Zinc Recovery from Abandoned Mine Drainage: Insights from the Freiberg Mining Region, Germany

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Abstract

The study was done in the Freiberg mining region of Saxony, Germany, where significant loads of zinc are released into the Elbe River. The study aimed to identify optimal conditions for zinc recovery through pretreatment of mine water, a series of 100 mL scale column experiments, and optimising the regeneration process. Initial tests showed that Aminophosphonic functionalized TP 260 resin had a high affinity for aluminium, occupying 93% of the resin's capacity, while zinc capacity was limited to 0.2 eq/L. Incomplete aluminium deloading necessitated pretreatment via selective precipitation of aluminium at pH 6.0, which resulted in increased zinc loading capacity to 1 eq/L. Under optimized conditions, a zinc concentrate of 18.5 g/L with 100% recovery was achieved, with sulfuric acid proving more effective than hydrochloric acid for elution. SEM EDX analysis indicated residual acid on the resin, suggesting the need for further study on the long-term effects of resin capacity variation. The study also revealed that three drainage galleries in the Freiberg area currently contribute nearly 85 tons of zinc load to river Elbe annually. This research elucidates the feasibility of efficient zinc recovery from these point sources of pollution via refined ion exchange processes, supporting circular economy initiatives and environmental conservation efforts.

Introduction

Old mine water discharge galleries, often referred as adits or drainage tunnels can have many importance in now a day. They basically help in managing water flow inside the mine and prevent accumulation of unnecessary levels of water in abandoned mines. However, old mines often have waste dumps and mined out areas that can generate acid mine drainage once they are exposed to water, oxygen, and necessary microbial processes (Wolkersdorfer, 2022). Therefore, sometimes the discharge galleries can transport metal loaded acidic waters to the recipient rivers causing negative impact on surrounding ecosystem and water sources. One main example of this process can be seen in Freiberg area, Germany. According to the literature, the mine water discharge galleries in the Freiberg area are particularly significant, contributing to 37% of the zinc contamination found at the end of the Elbe River (Martin *et al.*, 1994). However, due to water dilution, zinc concentrations at the mouth of the Elbe River are very low. However, if some or all of the zinc could be recovered at the discharge point, it would considerably reduce downstream contamination over the 400 km stretch and could also yield intermediate products that contribute to a circular economy.

Therefore, this study is focused on selectively recovering zinc from mining influenced water via ion exchange. As a first step, we characterized the different mine waters in the Freiberg area and compared the results with historical values from the literature (Baacke, 2000; Degner, 2003). Our results indicate that zinc loads have significantly decreased over the past two decades (Table 1). However, the Freiberg mine water galleries continue to discharge approximately 85 tons of zinc annually into the Mulde River. Moreover, sampling revealed elevated zinc concentrations of up to 20 mg/L and lower pH levels in water discharged from the VGS mine water gallery. Geochemical analyses revealed a considerable change in water composition in the VGS gallery during heavy rainfalls, while the waters in the other galleries show minimal changes (Fig. 1). Therefore, this study utilized water collected from the VGS mine water gallery (Königliche Verträgliche Gesellschaft Stollen) in Freiberg, Germany.

Based on many literatures, amino phosphonic-functionalized TP 260 resin was selected to recover zinc (Hubicki *et al.*, 2015; Jurrius *et al.*, 2014). After preliminary filtration using a 0.45-micron filter, the mining-influenced water was pumped into a 100 mL column containing TP 260 resin at a flow rate of 10 BV/h. It's important to note that in some of our earlier small-scale tests (1 BV = 10 mL), a flow rate of 10 BV/h was challenging to manage due to turbulence generated within the resin bed. However, at a 100 mL scale, the same flow rate was manageable, as the weight of the resin and the increased length of the resin bed mitigated the turbulence. Initial ion exchange experiments revealed that the TP 260 resin exhibited a strong affinity for aluminum in the water matrix (Fig. 2a), utilizing nearly 93% of its operational capacity (1.8 eq/L). The VGS water had an aluminum concentration between 4–8 mg/L. Due to the higher adsorption of aluminum, zinc was only loaded up to 0.2 eq/L. It seems that phosphonic group in the resin forms stronger coordination bond with Al^{3+} due to its higher oxidation state (+3). Therefore, most of the potentially toxic metals ions such as Cu^{2+}, Co^{2+}, and Ni^{2+}, which have lower oxidation state (+2) will be displace by the presence of Al^{3+} in a considerable concentration.

The de loading with 10% sulfuric acid was only able to elute 15% of the Al^{3+} loaded on to the resin. This result depicts that aluminum could not be entirely removed from the resin during deloading. This could mainly hinder the operational capacity and long-term sustainability of the resin. Further studies could be done with loaded resins to

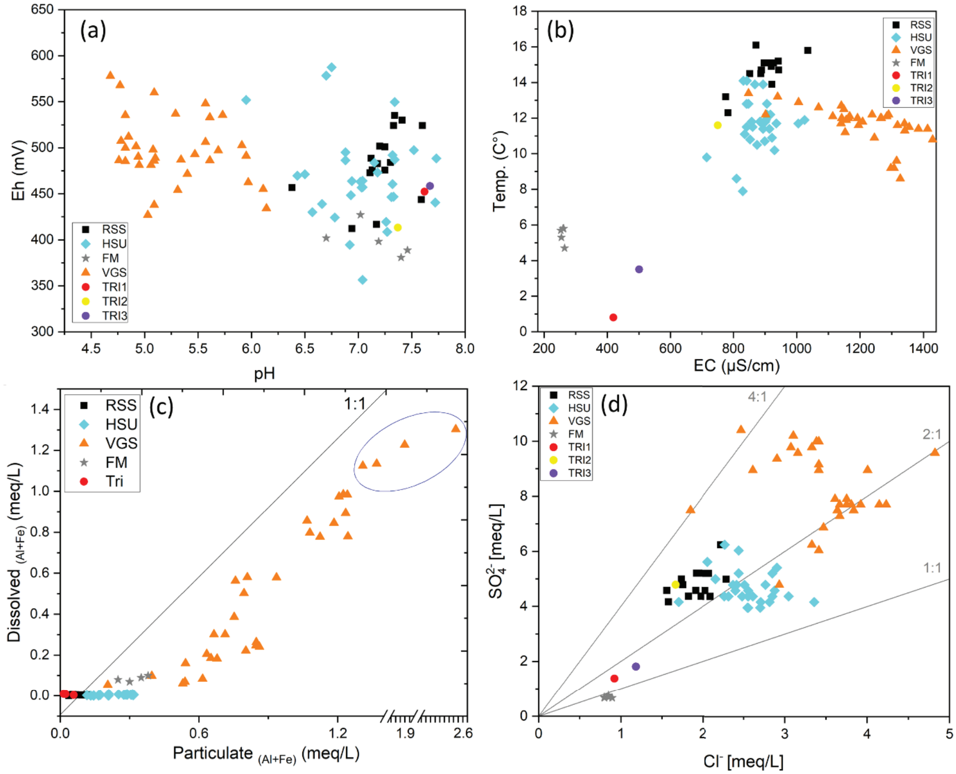

Figure 1 *a) Eh-pH diagram; b) Temperature versus electrical conductivity diagram of the Erzgebirge mine waters; c) Ratio of Particulate to dissolve Al+Fe; d) The relationship between Chloride and Sulfate (Rothschönberger Stollen – RSS; Hauptstolln Umbruch – HSU; Königliche Verträgliche Gesellschaft Stollen – VGS; Freiberger Mulde – FM; Triebisch River –Tri).*

understand the bonding between resin and Al^{3+}. However, due to the limited time, the study was primary focused on identifying a solution to remove Al^{3+} from the mining influenced water before the ion exchange process. Consequently, pretreatment step of the mining-influenced water was introduced to selectively precipitate and remove Al^{3+}. Raising the pH to 6 led to forming aluminum hydroxide precipitate, removing approximately 92% of the dissolved aluminum. Aluminum removal reached 100% at pH 7, but decreased slightly at pH 8 due to the redissolution of aluminum hydroxide. Zinc precipitation began around pH 5.5 and reached 100% at pH 8. Based on these findings, a pH of 6 was determined to be optimal for pretreatment, effectively removing most of the Al^{3+} with minimal zinc loss (approximately 15%).

When pre-treated water was introduced to 100 mL column filled with the TP 260 resin, the zinc loading capacity increased to 1 eq/L (Fig. 2b–2d). Even though some Al^{3+} were remained in the water (> 0.5 mg/L), it did generate a considerable effect on zinc loading. Under optimized conditions, the deloading process produced an 18.5 g/L zinc concentrate with 100% recovery (Fig. 2c). Sulfuric acid showed higher elution efficiency than hydrochloric acid during the deloading process. SEM EDX observation indicates that there are traces of acid composition on the resin surface even after washing the resins with distilled water, which might make the resin more acidic on the next loading cycle. Therefore, additional investigations are being conducted to evaluate the long-term sustainability of the resin and upscale the ion exchange system. The study also recommends

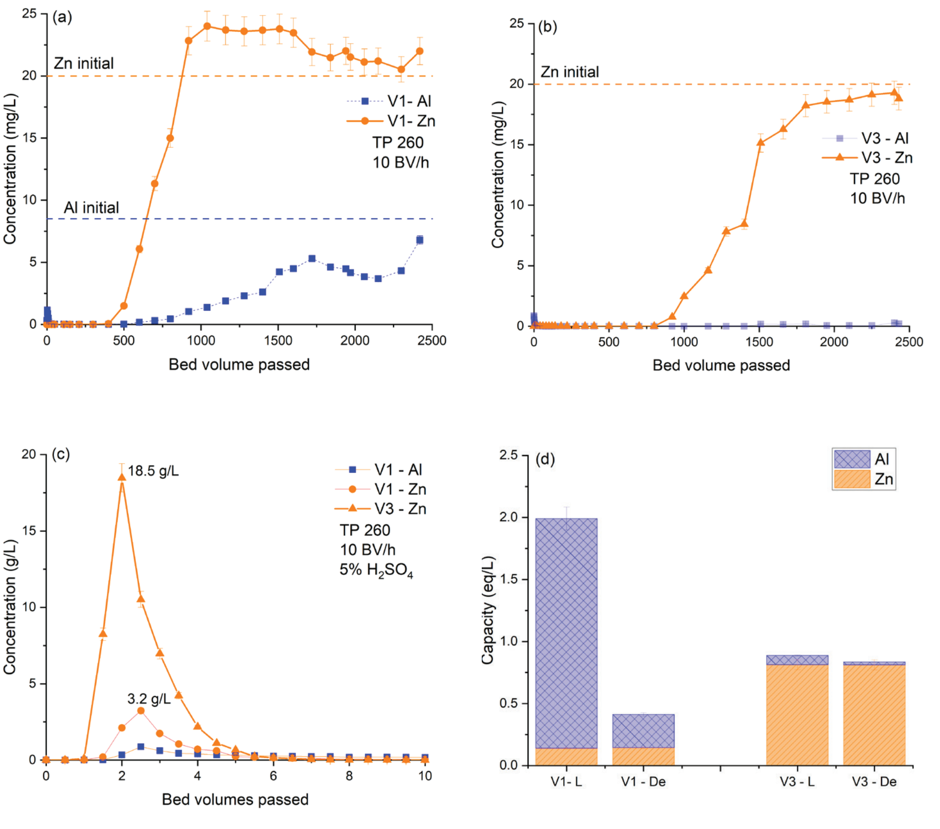

Figure 1 a) Breakthrough curves of untreated mine water (Zn and Al) loaded into IX column with TP 260 resin; b) breakthrough curves of pretreated minewater (after Al precipitation); c) De-loading curves of Zn and Al in untreated (column A) and pretreated (column B) mine waters; d) Mass balance of column A and B (L-loading, De-De-loading).

targeted sampling during extreme events and regular sampling of mine water discharges at Freiberg galleries to obtain more accurate freight determinations for recipient

Overall, through meticulous pretreatment to eliminate unwanted aluminium ions and refining deloading procedures, we have demonstrated the feasibility of efficient metal recovery from mining-influenced water via ion exchange. Scaling up the system will require evaluating water pretreatment strategies such as micro filtration or pH driven precipitation to maintain column performance while minimizing operational costs. Although aluminum was removed primarily to improve zinc recovery efficiency, future studies will examine the composition and potential value of the aluminum precipitate and its implications for material reuse or disposal. Moreover, successful implementation of this kind of technology has the potential to prevent significant amounts of metal loads from entering the recipient rivers and generate potentially exciting opportunities for metal recovery from point sources of contamination. The zinc concentrate produced in this study can be used for research purposes, such as developing new technologies or processes for zinc extraction or exploring novel applications for zinc-based materials. Moreover, it can also be used in environmental remediation such as soil stabilization where zinc can play a role in controlling pollution or promoting plant growth. Therefore, these endeavors contribute to a circular economy and serve as a pivotal measure in environmental conservation. Hence, further studies are recommended on upscaling the process.

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***Table 1** Comparison of Median Elemental Fluxes from Freiberg Mine Drainage Galleries to Receiving Rivers (This study vs Degner (2003)).*

Load (median)	HSU		VGS		RSS	
g/min	2003	2022	2003	2022	2003	2022
Na	51	96	140	67	1780	1021
K	11	16	19	10	250	141
Mg	65	80	178	76	970	697
Ca	180	261	410	240	3800	3097
Al	2.3	3	54	13	7.9	6
Fe	7.4	10	7	3	2.3	20
Mn	0.2	12	2	16	1.2	21
Si	NA	33	NA	18	NA	275
Zn	14	18	130	33	170	113
Cl	120	693	250	239	2180	2116
SO_4^{2-}	590	316	2200	851	11700	7243

Al, Fe, Mn, and Zn are given as total loads; other elements in dissolved loads; NA-: not available