



Comparison of adsorption equilibrium models for the study of Cl^- , NO_3^- and SO_4^{2-} removal from aqueous solutions by an anion exchange resin

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ABSTRACT

The removal of chloride, nitrate and sulfate ions from aqueous solutions by a macroporous resin is studied through the ion exchange systems OH^-/Cl^- , $\text{OH}^-/\text{NO}_3^-$, $\text{OH}^-/\text{SO}_4^{2-}$, and $\text{HCO}_3^-/\text{Cl}^-$, $\text{Cl}^-/\text{NO}_3^-$, $\text{Cl}^-/\text{SO}_4^{2-}$. They are investigated by means of Langmuir, Freundlich, Dubinin-Radushkevitch (D-R) and Dubinin-Astakhov (D-A) single-component adsorption isotherms. The sorption parameters and the fitting of the models are determined by nonlinear regression and discussed. The Langmuir model provides a fair estimation of the sorption capacity whatever the system under study, on the contrary to Freundlich and D-R models. The adsorption energies deduced from Dubinin and Langmuir isotherms are in good agreement, and the surface parameter of the D-A isotherm appears consistent. All models agree on the order of affinity $\text{OH}^- < \text{HCO}_3^- < \text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-}$, and distinguish high energy processes (OH^-/Cl^- , $\text{OH}^-/\text{NO}_3^-$, $\text{OH}^-/\text{SO}_4^{2-}$, $\text{Cl}^-/\text{SO}_4^{2-}$) from lower energy systems ($\text{HCO}_3^-/\text{Cl}^-$, $\text{Cl}^-/\text{NO}_3^-$). The D-A and D-R models provide the best fit to the experimental points, indicating that the micropore volume filling theory is the best representation of the ion exchange processes under study among other adsorption isotherms. The nonlinear regression results are also compared with linear regressions. While the parameter values are not affected, the evaluation of the best fitting model is biased by linearization.

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1. Introduction

The increasing levels of sulfate and nitrate in drinking and groundwater and their implication in environmental and health issues lead to a renewed interest in their removal from industrial wastewaters [1–3]. Likewise, chloride ions may also be involved in environmental issues and their removal from wastewaters should then be considered [4,5]. Moreover, the long half-life of the Cl radioisotope ^{36}Cl ($t_{1/2} = 3.01 \times 10^5$ years), its high β energy (709 keV), and its high ability of transferring to the environment, makes Cl a key element in the decontamination of nuclear wastewaters [6,7].

Ion exchange is considered as an attractive technology for removing chloride, nitrate and sulfate ions (Cl^- , NO_3^- and SO_4^{2-}) from aqueous solutions. It can be achieved quantitatively and independently of the solution pH, and the ion exchange resins can be regenerated thus offering long effective lifetime [1,2,8–13].

A good knowledge of the physicochemical process involved and of its characteristic parameters is a prerequisite for further industrial applications. Modelling the equilibria is a common approach to predict the relative affinities of the target and com-

peting ions, and their distribution in the resin-solution system during the purification process. The study of ion exchange equilibria is generally carried out by means of adsorption isotherms or ion exchange modelling. The use of adsorption isotherms to model ion exchange systems involves that it is interpreted as a sorption process, even though it is questionable in terms of physico-chemical theoretical bases [14,15]. According to their ease of use and their ability in roughly drawing the main characteristics of the ion exchange systems, the adsorption isotherms recently regained interest in evaluating the ability of an ion exchange resin to remove ionic species from aqueous solutions [1,2,13,16–19].

In the present study, we use adsorption isotherms to investigate several ion exchange systems related to the removal of the SO_4^{2-} , NO_3^- and Cl^- anionic species. The ion exchange systems are OH^-/Cl^- , $\text{OH}^-/\text{NO}_3^-$, $\text{OH}^-/\text{SO}_4^{2-}$, and $\text{HCO}_3^-/\text{Cl}^-$, $\text{Cl}^-/\text{NO}_3^-$, $\text{Cl}^-/\text{SO}_4^{2-}$ and the ion exchange material is the synthetic macroporous ion exchange resin Amberlite® IRN 9766. The removal of the anionic species is investigated through the most commonly used single-component adsorption isotherms, i.e. Langmuir, Freundlich, and Dubinin-Radushkevich. In addition, the Dubinin-Astakhov isotherm integrating a potentially relevant parameter related to the nature of the sorbent surface is also applied [20]. To our knowledge, this latter model is applied for the first time to anion exchange systems involving an ion exchange resin. The

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parameters and the fit of the models to the experimental data are discussed.

2. Experimental

2.1. Ion exchange resin

The ion exchange resin used in this study is a macroporous resin Amberlite® IRN 9766 strong anion exchanger (Rohm & Haas, France). The structure of macroporous resins is characterized by large pores (~150 nm diameter for IRN 9766) separated by highly reticulated areas. This gives to the resin some major advantages when it is applied to the treatment of industrial wastewaters. Even though the total ion exchange capacity of macroporous resins is generally inferior to what offered by gel-type resins, their constitution provides a high mechanical resistance and allows fast reaction kinetics. Thus, they can be used at high flow rates in industrial scale columns without any loss of efficiency [8]. Before all use, the resin is rinsed with ultrapure water on a frit glass filter connected to a vacuum pump, and is then referred as wet resin. The total anionic exchange capacity (AEC), the moisture content, and the density are determined experimentally.

The experimental determination of the AEC is carried out as follows; a known amount of wet resin is introduced in a glass column and approximately 15 bed volumes (BV) of a 1 M HCl (Merck, Germany) are flowed through the resin bed to guarantee its complete saturation with Cl⁻ ions. The resin bed is then rinsed with 15 BV of ultrapure water, and 15 BV of 1 M Na₂SO₄ (Merck, Germany) are flowed through the resin bed. The Cl⁻ ions are thus removed by the SO₄²⁻ ions, retrieved in a fixed volume downstream the resin bed, and finally measured by ion chromatography. The AEC is then obtained by simply dividing the quantity of Cl⁻ ions by the resin mass.

To determine the moisture content, an aliquot of resin is converted to the Cl⁻ form and rinsed on a frit glass filter connected to a vacuum pump, weighted and heated at 105 °C. The weight of the resin is controlled until stabilisation, and is then considered as dry resin. The moisture content τ is simply calculated as $\tau = 100 \times (1 - m_{\text{dry}}/m_{\text{wet}})$.

The characteristics of the resin, as given by the supplier and as determined experimentally, are presented in Table 1. The experimental values are in good agreement with the supplier data and are employed for all further purpose in this study.

2.2. Chemicals and analyses

The chloride, sulfate and nitrate stock solutions are prepared by dissolution of analytical grade CaCl₂, CaSO₄ and Ca(NO₃)₂ (Merck, Germany), respectively. Milli-Q ultrapure water (Millipore, France) is used for all purposes including the rinsing of the resin aliquots and the preparation of the stock and dilute solutions.

The analyses of the studied ions (Cl⁻, NO₃⁻ and SO₄²⁻) are realized by means of a DX-120 ion chromatograph (Dionex, France) equipped with an autosampler and an ion suppressor ASRS Ultra II. The separation of the anionic species is performed by a AS-14 column in the isocratic mode with a carbonate eluting phase constituted of 1.10⁻³ M NaHCO₃ and 3.5.10⁻³ M Na₂CO₃. The flow rate is set at 1 mL min⁻¹ and the total analysis time is 18 min. The detection limits for Cl⁻, NO₃⁻ and SO₄²⁻ are 3.10⁻⁷ M.

2.3. Batch ion exchange studies

When the ion exchange experiments are realized with the resin in the OH⁻ form (OH⁻/Cl⁻, OH⁻/NO₃⁻ and OH⁻/SO₄²⁻), the resin is simply rinsed and dried on frit glass filter as described earlier.

Then, known amounts of wet resin (corresponding to approximately 50 mg of dry resin) are introduced in 125 mL Nalgene® flasks (VWR, France), and 50 mL of a freshly prepared solution containing either Cl⁻, NO₃⁻ or SO₄²⁻ at the desired concentration are added.

In the case of HCO₃⁻/Cl⁻, or Cl⁻/NO₃⁻ and Cl⁻/SO₄²⁻ ion exchange experiments, it is necessary to change the ionic form of the resin into the HCO₃⁻ or Cl⁻ form, respectively. To convert the resin to its Cl⁻ form, weighted amounts of wet resin (corresponding to approximately 50 mg of dry resin) in the OH⁻ form are placed in flasks containing 50 mL of a 1 M CaCl₂ solution during 1 h 30 min, and gently agitated. The supernatant is removed and the resin is rinsed with 100 mL of ultrapure water and dried on a frit glass filter connected to a vacuum pump. The same procedure is used to convert resin aliquots to the HCO₃⁻ form, except that the contact time is extended to 24 h as the resin is expected to have a sensibly lower affinity for HCO₃⁻ than for Cl⁻. Additionally, the supernatant is removed after 2 h contact time and replaced by a fresh NaHCO₃ 1 M solution. This operation is repeated after 22 h contact time. It maintains the solution pH <8, were the carbonate species are almost exclusively in the form HCO₃⁻ (about 99%), and ensures the conversion of the resin to a strictly HCO₃⁻ form rather than to a mixed HCO₃⁻/CO₃²⁻ form. The supernatant is then removed and the resin is rinsed with 100 mL of ultrapure water and dried on a frit glass filter connected to a vacuum pump. Finally, each aliquot of resin is retrieved and placed in a 125 mL Nalgene® flask, and 50 mL of a solution containing either Cl⁻, NO₃⁻ or SO₄²⁻ at the desired concentration are added.

Initially, the pH of the latter solutions is in the range 6.5–6.8, and thus does not require any pH adjustment. The potential incidence of HCO₃⁻/CO₃²⁻ ions, originating from the dissolution of atmospheric CO₂, on the ion exchange equilibria is avoided by removing the air above the solutions with N₂ (>99.5%, AirLiquide, France) and by sealing the flasks hermetically. Preliminary experiments showed that the ion exchange equilibrium is reached after shaking about 1 h at 150 rpm on a G2 gyratory shaker (New Brunswick Sci. Co., USA). To ensure that the equilibrium is totally reached, the solution is still shaken during 24 h. The temperature is kept at 25 ± 1 °C. After the 24 h equilibration time, the concentration of the target ion remaining in the solution (c_e , mg L⁻¹) is measured by ion chromatography and the concentration in the resin phase (q_e , mg g⁻¹) is deduced from Eq. (1),

$$q_e = \frac{V}{m}(c_0 - c_e) \quad (1)$$

where V is the solution volume (L), m is the dry mass of resin (g) and c_0 is the initial concentration of the target ion (mg L⁻¹). Each experiment is repeated 3 times, and the results discussed here are the mean values. The calculated relative standard deviations (RSD) are all below 5% except for 2 experiments, the OH⁻/Cl⁻ and HCO₃⁻/Cl⁻ ion exchange experiments carried out at the highest Cl⁻ initial concentration levels (10.9% and 6.6%, respectively).

The influence of pH has been studied in the range 3–11, and did not have any significant impact on the adsorption rate of the anionic species under study.

3. Single-component sorption models

The equilibrium between a solute and an adsorbent surface is commonly represented by single-component adsorption isotherms, basically considering the following surface complexation reaction,



where R represents the sorbent in its initial form, X is the aqueous phase species, and RX is the species X in the resin phase.

Table 1
Characteristics of Amberlite® IRN 9766 strong anion exchange resin, as given by the supplier and determined experimentally (mean values and standard deviations of $N=6$ experiments).

General description	Macroporous PS-DVB spherical beads	
Functional group	$-\text{N}^+(\text{CH}_3)_3$	
Ionic form	OH^-	
Characteristics	Supplier	Experimental
Beads mean size	0.65 mm	nd
Uniformity coefficient	≤ 1.7	nd
Density	0.7	0.67 ± 0.01
Moisture holding (Cl form)	58–64%	$61.3 \pm 1.4\%$
Anionic exchange capacity (AEC)	3.20 meq g^{-1}	$3.17 \pm 0.08 \text{ meq g}^{-1}$

nd, Not determined.

The AEC are expressed as function of dry mass of resin.

3.1. Langmuir isotherm

The Langmuir model is semi-empirical and derives from Eq. (2) assuming a monolayer adsorption phenomenon on a homogeneous surface [21–23]. Considering Eq. (2) at equilibrium, the Langmuir parameter k_L (L mg^{-1}) representing the equilibrium constant can be expressed as,

$$k_L = \frac{[RX]}{[R][X]} \quad (3)$$

At equilibrium, the Langmuir equation arises from Eq. (3) considering $[X_{\text{aq}}] = c_e$; $[RX] = q_e$; and $[R] = q_0 - q_e$, where q_0 (mg g^{-1}) represents the maximum capacity of the resin. Eq. (3) then becomes,

$$k_L = \frac{q_e}{(q_0 - q_e)c_e} \quad (4)$$

And a simple modification leads to Eq. (5),

$$q_e = \frac{k_L q_0 c_e}{1 + k_L c_e} \quad (5)$$

The parameters k_L and q_0 are deduced from nonlinear regression. The adsorption energy of a solute on a sorbent is determined from the Langmuir isotherm as the corresponding change in Gibbs free energy ΔG° (kJ mol^{-1}), deduced from k_L as follows [24–26],

$$\Delta G^\circ = -RT \ln k_L \quad (6)$$

where k_L is expressed in L mol^{-1} , R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the temperature (K).

3.2. Freundlich isotherm

Unlike the Langmuir isotherm, the Freundlich isotherm [27] is an empirical model which does not imply a maximum adsorption capacity of the sorbent [15,22,28]. It is based on the following equation,

$$q_e = k_F c_e^{1/n_F} \quad (7)$$

where k_F ($\text{mg}^{1-1/n_F} \text{ L}^{1/n_F} \text{ g}^{-1}$) and n_F (dimensionless) are the Freundlich constants determined from the nonlinear regression. The value of the parameter n_F is representative of both the adsorption intensity and the surface heterogeneity. Despite the parameter n_F lacks of physical meaning, it is generally admitted that $0 < 1/n_F < 1$ indicates favourable adsorption, while $1/n_F = 1$ characterizes a linear adsorption phenomenon [22,26,28,29]. The k_F constant may be considered as a rough indication of adsorption capacity expressed in mg g^{-1} [16,29–31] or as a sorption affinity parameter [17,32]. Considering c_e and q_e expressed in mg L^{-1} and mg g^{-1} , respectively, k_F is expressed in $\text{mg}^{1-1/n_F} \text{ L}^{1/n_F} \text{ g}^{-1}$ [22,25]. Thus, when $1/n_F = 1$ (linear adsorption), then k_F is expressed in L g^{-1} and can be related to an adsorption energy, and when $1/n_F \rightarrow 0$, then $k_F \rightarrow q_e$ and k_F can

be roughly expressed in mg g^{-1} and considered as a rough evaluation of q_0 . As a conclusion, the Freundlich constants n_F and k_F appear to incorporate all the physico-chemical factors influencing the adsorption process [13].

Among the difficulties in interpreting the Freundlich parameters, the model has been recently criticized for its lack of thermodynamic basis and for not approaching Henry's law at low concentrations. Even though, its ability of fitting a broad set of experimental data still makes it a popular model in the study of adsorption and ion exchange phenomena [1,13,26,28].

3.3. Dubinin equations

The Dubinin-Radushkevich (D-R) and Dubinin-Astakhov (D-A) models are based on the Polanyi adsorption potential theory which defines an adsorption potential ε related to the free energy of change of a substance from the liquid to the resin phase [20,33,34]. In contrast to the Langmuir and Freundlich models, the Dubinin isotherms consider a micropore volume filling adsorption process [20,35,36], and are temperature dependent. The adsorption potential ε (J mol^{-1}) can be expressed as follows [37],

$$\varepsilon = RT \ln \left(1 + \frac{1}{c_e} \right) \quad (8)$$

where R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature (K). The Dubinin equation states that the quantity of adsorbed solute is a function of the adsorption potential, and considering an aqueous-phase adsorption system involving ions, the D-A isotherm is [20],

$$q_e = q_0 \exp \left[- \left(\frac{\varepsilon}{\sqrt{2E}} \right)^{n_D} \right] \quad (9)$$

where E is the adsorption energy (J mol^{-1}), n_D is the heterogeneity factor (dimensionless), and q_0 is the maximum adsorption capacity of the sorbent (mg g^{-1}). In the application of the D-A model to ion-exchange systems, the Eq. (9) is forced to match the experimental q_0 (corresponding here to the experimental AEC), and E and n_D are determined by nonlinear regression.

The D-R isotherm is a specific case of the D-A model where $n_D = 2$. The parameters E and q_0 are deduced from the nonlinear regression, and the D-R equation can be written as follows,

$$q_e = q_0 \exp \left[- \left(\frac{\varepsilon}{\sqrt{2E}} \right)^2 \right] \quad (10)$$

The interpretation of the D-R and D-A models results in two different approaches of the sorption phenomena. Like the Freundlich isotherm, the D-R model suggests that the sorption is not limited by a maximum capacity of the sorbent. On the other hand, the D-A model considers that the sorption capacity is limited to a maximum q_0 which has to be determined experimentally. Unlike the

D-R isotherm, it also implies that the heterogeneity parameter of the sorbent is not fixed arbitrarily.

4. Results and discussion

The characteristic parameters of the ion exchange systems are deduced from nonlinear regression using the mean square method with the SigmaPlot® software (version 10.0). The isotherms obtained for the 6 ion exchange systems are presented in Figs. 1–3. The fitting of the models to the experimental data is evaluated through the coefficients of correlation (R^2), the sum of squares of errors (SSE), and the average relative errors (ARE). It should be noted that while R^2 and ARE may be used to compare the fittings of the different models for all the ion exchange systems, SSE is restricted to comparisons within the same ion exchange system as the SSE values are not normalized.

4.1. Langmuir isotherms

The parameters q_0 and k_L deduced from the nonlinear regressions are listed in Table 2, along with the experimental value of AEC converted in mg g^{-1} for each ion. The q_0 values deduced from the Langmuir isotherms are in good agreement with the experimental AEC independently of the anionic specie. The average value for q_0 is $3.04 \pm 0.31 \text{ meq g}^{-1}$, which is in the range of the AEC experimental ($3.17 \pm 0.08 \text{ meq g}^{-1}$) and supplier (3.20 meq g^{-1}) values.

For the 6 ion exchange systems under study, $\Delta G^\circ < 0$ indicates favourable and spontaneous sorption of the solutes. The $\text{HCO}_3^-/\text{Cl}^-$ and $\text{Cl}^-/\text{NO}_3^-$ ion exchange systems present sensibly lower energies while the sorption of the divalent SO_4^{2-} on the resin in both its Cl^- and OH^- forms are the highest energy processes. These two distinct behaviours are well observed graphically (Figs. 1–3), as the systems presenting higher adsorption energies (OH^-/Cl^- , $\text{OH}^-/\text{NO}_3^-$, $\text{OH}^-/\text{SO}_4^{2-}$ and $\text{Cl}^-/\text{SO}_4^{2-}$) reach a plateau corresponding to q_0 while the two systems of lower energy ($\text{HCO}_3^-/\text{Cl}^-$ and $\text{Cl}^-/\text{NO}_3^-$) exhibit a very progressive adsorption process and do not reach a plateau within the concentration range of the study. The ΔG° values suggest the following order of affinity of the resin for the studied anions, $\text{OH}^- < \text{HCO}_3^- < \text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-}$, which is consistent with the literature [8].

The Langmuir isotherms fairly fit with the experimental results, with $0.91 < R^2 < 0.98$ and ARE ranging from 7 to 13% (Table 2). It is interesting to note that the fit of the model is not dependent on whether the ion exchange system is a high or a low energy process. It can also be observed in Figs. 1–3 that the low concentration points are responsible of the major part of the relative errors (R^2 and ARE), while SSE seem equally distributed in the concentration ranges.

4.2. Freundlich isotherms

The Freundlich parameters are detailed in Table 3 along with the corresponding R^2 , SSE, and ARE values. All the results indicate favourable adsorptions ($0 < 1/n_F < 1$) and the same order of affinity of the studied ions for the resin than the one deduced from the Langmuir isotherms. On the other hand the k_F values do not reflect the total adsorption capacity of the resin q_0 .

All the experiments are carried out on the same adsorbent material, and the ionic form of the resin should not have any impact on the surface heterogeneity. Thus, the adsorption intensity should be the only factor influencing the n_F values. The $\text{HCO}_3^-/\text{Cl}^-$ and $\text{Cl}^-/\text{NO}_3^-$ ion exchange systems appear as lower energy adsorption processes ($1/n_F \sim 0.4$) than the other ion exchange systems ($1/n_F < 0.2$). In addition, the high $1/n_F$ values are associated with low k_F values and a high fitting of the model with the experimental values ($R^2 > 0.99$ and ARE $< 5\%$). Thus, the Freundlich multilayer sorption model appears to describe relatively well the lower energy

processes. However, extending the experimental data to higher concentrations may contradict this result [38], as the expected reaching of a maximum sorption plateau would probably be unfavourable to the quality of the fitting of the Freundlich isotherm.

Lower correlations are obtained for the other ion exchange systems ($R^2 < 0.97$ and ARE $> 9\%$), in particular for the highest energy $\text{OH}^-/\text{SO}_4^{2-}$ system. Except for the latter system, the fit is still slightly better than what obtained with Langmuir isotherms but the reach of the maximum of adsorption is better represented by the Langmuir isotherms. Therefore, extending the concentration range in the high concentration end would probably favour the Langmuir model compared to the Freundlich isotherm.

4.3. D-R and D-A isotherms

The parameters calculated by means of the D-R and D-A isotherms for the 6 ion exchange systems under study are presented in Table 4. The high adsorption energies ($E > 10 \text{ kJ mol}^{-1}$) deduced from both models indicate that all the ions are favourably adsorbed on the IRN 9766 resin. As observed for the other models, the ion exchange systems can be divided into two groups. The $\text{HCO}_3^-/\text{Cl}^-$ and $\text{Cl}^-/\text{NO}_3^-$ ion exchange systems present lower energies, in the range generally admitted for ion exchange ($8 < E < 16 \text{ kJ mol}^{-1}$) [20], and they show a better correlation with the D-R model than with the D-A model. The other ion exchange systems present high adsorption energies ($E \geq 16 \text{ kJ mol}^{-1}$) and fit the D-A model better than the D-R model, suggesting that high energy ion exchange processes are better characterized when a higher homogeneity of the resin is considered. The values of $E \geq 16 \text{ kJ mol}^{-1}$ may be explained by the polar nature of the adsorption sites and of the anionic species involved. It is indeed considered in an ideal application of the Dubinin-Radushkevich theory that both the sorbent and the sorbate are non-polar, and that E is strictly related to the sorbent surface characteristics [20,35,36]. The adsorption energies calculated from the D-R and D-A isotherms are in good agreement, even though the D-A values are generally higher. They are also consistent with the ΔG° values deduced from the Langmuir isotherms, and suggest the same order of affinity $\text{OH}^- < \text{HCO}_3^- < \text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-}$. The q_0 values deduced from the D-R model are all much higher than the experimental value and are not representative of the maximum adsorption capacity of the resin.

In the D-A isotherm, q_0 is forced to match the experimental value and the heterogeneity parameter n_D can be estimated. Inglezakis [20] showed that this parameter is mainly dependent on the adsorbent surface properties. Higher values of n_D indicate a greater homogeneity of the materials pore structure, homogeneous materials having typically $n_D > 3$. The n_D values calculated here are comparable for all ion exchange systems ($3.64 < n_D < 4.90$) except for the $\text{OH}^-/\text{SO}_4^{2-}$ system. It indicates that the homogeneity of the IRN 9766 pore structure is in the typical range for zeolites, and higher than carbon materials [20]. In addition, the results show that n_D is not dependent on the ionic form of the resin nor on the solute involved in the ion exchange, thus confirming that it is mainly related to the homogeneity of the pore structure. The high n_D value obtained for the $\text{OH}^-/\text{SO}_4^{2-}$ system is in contradiction with this conclusion and is probably due to the very high energy of this ion exchange process, as it has been reported that the n_D parameter could still be influenced by the solute nature in some particular cases [20,33,36].

Among all the adsorption isotherm models studied here, the D-R isotherms present the best fit with the experimental data of the two lower energy ion exchange systems ($\text{HCO}_3^-/\text{Cl}^-$ and $\text{Cl}^-/\text{NO}_3^-$), while the D-A model presents the best fits for the other four ion exchange systems. From these results, the superiority of the Dubinin equations to fit the experimental data suggests that micropore volume filling is the best representation

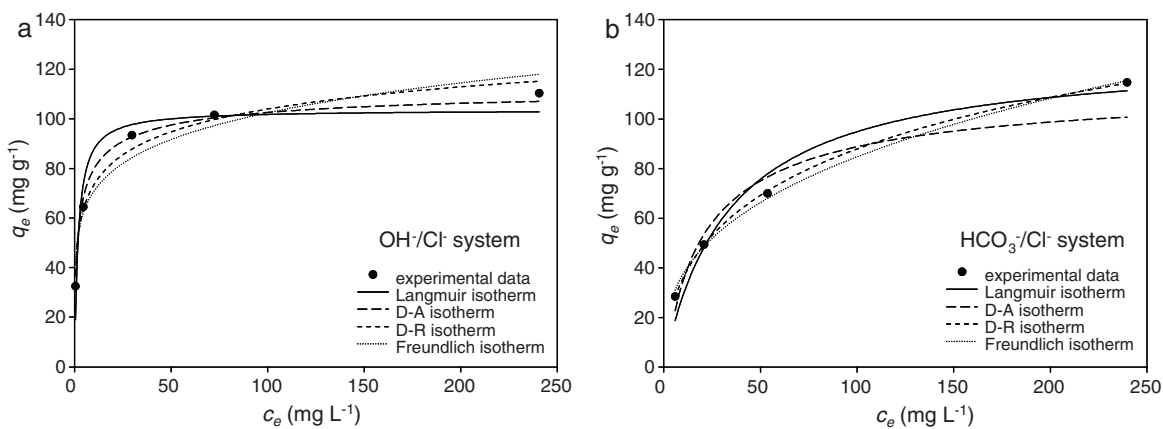


Fig. 1. Experimental data and adsorption isotherms determined by nonlinear regression of (a) the HO^-/Cl^- and (b) the $\text{HCO}_3^-/\text{Cl}^-$ ion exchange systems.

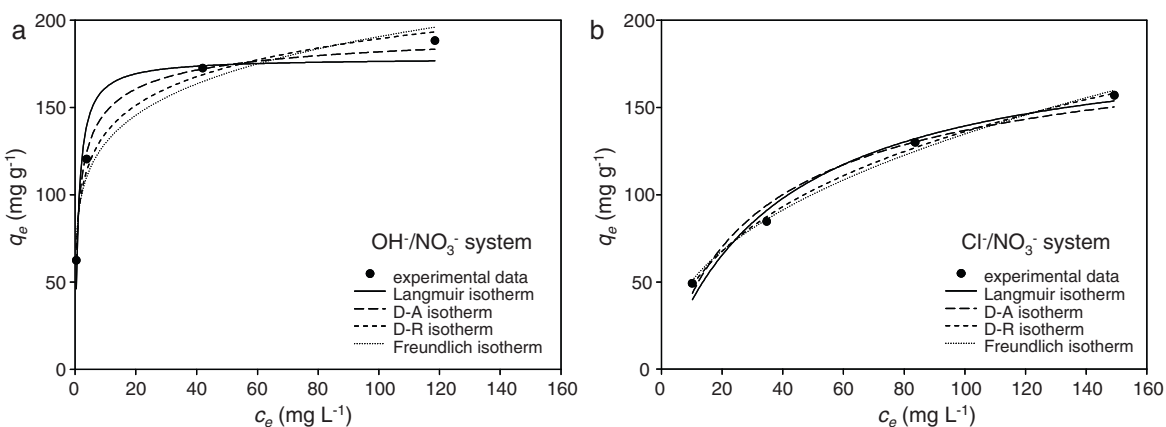


Fig. 2. Experimental data and adsorption isotherms determined by nonlinear regression of (a) the $\text{HO}^-/\text{NO}_3^-$ and (b) the $\text{Cl}^-/\text{NO}_3^-$ ion exchange systems.

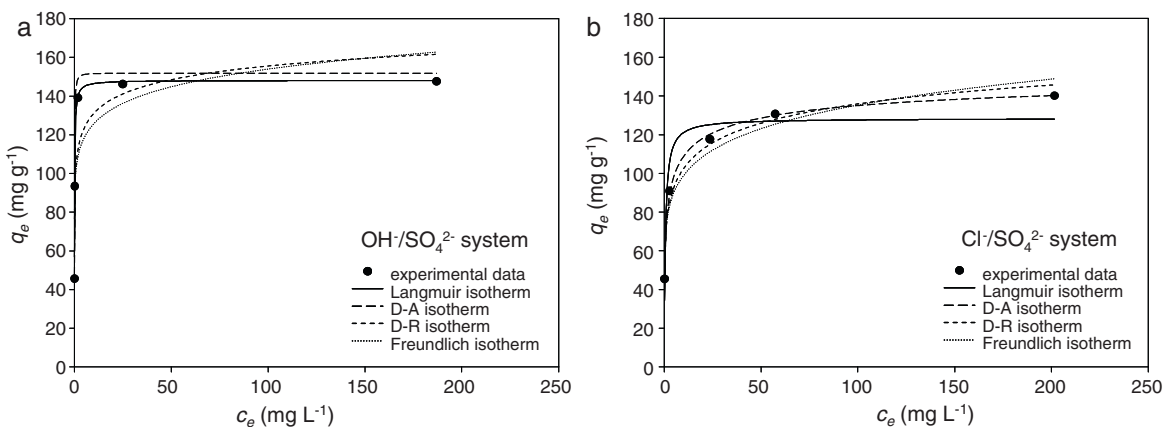


Fig. 3. Experimental data and adsorption isotherms determined by nonlinear regression of (a) the $\text{HO}^-/\text{SO}_4^{2-}$ and (b) the $\text{Cl}^-/\text{SO}_4^{2-}$ ion exchange systems.

Table 2
Langmuir parameters for the different ion exchange systems determined by nonlinear regression, correlation coefficients (R^2), sum of squares of errors (SSE), and average relative errors (ARE).

Ion exchange systems	AEC ^a (mg g^{-1})	q_0 (mg g^{-1})	k_L (L mg^{-1})	ΔG° (kJ mol^{-1})	R^2	SSE ($\text{mg}^2 \text{g}^{-2}$)	ARE (%)
OH^-/Cl^-	112.0	103.5	0.553	-24.4	0.917	336	13.4
$\text{HCO}_3^-/\text{Cl}^-$	112.0	127.1	0.029	-17.2	0.958	169	12.7
$\text{OH}^-/\text{NO}_3^-$	195.9	178.2	0.952	-27.2	0.923	752	12.1
$\text{Cl}^-/\text{NO}_3^-$	195.9	194.3	0.025	-18.2	0.980	140	7.5
$\text{OH}^-/\text{SO}_4^{2-}$	151.8	148.1	8.824	-33.8	0.970	239	7.3
$\text{Cl}^-/\text{SO}_4^{2-}$	151.8	128.4	1.651	-29.7	0.907	541	11.6

^a Experimental determination of the total anionic exchange capacity (see Section 2.1).

Table 3

Freundlich parameters for the different ion exchange systems determined by nonlinear regression, correlation coefficients (R^2), sum of squares of errors (SSE), and average relative errors (ARE).

Ion exchange systems	$q_0 \text{ exp}^a \text{ (mg g}^{-1}\text{)}$	$k_F \text{ (mg}^{1-1/n_F} \text{ L}^{1/n_F} \text{ g}^{-1}\text{)}$	$1/n_F$	R^2	SSE (mg ² g ⁻²)	ARE (%)
OH ⁻ /Cl ⁻	112.0	48.9	0.161	0.936	221	11.0
HCO ₃ ⁻ /Cl ⁻	112.0	16.6	0.355	0.997	12	3.6
OH ⁻ /NO ₃ ⁻	195.9	88.3	0.167	0.961	377	9.2
Cl ⁻ /NO ₃ ⁻	195.9	19.0	0.426	0.994	40	2.7
OH ⁻ /SO ₄ ²⁻	151.8	102.6	0.088	0.671	2598	22.9
Cl ⁻ /SO ₄ ²⁻	151.8	72.2	0.136	0.933	388	10.8

^a Experimental determination of the total anionic exchange capacity (see Section 2.1).

Table 4

D-R and D-A parameters for the different ion exchange systems determined by nonlinear regression, correlation coefficients (R^2), sum of squares of errors (SSE), and average relative errors (ARE).

Ion exchange systems	$q_0 \text{ exp}^a \text{ (mg g}^{-1}\text{)}$	$q_0 \text{ (mg g}^{-1}\text{)}$	$E \text{ (kJ mol}^{-1}\text{)}$	R^2	SSE (mg ² g ⁻²)	ARE (%)
Dubinin-Radushkevich						
OH ⁻ /Cl ⁻	112.0	150.8	16.8	0.979	84	5.9
HCO ₃ ⁻ /Cl ⁻	112.0	229.3	10.5	>0.999	2	1.1
OH ⁻ /NO ₃ ⁻	195.9	282.2	17.9	0.986	140	5.6
Cl ⁻ /NO ₃ ⁻	195.9	471.7	10.1	0.997	20	2.2
OH ⁻ /SO ₄ ²⁻	151.8	193.8	25.7	0.745	2016	20.2
Cl ⁻ /SO ₄ ²⁻	151.8	195.0	20.0	0.973	157	6.7
Ion exchange systems	$q_0 \text{ exp}^a \text{ (mg g}^{-1}\text{)}$	n_D	$E \text{ (kJ mol}^{-1}\text{)}$	R^2	SSE (mg ² g ⁻²)	ARE (%)
Dubinin-Astakhov						
OH ⁻ /Cl ⁻	112.0	4.06	18.6	0.993	29	3.2
HCO ₃ ⁻ /Cl ⁻	112.0	4.90	13.9	0.929	287	12.5
OH ⁻ /NO ₃ ⁻	195.9	4.41	20.4	0.996	41	2.2
Cl ⁻ /NO ₃ ⁻	195.9	4.72	14.0	0.977	160	6.7
OH ⁻ /SO ₄ ²⁻	151.8	15.43	24.5	0.980	154	3.8
Cl ⁻ /SO ₄ ²⁻	151.8	3.64	21.7	0.998	14	1.6

^a Experimental determination of the total anionic exchange capacity (see Section 2.1).

of the sorption processes involved in the studied ion exchange systems.

4.4. Comparison of nonlinear results with linear regressions

Modelling ion exchange with linearized adsorption isotherms is still commonly carried out, even though the linearization of the isotherm equations is often pointed out as a source of errors in the determination of the best fitting model and of the adsorption parameters [26,32,38–41]. Also, several studies suggest that the adsorption isotherm modelling of the removal of some com-

pound by a sorbent should be realized by both linear and nonlinear regression to select the optimal isotherm [38,41].

In the present study, we briefly compare the nonlinear with the linear regression results. The linear forms of the Langmuir, Freundlich, and D-A isotherms are, respectively given by Eqs. (11)–(13),

$$\frac{c_e}{q_e} = \frac{1}{q_0 k_L} + \frac{c_e}{q_0} \quad \left(\text{plot : } \frac{c_e}{q_e} = f(c_e) \right) \quad (11)$$

$$\log(q_e) = \log(k_F) + \frac{1}{n_F} \log(c_e) \quad \left(\text{plot : } \ln(q_e) = f(\ln(c_e)) \right) \quad (12)$$

Table 5

Langmuir, Freundlich, D-R and D-A parameters deduced from linear regressions for the 6 ion exchange systems, and comparison linear and nonlinear R^2 .

Model parameters	OH ⁻ /Cl ⁻	HCO ₃ ⁻ /Cl ⁻	OH ⁻ /NO ₃ ⁻	Cl ⁻ /NO ₃ ⁻	OH ⁻ /SO ₄ ²⁻	Cl ⁻ /SO ₄ ²⁻
Langmuir						
$q_0 \text{ (mg g}^{-1}\text{)}$	111.6	128.7	190.6	192.8	147.8	141.5
$\Delta G^\circ \text{ (kJ mol}^{-1}\text{)}$	-22.5	-17.4	-25.4	-18.4	-34.1	-27.0
R^2	>0.999	0.991	>0.999	0.989	>0.999	>0.999
Nonlinear R^2	0.917	0.958	0.923	0.980	0.970	0.907
Freundlich						
$k_F \text{ (mg}^{1-1/n_F} \text{ L}^{1/n_F} \text{ g}^{-1}\text{)}$	43.2	15.3	82.2	17.8	94.4	65.9
n_F	0.195	0.374	0.190	0.440	0.121	0.164
R^2	0.946	0.995	0.958	0.997	0.653	0.932
Nonlinear R^2	0.936	0.997	0.961	0.994	0.671	0.933
Dubinin-Radushkevitch						
$q_0 \text{ (mg g}^{-1}\text{)}$	160.5	225.1	298.5	464.4	253.4	251.4
$E \text{ (kJ mol}^{-1}\text{)}$	16.0	10.6	17.1	10.2	24.8	21.0
R^2	0.985	>0.999	0.985	0.997	0.712	0.966
Nonlinear R^2	0.979	>0.999	0.986	0.997	0.745	0.973
Dubinin-Astakhov						
n_D	4.05	4.57	4.42	4.42	10.2	3.67
$E \text{ (kJ mol}^{-1}\text{)}$	18.8	14.1	20.4	14.1	24.5	21.5
R^2	0.994	0.956	0.997	0.978	0.961	0.998
Nonlinear R^2	0.993	0.929	0.996	0.977	0.980	0.998

$$\ln(q_e) = \ln(q_0) - \left(\frac{1}{\sqrt{2E}}\right)^{n_D} \left[RT \ln\left(1 + \frac{1}{c_e}\right)\right]^{n_D}$$

(plot : $\ln(q_e) = f\{\varepsilon^{n_D}\}$) (13)

The linear form of the D-R isotherm is Eq. (13) where $n_D = 2$.

The parameters deduced from the linear regressions are listed in Table 5. They are consistent with the nonlinear results, and q_0 as calculated from the linearized Langmuir isotherms is $q_0 = 3.16 \pm 0.24 \text{ meq g}^{-1}$, while the non linear regressions give $q_0 = 3.04 \pm 0.31 \text{ meq g}^{-1}$, the experimental determination gives $AEC = 3.17 \pm 0.08 \text{ meq g}^{-1}$, and the supplier indicates $AEC = 3.20 \text{ meq g}^{-1}$.

No significant difference is observed between the R^2 values obtained from linear and nonlinear regressions for the Freundlich, D-R and D-A models. On the other hand, the quality of the fit of the linearized Langmuir model to the experimental data is much higher than what obtained from nonlinear regression for 5 of the 6 ion exchange systems under study. The determination of R^2 for the linearized Langmuir isotherms minimizes the errors originating from the points near the origin, where the highest deviations between the Langmuir model and the experimental data are observed by nonlinear regression (Figs. 1–3). Consequently, in this study the evaluation of errors using R^2 calculation on the linearized Langmuir isotherms would yield in major errors when estimating the best fit isotherms.

5. Conclusions

The macroporous resin IRN 9766 presents a very satisfying ability to remove all the anionic species of interest. The adsorption energies are particularly elevated for the OH^-/Cl^- , $\text{OH}^-/\text{NO}_3^-$ and $\text{OH}^-/\text{SO}_4^{2-}$ systems, while the $\text{HCO}_3^-/\text{Cl}^-$ and $\text{Cl}^-/\text{NO}_3^-$ systems present lower adsorption energies, suggesting that HCO_3^- and Cl^- have a potential incidence on the removal of Cl^- and NO_3^- , respectively. Unlike the Freundlich and Dubinin-Radushkevich (D-R) isotherms, the Langmuir model appears as an accurate model to predict q_0 . The heterogeneity parameter of the Dubinin-Astakhov (D-A) model is independent of the ion exchange system and seems to be a convenient parameter for the characterization of the sorbent surface. The D-A isotherm also presents the best fit to the experimental data obtained for the OH^-/Cl^- , $\text{OH}^-/\text{NO}_3^-$, $\text{OH}^-/\text{SO}_4^{2-}$ and $\text{Cl}^-/\text{SO}_4^{2-}$ ion exchange systems, while the D-R isotherms present better fits for the $\text{HCO}_3^-/\text{Cl}^-$ and $\text{Cl}^-/\text{NO}_3^-$ systems. This shows that the micropore volume filling model is the most appropriate to the investigation of the ion exchange systems studied here. Linear and nonlinear regression results are in agreement to estimate the isotherm parameters, but the fit of the linearized Langmuir isotherm based on R^2 determination is strongly overestimated. Therefore, nonlinear regression results obtained through the analysis of different error functions should be preferred to linear regression.

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