Selective Recovery Of Rare Earth Elements From Mining Influenced Water Using A Sulfonic Acid Resin: Evaluating Competitive Adsorption With Iron

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Abstract

Rare earth elements (REEs) are critical for modern technologies but sourcing them is environmentally hazardous and monopolized by certain regions. Mining influenced water (MIW) presents a potential sustainable alternative source. This study evaluates ion exchange (IX) for REE extraction in the presence of high iron (Fe) concentrations, assessing the selectivity of a sulfonic acid IX resin. Batch adsorption experiments were conducted, and equilibrium data were fitted to multicomponent isotherm models. Results indicate that while Fe exhibited high adsorption due to abundance, it had low selectivity, whereas REEs showed significantly stronger affinities. These findings highlight the potential of IX for sustainable REE recovery from MIW.

Keywords: Rare earth elements (REEs); Acid mine drainage (AMD); Ion exchange technology; Circular economy.

Introduction

Rare Earth Elements (REEs) Click or tap here to enter text.are essential for the production of high-performance magnets, electric vehicle (EV) batteries, wind turbines, and various electronic components. Their unique magnetic, optical, and catalytic properties make them indispensable in a wide array of industries, from renewable energy to defence applications (McLeod and Krekeler 2017). The global supply of REEs faces mounting challenges (including geopolitical tensions, environmental concerns, and economic dependencies) that threaten long-term sustainability (Massari and Ruberti 2013). A small number of regions dominate REE production (Fig. 1), creating a geographic monopoly that leaves global markets vulnerable to trade restrictions and political shifts (United States Geological Survey 2024).

Traditional REE extraction and processing generate hazardous waste, necessitating strict environmental regulation. Historically, REEs have been sourced from mineral ores such as bastnäsite, monazite, loparite, and lateritic ion-adsorption clays (Balaram 2019). However, with increasing pressure to reduce reliance on single-source suppliers, mitigate ecological impacts, and address the depletion of high-grade deposits, attention is shifting toward secondary sources. This strategy enables recovery from industrial waste, e-waste, and mine tailings. A particularly promising source is mining-influenced water (MIW), which often contain REEs and CRMs (Naidu *et al.* 2023). These streams offer both resource recovery and pollution mitigation by bypassing conventional processing, making them an attractive route for sustainable extraction.

Previous studies on REE recovery from MIW have focused on, and primarily

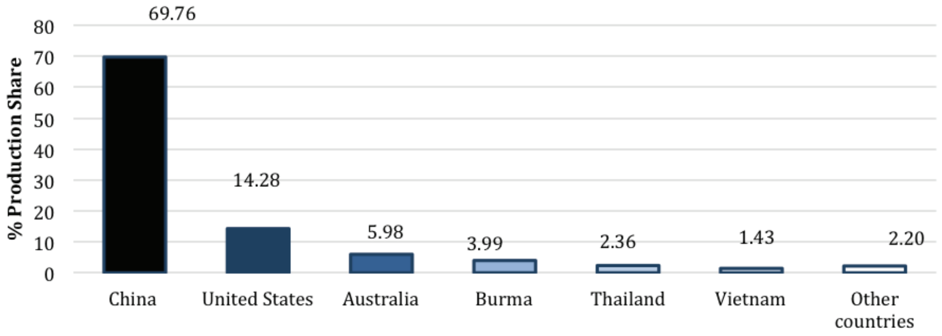

Figure 1 *Global REE Production Share 2023*

extracted, a select few elements, namely Y, La, Ce, Pr, and Nd, along with co-occurring metals such as Ca, Mg, and Fe (Smith *et al.* 2023). Techniques such as ion exchange (IX) have proven effective under specific conditions and are favoured in hydrometallurgy due to their metal affinity, stability, and reusability (El Ouardi *et al.* 2023). REEs span the lanthanide series, and each have distinct characteristics and uses – Eu in phosphors, Tb in magnets, and Gd in MRI contrast agents (Rademaker *et al.* 2013). Given their broad applications, a more inclusive recovery strategy is needed. This study aims to broaden this lens, focusing on the selectivity of a sulfonic acid cationic resin in extracting the full range of REEs from MIW in the presence of high amounts of Fe. This study evaluates resin selectivity using adsorption isotherms, specifically the Langmuir model, as well as empirical data.

Use of the Langmuir Model: The Langmuir isotherm describes monolayer adsorption on homogeneous surfaces, assuming no interaction between adsorbed species (Dada *et al.* 2012). Although these assumptions limit its use in complex, multicomponent systems, it remains a valuable predictive tool. Despite deviations from ideal behaviour, it has been shown to reasonably estimate adsorption capacities and equilibrium constants by capturing general trends. In MIW systems with competitive adsorption, it can still approximate equilibrium partitioning among available sites, offering insight into dominant interactions (Tangpromphan *et al.* 2016). Variants like the Multicomponent Competitive Langmuir Isotherm (MCL) improve applicability by incorporating ion competition (Misak 1995). Langmuir-based models have also been successfully applied to IX processes under non-ideal conditions (Jasim and Ajjam 2024).

In this study, the Langmuir model was selected due to its demonstrated success in similar systems (Calzaferri and Brühwiler 2024). While its assumptions limit predictive accuracy in complex, multicomponent systems like MIW, it is used here primarily as a tool to interpret adsorption behaviour and identify selectivity trends. Model refinements were introduced based on experimental data to better capture competitive effects; however, it is acknowledged that modifying isotherms outside their theoretical foundations (by empirically adding terms) compromises their general applicability. As such, the model's role here is illustrative rather than strictly predictive, with the core aim being the determination of REE selectivity coefficients.

Materials and Methods

A strongly acidic, gelular cation exchange resin, Lewatit® MonoPlus S 108 H (S108H), was sourced from CWENGA Technologies, South Africa, and Lanxess Deutschland. This styrene-divinylbenzene copolymer-based resin in H+ form was selected for its proven efficiency in metal removal and water demineralization, as supported by previous studies (Naidu *et al.* 2023). AMD samples were collected from a coal mine storage area in Emalahleni, Mpumalanga. Samples were stored in sealed polytetrafluoroethylene (PTFE) containers under constant temperature conditions. Seasonal and temporal variations in AMD composition were not accounted for, as these represent natural fluctuations encountered in real-world scenarios. To minimize adsorption losses in samples taken during the experiment, samples were preserved using nitric acid (0.6%), ensuring that dissolved metal adsorption onto container surfaces was negligible. Given that the MIW volume, the starting MIW conditions, resin quantity, and vessel type remained constant across all experiments, any potential variation was considered uniform and was assumed to not affect comparative adsorption results. The behavioural parameters of the IX system were evaluated through the following methods:

REE Content in AMD: The concentrations of REEs in the AMD samples were analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), following the methodology reported by Smith (2023).

Isotherm Parameters and Competitive Adsorption: Batch adsorption experiments were conducted using 900 mL AMD samples placed in glass bottles containing 45 mL of S108H resin. Samples were agitated for 72 hours at 23 °C at 200 RPM, after which the liquid phase was filtered through 0.45 µm syringe filters and analysed. Adsorption data were fitted to multiple isotherm models, including the extended MCL model to evaluate REE and CRM selectivity. To further enhance predictive accuracy, an interaction term was introduced into the MCL model. This term was iteratively determined by minimizing the difference between predicted and experimental adsorption results using nonlinear least squares optimization via the Levenberg-Marquardt algorithm. Additionally, empirical evidence, based on ratios of initial vs. final concentrations for each element, was used to validate the model predictions. Seven different AMD solutions with varying initial conditions (labelled 1–7) were used to assess system behaviour under different competitive adsorption scenarios.

Statistical analysis of adsorption variability was not conducted, as experiments were performed as single-pass trials without replicates; however, analytical precision was maintained through consistent experimental conditions and validated instrumental methods.

Results and Discussion

Initial Concentrations and Model Performance: The initial concentrations of selected elements in each experiment are presented in Table 1.

Adsorption data, representing equilibrium concentrations in each vessel, were fit to the simple Langmuir model. The residual plot for Nd illustrates the goodness-of-fit, with predicted values closely aligning with observed data (Fig. 2). This outcome confirmed the results of prior studies, reinforcing the Langmuir model's potential robustness in describing REE adsorption behaviour in multicomponent systems. Following the application of the simple Langmuir model, a modified Langmuir model was introduced to account for competitive adsorption effects. The resultant

***Table 1** Initial concentrations of Fe, Mg and select REEs in solution prior to resin contact*

	Elemental Concentration (mg/L)							
Experiment	**Fe**	**Mg**	**Ce**	**Nd**	**Eu**	**Gd**	**Yb**	**Lu**
1	6462	493.9	6.61	1.25	0.07	0.53	0.139	0.02
2	4006	477.4	8.27	1.18	0.07	0.53	0.128	0.018
3	1692.2	202.2	2.66	0.63	0.03	0.17	0.061	0.00913
4	781.3	101.3	1.27	0.30	0.01	0.08	0.029	0.00426
5	451.1	59.4	0.76	0.18	0.01	0.05	0.017	0.00259
6	187.9	26.3	0.34	0.08	0.004	0.02	0.008	0.00115
7	98.1	13.7	0.17	0.04	0.002	0.01	0.004	0.00057

equation from the iterative modeling process is presented below.

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

Where $Q_{e,i}$ is the equilibrium concentration of component i on the resin (mg/L), $Q_{e,i}$ is the maximum adsorption capacity for component *i* (mg/L), $K_{l,i}$ is the Langmuir affinity constant for component *i* (L/mg), $C_{e,i}$ is the equilibrium concentration of component *i* in solution (mg/L), $\eta_{l,i}$ is the interaction factor for component i, which modifies the competitive effect, and *N* is the total number of competing components in the system. The modification followed a similar approach to that used by Singh *et al.* (2024) for PFAS competitive adsorption equilibria on colloidal activated carbon. The equation quantifies how concentration-based competition (i.e., the presence of other ions) influences the Langmuir affinity constant (K_l) and maximum adsorption capacity (Q_m) for each element.

Initial guesses for Q_m and K_l were determined using the simple Langmuir model. Regression techniques were then used to obtain the optimal value for each term as well as the competition coefficient (η_l). Fig. 3 shows the normalized affinity coefficients obtained from this study which demonstrate that the resin exhibits a strong preference for REEs, with Fe and Mg showing substantially lower selectivity. Fe and Mg have selectivity coefficients which are 1 227 994 and 127 400 times less, respectively, than the REE with the highest affinity – Tm. Empirical data further support this trend; when comparing the average ratio of initial to final solution concentrations, Fe and Mg exhibited the lowest average adsorption relative to their initial concentrations (71 % and 76% respectively). Notably, in terms of measured concentrations, Ce demonstrated the highest average removal from solution (97%), deviating from model predictions. This discrepancy is likely due to Cerium's unique ability to exist in multiple oxidation states (Ce^{2+}, Ce^{3+} and Ce^{4+}), whereas other REEs predominantly exist in the trivalent state. The higher stability of Ce^{4+} in solution may result in enhanced adsorption relative to Ce^{2+} and Ce^{3+}, a factor not explicitly accounted for in the Langmuir model, which assumes a uniform adsorption mechanism. Consequently, the model provides an overall affinity for Ce without distinguishing between its oxidation states, potentially leading to an underestimation of its true selectivity. Further modelling or experimental validation is required to support this hypothesis.

Fit Assessment: Assessing the goodness of fit for non-linear models remains challenging, even when linear forms are applied. It is

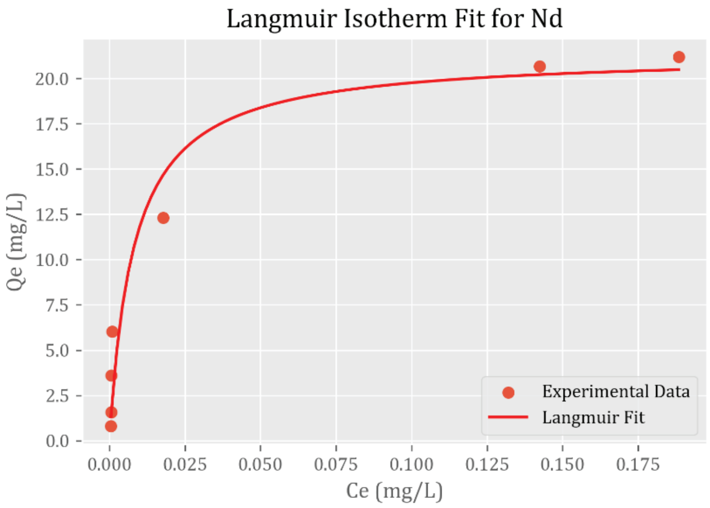

Figure 2 *Langmuir Isotherm Fit for Nd Adsorption onto Resin: Experimental Data vs. Model Prediction.*

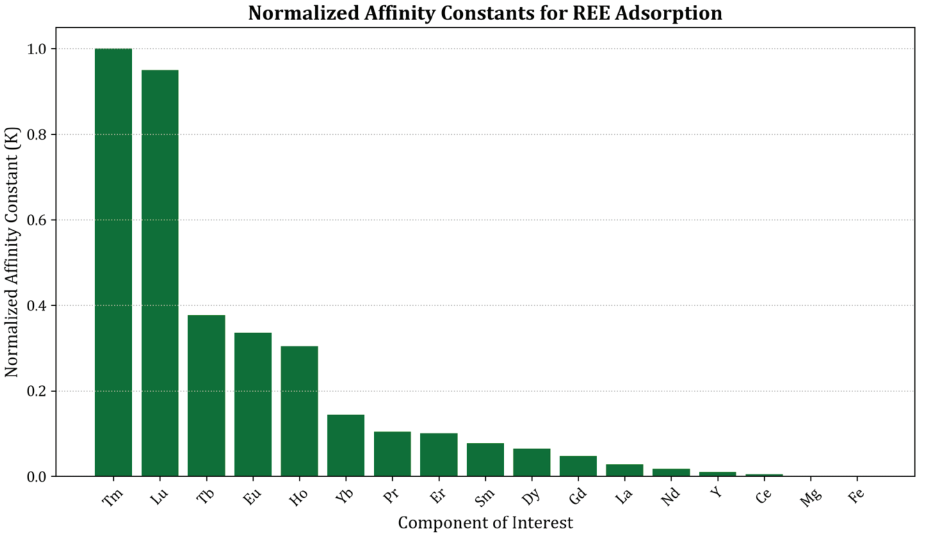

Figure 3 *Normalized selectivity of ions of interest in AMD solution using a modified extended Langmuir isotherm model.*

debatable whether using linear metrics like R^2 is mathematically valid post-linearization. Ideally, non-linear models should be evaluated in their original form for accuracy. During preliminary data analysis, multiple linearized versions of the Langmuir equation were explored (Mohammadi *et al.* 2012), to estimate initial Q_m and K_L values. Despite differences in transformation, a trend emerged: K_L values followed the same relative pattern, with Tm consistently showing the highest affinity. For mathematical reference, R^2 values for the linear fits are presented in Fig. 4.

The R^2 values indicate strong Langmuir fits for most REEs (all >0.99), except for Ce (0.96), Fe, and Mg (0.89–0.92). Ce's deviation is likely due to its variable oxidation states, which affect its adsorption behaviour compared to other predominantly trivalent REEs. Fe and Mg showed poorer fits due to several factors. Fe's high concentration, possible presence in both Fe^{3+} and Fe^{2+} forms, and low selectivity

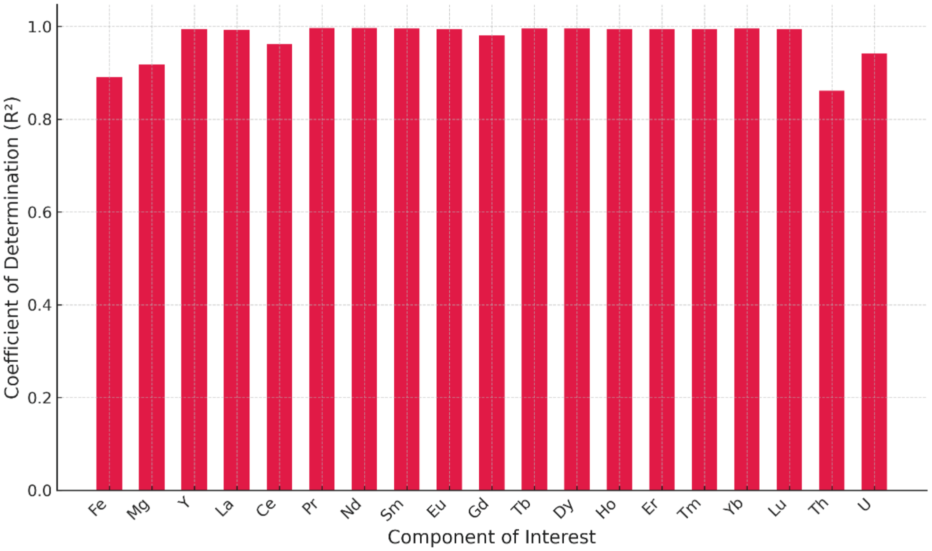

Figure 4 *Coefficient of Determination for all Elements analysed when fit to the simple Langmuir isotherm.*

for the resin likely led to non-ideal adsorption, including potential multilayer formation and competitive displacement. Mg, as a divalent ion, also deviates from the trivalent REE trend, weakening model applicability. These results underscore the limitations of the Langmuir model in complex systems with oxidation-state variation, competitive interactions, and non-monolayer adsorption.

Conclusions

Isotherm constants showed that Fe had high adsorption capacity (Q_m), consistent with its abundance in solution, but low selectivity (K_L), indicating adsorption driven by concentration rather than resin affinity. In contrast, REEs exhibited much higher selectivity, demonstrating strong binding to the resin even in the presence of excess Fe. The established selectivity sequence was: Tm > Lu > Tb > Eu > Ho > Yb > Pr > Er > Sm > Dy > Gd > La > Nd > Y > Ce >> Mg >> Fe. As shown in Fig. 4, REEs were adsorbed over Fe by several orders of magnitude, highlighting the S108H resin's potential for REE recovery. This sequence differs from earlier binary system studies (e.g., Hubicki *et al.* (1968)), likely due to the complex ion matrix of real AMD, which includes high sulfate levels and competing ions. Factors such as redox conditions, Al, Ca, and Total Organic Carbon may also influence selectivity, though not explicitly assessed here.

This study met its aim of evaluating REE selectivity in Fe-rich AMD using Langmuir-based modelling and empirical data. While Fe showed significant uptake, its poor selectivity reinforces the resin's potential for REE-focused separation. Future work should explore competing ion effects, optimize IX conditions, and assess performance in column systems. Cerium's unique behaviour, likely tied to redox variability, also merits deeper investigation.

Acknowledgements

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