

Modeling the Adsorption of Ions on Electrodes in a Flow Cell

R. Venkataraghavan¹, Tinto J Alencherry¹, Naveen Aerpula²

1.Unilever R&D Bangalore, Whitefield, Bangalore, India;

2.IISER Pune, Pashan, Pune, Maharashtra, India.

Introduction: Efficient and low cost deionization is a major technology challenge. Energy efficient technologies like Capacitive deionization (CDI) are possible emerging alternatives. In the present work, we simulate charge adsorption in a 2D flow cell to study its dependence on applied potential and flow rate, that can further help design a CDI system.

Physics: The problem is analyzed using a combination of laminar flow in a rectangular flow cell (Fig. 1), ion transport as given by Poisson-Nernst-Planck equation [1] and charge adsorption on the laterally placed electrodes using Langmuir adsorption model [2].

Modeling Scheme: Equations governing the physics that are used in the analysis are described below along with the boundary conditions and the parameters used in the analysis. The model is solved using graduated mesh with finer mesh near the electrodes (Fig. 1). The simulations are performed for varying applied potentials from 0.5 to 2 V and flow rates 0.41 to 41 ml/min.

Poisson equation: The electrostatic potential is calculated from the Poisson equation where one electrode is at a potential V, while the other is grounded.

$$\nabla \cdot (\epsilon_0 \epsilon_r E) = \rho, \rho = \sum_i z_i n_i e, E = -\nabla V$$

Navier Stokes equation:

Incompressible fluid flow with no-slip boundary condition on the walls, constant inlet flow rate and ambient outlet pressure is used.

$$\rho(u \cdot \nabla)u - \nabla \cdot [-pI + \mu(\nabla u + (\nabla u)^T)] - F = 0$$

$$\rho \nabla \cdot u = 0$$

Poisson-Nernst-Planck equation: The equations define the instantaneous concentration of the species, balancing diffusion, convection and electro-migration terms with the reaction rate. The ion concentration at the inlet is kept constant for both the anions and cations.

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - \frac{D_i z_i e}{k_B T} c_i \nabla \phi) + u \nabla c_i = R_i$$

Langmuir Monolayer adsorption model: Adsorption at the interface is governed by Langmuir adsorption.

$$R_i = K_{ads} c_i (\Gamma_s - c_s) - K_{des} c_s$$

Table 1: Parameters used in the analysis

| Parameters | | |
|------------|----------------------------|--------------------------------|
| | K_{ads} | 0.807 [m ³ /(mols)] |
| | K_{des} | 1[1/s] |
| | Γ_s | 3[mol/m ²] |
| | Diffusion coefficient (Na) | 1.33e-5[cm ² /s] |
| | Diffusion coefficient (Cl) | 2.03e-5[cm ² /s] |
| | C_{in} (Na) | 10 mM |
| | C_{in} (Cl) | 10 mM |

Results and Discussion: Figure 2 shows the resulting accumulation of counter-ions, accompanied by the depletion of the co-ions at the electrodes in response to the applied potential. This leads to a reduction in the concentration at the outlet, and consequent deionization of the inlet stream.

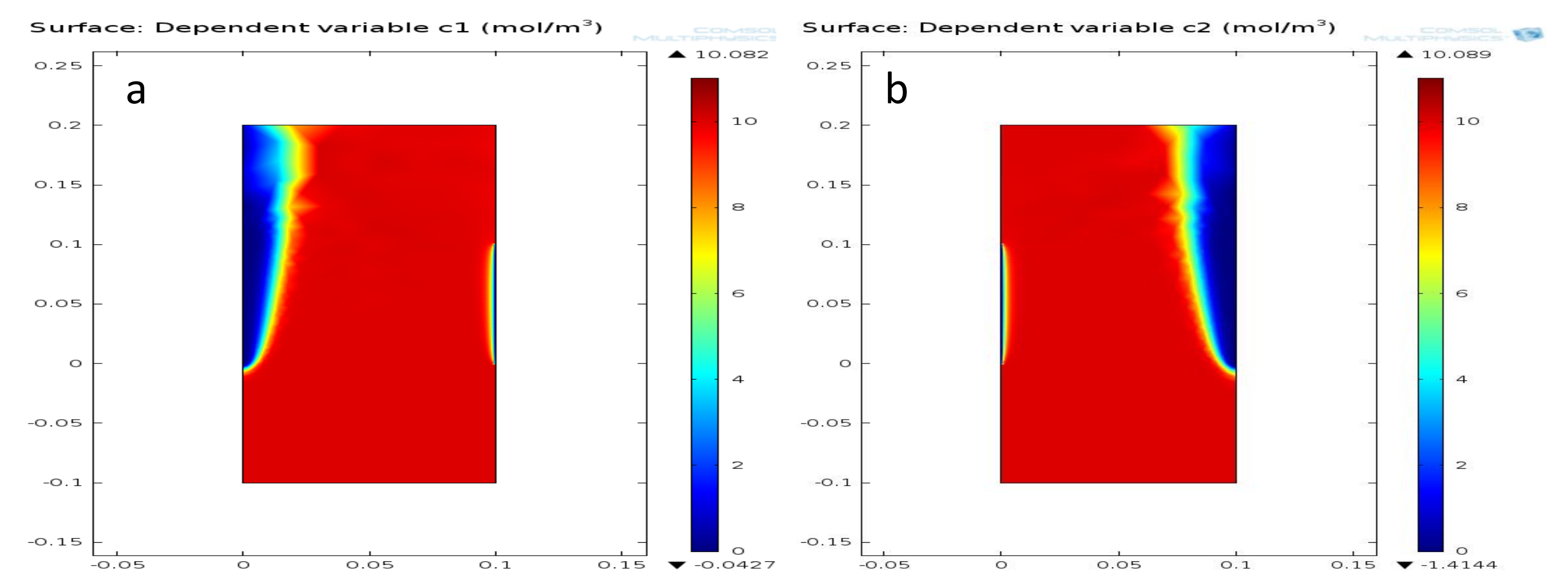


Fig. 2 Ion concentration in the flow channel (a) Na⁺ (b) Cl⁻

The ion concentration at the outlet is a function of applied potential (Fig.3a) and the influent flow rate (Fig. 3b). Salt removal increases with increasing applied potential because of enhanced charge adsorption and decreases with increasing flow rate, due to lower residence time in the flow cell [3].

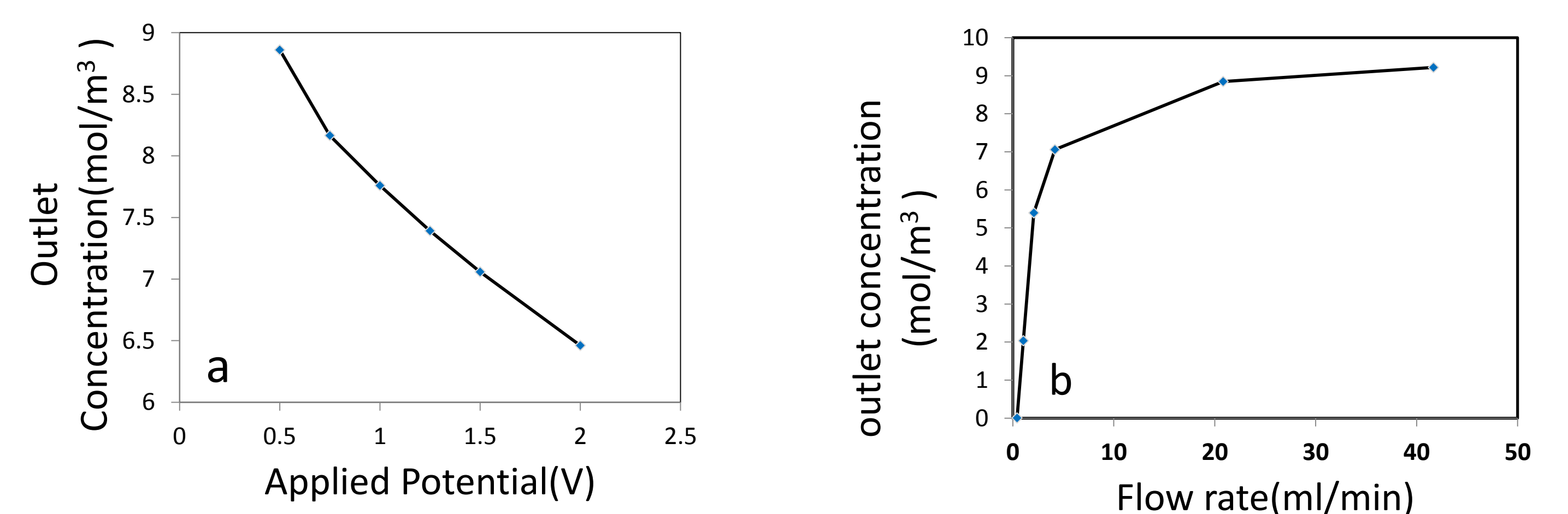


Fig. 3 Variation in output concentration as a function of (3a) Applied potential (V) (3b) Flow rate (ml/min)

It is also seen (Fig. 4) that adsorption is higher for species with higher charge and diffusion coefficient (adsorption of Ca²⁺ > Na⁺). This is also validated with experiments using NaCl and CaCl₂ solutions (Fig. 5).

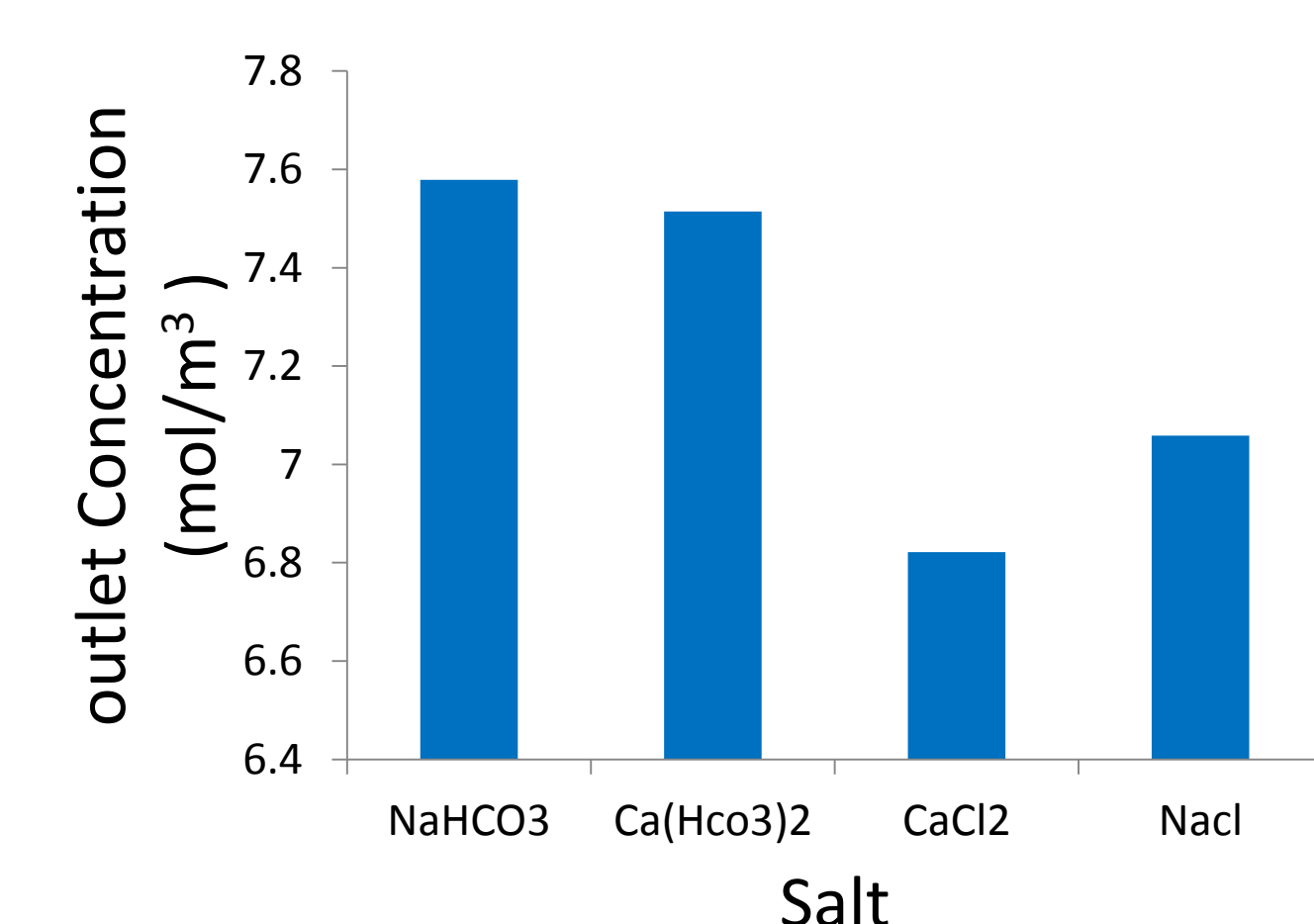


Fig. 4 Effect of Ionic species

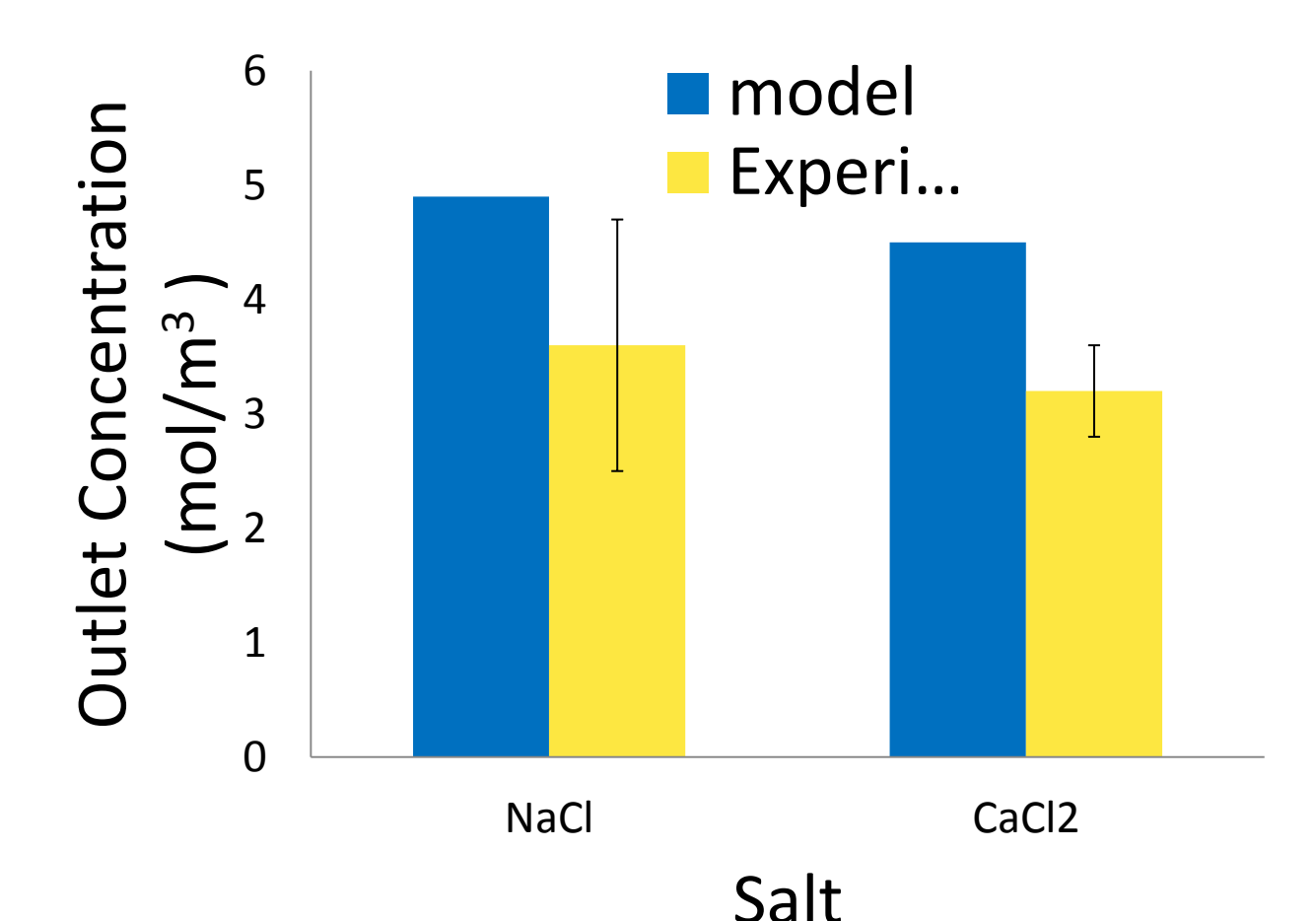


Fig. 5 Experimental validation

Conclusions:

- Ion adsorption is directly proportional to the applied potential and inversely proportional to the flow rate.
- The adsorption, and hence salt removal, is dependent on charge and diffusivity of the ions.
- The salt removal predicted by the model is 51%, as against 59% obtained experimentally.

References:

- Biesheuvel P.M. et al., J. Phys. Chem. C, 113, 5636 (2009).
- Haibo Li et al., Chemical Physics Letters, 485, 161 (2010).
- Jae-Hun Lee et al., Desalination, 159, 258 (2010).