

Numerical Modeling of Ion Chromatography in a Novel Microfluidic Device

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Abstract

A novel 3D-printed microfluidic device (MFDs) designed for online monitoring and separating rare earth elements (REE) via ion exchange was simulated using COMSOL Multiphysics®. Integrating numerical simulations and experimental validation can accelerate optimization for rare earth element separation development. To specifically optimize the separation of neodymium (Nd) using cation exchange resin (Dowex 50W-X8), several COMSOL modules were employed and replicated. The CAD Import Module was used to import full microfluidic geometries of various designs. The Ray Optics Module was used to investigate the impact of air mirrors on ultraviolet-visible absorption spectroscopy in the alternative device geometries, ultimately yielding a design that increased detector sensitivity and lowered detection limits. The Transport of Diluted Species in Porous Media Module was used to investigate laminar flow and Nd transport within a chromatographic column containing a single resin bead. A competitive Langmuir-isotherm adsorption model was used to simulate competitive adsorption between Nd and hydrogen cations, which required extremely fine meshing. A film diffusion-limited model was incorporated to reflect the mass transport into and inside the bead. The model closely matched time-resolved fluorescence measurements for loading on the bead up to 90% resin capacity. Above 90%, the model overpredicted loading, suggesting that micropores present in the resin with further reduced diffusion rates need to be included to fully match experiments. Through altering the affinity of hydrogen cations for the resin, the timescale of elution could be captured but not the exact profile. Results suggest further refinement is needed through addition of chemical species to promote more competition to reflect the gradual elution process in experiments. Following refinement and full flowsheet simulation, the resulting comprehensive model could guide large-scale rare earth element separation efforts and reduce experimental workload for rapid research and development of ion exchange materials.

Keywords: Microfluidic devices, ion exchange, resins, rare earth elements, neodymium, ultraviolet-visible (UV-VIS), separations, ion exchange chromatography.

Introduction

The demand for rare earth elements (REE) continues to grow due to their critical role in advanced technologies for electronics, renewable energy systems, and catalysis, yet they are vulnerable to supply chain disruptions [1]. Efficient separation and recovery of REE from waste streams is essential to ensure sustainable supply and the development of alternative sources. Ion exchange (IX) chromatography remains a widely used and highly effective method for REE separation - conventional packed columns can be sluggish and require extensive experimental optimization [2]. Recent advances in 3D printing microfluidic devices (MFD) enable novel platform fabrication for rapid online monitoring in microgram scale and separation of REE using IX resins in acidic solutions [3]. Innovative MFD experiments and simulations offer an increased throughput to reduce reagent consumption and enhance detector sensitivity in 3D printed devices.

Numerical modeling is increasingly recognized as a powerful tool to simulate complex transport and/or adsorption phenomena in microfluidic devices [4, 5]. By integrating ray optics, laminar flow, and transport in porous media modules, it is possible to accurately predict ion behavior and optimize device design for improved performance. For example, simulating the ultraviolet-visible (UV-Vis) cell of the MFD with the ray optics module can help in the design of MFD. These simulations can be used to promote internal reflection and transmission of UV-Vis light between source and detector, enhancing sensitivity and lowering the detection limit for absorption analysis in REE separation. Furthermore, combining transport in porous media and adsorption models in COMSOL enables detailed investigation of REE separation via ion exchange. Transport simulations are of interest considering the large role of diffusion in the kinetics of IX processes [6]. Adsorption simulations can capture interactions between chemical species and binding sites on the resin.

The current work investigated simulation of neodymium (Nd) separation from a strong acid cationic resin, Dowex 50W-X8, in a new microfluidic system [3]. Nd was used for evaluation of the MFD and initial simulations considering the molecule can not only adsorb light in the UV-Vis region but also fluoresce, allowing for unique on-line analysis of the IX process in the microfluidic device (Magnuson et al.) [3]. The fluorescence data captured directly on the resin bead allowed for a time profile of adsorption on the bead to be captured, which was used in the current study for validation. The unique dataset and microfluidic approach also allowed for a direct analysis and evaluation of the resin bead via simulations.

This paper presents a comprehensive approach to model ion chromatography in a novel 3D-printed MFD by integrating multiple COMSOL modules and validating experimental data. The results presented are expected to accelerate research and development for REE separation methods and advance MFD. Results suggest simulation of the loading of Nd on Dowex 50W-X8 resin is much faster through enhanced diffusion in the MFD compared to larger IX columns used in other studies. Loading and elution stages of the IX process were well captured.

Theoretical Background and Methods

Theoretical Background

The optical performance of the MFD is critical for online monitoring of REE separation. Ray optics theory simulated the propagation and focusing of UV-Vis light within the device. The resulting module evaluated design features such as printing thickness and air mirrors to enhance detector sensitivity and lower detection limits.

Separating REE via ion exchange chromatography is governed by fluid flow, mass transport, and competitive adsorption within the chromatographic medium (i.e., resin bead). For MFDs, these processes are further influenced by device geometry and operational parameters. The theoretical framework for this study is based on the convection-diffusion-reaction equation, i.e., the transport of Nd^{3+} and H^+ in the resin bead and surrounding solution. As flow in the chip is slow, Stokes flow was also applied. The adsorption model utilized the competitive Langmuir isotherm, which binds affinities for multiple ionic species with a shared resin capacity. This combined theoretical approach provided a robust foundation for both the simulation and experimental investigation of ion exchange processes in MFD platforms.

Methods

The experimental setup consisted of a novel 3D-printed MFD designed for online monitoring and extracting Nd using Dowex 50W-X8 cation exchange resin [3]. The full geometry of the MFD was imported into COMSOL Multiphysics® Version 6.2 using the CAD Import Module (**Figure 1**). The result allowed replication of experimental conditions in the simulation. The full geometry was manipulated to create simple geometries for the different analyses. One geometry isolated the flow channel (water) itself in the UV-Vis region (**Figure 2**). A 400-micron diameter circle was added to each end of the channel to represent the source and detector fiber optic cables with a numerical aperture of 0.22. On this geometry, different layers of increasing poly(methyl methacrylate) (PMMA) thickness, which were all surrounded by air, were tested to see how the thickness of the PMMA would affect transmission of light. Refractive indices for water, PMMA, and air were supplied by the COMSOL material library. From here, additional geometries with the inclusion of air mirrors were used to determine air mirror placement on light transmission (**Figure 3a** and **3b**). After determining the physical printing limitations of the 3D printer, a final MFD design was created and tested (**Figure 3c**). Rays were released with a source power of 1 W with a frequency of $3.819\text{E}14$ Hz, and the fraction of power deposited on the detector was used to evaluate the geometry. It was assumed all rays contributing to this deposited power were oriented within the receiving cone of the detector.



Figure 1. Full MFD Geometry.

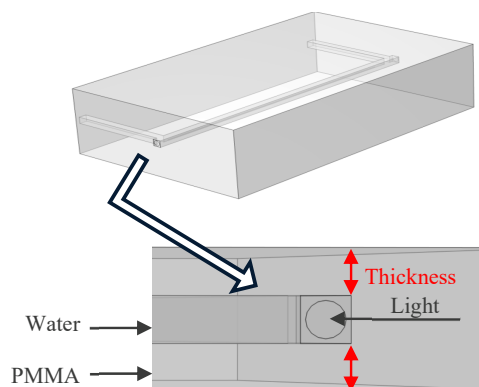


Figure 2. Simplified version of the UV-Vis flow region of the chip surrounded by air for Ray Optics simulations.

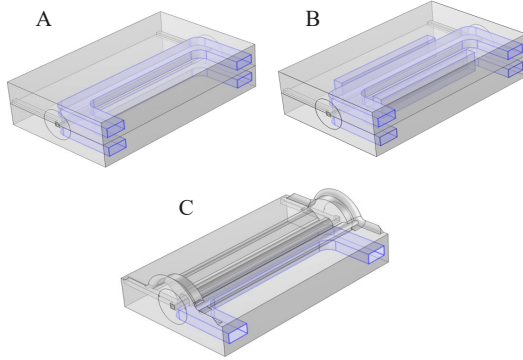


Figure 3. Various chip designs with air mirrors (highlighted in blue) used for Ray Optics simulations. C represents the final chip geometry.

For chromatographic experiments, a simplified conical geometry of the column was used to investigate the laminar flow around a static, spherical, and porous resin bead (Figure 4). The cutout of the column and resin bead were simplified to a 2D axisymmetric geometry for these simulations due to inherent symmetry, with the assumption that the resin bead is centered in the column. Time-resolved, fluorescence-emission spectroscopic measurements were taken directly on the resin bead to evaluate Nd loading and elution. The loading solution contained Nd^{3+} and H^+ ions at concentrations of 22.8 mol-m^{-3} and 100 mol-m^{-3} , respectively, to match those used in the experiments. A flowrate of $100 \text{ }\mu\text{L-min}^{-1}$ was used for loading and elution. The experimental elution solution contained no Nd and a significantly higher concentration of 4000 mol-m^{-3} H^+ ions to facilitate Nd^{3+} displacement from the resin.

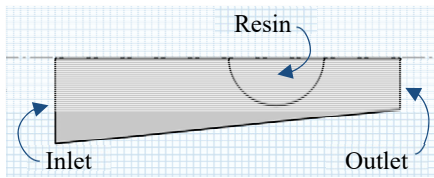


Figure 4. Axisymmetric geometry for adsorption modeling with a spherical resin bead.

For the adsorption model, a resin bead of 277 microns in diameter, capacity of $0.273 \text{ mol-kg}^{-1}$, [3] and porosity of 0.52 [7] was used. A Langmuir affinity constant for Nd^{3+} to Dowex 50W-X8 of $2.91 \text{ m}^3\text{-mol}^{-1}$ [8] from the literature was used, and as it was not reported, an affinity value of H^+ was assumed to be 1% of the Nd^{3+} affinity. A film diffusion layer of 100 micron thickness was used. Diffusion in the bulk was set to $1.25 \text{ E-9 m}^2\text{-s}^{-1}$ [9] and diffusion in the film and bead were varied between the bulk diffusion and $1.2\text{E-13 m}^2\text{-s}^{-1}$ [10].

Governing Equations, Boundary Conditions, and Numerical Model

Governing Equations

Ray equations are used for optics simulations. The propagation of light rays through the variable-index matrix was described by Hamilton's equations for geometric optics where, $\mathbf{q}$, is the ray position vector, $\mathbf{k}$, is the wave vector (related to direction and wavelength of the ray), and also, ω , is the angular frequency over time. These ray equations allowed the COMSOL model to trace how light bends and was propagated through the flow cell.

$$\frac{d\mathbf{q}}{dt} = \frac{\partial \omega}{\partial \mathbf{k}},$$

$$\frac{d\mathbf{k}}{dt} = -\frac{\partial \omega}{\partial \mathbf{q}},$$

The IX chromatography model inside the MFD was governed by combining transport and adsorption equations. The transport of Nd^{3+} and H^+ in the resin bead and surrounding solution was described by the convection-diffusion equation:

$$\frac{\partial C_i}{\partial t} + \mathbf{u} \cdot \nabla C_i = D_i \nabla^2 C_i - R_i,$$

where C_i is the concentration of species, i (Nd^{3+} or H^+), $\mathbf{u}$, is the velocity field, D_i , is the diffusion coefficient, and, R_i , is the reaction (adsorption and desorption) rate. This equation described how ions move through the system and how balanced physical transport from fluid flow (advection, $\mathbf{u} \cdot \nabla C_i$), molecular movement (diffusion, $D_i \nabla^2 C_i$), and local depletion/release as ions bound to or detached from the stationary phase (reaction, R_i).

Adsorption to the resin bead was modeled using a competitive Langmuir isotherm [11]:

$$Q_{e,i} = Q_{m,i} \frac{K_{L,i} C_{e,i}}{1 + \sum_{j=1}^N K_{L,j} C_{e,j}},$$

where, $Q_{e,i}$, is the equilibrium adsorbed amount of a species, $Q_{m,i}$, is the maximum adsorption capacity, $K_{L,i}$, is the Langmuir affinity constant, and, $C_{e,i}$, is the equilibrium concentration of species in solution. Since both Nd^{3+} and H^+ compete for the same physical exchange site on the resin bead, a single-component isotherm is inaccurate. This competitive isotherm models how the concentration of one species directly blocks and influences the adsorption and elution of the other.

To refine the transport model within complex regions like porous media (e.g., inside the resin bead or near its boundary film), the transport accounted for dispersive flux ($\mathbf{J}_i$) and external supply features (S_i):

$$\nabla \cdot \mathbf{J}_i + \mathbf{u} \cdot \nabla c_i = R_i + S_i,$$

$$\mathbf{J}_i = -(D_{D,i} + D_{e,i})\nabla c_i,$$

where, $\mathbf{J}_i$, is the total mass flux vector of species, c_i , is the local concentration of species, $D_{D,i}$, is the dispersion coefficient of species, $D_{e,i}$, is the effective diffusion coefficient of species in the porous medium, and, finally, S_i , is the general source or sink term (such as localized boundary inputs). These equations break the flux down to map how mechanical mixing is due to path tortuosity and how slowed molecular diffusion through complex pore networks impacted the local flow of species toward the active binding sites.

Key Initial and Boundary Conditions

For Ray Optics simulations, the detector boundary was set to freeze rays. Boundaries on the same face of the geometry as the source were set to make rays disappear, and the remaining faces were conditioned to reflect. Frequency of light in the simulation matched the 785 nm light used to induce fluorescence [3].

For IX simulations, initial concentrations of Nd^{3+} and H^+ in the MFD were established based on the experimental loading and elution solutions. Ramping functions were used for concentrations at the inlet to match calibration experiments from the work of Magnuson et al. that tracked Nd signal in an MFD with no resin bead [3]. At the channel walls, no-flux boundary conditions were implemented to prevent mass transfer across the boundaries. A constant flow rate was maintained at the channel inlet to replicate experimental conditions. The adsorption and desorption of ions at the surface and inside of the bead were governed by Langmuir isotherms, accurately modeling the competitive binding behavior between Nd^{3+} and H^+ ions during both the loading and elution phases of the ion exchange process.

Numerical Model and Other Assumptions

Simulations for this study were performed using COMSOL Multiphysics Version 6.2. Simulations with the Ray Optics module required zero meshing and based the results for transmitted laser power on a 1 ms time interval. For IX simulations, the resin bead was assumed to be fixed and rigid, allowing

for a 2D axisymmetric geometry to be used. The low flow rates and Reynolds number in the chip allowed for the bulk flow to be simulated with a stationary solver with the Laminar Flow Module. The simulated bulk flow was fed to time-dependent studies for adsorption modeling using a PARDISO solver. The 2D geometry was meshed finely with 76000 elements and an average quality of 0.9086; a triangular mesh and 2 boundary layers were used.

The adsorption model assumed $\text{Nd}(\text{NO}_3)_3(\text{H}_2\text{O})_6$ and HNO_3 used by Magnuson et al. [3] fully dissociated to calculate Nd^{3+} and H^+ cation concentration. These ions were assumed to follow monolayer binding under the Langmuir isotherm where H^+ has 3 times the capacity as Nd^{3+} due to the differences in charge. The affinity of H^+ was assumed to be 1% of Nd^{3+} for loading, which reflected the resin's higher selectivity for Nd and provided a starting point for tuning the model to experimental elution data.

Simulation Results and Discussion

Ray Optics

Optics simulations of varying thickness using the geometry in **Figure 2** showed that the thickness of PMMA between air and the liquid channel directly affected the transmission of light to the detector (**Table 1**). A PMMA thickness of 50 microns showed the highest transmission while increasing thickness resulted in decreasing transmission of laser power. These results highlighted that PMMA thickness should be kept as low as possible.

Table 1. Effect of PMMA thickness on light transmission.

Thickness (microns)	Fraction of power transmitted
50	13%
75	13%
100	13%
200	11%
300	10%
400	10%
500	8.5%
1000	7.5%

Air mirrors were added (**Figure 3**) to the simple design with PMMA thickness of ~350 microns between the mirrors, with results in **Table 2**. Initial testing with added mirrors showed a marginal increase in transmission and highlighted the need for more coverage with air. A circular channel around the flow cell was developed to minimize thickness of PMMA between the air and flow cell

to enhance internal reflection, resulting in a ~50% increase in power transmitted.

Table 2. Effect of air mirrors on light transmission.

MFD Design	Fraction of power transmitted
Figure 2	10%
Figure 3A	10%
Figure 3B	11%
Figure 3C	15%

Ion Exchange

Figure 5 illustrates the 3D velocity magnitude profile of a fluid flowing at $100 \mu\text{L}\cdot\text{min}^{-1}$ around the resin bead inside a conical nozzle. The fluid entered from the left inlet at a relatively low velocity and accelerated significantly as it was forced through the constricted annular spaces surrounding the resin, reaching a maximum velocity of $0.07 \text{ m}\cdot\text{s}^{-1}$. While moderate velocity increases were visible in the upper constriction and the wake region downstream to the right, the core of the central resin and the immediate boundaries of the channel wall displayed lower velocities, reflecting the importance of mass transport limitations to the bead being governed by diffusion.

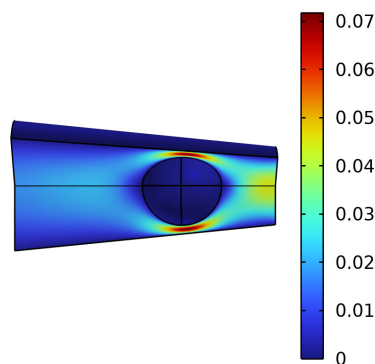


Figure 5. Velocity profile (in $\text{m}\cdot\text{s}^{-1}$) of fluid throughout the IX column at a $100 \mu\text{L}\cdot\text{min}^{-1}$ flowrate with the inlet on the left.

Flow and transport simulations for adsorption of Nd^{3+} on Dowex 50W-X8 required extremely fine mesh resolution to accurately resolve the non-linear adsorption kinetics and ensure convergence, as illustrated in **Figure 6**. The competitive Langmuir adsorption model was used to simulate the binding of Nd^{3+} and H^+ ions to the resin bead, capturing the sigmoidal shape and load time up to approximately 90% bead capacity (**Figure 7**). Above 90% capacity, the model overpredicted loading, which is

assumed to stem from micropores that control the remaining 10% capacity and have decreased diffusion rates.

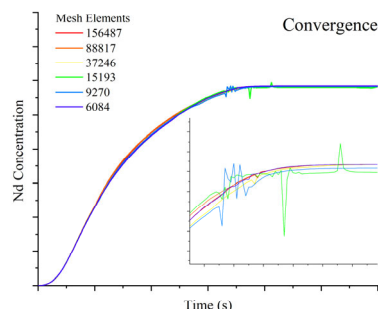


Figure 6. Convergence of simulated Nd concentration as a function of time for varying mesh element counts, demonstrating the need for fine meshing to resolve non-linear adsorption kinetics.

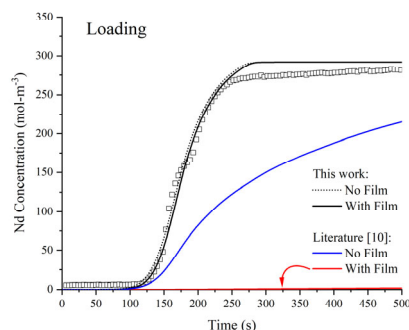


Figure 7. Comparison of simulated Nd loading profiles using parameters from this study versus literature values for intraparticle and film diffusion, illustrating improved model agreement with experimental data when using higher diffusion rates. Squares are experimental data from Magnuson et al. [3].

The best fit in this model was derived using a film diffusion model where both the film and intraparticle matched the bulk diffusion rate of $1.25\text{E-}9 \text{ m}^2\cdot\text{s}^{-1}$. Inclusion of the film resulted in marginal improvement on the predicted loading curve, but the findings suggest that film diffusion is greatly enhanced in the MFD. The loading process is much faster when compared to simulations using experimentally derived values of $1.4\text{E-}10 \text{ m}^2\cdot\text{s}^{-1}$ for film and $1.2\text{E-}13 \text{ m}^2\cdot\text{s}^{-1}$ for intraparticle diffusion from separation of other REEs on Dowex 50W-X8 in acidic conditions [10]. The results suggest that future evaluation of resins for IX separation within the MFD can occur on extremely faster timescales than full column studies due to the enhanced flux into the bead.

Parameter fitting was an essential part of the workflow for the elution simulations. The initial simulation with a factor of $X = 100$ showed significantly faster elution than suggested by the experimental data in **Figure 9**. The preliminary results indicated that the affinity for H^+ was too high, so the ratio of the affinity for Nd to H^+ was further increased up to a ratio of 1000:1. Decreasing the H^+ affinity slowed the elution of Nd in the adsorption model. Results suggest that the affinity of H^+ is ~ 1000 times lower than that of Nd^{3+} . The profile was not fully captured, as observed by the difference in the slope of the elution curves up to ~ 300 seconds in **Figure 9**, suggesting further refinement is needed.

While loading and elution results were captured well by the model, future work must be completed to address washing of the ion exchange resin during the IX process. Additionally, other cations, such as the various Nd nitrate complexes, almost certainly exist in the experiment and need to be included in the future. Addition of these other cations may improve loading simulations if the slow plateau in loading stems from competition with other cations as opposed to the hypothesized micropores. Elution predictions may also improve once all competition within the system is simulated.

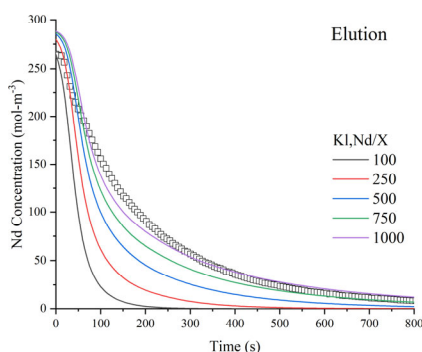


Figure 8. Comparison of simulated Nd elution profiles using different H^+ affinity values, illustrating improved model agreement with experimental data when using a lower H^+ affinity. An affinity ratio of 1000:1 for Nd and H^+ resulted in the closest approximation. Squares are experimental data from Magnuson et al. [3].

Conclusions

This work has simulated IX chromatography within a novel 3D-printed MFD for REE separation. The integration of ray optics, laminar flow, and transport in porous media modules enabled detailed simulation of both the optical and chromatographic performance of the device. Ray optics simulations revealed that the current MFD design transmitted up to 50% more light between the source and detector

compared to initial geometries, enhancing experimental UV-Vis absorption analysis.

The competitive Langmuir adsorption model was validated against experimental data. The adaptive model successfully predicted Nd loading profiles up to 90% bead capacity range. The use of higher diffusion rates than anticipated was required to match experiments on a single Dowex 50W-X8 bead. This critical finding suggests that evaluation of resins for REE separation using continuous flow and a single resin bead in a microfluidic device can be done significantly faster than evaluation with full columns or batch applications, providing an innovative screening tool to accelerate REE separations using IX. The modeling approach required fewer input parameters and less experimental calibration, which streamlines future simulation efforts.

These findings impact rapid prototyping and optimization of MFDs for REE separation. The ability to accurately simulate IX processes in MFDs could accelerate the development of efficient and high-throughput analytical platforms for both research and industrial applications. Future simulations will focus on the washing step in the IX process and incorporating all cations in solution. Once validated, the future model can be used to simulate entire separation flowsheets on the microfluidic device. This model will serve as a critical tool (i.e., digital twin) to predict optimal experimental conditions in the MFD for evaluation of IX resins to enhance large-scale REE separations.

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