Proton / Magnesium (II) Ion Exchange Equilibrium on Sulfonated Hyper-Crosslinked Resin
Sorption and Surface Complexation Models

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The macronet sulfonated Purolite MN500 resin is a new ion exchanger with a hypercrosslinked styrene-divinylbenzene matrix, which seems to be a good sorbent in water and wastewater treatment, but scarcely investigated until now. Proton/magnesium(II) ion exchange isotherm on this resin was measured at 298 K and 0.01 total equivalent concentration of aqueous external solution using atomic absorption spectrometry. Several adsorption isotherms and surface complexation model were used to model the experimental data. The Freundlich isotherm was the best fitted equation. The surface complexation constants were determined and subsequently used to predict the ion exchange isotherm. The results are in good agreement with the experimental data and can be used in modeling multicomponent ion exchange equilibria on the new strong acid hyper-crosslinked ion exchanger.

Keywords: ion exchange equilibrium; sorption models; surface complexation model; sulfonated macronet resin; hyper-crosslinked matrix

Water treatment by ion exchange is a common procedure in chemical, petrochemical, metallurgical and utility plants [1a]. The ion exchangers are used for ionic or organic pollutants removal from wastewaters [2,3]. Magnesium ion removal from water occurs in softening process in order to prevent the formation of crusts in pipes and boilers. Magnesium ion is also eliminated by ion exchange in demineralization processes, ultra pure water being necessary in nuclear, electronic and pharmaceutical industries.

The design of a new ion exchange separation procedure is accompanied by simulation of the behaviour of the corresponding multicomponent system, in given conditions. The models usually use the ion exchange equilibrium constants of the binary ion exchange systems on a given ion exchanger. So, the accurate experimental determination of the ion exchange isotherms and modeling of the data with different models for many ions on the same ion exchanger is worthy, because enriches the open literature with results that can be used in the development of new ion exchange procedures.

A new class of styrene-divinylbenzene polymers was developed in [4,5] and manufactured by Purolite International under the trade name “Macronet Hypersol” [6]. This represents a third generation of styrene-divinylbenzene copolymers, after the traditional gel-type and macroporous resins [7]. These polymers were obtained from spherical beads of styrene-divinylbenzene copolymers swelled in a solvent in excess and post-crosslinked with conformational rigid methylenic bridges. The new inert material Purolite MN200 has a bulk density of ~0.5 g/cm³, and apparent density of ~1.1 g/cm³, a total cumulative pore volume of ~1.1 cm³/g, porosity of ~55%, and a specific surface area measured by BET method using dinitrogen of ~1000 m²/g [8]. The hyper-crosslinked polymer has micro-, meso-, and macropores. The ion exchanger selected in this work was Purolite MN500 obtained by sulfonation of the inert MN200 material. The sulfonation reaction produces a notable change of the structure and texture of the inert polymer [8]. Thus, the above properties become: bulk density ~0.75 g/cm³, apparent density ~1.50 g/cm³, total cumulative pore volume ~0.65 cm³/g, porosity ~49%, BET surface area ~350 m²/g [8]. The scanning electron micrographs show a cauliflower-like structure for both inert and sulfonated polymers due to a phase separation during synthesis [8]. After sulfonation the structure of the inert polymer is modified, the primary gel microparticles being redistributed inside the macronet bead in different clusters in a more close packing. The drastic decrease of the pore volume in MN500 resin compared with the inert MN200 polymer supports the densification.

The ion exchange equilibria on the new strong acid macronet resin were scarcely investigated in literature. The ion exchange equilibria on MN500 for H⁺/Na⁺, K⁺ [9], H⁺/NH₄⁺ [10], and H⁺/Cu²⁺, Zn²⁺, Cd²⁺ [11], and ion exchange kinetics [12] were reported in the last years. The aim of the present work was to obtain the H⁺/Mg²⁺ ion exchange isotherm at 298 K on the new MN500 strong acid macronet ion exchanger and to analyze the data using different theoretical models. One group of models relies on the adsorption phenomena and can reveal the energetic homogeneity or heterogeneity of the sorbent surface towards magnesium ion [13]. Another approach is based on the surface complexation model (SCM) extended by Höll and co-workers from the metal oxides surfaces to polymeric ion exchangers [14]. The major advantage of this model is the prediction of the ion exchange equilibria in multicomponent systems using the constants of the model determined for binary systems. The SCM constants reported for new systems enrich the specialized literature. The H⁺/Mg²⁺ equilibrium on the sulfonated macronet polymer was not investigated until now.

Sorption isotherms
Ion exchange equilibria were frequently described using adsorption isotherms [1b]. In the adsorption processes...
neutral species are adsorbed on the neutral surface of the sorbent due to weak van der Waals forces. The potential energy fluctuates periodically and the troughs of the energy fluctuation are acting as adsorption sites [13]. In the ion exchange processes the solid ion exchanger carries ionized functional groups and the sorbate species are counter-ions which exchange each other (equivalent to equivalent) in the near neighborhood of the fixed ionic charges. The process implies strong coulombian forces. The potential energy also fluctuates periodically. The equations of the adsorption isotherms were deduced without taking into account the nature and the magnitude of the interaction forces which occur between the adsorbent and the adsorbate, explaining why these equations describe also the ion exchange equilibria. The Langmuir model describes the ideal case of a monolayer adsorption of a single component from an ideal fluid medium on an uniform surface without lateral interactions [13, 15]. The real systems are formed from non-ideal fluids and solid surfaces, exhibiting intrinsic and/or adsorbate induced energetic heterogeneities [13, 15]. Empirical equations were proposed for the real adsorption systems, like Freundlich, Sips, Tóth or Unilan isotherms. These equations were later derived assuming a patchwise topography of the adsorption sites, with local uniform surface described

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir (L)</td>
<td>( q = \frac{a L \cdot KC}{1 + KC} )</td>
<td>Ideal bulk and surface phase; localized adsorption; monolayer; energetically homogeneous surface; has Henry law limit; finite saturation limit;</td>
</tr>
<tr>
<td>Freundlich (F)</td>
<td>( q = k C^n ), ( n &gt; 1 )</td>
<td>Heterogeneous surface, patchwise topography with local Langmuir isotherm and exponential decay energy distribution function; does not have Henry law limit and no saturation limit;</td>
</tr>
<tr>
<td>Sips (S) or</td>
<td>( q = \frac{a S \cdot (KC)^n}{1 + (KC)^n} ), ( n \neq 1 ); usually ( n &gt; 1 )</td>
<td>Surface heterogeneity; patchwise topography with local Langmuir isotherm and symmetrical quasi-gaussian energy distribution (exponentially decreasing</td>
</tr>
<tr>
<td>Langmuir-Freundlich (LF)</td>
<td>( q = \frac{a LF \cdot KC}{1 + (KC)^n} ), ( n \neq 1 ); usually ( n &lt; 1 )</td>
<td>distribution of adsorption energy on both sides; localized adsorption; reduces to Freundlich equation for low adsorption values; does not have Henry law limit; for high adsorptions becomes similar to Tóth equation; finite saturation limit;</td>
</tr>
<tr>
<td>Tóth (T)</td>
<td>( q = \frac{a T \cdot \ln \left( \frac{1 + K \cdot C \cdot \exp(-s)}{1 + K \cdot C \cdot \exp(s)} \right)}{2s} ), ( s = \frac{E_{ad} - E_{eq}}{2RT} )</td>
<td>Surface heterogeneity; patchwise topography with local Langmuir isotherm and asymmetrical quasi-gaussian energy distribution (exponentially decreasing distribution of adsorption energy on both sides with bigger tail for low adsorption energies); monolayer; reduces to Henry equation for low adsorption values and becomes similar to LF for high adsorption values; has finite saturation limit;</td>
</tr>
<tr>
<td>Unilan (U)</td>
<td>( q = \frac{a U}{2s} \cdot \ln \left( \frac{1 + K \cdot C \cdot \exp(x)}{1 + K \cdot C \cdot \exp(-x)} \right) ), ( s = \frac{E_{ad} - E_{eq}}{2RT} )</td>
<td>Surface heterogeneity; patchwise topography with local Langmuir isotherm and uniform energy distribution function (the name Unilan comes from uniform and Langmuir); monolayer; has Henry law limit and finite saturation limit;</td>
</tr>
</tbody>
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Table 1

<table>
<thead>
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Surface complexation model

The surface complexation model (SCM) has been developed for ion adsorption from aqueous solutions to hydrous oxides minerals as goethite, gibbsite, clay minerals, etc. [14]. Höll and co-workers extended this model to ion exchange processes on polymeric ion exchangers [14]. Besides the adsorption models the SCM takes into account the contribution of the electrical forces to the ion exchange process. It is supposed that the ion exchanger is a fictitious plane surface carrying ionized functional groups (proton donor/acceptor) uniformly distributed. The counter-ions form Stern layers parallel to the resin surface, with the same area and located at well defined distances, determined by the intrinsic ionic size and solvated ionic radius. Each kind of counter-ions forms a separate Stern layer at a definite distance from the surface. Some other simplifying assumptions were accepted: a) the swelling and the shrinking effects were not taken into account; b) negligible quantity of counter-ions exists in a diffuse layer; c) no repulsive forces between the counter-ions within the same or adjacent Stern layers; d) the activity coefficient of a species in the resin phase is equal to unity; e) the relative permittivity in the resin phase is constant. The counter-ions of one kind located in their corresponding Stern layer form “surface complexes” with the ionic charges distributed on the resin surface through all kinds of physical and chemical interactions [14]. The electric potential generated by the fixed charges on a strong electric field as:

$$C(i)_{S,i} = C(i)_{\text{liquid phase}} \exp\left(\frac{z(i)E}{RT}\right)$$  \hspace{1cm} (7)

where $$\frac{z(i)E}{RT}$$ is the difference of the unknown electric potentials in the Stern layer.

The two Stern layers form an electric capacitor. Supposing that the proton Stern layer is the second one from the surface, equation (6) becomes:

$$K_m^H = \frac{K_m^M}{K_n^M} = \frac{C(R-H_z)|C(H^+)_{S,H}|^2}{C(R-H_z)|C(M^{-2})_{S,M}|^2}$$ \hspace{1cm} (8)

The difference of the unknown electric potentials in the two Stern layers can be obtained from the electric capacitance C(M,H) of the capacitor formed by the two Stern layers and the charge density in the second Stern layer [14]. The ratio of the concentration of the surface complexes was replaced with the ratio of the resin loading with the corresponding two counter-ions, supposing that all counter-ions in the resin phase are involved in surface complexes. After transformations [14] equation (8) becomes:

$$\log Q_H^M = \log \frac{w_H^2}{w_M} C_{M^2} + \log K_m^H +$$

$$\frac{1}{\ln 10} \frac{F^2 q_{\text{max}}}{A_c C(M,H)RT} y_{H_z} = \log K_m^M + m(M,H) y_M,$$  \hspace{1cm} (9)

where $$Q_H^M$$ is called the generalized separation factor, which can be measured at different resin loadings. The intercept of the linear regression of $$\log Q_H^M$$ vs. $$y_M$$ is the logarithm of the ion exchange constant. The slope $$m(M,H)$$ is also an important constant of SCM, because equation (9) can be also used to predict an ion exchange isotherm in the surface complexation model if $$\log K_m^M$$ and $$m(M,H)$$ are known. The slope is positive if the sequence of the two Stern layers is correctly assumed.

Experimental part

The ion exchange resin and reagents

The commercial Purolite MN 500 macronet (hyper-crosslinked) resin with polystyrenic matrix and sulfonic acid functional groups was dried at room temperature, screened by sieving and the size fraction selected between [-710+600] was purified. The separation in size fractions of the resin was done in order to have a more uniform material, because the particles with different sizes could have different cross-linking degrees. The purification of the resin was done in three cycles of successive treatments with 1M HCl solution, demineralized water with specific conductivity of 0.05μS/cm, 1M NaOH solution, demineralized water. The final form of the resin was H+ form, and the final washing was done with demineralized water until the effluent had a specific conductivity less
than 1 μS/cm. After purification the resin was air-dried, and kept in a desiccator on a saturated sodium chloride solution, in order to sorb water vapors and to reach a constant mass at room temperature. The total ion exchange capacity was of 2.48 meq/g, measured using the standard method based on the treatment of a known quantity of the resin in H+ form saturated with water vapors with an excess of the sodium hydroxide solution and re-titration of the excess with standardized 0.1 M HCl solution, using phenol red as indicator.

The external solution was prepared from Mg(NO₃)₂·6H₂O p.a. Merck, using demineralized water (0.055 μS/cm). HCl 36% and NaOH p.a. Merck were used for the preparation of the other solutions.

The determination of the ion exchange isotherm

Known quantities of the resin saturated with water vapors were introduced in 100 mL salt solution 0.01N in glass bottles with lid, kept at 25°C in a climatized laboratory during one week and stirred from time to time. The concentrations of the magnesium ion in the initial solution and at equilibrium were analyzed using atomic absorption spectrophotometric method, and AA100 Perkin – Elmer spectrophotometer. The calibration stock solution was from Merck. The isotherm was obtained from three independent runs, namely from new prepared external solutions. For each point the experiments were done in duplicates. The measured pHs of the external solutions at equilibrium ranges between 2.042 and 3.660 depending on the amount of resin introduced in the salt solution. The obtained isotherm contains 52 points.

Results and discussions

The experimental H⁺/Mg²⁺ ion exchange isotherm on the strong acid hypercrosslinked resin MN500 is given in figure 1. The equations given in table 1 were fitted on the experimental curve, using a nonlinear regression analysis. Figure 1 contains also the fitted Langmuir, Freundlich, Sips, Tóth and Unilan isotherms. The obtained adsorption constants (with 95% confidence limits) are presented in table 3, together with the parameters of goodness of fit, coefficient of determination r² and F-statistic.

The best fitted equation is the Freundlich isotherm, having the higher value of F and residuals with a quite random distribution. The Sips, Tóth and Unilan adsoption equations are disclosed because the lower confidence limits for 95% probability of the obtained adsorption constants are negative, and consequently meaningless, even if r² and F are significant. The best fitted Freundlich isotherm indicates an energetic heterogeneity of the macronet strong acid ion exchanger MN500 toward magnesium ion (exponential decay energy distribution function) and the absence of a saturation limit. The differences in the sorption energy of Mg²⁺ ion on the sulfonic acid groups of the hypercrosslinked resin could be understood if the interactions between magnesium ion and π electrons of the aromatic rings are also considered. The cation-aromatic ring distance and the energy of interaction could be different in macropores, mesopores, and micropores of the resin, due to the resin local structure and to the changes of the cation hydration shell.

Figure 2 gives the variation of the generalized separation factor with the ionic fraction in the resin phase of the counter-ion forming the second Stern layer from the resin surface (yₜ), for H⁺/Mg²⁺ ion exchange equilibrium on MN500 resin and the obtained SCM constants.

<table>
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<th>r²</th>
<th>F-statistic</th>
<th>qₑₓ x 10⁷ / (mol/g)</th>
<th>K x 10⁻⁴</th>
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<td>Langmuir</td>
<td>0.9183</td>
<td>573</td>
<td>1.036 ± 0.040</td>
<td>20.1 ± 3.0</td>
<td>5.12 ± 0.32</td>
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<tr>
<td>Freundlich</td>
<td>0.9607</td>
<td>1246</td>
<td>3.65 ± 0.35*</td>
<td>4.2 ± 4.6</td>
<td>2.40 ± 0.57</td>
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<tr>
<td>Sips</td>
<td>0.9717</td>
<td>859</td>
<td>1.52 ± 0.31</td>
<td>648 ± 1440</td>
<td>0.27 ± 0.12</td>
</tr>
<tr>
<td>Tóth</td>
<td>0.9724</td>
<td>881</td>
<td>1.77 ± 0.60</td>
<td>1.7 ± 3.7</td>
<td>2 ± 28</td>
</tr>
<tr>
<td>Unilan</td>
<td>0.9731</td>
<td>903</td>
<td>1.7 ± 3.7</td>
<td>5.6 ± 13**</td>
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</table>

* “K” in Freundlich’s equation; ** “s” in Unilan equation

Table 3

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<th>Isotherm</th>
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<th>F-statistic</th>
<th>qₑₓ x 10⁷ / (mol/g)</th>
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* “K” in Freundlich’s equation; ** “s” in Unilan equation
Using the obtained SCM constants and a computer program previously developed by [14], the H⁺/Mg²⁺ ion exchange isotherm on MN500 ion exchanger was predicted. The results are presented in figure 3 together with the fitted Freundlich isotherm. They are in good agreement with the experimental data.

The SCM constants for binary proton/divalent ion exchange systems on the hyper-crosslinked sulfonated ion exchanger reported previously in literature [11] are compared in table 4 with the data obtained in this work.

The increasing selectivity series observed for the sulfonated macronet resin MN500 is: Mg²⁺ < Cu²⁺ < Zn²⁺ < Cd²⁺. The selectivity sequence for the common cation exchangers was given as Mg²⁺ < Zn²⁺ < Cu²⁺ < Cd²⁺ [16]. The results obtained in this work show that the new macronet strong acid resin is less selective for magnesium(II) ion than for divalent transition metal cations, as the sulfonated styrene-divinylbenzene cation exchangers gel-type or macroporous.

The equilibrium constants determined for H⁺/Mg²⁺ ion exchange on the MN500 resin were obtained using a magnesium nitrate salt solution of 5·10⁻³ M. The nitrate ion is known to be a weak ligand for metallic ions in aqueous solution in competition with water molecule [17] and it is realistic to neglect the formation of 1:1 complexes. To our knowledge, the formation constant of Mg(NO₃)⁺ complex was not reported in literature, and it can be supposed with good accuracy that in our experiments (5·10⁻³ M Mg(NO₃)₂ solution, pH 2-6.5) all magnesium ions were free aquaions in the external solution. It is important to know if the obtained equilibrium constants are true also for H⁺/Mg²⁺ ion exchange equilibrium on the same resin in the presence of Cl⁻ or SO₄²⁻ ligands. So, the magnesium ion speciation must be analyzed. In table 5 are given the thermodynamic formation constants of magnesium hydroxoaquaions and complexes with Cl⁻, SO₄²⁻ and NO₃⁻ ligands.

The concentration of the magnesium species, free magnesium aquaion Mg²⁺, hydroxoaquaion MgOH⁺, the complex MgCl⁺ which is a contact ion pair [21], in aqueous solution of 5·10⁻³ M magnesium, at pH in the range 0.1 - 6.5 were obtained solving the system of equations 10-13, for α = 5·10⁻³ M, K₁ = 10⁻¹¹.70⁴, and K₂ = 0.77:

\[
K_1 = \frac{\text{[MgOH}^+\text{][H}^+\text{]}}{\text{[Mg}^2+\text{]}} \quad (10)
\]

\[
K_2 = \frac{\text{[MgCl}^+\text{][Cl}^-\text{]}}{\text{[Mg}^2+\text{][Cl}^-\text{]}} \quad (11)
\]

\[
\text{[Cl}^-\text{]_{total}} = \text{[Mg}^2+\text{]} + \text{[MgOH}^+\text{]} + \text{[MgCl}^+\text{]} = \alpha \quad (12)
\]

\[
\text{[Cl}^-\text{]_{total}} = \text{[Cl}^-\text{]} + \text{[MgCl}^+\text{]} = 2\alpha \quad (13)
\]

In this analysis the solvent separated ion pair [Mg²⁺(OH)₃(OH)Cl⁻]⁻ and the solvent shared ion pair [Mg²⁺(OH)₂Cl⁻]⁻ were not taken into account as distinct species. Recently, in [21] has been shown that in 0.22 M MgCl₂ aqueous solution the percentage distribution was: free magnesium aquaion Mg²⁺ ~50%, [Mg²⁺(OH)₃Cl⁻]⁻ ~30%, and [Mg²⁺(OH)₂(OH)Cl⁻]⁻ ~20%. The formation of solvent shared and solvent separated ion pairs can be neglected in more diluted solution of MgCl₂ (5·10⁻³ M). Using these approximations the obtained results for magnesium ion speciation in presence of Cl⁻ ligand are given in figure 4, and show that the main species are the free magnesium aquaion, while MgCl⁺ and MgOH⁺ are trace species.

The concentration of the magnesium species in solution of MgSO₄ were obtained by solving the system of equations (10, 14-16) for pH = (0.1 - 6.5), α = 5·10⁻³ M, K₁ = 10⁻¹¹.70⁴, and K₂ = 10²-36. (the highest value of this complex formation was selected, table 5):
Table 5

<table>
<thead>
<tr>
<th>Equilibrium reaction</th>
<th>logK</th>
<th>K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg^{2+} + H_{2}O(l) ⇌ MgOH^- + H^+</td>
<td>-11.794</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.45</td>
<td>19</td>
</tr>
<tr>
<td>Mg^{2+} + 2H_{2}O(l) ⇌ Mg(OH)_{2} + 2H^+</td>
<td>-27.99</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>Mg^{2+} + HO^- ⇌ MgOH^-</td>
<td>2.56</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Mg^{2+} + Cl^- ⇌ MgCl^-</td>
<td>0.77 ± 0.23 exp</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.645 calculated</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.656 calculated</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>Mg^{2+} + 2Cl^- ⇌ MgCl_2</td>
<td>-0.03</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>Mg^{2+} + NO_3^- ⇌ Mg(NO_3)^+</td>
<td>0.67</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>Mg^{2+} + 2NO_3^- ⇌ Mg(NO_3)_2</td>
<td>0.01</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>Mg^{2+} + SO_4^{2-} ⇌ MgSO_4</td>
<td>2.250</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>2.23</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>2.36</td>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>

The molar fraction of the magnesium free aquaion, hydroxoaquaion and MgSO_4 complex are given in figure 4, and it can be observed that the free aquaion is ~60% and the ion pair MgSO_4 is ~40%. The hydrolysis of aquaion is negligible for pH < 6.5.

Fig. 4. Speciation of magnesium ions in 5·10^{-3} M chloride and sulfate solutions, respectively, at 298 K at different pHs

\[
K_z = \frac{[\text{MgSO}_4]}{[\text{Mg}^{2+}][\text{SO}_4^{2-}]} \quad (14)
\]

\[
[Mg^{2+}]_{\text{total}} = [Mg^{2+}] + [\text{MgOH}^+] + [\text{MgSO}_4] = a \quad (15)
\]

\[
[\text{SO}_4^{2-}]_{\text{total}} = [\text{SO}_4^{2-}] + [\text{MgSO}_4] = a \quad (16)
\]

The molar fraction of the free magnesium aquaion obtained in these conditions was of 0.99.

The speciation in magnesium ion in nitrate solution was estimated, taken into account the formation of the complex Mg(NO_3)_2, with the formation constant \( K_z = 10^{-0.01} \). The aquaion hydrolysis was neglected for pH < 6.5. The simplified system given by equations (17-19) was solved for \( a = 5·10^{-3} \) M:

\[
K_z = \frac{[\text{Mg(NO}_3)^2_2]}{[\text{Mg}^{2+}][\text{NO}_3]^{2}} \quad (17)
\]

\[
[Mg^{2+}]_{\text{total}} = [Mg^{2+}] + [\text{Mg(NO}_3)_2] = a \quad (18)
\]

\[
[\text{NO}_3^-]_{\text{total}} = [\text{NO}_3^-] + 2[\text{Mg(NO}_3)_2] \equiv 2a \quad (19)
\]

The molar fraction of the free magnesium aquaion in nitrate solutions, respectively, at 298 K at different pHs

Conclusions

A new sulfonated hyper-crosslinked ion exchanger Purolite MN500, which represents a third generation of styrene-divinylbenzene resins, was evaluated for magnesium ion removal from aqueous solutions. The H^+/Mg^{2+} ion exchange isotherm was measured at 298 K and 0.01 N total equivalent concentration of nitrate solution using atomic absorption spectrometry. The results were
modeled with Langmuir, Freundlich, Sips, Tóth, Unilan adsorption isotherms and with a surface complexation model proposed by Höll and co-workers for polymeric ion exchangers. The results show that the Freundlich isotherm was the best fit of the experimental data, indicating the energetic heterogeneity for the ionized sulfonic groups bent on the resin matrix which are interacting with the magnesium ions. The surface complexation constants for the investigated system were obtained and used subsequently to predict the ion exchange isotherm. The predicted isotherm in surface complexation model is in good agreement with the experimental isotherm. The macronet strong acid resin is less selective for magnesium ions as compared to divalent transition metallic cations, like the gel-type and macroporous styrene-divinylbenzene sulfonated resins. A speciation analysis has shown that in nitrate and chloride solutions of 0.01 N the free aquaion is the dominant species (>99%), but in sulfate solution is only 60%, the amount of MgSO₄ ion pairs being of 40%. The ion exchange equilibrium constants determined in nitrate solutions are valid within the experimental errors also for chloride solutions, but in sulfate solutions the loading at equilibrium could be lower.

Symbols

\( A_s \) – specific surface area of the fictitious plane surface representing the ion exchanger in SCM (m²/g)

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

\( C(i) \) – concentration of ions “i” in the external solution at equilibrium (M)

\( C(i)_{\text{eq}} \) – concentration of free ions “i” in the Stern layer formed by these ions (M)

\( C(M,H) \) – specific electric capacitance of the capacitor formed by the Stern layers of metallic counter-ions and protons (F/m²)

\( C(R) \) – equilibrium concentration of pairs of two sulfonic acid groups on the resin surface (M)

\( C(R-H) \) – equilibrium concentration of the surface complex formed by two protons from the proton layer with two monovalent functional groups from the resin surface (M)

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

\( F \) – Faraday constant (96500 C/mol)

\( k \) – parameter of Freundlich equation

\( K \) – thermodynamic constant of formation of surface complexes R-H* (dimensionless)

\( K' \) – thermodynamic constant of formation of surface complexes R-H₂ (dimensionless)

\( K'' \) – thermodynamic constant of formation of surface complexes R-M (dimensionless)

\( K'\perp = K''/K' \) – thermodynamic ion exchange constant defined in SCM (dimensionless)

\( m(M,H) \) – SCM constant; the slope of the linear regression logQₘ

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

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

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

\( Qₘ \) – generalized separation factor defined in SCM (dimensionless)

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

\( T \) – temperature (K)

\( y_{M,i} \) – 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 our case \( z(R) = -2 \)

\( w' \) – stoichiometric coefficient of ion “i” defined in SCM

Greek symbols

\( \psi_{ik} \) – the electric potential in the Stern layer of ions “i” (V)

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