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Deployment of Ion-Exchange Fluoride Capture and Recovery Technology Resins and Adsorption in High-Fluoride Regions of Tanzania

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Abstract

Fluoride contamination in water emerges as a major public health challenge in Tanzania. Elevated fluoride levels lead to severe health issues, such as dental and skeletal fluorosis and neurological impairment. While current fluoride mitigations techniques such as chemical precipitation and metal-based adsorbents facilitate the removal of fluoride efficiently up to 95%, these methods are hampered by poor ion-selectivity in complex water matrices, operational inflexibility, and the generation of secondary toxic waste. Hence, there is a crucial need for a selective and sustainable technique that not only removes fluoride but also enables the potential resource recovery of fluoride. This study aims to address these gaps by comprehensively evaluating the effectiveness of three chelating cation-exchange resins—synthesized and functionalized with Aluminum (Al), Cerium (Ce) and Lanthanum (La), for the selective adsorption of fluoride in aqueous solutions. The resins were tested against a simulated Tanzanian groundwater solution that was replicated containing competing co-ions. Batch adsorption experiments revealed that the Iminodiacetic Acid (IDA) resins loaded with Al (4.48 *mg/g*) demonstrated superior adsorption performance and affinity. The high selectivity for fluoride was further validated in continuous-flow column studies, confirming the robustness and selectivity of the IDA-Al resin system under dynamic conditions. These results highlight the potential of IDA-Al as an efficient and scalable solution for fluoride remediation in real-world applications.

Introduction

Fluoride exposure is a prime public health concern for many communities in Tanzania. The fluoride ion is formed when the highly electronegative element fluorine gains an electron. It is particularly found in the East African Rift Valley, which extends through Tanzania. The groundwater is reported to be a high fluoride zone where fluoride from underlying rocks contaminates water sources (Foat et al., 2023; Grandjean, 2019; Shaji et al., 2023). Moreover, the discharge of solid and aqueous waste from different industries could contribute to the contamination of water sources.

Individuals primarily consume fluoride predominantly through drinking water (Foat et al., 2023). Generally, the World Health Organisation recommends the optimal range of fluoride in drinking water is 0.5 mg/L to 1.5 mg/L in order for it to be beneficial to protect against cavities and develop bones (Fawell et al., 2004). However, long-term ingestion of fluoridated water above the suggested limits leads to adverse health effects such as dental and skeletal fluorosis (Bakar et al., 2025; Foat et al., 2023). Dental fluorosis is indicated by teeth discoloration and mottling of teeth, while skeletal fluorosis involves weakened bones and joints. Furthermore, Grandjean (2019) accumulated evidence arguing that prolonged consumption of excessive fluoride has further risks. Fluoride has neurotoxic effects in the early developmental stages of children. Exposure to fluoride in drinking water is associated with cognitive deficits in children. This issue of fluoride contamination in groundwater is a global problem, affecting not only Tanzania but also other countries such as Argentina, India and China (Shaji et al., 2023).

Current Techniques for the Defluoridation of Water

Chemical precipitation

Previous literature has documented multiple available defluoridation technologies used in Tanzania such as chemical precipitation, membrane technologies and metal-based adsorbents. Chemical precipitation is a conventional technique to extract fluoride from industrial wastewater. This method concerns converting soluble impurities to form an insoluble solid (precipitates), followed by the separation of these precipitates from water (Pathak et al., 2023). It involves lime (Ca(OH)_2) reacting with free fluoride in water to form fluorite (CaF_2), an insoluble compound that can be extracted and then recycled. With the additional introduction of alum which is the salts of aluminium (AlCl_3 or $\text{Al}_2(\text{SO}_4)_3$), aluminium serves as a coagulant and hydrolyses to form aluminium hydroxide (Devasthali et al., 2023). The remaining fluoride ions are adsorbed on to the flocks of aluminium hydroxide. Zhang et al. (2017) outline that precipitation allows for the extraction of 90-95% of fluorite from a pure sodium fluoride (NaF) feed. Whereas, only 78% of fluorite was recovered from industrial wastewater (Ezzeddine et al., 2014). Fluoride readily forms complexes since it can has high affinity towards multivalent cations. The presence of co-contaminants with fluoride complicates the removal and recovery of fluoride (Robshaw, 2020). While this method is effective in ideal conditions, it is less effective in recovering fluoride from an impure stream such as industrial water due to interference of other ions. Moreover, significant amounts of water-rich sludges are produced by this technique (Aldaco et al., 2007; Pathak et al., 2023; Yegon et al., 2025). Toyoda and Taira (2000) theorised that the water-rich sludges can potentially be recycled to attempt to eliminate sludges and costs. However, Aldaco et al. (2007) later found that fluoride could not be recovered as a valuable resource using precipitation and the process is highly energy-intensive.

An adaption of the chemical precipitation method used in Tanzania is the Nalgonda process (Devasthali et al., 2023). While general chemical precipitation emphasises the generation of fluorite to remove fluoride, this technique focuses on the co-precipitation part for fluoride to adsorb onto aluminium hydroxide. This technique also includes a bleaching step using bleaching powder ($\text{Ca}(\text{OCl})_2$) to disinfect water. This process is also prone to releasing highly concentrated alum, making it unsuitable for fluoride recovery (Yegon et al., 2025). Hence, these limitations emphasise the need for more eco-friendly and safer alternatives for fluoride remediation.

Membrane technologies

Another existing technique to separate fluoride is using membrane techniques such as reverse osmosis, nano filtration and electrodialysis. In this technique, molecules are isolated based on the molecular size, charge and diffusion properties through a thin semi-permeable membrane, removing all ions and minerals (Waghmare & Arfin, 2015). While membrane methods work effectively in low temperatures and function in automated conditions, large volumes of water are discarded in the form of brine (Mobeen & Kumar, 2017; Yegon et al., 2025). An additional remineralisation process will also be required to provide essential minerals in the water. This increases operational complexity to the process of recovering fluoride, making it less viable in developing settings where resources are limited.

Metal-based adsorbents

Comparatively, adsorption is the most used defluoridation technique to treat aqueous streams since its simple to operate, has an exceptional removal efficiency and are reusable (Yegon et al., 2025). Adsorption refers to the process of pollutants adhering from a liquid state onto a solid surface (Sinharoy & Chung, 2024). Activated carbon, alumina and chitosan are

frequently used as adsorbents. Loading metals allowed for higher capacity fluoride removal than unmodified adsorbents (Robshaw, 2020). However, these metal-based adsorbents lack the porous structures and functionalisation to selectively bind to target contaminants. There are also potential risks of leaching of these toxic metals into treated water, presenting a significant challenge to water remediation (Robshaw, 2020). Thus, while adsorption has potential for fluoride removal, there is a critical need for an adsorbent that combines high selectivity for fluoride, superior structural stability and eliminate the risk for secondary contamination. Given this gap in the literature, it motivates the investigation of functionalised resins as a safer and more efficient alternative.

Mechanism of Cation-Exchange Resins

To address these requirements, ion-exchange resins emerge as a promising candidate for fluoride removal. Resins are typically synthesised through free radical polymerisation of styrene, loosely crosslinked with minimal divinylbenzene (DVB) (“Building Plastic,” 2011). There are two types of commercially available resins which are generally used, gel type and macroporous type. The latter type contains an increased amount of DVB incorporated into the polymer chains (Robshaw, 2020). Although gel-type resins do have a greater ion-exchange capacity than macroporous type resins, they have lower mechanical strength making them less durable under high osmotic pressure (Robshaw, 2020). For this investigation, the macroporous type was selected to ensure structural stability under operational conditions.

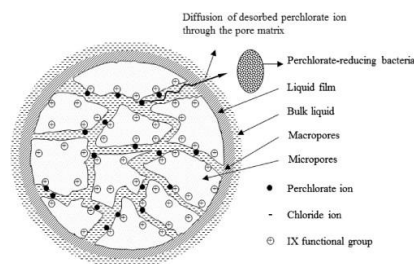


Figure 1: A Conceptual Model of a Resin's Structure illustrating the porous matrix and sites essential for ion-exchange (Sharbatmaleki et al., 2015)

Ion exchange refers to a reversible chemical process where ions in a solid phase (resins) and liquid phase (water) are transposed (Sinharoy & Chung, 2024). Literature has demonstrated that the standard anion-exchange resins are ineffective for the removal of fluoride. This is due to the order of these anionic species to select for these resins which is: citrate > SO_4^{2-} , oxalate > I^- > NO_3^- > CrO_4^{2-} > Br^- > SCN^- > Cl^- > formate > acetate > F^- (Helfferich, 1995). Since fluoride is the least selective ion, it can be easily displaced by other competitive co-existing ions in water, making it less effective in fluoride removal.

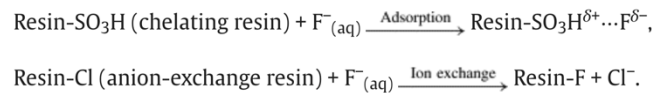


Figure 2: Chemical equation illustrating the mechanism of anion-exchange and cation-exchange resins (Meenakshi & Viswanathan, 2007)

Due to the limitations of existing anion exchange resins, cation-based exchange resins or chelating resins will be subsequently employed in this investigation for the target solution (Meenakshi & Viswanathan, 2007). Unlike anion-exchange resins, these resins function by leveraging the strong affinity of multivalent metal cations which are loaded onto the resin's functional groups (Liu et al., 2011). These immobilised cations can selectively bind to fluoride, forming strong inner-sphere complexes through ligand exchange (Robshaw, 2020).

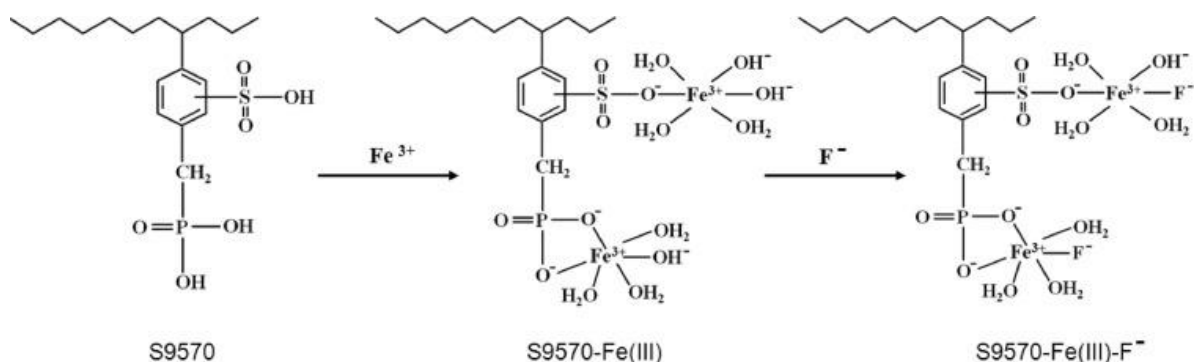


Figure 3: Depicts the Proposed Mechanism of Sulfonic and Phosphonic Cation-Exchange Resin, showing how cation can be immobilised exchanging a hydroxyl group(OH⁻) for a fluoride ion (F⁻) (Li et al., 2019)

Objectives

This present study evaluates the effectiveness of metal-loaded strong-acid and chelating-base cation exchange resins in the removal of fluoride from aqueous solutions. The experimental procedure was adapted and designed from the protocol established by Robshaw (2020). In this study, we report the adsorption capacity of these functionalised cation resins for fluoride with a detailed comparison under concentrated groundwater conditions. Understanding the adsorption capacity will allow for the real-world deployment of treating fluoridated water, bridging scientific innovation with public health crises.

Methodology

Adsorbent Material

This investigation employed three primary resin types: Aminomethylphosphonic Acid (AMPA), Iminodiacetic Acid (IDA) and Sulfonic Acid (SULF). These resins are characterised by their strong ability high affinity to heavy metal ions and demonstrated effective performance in conventional hydrometallurgical applications (Page et al., 2017). Macroporous variants of resins were selected for their ability to withstand high osmotic pressure encountered during frequent regeneration and reuse of sorbent bed. To enable selective fluoride adsorption, the metal ions Aluminium Al³⁺, Cerium Ce³⁺ and Lanthanum La³⁺ were loaded onto the functional groups of the resins. These metals were chosen based on abundance and high stability to form complexes with fluoride (Robshaw, 2020).

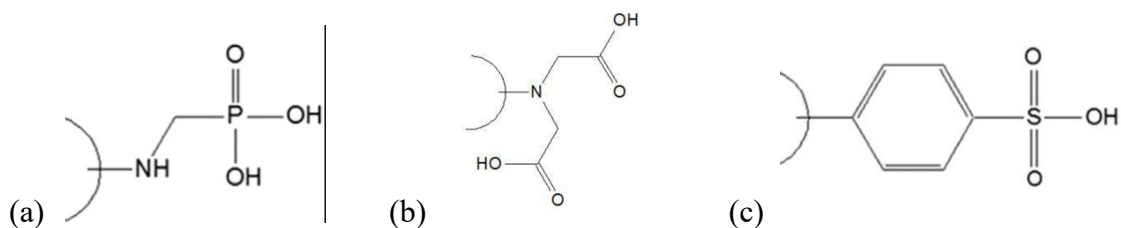


Figure 4: Chemical Structures of the Functional Groups Defining this Cation-Exchange Resins used in this investigation: (a) AMPA, (b) IDA, (c) SULF (Page et al., 2017)

Experimental Protocol

Pre-conditioning and Metal-Loading of the Resin

All the resins were purchased from commercial suppliers in their sodium (Na) form. Prior to loading the resins with metals, the resins need to be converted to their protonated form (H^+) to allow their functional groups to stabilise and selectively bind to the metals. This was achieved by mixing 25g of wet resin with 1 L of 1M Nitric Acid (HNO_3) in a volumetric flask. The mixture was placed on the orbital shaker and agitated for an hour at 500 rpm. Then, the resins were washed with deionised water. The resins were treated with Al by mixing 25g of wet resin with 1L of $10g \cdot L^{-1} Al^{3+}$. This metal ion solution was prepared by dissolutions of the chloride salts in deionised water. They were mixed in the orbital shaker and washed with deionised water, as previously done, which was followed by drying at air-flown oven at $50^\circ C$ for at least 24 hours. All the following experiments were repeated for the Ce^{3+} and La^{3+} loaded resins.

Batch Adsorption Experiments

Batch experiments were conducted at ambient temperature to analyse which loading metal ion would be appropriate to extract fluoride. Experiments were conducted in duplicate for each resin type at two initial fluoride concentrations: a low concentration and a high concentration. These concentrations were selected to simulate the groundwater conditions in Tanzania. In the standard process, 0.25 g of dry mass resins was contacted with 20 mL of known fluoride concentration solution in a 50 mL polypropylene screw-top tube. These tubes were tightly sealed and placed on the orbital shaker at 100 rpm for 24 hr. Afterwards, the solutions were analysed using a Cole Parmer Fluoride Ion-Selective Electrode. The concentrations of

fluoride in the samples were measured after contacting with the resin. The equilibrium adsorption capacity of fluoride was determined using the following equation below:

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

Where C_0 is the initial and C_e is the equilibrium fluoride concentration. V is the volume of solution (L) and m is the dry mass of adsorbent used.

Table 1: A Summary Table of the Experimental group Conditions of 36 Samples

Experimental Group	Type of Specimen	Number of trials (n)
Low Fluoride Adsorption (2 mg L ⁻¹)	AMPA-A1	2
	AMPA-Ce	2
	AMPA-La	2
	IDA-A1	2
	IDA-Ce	2
	IDA-La	2
	SULF-A1	2
	SULF-Ce	2
	SULF-La	2
High Fluoride Adsorption (200 mg L ⁻¹)	AMPA-A1	2
	AMPA-Ce	2
	AMPA-La	2
	IDA-A1	2
	IDA-Ce	2
	IDA-La	2
	SULF-A1	2
	SULF-Ce	2
	SULF-La	2

Adsorption Column Experiment

Following the batch experiments, the regeneration capacity of the IDA-Al sorbent was investigated using column experiments. Wet resin beads were loaded in a syringe column of 5 cm^3 in order to establish a zone where adsorption can actively occur (Robshaw, 2020). The simulant Tanzanian groundwater solution was passed through the column set-up in a flow rate of 4 $bv\ hour^{-1}$ using a peristaltic pump. Elution was then performed using 0.5M of sodium bicarbonate ($NaHCO_3$) solution. Subsequently, the column was rinsed with deionised water to flush out interstitial $NaHCO_3$. This was repeated 4 more times through the column until the column is completely exhausted.

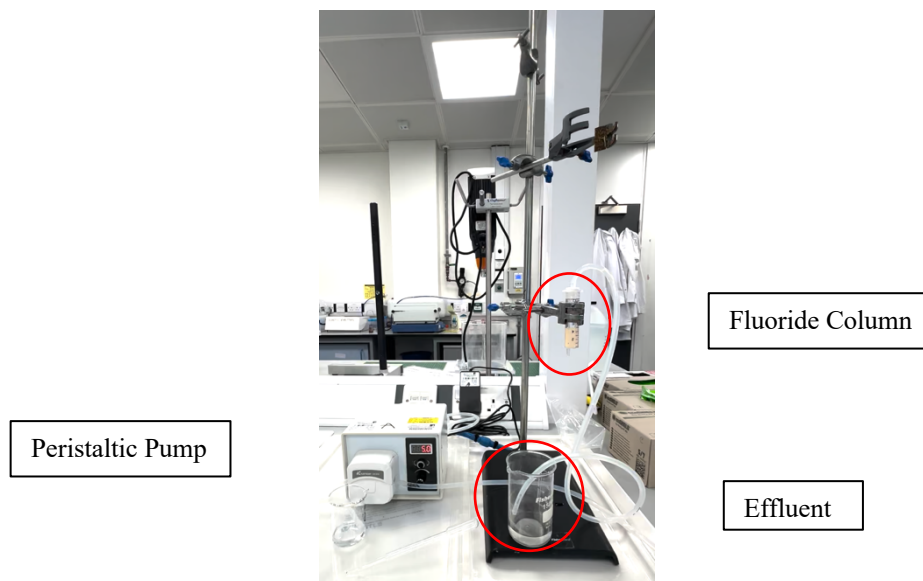


Figure 3: Laboratory Set-up for the Fixed-Bed Column Adsorption Column for Fluoride Removal

Statistical Analysis

A breakthrough profile was plotted by measuring the relative effluent concentration (C_e/C_0) against the volume of effluent. By integrating the area above the breakthrough curve, the dynamic adsorption capacity was determined. The curve also identifies other critical parameters such as the breakthrough time and the exhaustion time.

Results

Batch Adsorption Experiment

Table 1 Reveals the Equilibrium Adsorption Capacities of Low and High Concentration Across Different Adsorption Systems

System	Low Fluoride Concentration		High Fluoride Concentration	
	Average Adsorption Capacity (q_e , mg/L)	Uncertainty	Average Adsorption Capacity (q_e , mg/L)	Uncertainty
AMPA Al	0.0963	0.0070	3.76	0.07
AMPA Ce	0.117	0.004	1.10	0.05
AMPA La	0.0926	0.0042	1.12	0.01
IDA Al	0.128	0.001	4.48	0.54
IDA Ce	0.0623	0.0003	0.839	0.058
IDA La	0.0317	0.0386	0.474	0.200
SULF Al	0.117	0.003	3.50	0.17
SULF Ce	0.101	0.033	0.26	0.15
SULF La	0.0656	0.0329	-0.219	0.373

The q_e of all synthesised systems was evaluated in batch experiments at low initial fluoride concentrations to assess their performance (*Figure 4.1*). The adsorption capacity varied significantly cross different adsorbents. The results from the experiment revealed that IDA-Al has the highest adsorption capacity in comparison to other resins (0.128 mg/g), followed by SULF-Al and AMPA-Ce (0.117 mg/g). Notably, the La-loaded resins performed poorly in comparison to other resins in adsorbing fluoride. IDA-La (0.0317 mg/g) and SULF-La (0.0657 mg/g). Additionally, the La-based systems exhibited high uncertainty between replicates, particularly in IDA-La (± 0.0387), suggesting inconsistent adsorption behaviour or experimental challenges with this specific adsorbent. The low adsorption capacity and high variability of La-based systems indicate that this material is unsuitable for application under these conditions.

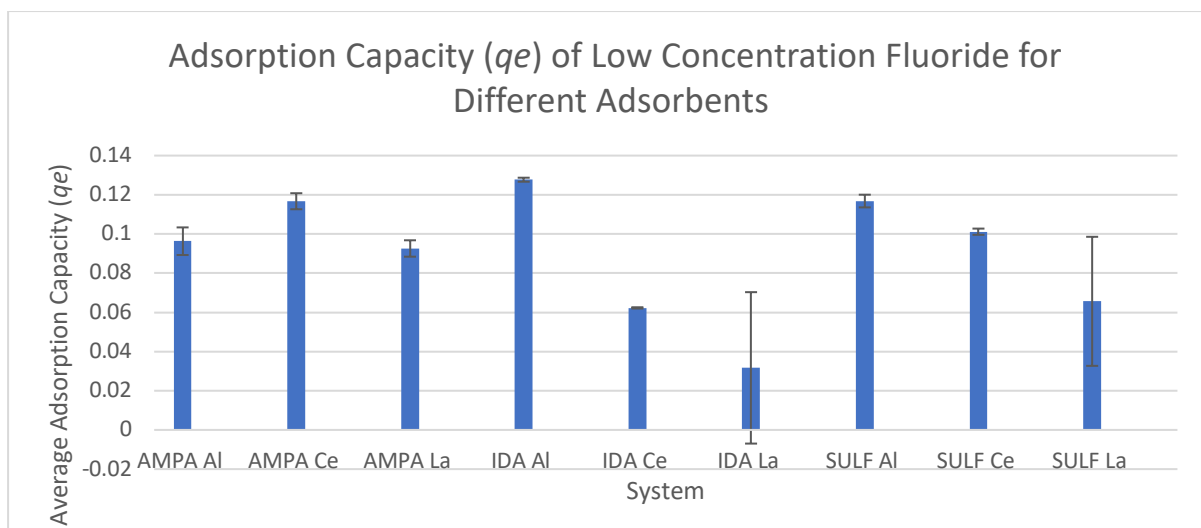


Figure 4.1 compares the adsorption capacity of low fluoride concentration across different adsorbents

In direct comparison with the q_e of the low fluoride concentrations, the q_e of the synthesised systems at high fluoride concentrations suggest that the Al-based systems has superior adsorption performance. Similar to the low concentrations, IDA-Al (4.48 mg/g) performed the best. In stark contrast, both the Ce-based and La-based systems yielded remarkably minimal adsorption capacities, with SULF-Ce (0.260 mg/g). Hence, IDA-Al was selected for the following fluoride column experiment.

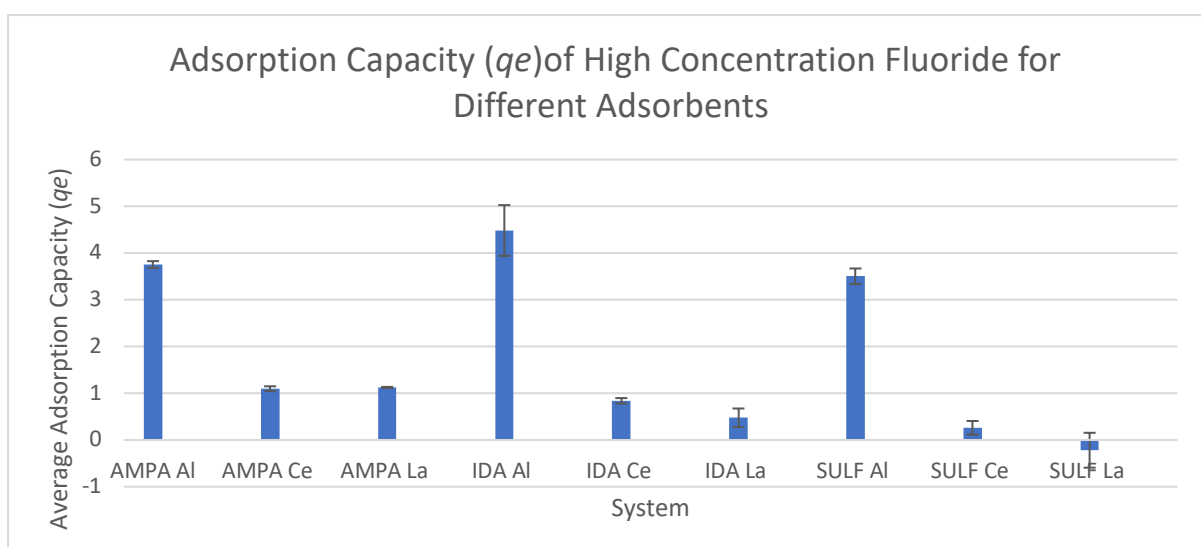


Figure 4.2 compares the adsorption capacity of high fluoride concentration across different adsorbents

Column Experiment

Table 3 Shows the Fluoride Breakthrough Data for IDA-Al

Fraction	Volume of eluent (mL)	Fluoride Concentration [F-]	[F-] uncertainty
1	7	1.02	0.23
4	28	1.93	0.05
7	49	2.63	0.00
10	70	4.16	0.00
13	91	7.77	0.23
16	112	12.4	0.2
19	133	12.7	0.1
22	154	19.3	0.1
25	175	22.2	0.0
28	196	24.5	8.2
31	217	22.6	0.7
34	238	22.9	4.2

The breakthrough profile was generated based on Breakthrough data presented in *Table 3*. The breakthrough profile in *Figure 5* exhibits a characteristic gradual sigmoidal S-shaped slope. Initially, the curve begins with a slow increase in fluoride concentration (7-91 mL), indicating that the adsorbent is highly effective in the beginning at removing fluoride. There is significant and consistent increase from 112 mL to 196 mL defining the mass transfer zone. This zone is when the fluoride concentration particularly transitions from high to zero. The extended length of this zone signifies slow adsorption kinetics. The process is likely restricted by the kinetics of intra-particle fluoride diffusion rather than the availability of adsorption sites (Ahamad et al., 2018; Valdez-García & Leyva-Ramos, 2023). The curve subsequently approached a plateau between 196 mL and 238 mL, revealing the volume range at which the adsorbent was completely saturated and no longer able to remove fluoride. The low uncertainties during the initial and rising phases of the curve emphasise the high reliability of the data. The curve seems to have higher uncertainties as it began to reach a plateau which is a

common phenomenon, resulting from concentration fluctuations as the system reached equilibrium.

The Dynamic Breakthrough Curve

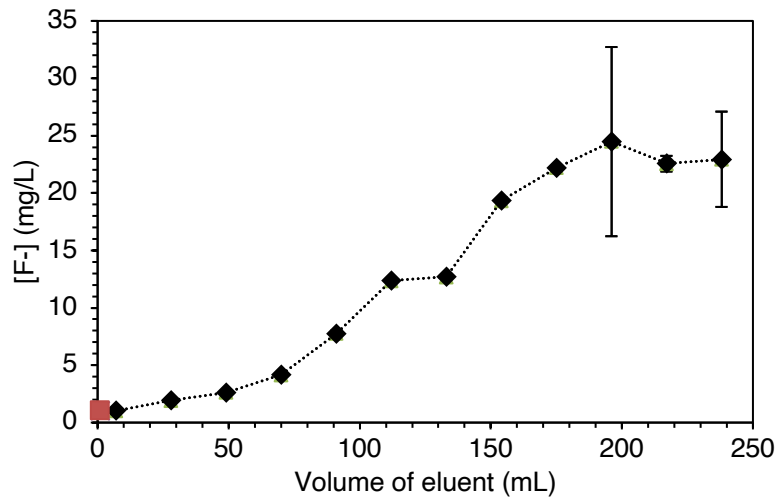


Figure 5: The Breakthrough Profile

Discussion

This study evaluated the efficacy three types of cation-functionalised resins for fluoride removal. The results show the potential for IDA-Al to be used for fluoride removal at high concentrations, exhibiting strong adsorption under operational settings using fluoridated columns. Al-based systems performed better compared to the Ce and La counterparts. This demonstrates that choice of metal ion used is critical factor in designing effective fluoride adsorption systems.

Batch Adsorption Experiment

The batch experiments provided a clear initial screening of the synthesised system. As shown in Figure 4.1 and 4.2, IDA-Al has significantly higher q_e values compared to other resins. Our findings were in line with previous research investigating adsorption behaviour of

IDA-chelating resins (Liu et al., 2011). Resins with the IDA functional groups are unique for having high capacity and selectivity for the features of metal ions including electronegativity and hydration energies (Liu et al., 2011). This was particularly evident in the Al-based systems which revealed as superior performance in fluoride removal. In reference to Pearson's Lewis acid-base theory, hard acidic Al exhibit a strong affinity towards hard basic fluorides (Ma et al., 2025; Robshaw, 2020). The first-coordination constant to form Al-F complexes is high ($\text{Log } K_1 = 6.10$) allowing it to form a stable complex indicating a favourable reaction, making Al-based systems highly efficient for defluoridation applications (Ma et al., 2025). However, our findings contradicted literature that described La-based adsorbents to be highly effective in fluoride removal due to high electronegativity (Yang et al., 2022; Yu et al., 2014). The poor performance of the La-based system in our research can be attributed to the high experimental uncertainties, indicating potential issues with inconsistency in ligand loading or synthesis reproducibility. While La-based systems have theoretical potential, producing effective La-based systems may present practical challenges. The drastically high performance of IDA-Al system in high fluoride concentration prompted its selection for further evaluation in a continuous-flow system.

Column Experiment

The breakthrough curve obtained for the IDA-Al column validates its effectiveness in a practical setting with a continuous flow. The characteristic S-shape curve illustrated in *Figure 5* is a typical breakthrough profile produced by fixed-bed adsorption. The extended mass transfer zone of reveals a strong adsorption capacity, as the column continued to remove fluoride for a significant time even after breakthrough. Moreover, the gradual slope implies that the process of is not instantaneous. The limited kinetics is likely governed by the intra-particle diffusion, where fluoride ions take time to migrate through the pores of the sorbent bed

rather than the scarce binding site (Ahamad et al., 2018; Valdez-García & Leyva-Ramos, 2023).

Limitations of Ion-Exchange Resins

A major limitation of this study is that the breakthrough profile was not modelled quantitatively. Given the short period of research, a complete dataset could not be collected to model the data. Future research should fit the data using models such as Thomason Model to determine precise rate constants (Robshaw, 2020). Additionally, the adsorption of fluoride using ion-exchange resins requires the production of significant amounts of pure water, representing another waste point as the resins must be regularly replaced upon exhaustion (Paudyal et al., 2017). While commercial ion exchange resins are effective and have a long operational lifespan, their high cost and the chemical waste generated limit their sustainability (Yegon et al., 2025). The stability of the IDA-Al should also be evaluated for the potential risk of leaching (Le et al., 2025). This emphasises the demand for novel, sustainable and high-capacity adsorbents without creating secondary waste streams.

Conclusion

In conclusion, IDA-Al has been identified as an effective adsorbent for fluoride removal. Its superior performance in batch tests and continuous column flow systems confirms its potential. It is a promising innovation that requires further development and optimisation to be used in water systems in Tanzania.

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Appendix

Batch Experiment Raw Data

Table 4.1: Adsorption Capacities (q_e) of Low Concentration Fluoride by Different Adsorbents

System	Trial	q_e	Average q_e	Uncertainty
AMPA Al low	AMPA Al low R1	0.09133031	0.0963099	0.00704221
	AMPA Al low R2	0.10128949		
AMPA Ce low	AMPA Ce low R1	0.11380979	0.11670323	0.00409195
	AMPA Ce low R2	0.11959667		
AMPA La low	AMPA La low R1	0.09555186	0.09259371	0.00418345
	AMPA La low R2	0.08963556		
IDA Al low	IDA Al low R1	0.12841617	0.12769799	0.00101567
	IDA Al low R2	0.1269798		
IDA Ce low	IDA Ce low R1	0.06205026	0.06227603	0.00031929
	IDA Ce low R2	0.0625018		
IDA La low	IDA La low R1	0.00434473	0.03166718	0.03863977
	IDA La low R2	0.05898962		
SULF Al low	SULF Al low R1	0.11909428	0.11680497	0.00323758
	SULF Al low R2	0.11451565		
SULF Ce low	SULF Ce low R1	0.10227763	0.1011536	0.00158962
	SULF Ce low R2	0.10002956		
SULF La low	SULF La low R1	0.08891452	0.06562969	0.03292973
	SULF La low R2	0.04234485		

Table 4.2: Adsorption Capacities (q_e) of High Concentration Fluoride by Different

Adsorbents

System	Trial	q_e	Average q_e	Uncertainty
AMPA Al high	AMPA Al high R1	3.80577524	3.75522138	0.07149395
	AMPA Al high R2	3.70466753		
AMPA Ce high	AMPA Ce high R1	1.06166058	1.09772657	0.05100502
	AMPA Ce high R2	1.13379257		
AMPA La high	AMPA La high R1	1.11601247	1.12405086	0.011368
	AMPA La high R2	1.13208925		
IDA Al high	IDA Al high R1	4.09834478	4.48256322	0.54336693
	IDA Al high R2	4.86678166		
IDA Ce high	IDA Ce high R1	0.7981447	0.8388957	0.05763062
	IDA Ce high R2	0.8796467		
IDA La high	IDA La high R1	0.33298963	0.47420702	0.19971156
	IDA La high R2	0.61542442		
SULF Al high	SULF Al high R1	3.62126157	3.50310404	0.16709998
	SULF Al high R2	3.38494651		
SULF Ce high	SULF Ce high R1	0.1567498	0.26016646	0.14625324
	SULF Ce high R2	0.36358313		
SULF La high	SULF La high R1	0.04426329	-0.219497	0.37301342
	SULF La high R2	-0.4832574		

Table 5: Raw Data of Breakthrough Profile

Fraction	Volume of eluent (mL)	t (min)	C _e (mg/L)	C _e /C ₀
1	7	16.509434	1.0223929 8	0.0408957 2
4	28	66.037735 8	1.9334967 6	0.0773398 7
7	49	115.56603 8	2.6274946 9	0.1050997 9
10	70	165.09434	4.1625726 7	0.1665029 1
13	91	214.62264 2	7.7680540 6	0.3107221 6
16	112	264.15094 3	12.357126 1	0.4942850 4
19	133	313.67924 5	12.694452 8	0.5077781 1
22	154	363.20754 7	19.334344 8	0.7733737 9
25	175	412.73584 9	22.214398 4	0.8885759 4
28	196	462.26415 1	24.482417 1	0.9792966 8
31	217	511.79245 3	22.558594 1	0.9023437 6
34	238	561.32075 5	22.944140 9	0.9177656 4