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Review Article

Selective Recovery of Rare Earth Elements and Valuable Metals from Mining Wastewater by Membrane/Adsorption Hybrid Systems

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Abstract

Acid mine drainage (AMD) is a major global environmental issue and requires urgent sustainable treatment solution. There is a growing interest in recovering valuable materials from AMD as a way to offset treatment costs. In this study, two novel adsorbent materials—Cr-MIL-PMIDA (a chromium-based metal-organic framework) and SBA15-NH-PMIDA (a surface-modified mesoporous silica)—were developed and selectively recovered europium (Eu) from real acid mine drainage. Both adsorbents are highly effective for selective Eu adsorption; SBA15-NH-PMIDA offers superior capacity, selectivity, and regeneration potential; Membrane distillation combined with SBA15-NH-PMIDA enhanced both water reclamation and Europium concentration; The integrated approach transforms AMD into a resource stream, supporting both environmental and economic goals.

Keywords: Acid mine drainage; membrane distillation; selective adsorption; water recovery; rare earth elements

Introduction

Rapid industrial growth has led to considerable environmental degradation, with acid mine drainage (AMD) emerging as a major global issue. AMD forms when water infiltrates through mine waste, exposed rock surfaces, and sulfide-rich soils, leading to the formation of acidic, metal-laden effluents [1]. If left untreated, these acidic discharges pollute nearby water systems, contributing high concentrations of dissolved metals, sulphates, and acidity, which can severely disrupt aquatic ecosystems. Contaminated water poses significant risks to both human and animal health. Consequently, the search for efficient and economically viable AMD treatment solutions has become increasingly urgent [1]. The rising expenses associated with mining and tighter environmental regulations have made AMD treatment a financial burden for the industry [2]. This has sparked growing interest in recovering valuable materials from AMD as a way to offset treatment costs. With the depletion of conventional mineral sources, the mining sector is actively exploring alternative methods for metal recovery.

Conventional AMD treatment typically aims to neutralize pH levels and remove contaminants prior to discharge. While passive treatment methods are cost-effective, they often fail to meet regulatory standards without further refinement. As a result, more advanced treatment technologies—such as reverse osmosis, nanofiltration, and membrane distillation—are being considered. However, these options involve high installation and maintenance costs, especially due to the need for pre-treatment and frequent membrane replacement, making them less appealing for widespread adoption. To improve the economic feasibility of AMD treatment, the concept of resource recovery—particularly the extraction of valuable elements—is gaining momentum. Among these, rare earth elements (REEs) represent a promising opportunity. The global market for REEs was valued at approximately USD 2.8 billion in 2018 and is projected to grow at a compound annual growth rate of 10.4% between 2019 and 2025 [3]. Harnessing REEs from AMD could simultaneously support environmental protection and generate revenue, enhancing the overall sustainability of mining operations.

Several techniques have been explored for recovering REEs from AMD, including precipitation, adsorption, ion exchange, and solvent extraction [4-7]. Membrane-based methods—such as reverse osmosis, nanofiltration, and membrane distillation—have also been employed to concentrate REEs prior to recovery [8]. Among these, adsorption stands out for its simplicity and efficiency in extracting both REEs and heavy metals from contaminated water [4]. Various advanced adsorbent materials have shown significant potential for REE recovery. Notable examples include nanocarbon shells [9], magnetic nanoparticles [10], metal-organic frameworks [11], silica-based composites [10,12], and biosorbents [13]. These materials demonstrate high effectiveness in removing REEs from aqueous environments, positioning them as promising tools for sustainable AMD treatment and resource recovery. A significant limitation of current treatment technologies lies in their high operational costs and limited potential for regeneration, which hinders their implementation at operational mining sites [14]. As a result, there is a clear research need to identify affordable, efficient, and regenerable adsorbents that can be sourced easily and deployed effectively within the mining industry. Gaining insight into the economic value of recovered resources and deploying cost-effective, proven technologies can help reduce the reliance on primary mining operations. This not only mitigates additional environmental degradation but also supports the transition towards a circular economy by reclaiming valuable metals from waste streams.

The remediation of acid mine drainage (AMD), coupled with the recovery of valuable elements, aligns with the core principles of sustainable mining. These include minimizing environmental impact, managing waste more efficiently, and optimizing resource use. AMD is known to contain a range of valuable metals, such as rare earth elements (REEs). Extracting these from mine wastewater reduces pressure on natural resource extraction, reinforces circular economy strategies, and enhances sustainability in the sector. Economically, the recovery of such metals transforms waste into a profitable resource, supporting “by-product economics”—a model where previously discarded materials contribute to revenue generation. In this study, we focused on the targeted extraction of europium (Eu) from dissolved zinc mine tailings using specially engineered Chromium-based metal-organic frameworks (MOFs). Recognizing that powdered adsorbents are not practical for field-scale operations, we developed granulated forms of a novel modified mesoporous silica, SBA15-NH-PMIDA, to facilitate selective europium recovery from real-world mining effluent. Furthermore, we integrated this material into a hybrid treatment system combining direct contact membrane distillation (DCMD) and adsorption for simultaneous water purification and selective Eu recovery.

Targeted Europium Extraction Using Functionalized MOFs

We synthesized a functionalized Chromium-based MOF, Cr-MIL-PMIDA, designed for selective europium recovery from zinc-rich mining wastewater [15]. Characterization of the material confirmed key components such as chromium (Cr), nitrogen (N), and phosphorus (P). The Cr-MIL MOF displayed an exceptionally high surface area (exceeding 1000 m^2/g). FT-IR spectral analysis confirmed the presence of functional groups—hydrogen, carboxyl, carbonyl, and amine—indicating successful integration of the PMIDA moiety onto the MOF surface. Europium adsorption was found to be strongly pH-dependent, with optimal recovery observed at an equilibrium pH of approximately 5.5. At this pH, the surface of the adsorbent exhibited a strongly negative charge (zeta potential ~ -25 mV), resulting from the deprotonation of its functional groups. The Cr-MIL-PMIDA material demonstrated excellent selectivity for europium, even in the presence of high concentrations of other transition and alkaline earth metals. This selectivity can be attributed to the synergistic action of phosphonic and carboxylate functionalities, alongside residual amine groups, which enhance affinity for hard acidic REEs like Eu through specific electrostatic and coordination interactions.

Selective Recovery of Europium from Real Acid Mine Drainage by Using Novel SBA15-NH-PMIDA Adsorbent

This research focused on evaluating the performance of the newly developed SBA15-NH-PMIDA material for europium (Eu) adsorption and exploring the application of Direct Contact Membrane Distillation (DCMD) in acid mine drainage (AMD) treatment. SBA15-NH-PMIDA was synthesized using a novel two-step sequential functionalization process, marking its first-time preparation. A detailed suite of chemical and physical characterization techniques was employed to validate the successful synthesis and elucidate the adsorption mechanism [15,16]. Initial experiments were conducted using synthetic single-solute Eu solutions to determine optimal adsorption conditions. The most effective pH for Eu uptake was identified as 4.8. Equilibrium was achieved within 2 hours, and the material demonstrated a high adsorption capacity of 86.21 mg/g. To assess selectivity, further tests were carried out using real AMD samples sourced from an abandoned mine site in northern Norway. Results showed that SBA15-NH-PMIDA could selectively capture more than 80% of europium present in the AMD, while adsorption of other competing metals remained below 10%.

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It was observed that modifying the pH of the AMD not only prevented protonation of the adsorbent's functional groups but also facilitated the removal of competing ions such as iron and aluminum via precipitation, thereby improving selectivity for Eu. Infrared spectral analysis of the used adsorbent confirmed that selective uptake of Eu was driven by strong coordination interactions between Eu ions and functional groups such as phosphonates and carboxyls on the SBA15-NH-PMIDA surface. In terms of durability, the adsorbent retained over 90% of its original adsorption capacity across ten reuse cycles, highlighting its suitability as a cost-effective and sustainable option for europium recovery. Despite these promising results, granulating SBA15-NH-PMIDA remains essential for real-world application. Granulation enhances practical usability by improving material handling, minimizing pressure drop, increasing mass transfer efficiency, and supporting consistent performance at larger scales.

Membrane Distillation/Adsorption System for Selective Eu Recovery and Water Reuse from Mining Wastewaters

To enhance the practicality of SBA15-NH-PMIDA for industrial applications, the powdered adsorbent was granulated using a technique based on sodium alginate and calcium chloride, as described in previous studies [17]. Specifically, 1 gram of SBA15-NH-PMIDA powder was dispersed in 10 mL of a 1.5% sodium alginate solution. This mixture was then transferred into a 50 mL syringe and slowly dispensed into a 0.05 M $CaCl_2$ solution under gentle stirring at 100 rpm. The resulting spherical granules (average diameter: 2.0 ± 0.1 mm) were collected, sieved, and dried at 70°C for 12 hours. Further procedural details can be found in Ryu et al. [17] and Fonseka et al. [16]. To evaluate the viability of water reclamation and europium enrichment, Direct Contact Membrane Distillation (DCMD) experiments were conducted using synthetic AMD formulated to reflect the composition of actual AMD. The objective was to test the DCMD system's ability to produce clean water and concentrate trace-level europium for subsequent recovery [18].

The DCMD apparatus featured a flat-sheet membrane module (surface area: 40 cm^2) integrated with a double-jacketed reactor. A commercial hydrophobic flat-sheet membrane made of polytetrafluoroethylene (PTFE) was sourced from General Electric (USA), with specifications including an average pore diameter of 0.22 µm, porosity of 70–80%, and thickness of 179 µm. The feed solution was maintained at 60 ± 0.5°C using a heat-controlled double-walled vessel, while the permeate was cooled to 20 ± 0.5°C with a chiller [19]. Both streams were circulated at a flow rate of 1.0 L/min using a gear pump. Permeate accumulation was monitored continuously via an analytical balance connected to a data acquisition system (AdamDU). Water samples were collected from the feed and permeate tanks at the start and end of each run, filtered through 0.45 µm syringe filters, and analysed for dissolved metals using ICP-MS (Agilent 7900, USA). Initial tests focused on quantifying Eu concentration and membrane solute rejection. Subsequently, trials were conducted by adding pre-weighed amounts of granulated SBA15-NH-PMIDA directly into the feed tank to evaluate combined water purification and selective europium adsorption [20].

Results demonstrated that SBA15-NH-PMIDA is both an economical and effective material for the selective capture of europium from mining wastewater. A novel cost-benefit analysis revealed that processing 1000 m^3 of AMD could yield 193.2 g of high-purity (99%) $EuCl_3$. Additionally, the clean water recovered via membrane distillation could be reused within mining operations, particularly beneficial in water-scarce environments. This integrated approach underscores the feasibility of combining water treatment and resource recovery to advance sustainable mining practices. The dual benefits—economic value from metal recovery and environmental gains from water reuse—align with global goals for sustainable development. By adopting such circular resource management strategies, industries can simultaneously reduce ecological footprints and support the transition to renewable, resilient systems.

Conclusions

Rare earth elements (REEs) are critical components in a wide range of modern technologies, including renewable energy systems and advanced electronics. Due to the ongoing depletion of conventional REE-rich mineral reserves, it has become increasingly important to explore alternative recovery sources to meet growing global demand. In this study, two novel adsorbent materials—Cr-MIL-PMIDA (a chromium-based metal-organic framework) and SBA15-NH-PMIDA (a surface-modified mesoporous silica)—were developed and evaluated for their effectiveness in selectively recovering europium (Eu) from mining wastewaters. The Cr-MIL-PMIDA adsorbent was synthesized to isolate Eu from a complex leachate derived from zinc ore. Adsorption studies indicated a maximum uptake of 69.14 mg/g at an optimal pH of 5.5. The material demonstrated strong selectivity for Eu, achieving 88% recovery in the presence of various coexisting ions (Na, Mg, Al, Ca, Mn, Fe, Ni, Cu, Co, Zn), which are commonly found in mining leachates.

Additionally, the SBA15-NH-PMIDA adsorbent was produced through a two-step surface functionalization using 3-aminopropyltriethoxysilane (APTES) followed by N-phosphonomethyliminodiacetic acid (PMIDA). Initial tests using single-component Eu solutions revealed rapid adsorption equilibrium within two hours and a maximum Langmuir capacity of 86.21 mg/g at pH 4.8. When applied to real acid mine drainage (AMD) collected from a disused mining site in northern Norway, the modified SBA15 material recovered over 80% of Eu while limiting the uptake of other metals to under 15%. The adsorbent maintained more than 90% of its original capacity across ten regeneration cycles, demonstrating strong durability and reusability for potential large-scale deployment.

To further evaluate practical application, granulated SBA15-NH-PMIDA was integrated into a Direct Contact Membrane Distillation (DCMD) system. The hybrid setup enabled simultaneous water purification and Eu recovery from synthetic AMD. The DCMD module, operated under optimized conditions, achieved approximately 80% water recovery and maintained a stable permeate flux of 7.0 ± 0.5 L/m²·h. As water was removed, Eu concentrations in the feed tank increased, which in turn enhanced the material's selective adsorption performance. The granulated adsorbent recovered nearly 90% of Eu, with minimal uptake of other metals, confirming its high selectivity and efficiency. Furthermore, the material demonstrated consistent performance across ten reuse cycles. The economic and environmental benefits of this approach are substantial. Recovering Eu from AMD not only helps address water contamination but also provides a source of valuable materials that would otherwise require costly mining operations. This dual benefit—waste remediation and resource recovery—supports a transition toward circular economy practices and more sustainable management of critical raw materials. DCMD combined with SBA15-NH-PMIDA enhances both water reclamation and REE concentration; The integrated approach transforms AMD into a resource stream, supporting both environmental and economic goals.

References

1. Naidu G, Ryu S, Thiruvenkatachari R, Choi Y, Jeong S, et al. (2019) A critical review on remediation, reuse, and resource recovery from acid mine drainage. Environmental Pollution 247(1): 1110-1124.
2. Nordstrom DK (2011) Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters. Applied Geochemistry 26(11): 1777-1791.
3. Research GV (2019) Rare Earth Elements Market Size, Share & Trends Analysis Report By Product (Cerium, Dysprosium, Erbium), By Application (Magnets, Catalyst), By Region, And Segment Forecasts, 2019 - 2025.
4. Anastopoulos I, Bhatnagar A, Lima EC (2016) Adsorption of rare earth metals: A review of recent literature. Journal of Molecular Liquids 221(6): 954-962.
5. Chen T, Yan B, Lei C, Xiao X (2014) Pollution control and metal resource recovery for acid mine drainage. Hydrometallurgy 147-148(1): 112-119.
6. Felipe ECB, Batista KA, Ladeira ACQ (2020) Recovery of rare earth elements from acid mine drainage by ion exchange. Environ Technol 42(17): 2721-2732.
7. Motsi T, Rowson NA, Simmons MJH (2009) Adsorption of heavy metals from acid mine drainage by natural zeolite. International Journal of Mineral Processing 92(1-2): 42-48.
8. Ambiado K, Bustos C, Schwarz A, Bórquez R (2016) Membrane technology applied to acid mine drainage from copper mining. Water Science and Technology 75(3-4): 705-715.
9. Xiaoqi S, Huimin L, Mahurin SM, Rui L, Xisen H, et al. (2016) Adsorption of rare earth ions using carbonized polydopamine nano carbon shells. Journal of Rare Earths 34(1): 77-82.
10. Zhang H, McDowell RG, Martin LR, Qiang Y (2016) Selective Extraction of Heavy and Light Lanthanides from Aqueous Solution by Advanced Magnetic Nanosorbents. ACS Appl Mater Interfaces 8(14): 9523-9531.
11. Lee YR, Yu K, Ravi S, Ahn WS (2018) Selective adsorption of rare earth elements over functionalized Cr-MIL-101. ACS Applied Materials & Interfaces 10(28): 23918-23927.
12. Hu Y, Drouin E, Larivière D, Kleitz F, Fontaine FG (2017) Highly Efficient and Selective Recovery of Rare Earth Elements Using Mesoporous Silica Functionalized by Pre-Organized Chelating Ligands. ACS Applied Materials & Interfaces 9(44): 38584-38593.
13. Das N, Das D (2013) Recovery of rare earth metals through biosorption: an overview. Journal of Rare Earths 31(10): 933-943.
14. Lèbre É, Corder G, Golev A (2017) The role of the mining industry in a circular economy: a framework for resource management at the mine site level. Journal of Industrial Ecology 21(3): 662-672.
15. Fonseka C, Ryu S, Choo Y, Naidu G, Kandasamy J, et al. (2024b) Selective recovery of europium from real acid mine drainage by using novel amine based modified SBA15 adsorbent and membrane distillation system. Journal of Water Process Engineering 56(4): 1045514-1045519.
16. Fonseka Charith (2024a) Selective Recovery of Rare Earth Elements and Valuable Metals from Mining Wastewater by Membrane/Adsorption Hybrid Systems. Doctor of Philosophy (PhD), University of Technology Sydney, Australia.
17. Ryu S, Fonseka C, Naidu G, Loganathan P, Moon H, et al. (2021) Recovery of rare earth elements (Lu, Y) by adsorption using functionalized SBA-15 and MIL-101 (Cr). Chemosphere 281(1): 130869-130875.
18. Gaikwad DR, SAM Dhirendra, DVG (2009) REMOVAL OF COPPER IONS FROM ACID MINE DRAINAGE (AMD) BY ION EXCHANGE RESINS: INDION 820.
19. Fonseka C, Ryu S, Choo Y, Mullett M, Thiruvenkatachari R, et al. (2021) Selective Recovery of Rare Earth Elements from Mine Ore by Cr-MIL Metal–Organic Frameworks. ACS Sustainable Chem Eng 50(9): 16896-16904.
20. Chen Z, Li Z, Chen J, Kallem P, Banat F, et al. (2022) Recent advances in selective separation technologies of rare earth elements: A review. Journal of Environmental Chemical Engineering 10(1): 107104-107108.