Simplified Prediction of Ion Removal in Capacitive Deionization of Multi-Ion Solutions

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ABSTRACT: Capacitive deionization (CDI) is an upcoming desalination technology being increasingly considered to be a simple and cost-effective solution for brackish water, where electrosorption leads to the removal of charged species from water. Real-world water samples typically contain a multitude of ions that must be considered apart from sodium–chloride salt. In this work, we have developed a method to quantify the competitive adsorption of different ionic species during CDI processes. The method is straightforward, requiring a single calibrating experiment to extract a ‘periodic table’ of competitiveness scores for all ions present in the experiment. Using a dynamic Langmuir model that was developed by our group, it is shown that these scores could subsequently be used to predict the adsorption of any ion species in a multi-ion solution. Excellent agreement with data from the literature could be achieved with this model, and the method is especially well-suited for trace ions as these can be predicted directly. The derived method is simple and accurate for quantifying and predicting adsorption in multi-ion solutions and could be valuable for predicting the effect when applying CDI to real-world water samples.

INTRODUCTION

The increasing global water scarcity necessitates the development of new and improved methods of producing clean water. To this end, desalination techniques which remove sodium chloride (NaCl) salt from water have been developed to tap into earth’s large supplies of brackish and seawater. While a lot of effort has been directed toward removing NaCl from water, there are often other trace-level ions that must be considered when producing drinking water or when used for industrial applications, such as calcium, magnesium, fluoride, sulfates, arsenic, or nitrates.

Capacitive deionization (CDI) is an emerging environmentally-friendly and energy-efficient technique for removing ions from water, which has been gaining increasing attention in the last few years. A CDI cell comprises two porous carbon electrodes separated by a spacer, and water is flown through the electrodes (Figure 1). Ions are removed when a potential is applied to the electrodes, and the cell is cleaned (regenerated) by removing the potential to desorb the ions from the electrodes.

The CDI process is strongly dependent on structural and operational parameters. For multi-ion systems, ion valency, ion size, and electrode pore size distribution have been identified as some critical parameters, determining the relative adsorption of the ionic species. Studies have reported on the adsorption properties of specific ions or adsorption in competitive mixtures of anions and cations.
Recently, using a dynamic Langmuir (DL) model, a relationship to describe the relative adsorption of ionic species in terms of their equilibrium concentrations has been reported. In the current work, we derive a simple relationship to describe the relative adsorption of ionic species adsorption rate of surface sites that are covered, the adsorption and desorption rates (eq 2). Here, \( K_s = k_{\text{ads}}/k_{\text{des}} \) is a constant and \( \theta \) is equilibrium fractional surface coverage. The Langmuir isotherm has previously been also adapted to describe liquids by exchanging \( p_A \) with \( c \) (the concentration in the liquid of the species being adsorbed), which was used to describe salt adsorption in the equilibrium state in CDI.40–46

\[
\frac{d\theta}{dt} = R_{\text{ads}} - R_{\text{des}} = k_{\text{ads}}p_A(1 - \theta) - k_{\text{des}}\theta \tag{1}
\]

\[
\theta_e = \frac{K_s p_A}{1 + K_s p_A} \tag{2}
\]

**DL Model.** A fundamental property that is shared between salt adsorption in a CDI system and typical Langmuir isotherms used for describing gas adsorption is that adsorption is fast in the beginning and becomes slower as the process approaches equilibrium. This has been adapted to describe the ion adsorption/desorption in CDI through the DL model.57

To adapt the principles behind Langmuir adsorption to CDI, it is assumed that the adsorption occurs onto voltage-induced sites “S”. Taking these sites to be proportional to the voltage which is applied to the electrodes ensures that the model agrees with the basic principles in supercapacitors that the charge storage is proportional to the applied voltage. Because the CDI process is driven by the applied voltage, it is further assumed that charge storage is the fundamental mechanism in CDI. Thus, eq 1 can be modified to eq 3 to describe electrosorption in CDI systems. Here, \( \sigma \) denotes the concentration of charged species in the liquid, and the subscript “ads” denotes the corresponding adsorbed quantity, while the subscript “des” denotes desorption.

\[
\frac{d\sigma_{\text{ads}}}{dt} = k_{\text{ads}}\sigma(S - \sigma_{\text{ads}}) - k_{\text{des}}\sigma_{\text{ads}} \tag{3}
\]

In an ideal system, the concentration of adsorbed ions would be directly related to the stored charge through the simple relationship \( \sigma = cz \), where \( z \) is the ion valency (eq 4). However, in reality, there are several effects that prevent some charges from contributing to adsorption.57 Here, co-ion expulsion will be considered as the primary factor, meaning that the applied voltage pushes away co-ions rather than adsorbing counterions. Co-ion expulsion could be interpreted as a blockage of sites because the applied voltage is being used for pushing away these ions instead of adsorbing. Thus, eq 4 could still be used if the number of sites, \( S \), is exchanged for an effective number of unblocked sites, \( S' \).

\[
\frac{d\sigma_{\text{ads}}}{dt} = k_{\text{ads}}c(S - c_{\text{ads}}^2) - k_{\text{des}}\sigma_{\text{ads}} \tag{4}
\]

Two key mechanisms can be identified that lead to co-ion expulsion. First, there will be ions of both charge signs passively close to the electrode wall, and this contributes to a blockage proportional to the initial ion concentration in water (\( S \) reduced by \( \beta_i c_0 \), where \( \beta_i \) is a constant). Also, charged surface groups on the electrodes will be neutralized by ions from the solution before the voltage is applied to the cell to start the desalination process, meaning that there is a fixed blockage of sites even at low concentrations (\( S \) reduced by \( \beta fi \), a constant). Assuming that there are fewer adsorption sites than the charge storage sites with a difference determined by the size of this blockage (\( S' = S - \beta fi - \beta fi c_0 \)), the adsorption can be described by eq 5.

\[
\frac{d\sigma_{\text{ads}}}{dt} = k_{\text{ads}}c(S - \beta fi - \beta fi c_0 - c_{\text{ads}}) - k_{\text{des}}\sigma_{\text{ads}} \tag{5}
\]

**Multicomponent Electrolytes.** As the Langmuir isotherm considers the partial pressure of gas, similarly, the DL model can be used to describe the adsorption of individual ion species by considering their concentrations separately. This is shown in eq 6, where superscripts \((i)\) denote the ion species considered. Note that, \( S \) symbolizes the total capacity for storing charges and the number of free sites is, therefore, \( S \) minus the total accumulated charges summed over all species (hence the sum in eq 6).

\[
\frac{d\sigma_{\text{ads}}^{(i)}}{dt} = k_{\text{ads}}^{(i)}c(S - \beta fi - \beta fi c_0 - \sum_i z_i^{(i)}c_{\text{ads}}^{(i)}) - k_{\text{des}}^{(i)}\sigma_{\text{ads}}^{(i)} \tag{6}
\]

As this expression can be complicated to use, a simpler result is derived for the relative adsorption of two ion species \((i)\) and \((j)\) of the same charge sign at equilibrium. At equilibrium, the derivatives will be zero, meaning that \( k_{\text{ads}}^{(i)}/k_{\text{des}}^{(i)} = k_{\text{ads}}^{(j)}/k_{\text{des}}^{(j)} = \alpha^{(i)}/\alpha^{(j)} = \sum z_i^{(i)}/\sum z_j^{(j)} \). Next, we divide this expression for one species \((i)\) by the corresponding expression for another species \((j)\). To finally reach the simplified expression, we assume that the charge efficiency is similar between the species, so the two factors containing \( S \) cancel. This assumption has previously been shown to be reasonable57 and an example of an experimental study showing a similar charge efficiency for different species can be seen in the work by Hassanvand et al.49

The result of the derivation is shown in eq 7, which demonstrates that the relative adsorption between the species is proportional to their relative equilibrium concentration.

\[
\frac{z_i^{(i)}c_{\text{ads}}^{(i)}}{z_j^{(j)}c_{\text{ads}}^{(j)}} = \frac{k_{\text{ads}}^{(i)}/k_{\text{des}}^{(i)}}{k_{\text{ads}}^{(j)}/k_{\text{des}}^{(j)} \alpha^{(i)}/\alpha^{(j)} = \alpha^{(i)}/\alpha^{(j)}} \tag{7}
\]

In continuous-mode operation, the equilibrium concentration inside the cell will be the same as the influent concentration \( c_p \). In batch-mode operation, the equilibrium batch concentration is not the same as the initial concentration. However, because the total salt quantity is constant in the batch-mode operation, \( c_i^{(i)} = c_i^{(i)} + c_i^{(j)} \). Substituting this in
eq 7 reveals that relative adsorption can be uniquely related to (and thus calculated from) the initial concentrations. Additionally, the batch-mode relative concentrations also depend linearly on the relative initial concentration for the case where the batch reservoir is large (the relative adsorption is small) or if the adsorption of the two species is similar ($\alpha \approx 1$), as shown in eq 8.

$$\frac{c_{ads}(i)}{c_{ads}(j)} = \frac{c_{e}(i)}{c_{e}(j)} = \alpha \frac{c_{e}(i)}{c_{ads}(i)} \frac{c_{e}(j)}{c_{ads}(j)}$$

$$\rightarrow \frac{c_{e}(i)}{c_{e}(j)} = \alpha \frac{c_{e}(i)}{c_{ads}(i)} \frac{c_{e}(j)}{c_{ads}(j)}$$

$$\rightarrow \frac{c_{e}(i)}{c_{e}(j)} - 1 = \alpha \left( \frac{c_{e}(i)}{c_{ads}(i)} - 1 \right)$$

$$\rightarrow \frac{c_{e}(i)}{c_{e}(j)} = \alpha \frac{c_{e}(i)}{c_{ads}(i)} + (1 - \alpha)$$

$$\rightarrow \frac{c_{e}(i)}{c_{e}(j)} = \alpha \frac{c_{e}(i)}{c_{ads}(i)} + (1 - \alpha) \frac{c_{e}(i)}{c_{e}(j)}$$

(8)

Competitiveness Metric. Based on the results mentioned above, the competitiveness of an ion compared to any other ion in the solution of the same charge sign can be quantified by the parameter $\alpha$. Crucially, $\alpha$ is independent of the other ions present in the solution and could be extracted for all pairs of ions in a solution containing multiple ion species. However, it is not imperative to know the $\alpha$ values relating each ion in the solution to every other ion in the solution to be able to predict the relative adsorption of any two species. Consider the case where one or more separate experiments for the same CDI device have revealed the $\alpha$ values for (b) in relation to (i) and (j) in relation to (j). Then, the relative adsorption of (i) and (j) can be predicted as in eq 9.

$$\frac{c_{ads}(i)}{c_{ads}(j)} = \frac{c_{e}(i)}{c_{e}(j)} = \frac{\alpha_{i,b}c_{e}(i)}{\alpha_{j,b}c_{e}(j)} = \alpha_{i,b} \frac{c_{e}(i)}{c_{e}(j)}$$

$$\alpha_{i,j} = \frac{\alpha_{i,b}}{\alpha_{j,b}}$$

(9)

(10)

Note that the last step in eq 9 follows from the definition of $\alpha$, as derived in eq 7. This derivation shows that there is a simple relationship between the $\alpha$ parameters for different species (eq 10), that is, the $\alpha$ value relating to the two species (i), and (j) is equal to the fraction of their $\alpha$ values compared to some other species (b). The value of this finding is that one could build a “periodic table” containing the $\alpha$ value of all ion species in relation to a fixed baseline (b). These values could then be used to predict the relative adsorption of any combination of ions by using the relationship in eq 7.

As a side note, inverting eq 9 reveals that $\alpha_{i,j} = 1/\alpha_{j,i}$, because of the proportionality relationship. Consequently, one does not need to calculate separate $\alpha$ values to be able to alternate between calculating (i) as a fraction of (j) or vice versa.

So far, only the relative adsorption between pairs of species has been described. However, if there are multiple ions in the solution, it is also interesting to predict preferential adsorption of specific species in comparison to the total adsorption of all species. Consider the case where there are multiple ions in a solution where a specific ion (i) is of interest. Summing eq 9 for all ion species ($\sum$ denotes the sum over species s) with (i) in the denominator leads to eq 11. Inverting this equation leads to eq 12, stating that the adsorption of (i) compared to the total adsorption of all species is equal to the equilibrium concentration of (i) compared to a weighted sum of other concentrations by their corresponding $\alpha$ values. Note also that the $\alpha$ values have been exchanged for the corresponding values compared to a base (b) as per eq 10.

$$\sum_{s} \frac{c_{ads}(i)}{c_{ads}(s)} = \frac{\sum_{s} \alpha_{i,s}c_{e}(s)}{c_{e}(i)}$$

(11)

$$\sum_{s} \frac{c_{ads}(i)}{c_{ads}(s)} = \frac{\sum_{s} \alpha_{i,b}c_{e}(s)}{c_{e}(i)}$$

(12)

Trace Ions. Generally, the relative adsorption between pairs of ion species or between a species and the total adsorption can be predicted. In the case of trace ions, the exact level of adsorption can be predicted as well.

Consider a solution that contains a majority ion (m) and trace ions, which include the species (i) (eq 13, directly taken from eq 7). Varying the concentration of the trace ion will have a negligible effect on the adsorption of the majority ion because the trace ion constitutes a negligible fraction of all ions adsorbed. Thus, if the major-ion concentration is kept constant, the major-ion adsorption can be considered as a constant parameter as well. This implies that the adsorption of the trace ion is directly proportional to the concentration of the trace ion.

Note that the proportionality constant in eq 13 can be derived either indirectly from a known/calibrated $\alpha$ value and the adsorption of the majority ion at the concentration of interest or directly by simply measuring trace-ion adsorption for a given trace-ion concentration at the desired majority ion-background concentration.

$$c_{ads}(i) \approx \left( \frac{c_{ads}(m)}{c_{e}(m)} \right) c_{e}(i)$$

(13)

EXPERIMENTAL VALIDATION

To validate the claims put forth in the model developed herein, data were extracted from various reports on adsorption in multi-ion solutions from the literature. This was done using WebPlotDigitizer software, which allows numerical data points to be extracted from graphs. Both steady-state and time-varying concentrations were considered, and reports were chosen based on whether the results had a large set of investigated ions, preferably in different concentrations.

RESULTS

Multi-Ion Solutions. Despite the complicated mechanisms involved, the DL model has shown that multi-ion adsorption for a given system follows a simple principle: the relative adsorption between two species is proportional to their relative initial concentration (eq 7). A crucial point to note regarding the pairwise relationship is that an experiment to extract the competitiveness score $\alpha$ between two ions does not need to be conducted for the ion species separately. Rather, a single experiment could be conducted, where the treated water contains lots of different ionic species, and the competitiveness scores between all ions could be extracted at the same time.
Hou et al.\textsuperscript{34} investigated electrosorption of ions in a competitive environment containing multiple cations, using a solution with potassium, sodium, calcium, and magnesium. In this solution with four ions, a linear trend can be noted when the relative adsorption between potassium and sodium (Figure 2a) is compared to that between calcium and sodium (Figure 2b). In their system, K\textsuperscript{+} shows slightly better adsorption than Na\textsuperscript{+} ($\alpha \approx 1.1$). Ca\textsuperscript{2+} was the most competitive ($\alpha \approx 1.2$), which could partly be attributed to its higher valency state.

Calculating New Ion Combinations. By fitting the $\alpha$ value to the experimental data between two ion species, as shown above, it is possible to predict the relative adsorption at different initial concentrations of these ion species for the same device. However, eq 10 further suggests that it could be possible to predict the relative adsorption between two species without experimentally extracting $\alpha$. Rather, it could be calculated if their competitiveness relative to some other ions is known.

To illustrate the principle, let us consider the data set with potassium, sodium, calcium, and magnesium in the solution as discussed above. Using eq 10, the $\alpha$ value relating K\textsuperscript{+} to Ca\textsuperscript{2+} could be calculated as a fraction of their $\alpha$ values with respect to Na\textsuperscript{+}. The obtained model results based on this calculated value correspond well with the experimental data for the relative adsorption of K\textsuperscript{+} and Ca\textsuperscript{2+} (Figure 3).

Fraction of Total Adsorption. So far, all calculations have focused on pairwise relationships between two ions in a multi-ion solution. However, the adsorption of one species compared to the total adsorption of all species present in the solution could be calculated as well. From eq 12, adsorption of one species compared to the total adsorption of all species is equal to the relative equilibrium concentration between the species and the weighted sum of the individual species. Here, the weighted sum is generated by multiplying each ionic species with its corresponding $\alpha$ value.

For the solution with K\textsuperscript{+}, Na\textsuperscript{+}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+}, consider the adsorption of Na\textsuperscript{+} relative to the total adsorption. Because the adsorption and concentrations of all ion species are known, all $\alpha$ values relative to Na\textsuperscript{+} could be calculated and then used to generate the weighted total concentration. There is a clear agreement between the experimental data and the linear model, as shown in Figure 4a. Using the same principle, the

Figure 3. Graph showing the experimental relative adsorption between K\textsuperscript{+} and Ca\textsuperscript{2+} from the data set used in Figure 2. Note that, based on the $\alpha$ values relating K\textsuperscript{+} to Na\textsuperscript{+} (Figure 2a) and Ca\textsuperscript{2+} to Na\textsuperscript{+} (Figure 2b), the $\alpha$ value relating K\textsuperscript{+} to Ca\textsuperscript{2+} can be calculated using eq 10. This calculated value for $\alpha$ was used to generate the model line rather than fitting it.

Figure 4. Graph using the same data set as in Figure 2. With all $\alpha$ values and concentrations known, eq 12 can be used to plot the adsorption of an ion to the total adsorption of all ions as a function of the weighted average between the concentrations of the ion species and their corresponding $\alpha$ values. Na\textsuperscript{+} was chosen as the baseline ion in all graphs, and the investigated ions were (a) Na\textsuperscript{+}, (b) K\textsuperscript{+}, and (c) Ca\textsuperscript{2+}.
adsorption of K⁺ (Figure 4b) and Ca²⁺ (Figure 4c) could also be calculated with respect to the total. Note that, following eq 12, the weighted total is always measured with respect to the baseline Na⁺, while the slope is the α parameter between the ion of interest and the baseline.

**Trace Ions.** For a solution with varying trace-ion concentrations but a fixed major-ion background, not only the relative adsorption but also the absolute adsorption of the trace ion can be predicted. This is because varying the trace-ion concentration has a negligible effect on the major-ion adsorption, so both \( c_{m}^{(m)} \) and \( c_{ads}^{(m)} \) are constants in eq 13.

The proportionality constant in eq 13 can be determined through calibration of \( \alpha, c_{e}^{(m)} \), and \( c_{ads}^{(m)} \). In a report by Tang et al., the authors investigated the adsorption in a solution containing varying amounts of NaCl (such as 2 g/L) and a small fixed amount of NaF (ref 13, Figure 4). From this experiment, \( \alpha = 0.974 \) can be extracted along with the total adsorption for the system, where NaCl (2 g/L) is the major ion (Figure 5a). Alternatively, it can simply be noted that in the same experiment, 68% of the F⁻ was removed when the background concentration was 2 g/L NaCl (eq 14). Note also that the relative adsorption of F⁻ and Cl⁻ are similar so that the equilibrium concentration can be substituted for the initial concentration.

In the same report, other batch-mode experiments are presented in which the NaCl concentration is fixed at 2 g/L, while the concentration of F⁻ is varied (ref 13 Figure 3). The derived trend (eq 13) demonstrates an excellent agreement with the experimental results (Figure 5b). This result is important for two reasons. First, it demonstrates that it is possible to use the methods presented in this work for predictions. Second, it shows that it is possible to model the exact adsorption of trace ionic species in multi-ion solutions.

\[ c_{ads,F} = 0.68c_{F} \]  

**Implementation Details.** In the previous sections, the results when applying the DL model to various experimental data have been shown. In this section, three key points are presented that are important to note when applying the DL model to a new system.

First, as previous reports have extensively shown that there are differences between devices (because of electrodes, configuration, etc.), it is not expected that the relative adsorption and thus competitiveness scores should translate exactly between devices. For accuracy, we recommend calibrating the competitiveness scores to the desired device and operating conditions.

Second, to build a table of competitiveness scores, baselines for cations and anions are required. For this, we recommend Na⁺ and Cl⁻ because they are the most commonly investigated ions. As the number of ion species in a solution is not a limitation for the model, we suggest calibrating a system by using a standard solution containing all ions that are being investigated. By extracting the data on performing CDI until equilibrium is reached while measuring the concentration and total adsorption of all ions, eq 7 could be used to generate a competitiveness score \( \alpha \) for every ion with respect to Na⁺ (for cations) or Cl⁻ (for anions).

Third, having the table of competitiveness scores, predictions could then be made for any solution containing a subset of the ions for which the competitiveness scores have been extracted (eqs 12, or 7, and 10). Note that if a continuous-mode operation has been used or a batch-mode operation where either all \( \alpha \approx 1 \) or the adsorption is small in comparison to initial ionic concentrations, the adsorption/concentration trend is linear in the initial concentration and the equilibrium concentration. Thus, it would be possible to calculate the relative adsorption of one ion with respect to other ions without performing any additional experiments.

As a side note, while most calculations shown here have been on relative adsorption, it is especially interesting to note that exact adsorption can be predicted for trace substances mixed with more concentrated species. For instance, if the adsorption for a NaCl-only solution is known, the adsorption could be predicted for such a solution mixed with any combination of trace ions, such as arsenic and fluoride.

**CONCLUSIONS.** In this work, a new metric has been developed for CDI processes to quantify and predict the adsorption competitiveness of ions in a solution containing multiple ionic species.

Using the DL model, it was shown that the relative adsorption between a pair of ion species is proportional to their relative concentration. By conducting a single experiment where the adsorption is measured for a CDI process using a standard solution with multiple ions, the proportionality constants could be derived with respect to a common baseline ion to build a “periodic table” of competitiveness scores (competitiveness table). Having these scores, one could calculate and predict the performance of a given ion compared to other ionic species in the solution. The method is especially well-suited for trace ions as the adsorption of such ions could be predicted directly.

It is hoped that the metric derived here could be used by researchers in future experiments to quantitatively compare adsorption characteristics between ions and to predict the
performance of CDI for multi-ion solutions and especially for solutions with trace ions.

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**Notes**

The authors declare no competing financial interest.

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