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Enhancing Parameter Identifiability in Capacitive Deionization: A Model-Based Design of Experiments Approach

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ABSTRACT

Capacitive Deionization (CDI) is an emerging electrochemical technology for energy-efficient brackish water desalination. However, the rigorous design and scale-up of CDI systems are frequently hindered by the complexity of validating predictive models. The coupling of electrochemical double-layer kinetics with macroscopic mass transport often leads to structural parameter correlations, where multiple combinations of kinetic rates yield indistinguishable effluent trajectories. This paper addresses these challenges by proposing a simulation-driven Model-Based Design of Experiments (MBDoE) framework. We develop and implement a reduced-order Dynamic Langmuir (DL) model within the gPROMS platform, designed to capture cyclic adsorption-desorption dynamics with high computational efficiency. Sensitivity analysis reveals that information content is highly transient, concentrated primarily in the short time windows following voltage switching, and that the effluent concentration is significantly more sensitive to desorption kinetics than adsorption. Fisher Information Matrix (FIM) analysis of baseline experimental data confirms a strong negative correlation between kinetic parameters, resulting in a poorly conditioned estimation problem. To resolve this, a large-scale in-silico screening of the experimental design space—spanning inlet concentration, flow rate, and cell volume—is conducted using a D-optimality criterion. The simulation results demonstrate that operating at low flow rates and large effective cell volumes maximizes parameter identifiability by enhancing the separation of dynamic signatures. This work illustrates the critical role of dynamic simulation in guiding experimental strategy, minimizing trial-and-error effort, and improving the robustness of process models.

Keywords: Desalination, Capacitive Deionization, Modelling and Simulation, System Identification, Design of Experiment

1. INTRODUCTION

Freshwater scarcity is a growing global constraint, driving the demand for reliable and energy-efficient desalination technologies. Capacitive Deionization (CDI) has emerged as a promising alternative to reverse osmosis, particularly for the treatment of low-to-moderate salinity brackish water [1]. The technology operates on the principle of electrosorption, where dissolved ions are removed from a feed stream by applying a low voltage across porous carbon electrodes, storing them in electrical double layers (EDLs) [2]. Unlike steady-state membrane processes, CDI is inherently dynamic and cyclic, alternating between a charging or purification phase and a discharging or regeneration phase.

The optimization of CDI cycles—balancing salt removal, energy consumption, and water recovery—requires robust predictive models. However, the modelling of CDI systems presents a significant fidelity-cost challenge [3]. High-fidelity models, such as those based on Poisson-Nernst-Planck (PNP) equations or modified Donnan theory, offer detailed resolution of pore-scale electrochemistry but are often computationally prohibitive for real-time control or extensive design screening [4]. Conversely, simple equivalent-circuit models (RC circuits) are computationally inexpensive but lack mechanistic insight into mass transfer limitations, making them poor tools for process scale-up.

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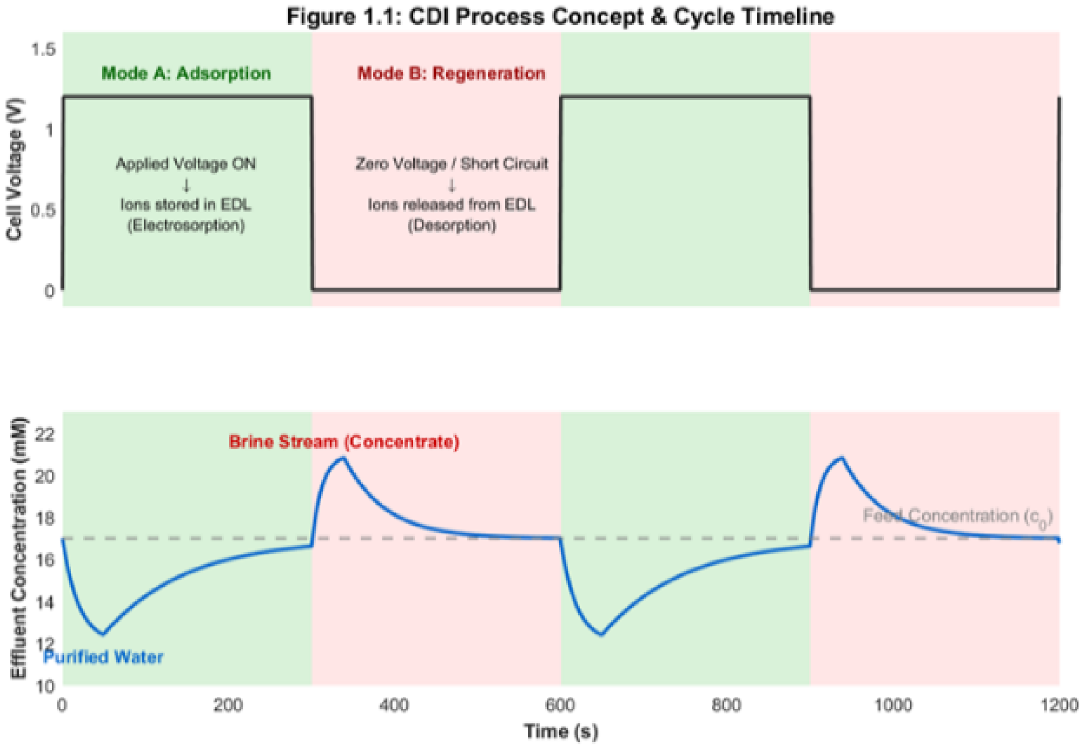

Figure 1. Ideal CDI process concept and timeline

An intermediate class of models, such as the Dynamic Langmuir (DL) model, offers a compelling compromise by describing the macroscopic adsorption dynamics with a compact set of parameters [5]. Yet, even simplified mechanistic models face the challenge of parameter identifiability. The coupling of reaction kinetics with fluid dynamics in a flow-through cell often leads to strong correlations between parameters. For instance, a faster adsorption rate might be mathematically indistinguishable from a different mass transfer coefficient under certain flow conditions. Standard experimental approaches, which often rely on normal one by one sweeps, is hard to generate data that can decouple these effects, leading to models with large predictive uncertainties [6].

Figure 1 shows the ideal CDI process concept and the adsorption regeneration cycle timeline. The top panel shows the applied cell voltage profile, which changes between a charging step (Mode A) where a constant voltage is applied to drive absorption, and a regeneration step (Mode B) where the voltage is removed or reversed. The bottom panel shows the corresponding effluent concentration response (blue line) relative to the constant feed concentration. During Mode A, ion removal causes the effluent concentration to drop, producing purified water. Conversely, in Mode B, the release of stored ions creates a concentration peak, resulting in a concentrated brine stream. These transient responses highlight why understanding dynamics and cycling is important to both system operation and model development.

Calibrating mechanistic models for CDI is challenging because different combinations of kinetic and transport parameters often yield indistinguishable effluent profiles, leading to poor parameter identifiability [7]. Traditional experimental design strategies, which typically rely on intuition or broad factorial sweeps, are often inefficient at resolving these correlations and can result in high experimental costs without reducing parameter uncertainty.

To address this, we employ Model-Based Design of Experiments (MBDoE) [8, 9]. Unlike classical design approaches that aim for broad empirical coverage, MBDoE uses the mechanistic model itself to quantitatively predict the information content of future experiments [10]. By analyzing dynamic sensitivities and the Fisher Information Matrix (FIM), MBDoE identifies specific operating windows, such as precise flow rates or cycle timings, that maximize the sensitivity of the measured outputs to the target parameters. This approach guides the selection of experimental conditions to decouple correlated parameters and minimize the variance of estimates with the least possible experimental effort [11]. Similar work in electrodialysis successfully minimise the number of trials and resources required for model identification [12].

This paper uses modelling and simulation as a tool to solve this experimental design problem. We propose a MBDoE framework to systematically identify operating conditions that maximize the information content of collected data.

2. METHODOLOGY: MODELLING AND SIMULATION FRAMEWORK

2.1 The Dynamic Langmuir (DL) Model

To enable the rapid, repeated simulations required for extensive design screening ($N > 1000$ runs), we adopt a reduced version of the Dynamic Langmuir model. The original DL framework describes ion removal as a competitive adsorption process on voltage-induced sites.

The full kinetic description typically depends on the real-time free ion concentration inside the cell, $c(t)$. However, in this work, a key simplification to improve structural identifiability and computational speed was introduced [13]: It assume that for the purpose of the adsorption driving force, the cell concentration can be approximated by the constant inlet concentration, i.e., $c(t) \approx c_0$ in the kinetic rate term. This assumption transforms the nonlinear adsorption dynamics into a linear Ordinary Differential Equation (ODE) for the adsorbed concentration state, c_{ads} (mM)[14]:

$$\frac{dc_{ads}}{dt} = K_a - K_b c_{ads} \tag{1}$$

Here, K_a (mM/s) represents an effective adsorption rate that lumps together the site availability, voltage dependence, and feed concentration effects.K_b (s^{-1}) represents the effective desorption or relaxation rate constant.

The macroscopic mass balance for the cell is modelled as a Continuous Stirred Tank Reactor (CSTR). The change in free ion concentration c (mM) is driven by the net removal of ions to the electrode (adsorption sink) and the convective transport through the cell [14]:

$$\frac{dc}{dt} = -\frac{dc_{ads}}{dt} + \frac{Q}{V}(c_0 - c) \tag{2}$$

where Q is the volumetric flow rate (mL/s) and V is the effective free cell volume (mL). This structure retains the essential dynamic features of CDI, which is the rapid drop during charging and the concentration overshoot during regeneration, while reducing the estimation problem to two primary kinetic parameters, $\theta = [K_a, K_b]^T$.

2.2 Model-Based Design of Experiments (MBDoE) Formulation

The objective of the MBDoE framework is to determine the experimental design vector $\varphi = [c_0, Q, V]^T$ that minimizes the statistical uncertainty of the estimated parameters θ.

Sensitivity Analysis: The foundation of the analysis is the dynamic local sensitivity matrix $Q(t)$, which quantifies the influence of parameters on the measured output $y(t) = [c(t), c_{ads}(t)]^T$:

$$Q_{ij}(t) = \frac{\partial y_i(t)}{\partial \theta_j} \tag{3}$$

In this study, sensitivities were computed using a finite-difference perturbation method ($\delta = 1\%$) implemented directly within the simulator. Large sensitivity values indicate that the output is strongly responsive to the parameter, implying that the data contains significant information for estimation.

Fisher Information Matrix (FIM): To aggregate this information over the duration of a dynamic experiment (T), we compute the cumulative Fisher Information Matrix, $H(\theta)$. Assuming Gaussian measurement noise with variance σ^2, the FIM is defined as [8]:

$$H(\theta) = \frac{1}{\sigma^2} \int_0^T Q(t)^T Q(t) dt \tag{4}$$

The inverse of the FIM approximates the parameter covariance matrix ($Cov(\theta) \approx H^{-1}$). Therefore, “maximizing” the FIM corresponds to minimizing the variance and covariance of the parameters.

D-Optimality Criterion: Since the FIM is a matrix, a scalar metric is required for optimization. We employ the **D-optimality criterion**, which maximizes the determinant of the FIM [8]:

$$\Phi_D(\varphi) = \mathrm{logdet}\big(H(\varphi)\big) \tag{5}$$

Geometrically, maximizing the determinant minimizes the volume of the joint confidence ellipsoid in the parameter space. This is particularly critical in CDI modeling, where parameters are often highly correlated; D-optimality specifically penalizes designs that result in flattened, elongated confidence regions.

2.3 Implementation in gPROMS

The simulation framework was implemented in gPROMS ModelBuilder. The architecture was designed for scalability, consisting of two layers:

Unit Model: A rigorous dynamic model of a single CDI cell solving the mass balance and kinetic equations (Eqs. 1-2) under a cyclic voltage schedule].

Manager Model: A high-level wrapper that instantiates an array of unit models. This allows for the simultaneous execution of a full-factorial Design of Experiments (DoE) grid.

This architecture enabled the screening of $N_{exp} = 1000$ virtual experiments in a single simulation job, ensuring consistency across initial conditions and solver settings.

3. RESULTS AND DISCUSSION

3.1 Dynamic Behaviour and Sensitivity Analysis

The reduced model was first evaluated under baseline conditions ($c_0 = 17$ mM, $Q = 1$ mL/s, $V = 10$ mL) to establish the dynamic characteristics of the system. . The simulation successfully reproduces the classic CDI response: upon voltage application, the effluent concentration drops sharply as ions are electrosorbed, followed by a gradual saturation. During regeneration (voltage removal), a concentration peak (overshoot) is observed as stored ions are released back into the bulk

The agreement between the model predictions using the estimated parameters and the measured data is illustrated in Figure 2 The solid line represents the simulated effluent concentration, while the symbols with error bars denote the experimental measurements and their standard deviations based on the estimated variance model. The figure shows that the model captures both the rapid initial decrease in effluent concentration during adsorption and the subsequent recovery and slight overshoot during regeneration. All measured points lie within the ±1σ confidence bands, and no systematic deviation can be observed over time.

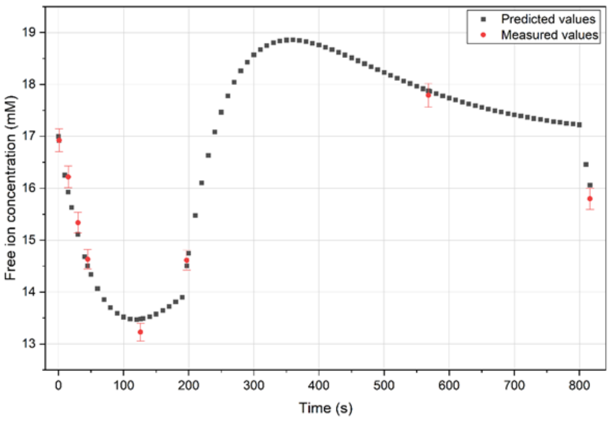

Figure 2. Comparison between measured and model-predicted effluent concentration c for the sample experiment

A critical finding from the sensitivity analysis is the disparity in parameter influence. The sensitivity of the effluent concentration to the desorption rate (K_b) is approximately an order of magnitude larger than that to the adsorption rate (K_a). Specifically, sensitivity to K_b peaks at values around 3×10^2, while sensitivity to K_a remains within ± 20.

Furthermore, the information content is highly localized in time. The sensitivity profiles exhibit sharp peaks immediately following the voltage switching events (charging and discharging steps) and decay to near zero during the steady-state phases. This temporal analysis suggests that measurements taken during the transient "switching windows" are exponentially more valuable than those taken at steady state. It confirms that dynamic operation is not just a feature of CDI but a necessity for accurate model calibration.

3.2 Parameter Estimation and Identifiability Issues

Using experimental data from a single charging cycle taken from literature, the kinetic parameters were estimated as $K_a \approx 0.0814$ mM/s and $K_b \approx 0.0071$ s^{-1}. While the model achieved a statistically valid fit (passing χ^2 and lack-of-fit tests), the FIM analysis reveals severe underlying identifiability issues.

The cumulative FIM at the end of the experiment showed a condition number of approximately 2.4×10^2, indicating a highly ill-conditioned estimation problem. The off-diagonal element of the covariance matrix revealed a correlation coefficient between K_a and K_b of $\rho \approx -0.83$. This indicates a strong negative correlation between Ka and Kb: an increase in one parameter can be partially compensated by a decrease in the other while still producing similar model responses. Geometrically, the confidence region in the (K_a, K_b)-plane is expected to be an elongated ellipse with a major axis tilted away from the coordinate axes.

Geometrically, this strong negative correlation results in a highly elongated joint confidence ellipse. This implies that K_a and K_b are coupled: an error in estimating the adsorption rate can be compensated by a proportional error in the desorption rate, leaving the model prediction largely unchanged. This "parameter compensation" effect is a primary cause of poor model predictive capability when operating conditions change.

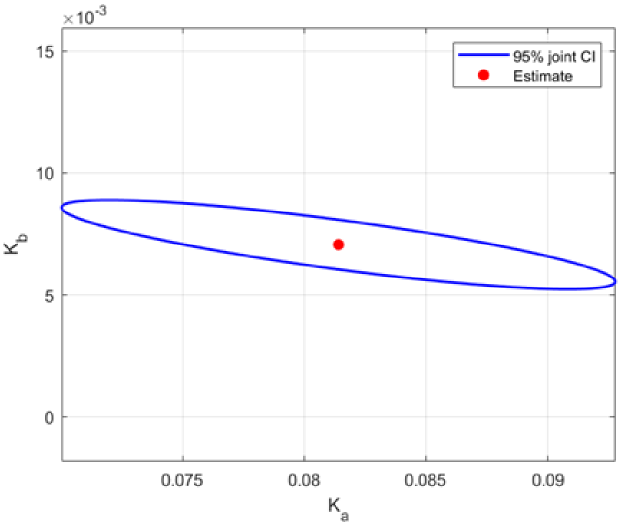

Figure 3. Joint 95% confidence region for the kinetic parameters $K_a$and K_b

Table 1. Estimated kinetic and variance-model parameters for the experiment data

Parameter	Final value	Initial guess	Std. dev.	95% CI lower	95% CI upper	t-value
K_a [units]	0.0814	0.0976	0.0046	0.059	0.119	6.82
K_b [s^{-1}]	0.00706	0.00880	0.00075	0.00530	0.00919	3.68
ω [–]	0.0130	0.0100	0.0049	0.0093	0.0185	1.10

Table 1 summarises the final parameter estimates, together with their standard deviations and 95% confidence intervals as reported by gPROMS. Starting from the literature-based initial guesses, the optimisation converged to slightly lower values for both kinetic parameters: K_a decreases from 0.0976 to approximately 0.081, while K_b decreases from 0.0088 to around 0.0071. These shifts indicate that the originally assumed rates moderately overestimated both the adsorption and desorption kinetics for the dataset considered.

3.3 Optimal Design Screening via Simulation

To break this parameter correlation, the simulation framework was used to screen the design space for conditions that maximize the D-optimality score. A full-factorial grid was evaluated:

- Inlet concentration $c_0 \in [0.1, 100]$ mM
- Flow rate $Q \in [0.05, 5.0]$ mL/s
- Cell volume $V \in [1, 100]$ mL.

The analysis of the resulting 1000 design points (Figure 4) yields three key insights for process engineering:

Invariance to Concentration: The D-optimality score showed negligible sensitivity to the inlet concentration c_0. This is consistent with the linear structure of the reduced model, suggesting that experimenters have flexibility in choosing c_0 based on safety or material constraints without compromising information quality.

Dominance of Flow Rate: The flow rate Q emerged as the most critical design factor, showing a strong negative correlation with the D-score ($r \approx -0.68$). Reducing the flow rate from 5.0 mL/s to 0.05 mL/s improved the determinant of the FIM by nearly a factor of three. Physically, lower flow rates increase the residence time of fluid in the cell. This allows the kinetic signature of the adsorption process to manifest more clearly against the background of convective transport, effectively "amplifying" the signal of the kinetic parameters.

Benefit of Cell Volume: Larger cell volumes were found to improve identifiability ($r \approx +0.31$). Similar to flow rate, a larger volume stretches the characteristic time of the mass balance, enhancing the separation of adsorption and desorption dynamic modes.

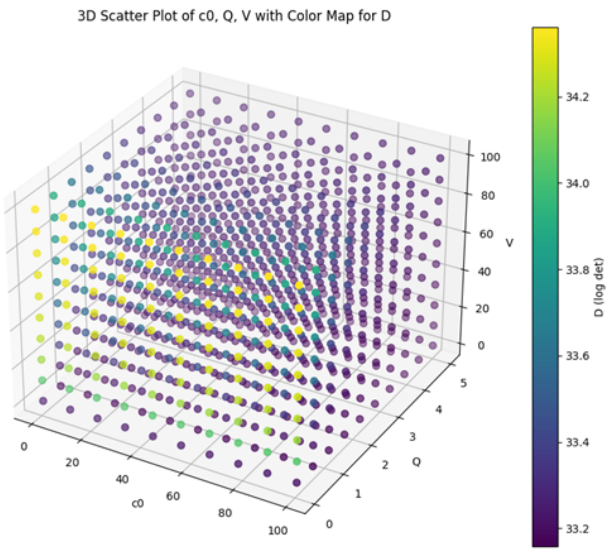

Figure 4. Three-dimensional scatter plot of the DOE design space (c_0, Q, V) coloured by the final D-criterion $D_{\log}(t_f)$, indicating the regions of highest and lowest information content for estimating K_a and K_b.

3.4 Recommended Design Strategy

Based on these simulation results, the optimal strategy for characterizing CDI kinetics is to operate at the **lowest feasible flow rate** and using a **larger effective cell volume**. The "worst-case" design was identified as a high-flow, small-volume configuration ($D_{log} \approx 33.16$), while the "best-case" design was a low-flow, large-volume configuration ($D_{log} \approx 34.36$). By shifting experiments to this optimal region, researchers can significantly reduce the volume of the parameter confidence ellipsoid, decoupling the kinetic rates and ensuring a more robust model calibration.

4. CONCLUSION

This study demonstrates the power of modelling and simulation as a core pillar of Computer Aided Process Engineering (CAPE) for emerging water technologies. By formulating a reduced-order dynamic model for Capacitive Deionization and integrating it with a rigorous MBDoE framework, we successfully quantified the information content of experimental data.

The simulation results highlight that "standard" experimental conditions often yield poor parameter identifiability due to intrinsic correlations between adsorption and desorption kinetics. However, by using the model to navigate the design space, we identified that operating regimes with high residence times (low flow, large volume) maximize the D-optimality criterion. This approach moves beyond trial-and-error experimentation, providing a systematic workflow to minimize experimental effort while maximizing the reliability of process models. Future work will extend this framework to include multi-objective optimization, incorporating energy consumption and thermodynamic efficiency into the design criteria.

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