Environmental Protection Agency, Office of Research and Development, Washington, DC
- 21.SPOSITO, G., HOLTZCLAW, K.M., Soil Sci. Soc. Am. J. **43**, 1979, p. 47
- 22.FEDOROV, V.A., ROBOV, A.M., SHMYD'KO, I.I., MIRONOV, V.E., Russian J. Inorg. Chem., **18**, 1973, p. 180
- 23.KITAMURA, S., KIRISHIMA, A., SAITO, T., SHIBUTAN, S., TOCHIYAMA, O., JAEA Thermodynamic Database for Performance Assessment of Geological Disposal of High-level and TRU Wastes: Selection of Thermodynamic Data of Cobalt and Nickel, JAEA-Researh 2009-037, Table 18. p.48, November 2009, Japan Atomic Energy Agency

Manuscript received: 27.10.2011