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TECHNICAL ARTICLE

Field Experimental Study of Sulfuric Acid Extraction from Acid Mine Drainage

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Abstract

This study presents a novel approach for extracting sulfuric acid from AMD. The proposed method comprises three stages: AMD pre-treatment, sulfate extraction, and electrolysis of sodium sulfate solution to produce sulfuric acid. Field experiments were conducted to evaluate the efficacy of sulfuric acid extraction from AMD. Results indicate that nano-zirconia hydroxide particles exhibit promising selectivity in adsorbing sulfate from AMD under low pH conditions. The sulfate adsorption rate reached 80%, with an energy consumption of 0.25 kW·h/kg for sulfuric acid generation. Techno-economic analysis reveals a levelized cost of sulfuric acid (LCS) of $0.83/kg, indicating the economic viability of the proposed method. This innovative approach addresses environmental concerns associated with AMD and presents a sustainable pathway for sulfate resource recovery and commercialized valorization.

Keywords Bipolar membrane electrodialysis device (BMED) · Nano-zirconium hydroxide particles · Resource utilization of acid mine drainage · Selective adsorption of sulfate

Introduction

Acid mine drainage (AMD) poses environmental challenges globally, arising from the accumulation of groundwater, surface infiltration, and production drainage during mining operations (Kefeni et al. 2018; Park et al. 2018). Characterized by a pH < 6.0, AMD is prevalent in major coal-producing nations, often leading to severe pollution issues (Geoffrey et al. 2014; Kefeni et al. 2017).

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A range of sustainable solutions has emerged to recover valuable resources such as sulfuric acid (H_2SO_4), non-ferrous metals, and rare earth elements from AMD (Aydin et al. 2019; Lopez et al. 2019; Park et al. 2013; Roa et al. 2024). The recovery of sulfuric acid within the chalcopyrite mining industry was initially proposed using an electrodialysis (ED) membrane process, with a case study conducted using wastewater from a chalcopyrite mine in Turkey (Aydin et al. 2019).

In the process of treating AMD, specific adsorption materials have been extensively developed and researched. Zirconium hydroxide nanoparticles have emerged as promising adsorbents with the capability to adsorb arsenic, sulfur dioxide, nitrogen dioxide, and sulfate from waters (Peng et al. 2022; Singh et al. 2012). Magnetic nanometer zirconia hydroxide, synthesized via the sol–gel method with nanometer ferric oxide, has been investigated for its adsorption performance regarding sulfate ions through static adsorption experiments. The study revealed a desorption rate of 90% and an adsorption capacity of 90 mg/g when sodium hydroxide (NaOH) solution was employed for desorption and subsequent readsorption of saturated magnetic nano zirconia. Experimental findings suggest that magnetic nano zirconia serves as an effective sulfate ion adsorbent and can be reused (Li et al. 2013).

The research results reported in the current literatures indicate that sulfate ions in water can be selectively adsorbed and desorbed, and form sodium sulfate. However, there have been no reports of field experiments of sulfuric acid extraction from AMD. So, we evaluated a sulfuric acid extraction technology for AMD using nano-zirconia hydroxide particles as a case study of the circular economy concept. This method contributes to both the treatment and resource utilization of AMD and demonstrates the potential for swift commercialization and valorization.

Principles and Technical Approaches

Sulfate ions (SO_4^{2-}) can be selectively adsorbed from AMD using nano-zirconium hydroxide ($ZrO(OH)_2$) under acidic environmental conditions (Li et al. 2013; Peng et al. 2022). Nano-zirconium hydroxide exhibits the unique ability to selectively adsorb sulfate ions from AMD under acidic environmental conditions (with the optimum pH value falling within the range of 2.0–3.0), demonstrating a distinctive performance in selective adsorption (Lu 2006). Once the adsorption capacity of the nano-zirconium hydroxide adsorbent is saturated, it transforms into $ZrOSO_4$, losing its ability to further adsorb sulfate ions. Regeneration of $ZrOSO_4$ is achieved through treatment with NaOH solution, converting it back to zirconium hydroxide ($ZrO(OH)_2$) and restoring its adsorption capacity. The resulting solution is sodium sulfate solution (Na_2SO_4), which undergoes electrolysis using a bipolar membrane electrodialysis device (BMED) in a subsequent stage. During the electrodialysis process, sulfuric acid (H_2SO_4) solution is generated in the anode chamber as an industrial product, while sodium hydroxide solution is produced in the cathode chamber (Aydin et al. 2019), which can be recycled as the regenerant for $ZrOSO_4$.

The nano-zirconium hydroxide adsorbent acts as ion exchanger, selectively adsorbing sulfate ions from the AMD. The adsorption chemical reaction is illustrated in Eq. 1.

$$ZrO(OH)_2 + SO_4^{2-} \rightarrow ZrOSO_4 + 2OH^- \quad (1)$$

The sulfate ion can be desorbed from the saturated adsorbent $ZrOSO_4$ by soaking it in a saturated NaOH solution. The chemical equation representing the desorption or regeneration reaction is illustrated in Eq. 2.

$$ZrOSO_4 + 2NaOH \rightarrow ZrO(OH)_2 + Na_2SO_4 \quad (2)$$

The production of sulfuric acid through sodium sulfate electrolysis in a bipolar membrane electrodialysis (BMED) device is illustrated in Eqs. 3 and 4.

$$H_2O \rightarrow 2H^+ + OH^- \quad (3)$$

$$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-} \quad (4)$$

In the BMED, sulfuric acid (H_2SO_4) solution is generated in the anode chamber, while NaOH solution is produced in the cathode chamber in Eqs. 5 and 6. (Aydin et al. 2019).

$$2H^+ + SO_4^{2-} \rightarrow H_2SO_4 \quad (5)$$

$$Na^+ + OH^- \rightarrow NaOH \quad (6)$$

Under the action of an external DC electric field, cations in the salt chamber permeate through the cation permeable membranes into the alkali chamber. Simultaneously, water in the alkali chamber undergoes electrolysis to produce hydroxide ions, resulting in the generation of alkali. Similarly, anions in the salt chamber permeate through anion permeable membranes into the acid chamber. In the acid chamber, water undergoes electrolysis to produce hydrogen ions, leading to the generation of acid. The process of sulfuric acid extraction from AMD is shown in the following schematic diagram (Fig. 1).

The main process of extracting sulfuric acid from AMD involves three stages: pre-treatment of AMD, extraction of

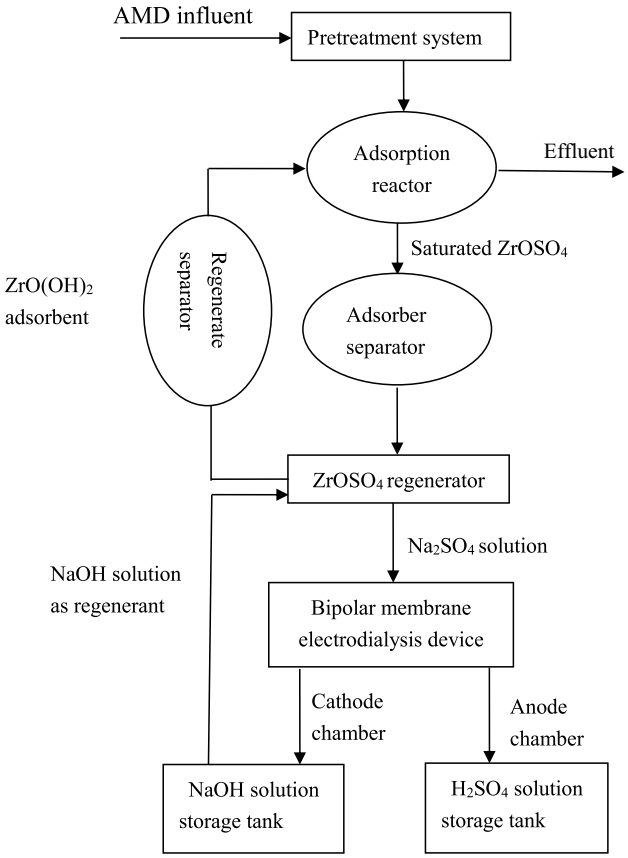


Fig. 1 Schematic diagram of sulfuric acid extraction from AMD

sulfate from AMD, and electrolysis of sodium sulfate to generate sulfuric acid.

Materials and Methods

AMD Water Sample

The experimental site was an abandoned coal mine in the Yudong River basin in southwest China, characterized by karst topography. The AMD in this area had sulfate (SO_4^{2-}) concentrations of 3,500–4,000 mg/L, iron ions Fe (II) ranging from 120 to 350 mg/L, manganese ions Mn (II) between 8.0 and 12.0 mg/L, and a pH of 2.5–3.5 (Guo et al. 2021). The AMD flowrate for the experiment was designed to be 1.0 m^3/h.

Adsorbent Materials

The sol–gel process was employed to fabricate nano-zirconium hydroxide, an adsorptive material, following established methods (Li et al. 2013; Lu 2006).

- Preparation method: sol-gel process.
- Raw materials: $ZrOCl_2{\cdot}2H_2O$, ammonia, deionized water, $AgNO_3$, anhydrous ethanol, polyethylene glycol (PEG2000).
- Process

  Stage 1: Prepare 2.0 mol/L ammonia aqueous solution and 1.0 mol/L $ZrOCl_2$ solution with a 5 wt% PEG2000 as a dispersant.

  Stage 2: Precursor mixing: simultaneously add $ZrOCl_2 \cdot 2H_2O$ and ammonia solutions into the reactor while adjusting addition rates via valves to maintain pH around 10. Stir continuously at an appropriate speed to ensure thorough mixing and reaction.

  Stage 3: Sol (colloidal suspension) formation: Prepare sol within 6 min, maintaining a 1:1 ratio of $ZrOCl_2$ solution to ammonia solution. Age the sol according to specified conditions. Wash and filter repeatedly with deionized water until chloride ions are absent. Confirm absence using 1 wt% $AgNO_3$ solution.

  Stage 4: Ethanol treatment: Inject anhydrous ethanol (sol amount to the anhydrous ethanol ratio 10:1) into the filter cake, mixing and stirring homogeneously. Dry in a constant temperature drying oven to obtain the sample.
- Influential factors or operation conditions: aging time 30 min, aging temperature 20 ℃, ultrasonic time 30 min (cycle time of 1:3), and drying temperature 80 ℃.

Since this study was a production experiment requiring a large quantity, the adsorbent was produced by Jiupeng New Materials Co., Ltd. in Hangzhou, China. This company specializes in new nano materials. (URL: www.jiupengap.com).

Experimental Device

The experimental device mainly comprised three modules: a pretreatment module, a sulfuric acid extraction module, and a sodium sulfate solution electrolysis module.

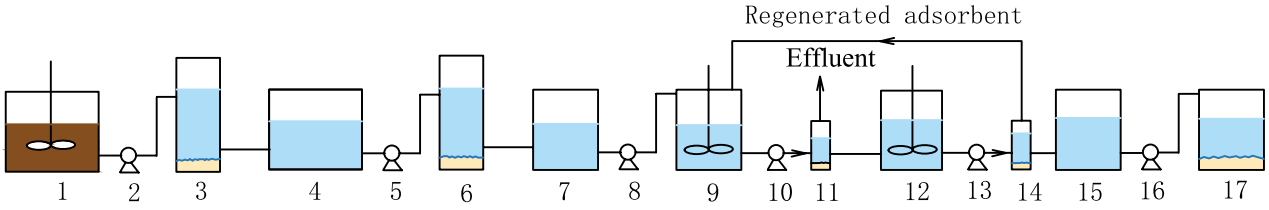
The pre-treatment module included a coagulation reactor, a quartz sand filter, and a manganese sand filter. Its primary function was to remove suspended solids (SS), iron ions, and manganese ions from the raw AMD to ensure the normal operation of the subsequent sulfuric acid extraction module.

The sulfuric acid extraction module comprised an adsorption reactor, a regeneration reactor, and a precision separation filter. The adsorption reactor selectively adsorbed sulfate ions from the pre-treated AMD using nano zirconia hydroxide adsorbents. The regeneration reactor was to restore the adsorptive capability of the saturated adsorbents.

The sodium sulfate solution electrolysis module's main function was to use a bipolar membrane electrodialysis device (BMED) to electrolyze the regenerated sodium sulfate solution. This process generated sulfuric acid solution in the anode chamber and sodium hydroxide solution in the cathode chamber. The BMED (Model JABCM-8040/20) was manufactured by the Beijing Tingrun Membrane Technology Development Co., Ltd in P.R. China, with the performance parameters of the ion exchange membranes shown in Table 1. The experimental device is shown in Figs. 2 and 3.

Table 1 Performance parameters of the ion exchange membranes

Membrane types	Resistance of membrane surface ($\Omega{\cdot}cm^2$)	Membrane thickness (mm)	Exchange capacity of membrane ($mmol{\cdot}kg^{-1}$)	Rate of water content (%)	Ion transference rate	Specifications (mm)
FAB anion exchange membrane	3	0.11–0.13	3.9×10^{-2}	25–30	0.98	800×400
FKB cation exchange membrane	5	0.11–0.13	4.3×10^{-2} 4.6×10^{-2}	25–30	0.96	800×400



Legends

1. Coagulation reactor
2. Feeding pump
3. Quartz sand filter
4. Intermediate water tank
5. Feeding pump
6. Manganese sand filter
7. Intermediate water tank
8. Feeding pump
9. Adsorption reactor
10. Feeding pump
11. Precision filter
12. Regeneration reactor
13. Feeding pump
14. Precision filter
15. Intermediate water tank
16. Feeding pump
17. BMED

Fig. 2 Schematic diagram of the field experimental device

Fig. 3 Photo of the field experimental devices

Water Quality Testing Methods

The Lab QC/QA adhered to the guidelines outlined in the "Measures for Quality and Safety Management of Water Quality Monitoring" Hydrology [2022] No. 136 issued by the Ministry of Water Resources of China and the water quality detection methods followed standards issued by the environmental protection departments of the Chinese government (Guo et al. 2021).

The pH was measured using the "glass electrode method", utilizing a PHS-3C meter manufactured by Shanghai Scientific Instrument Co., Ltd, China. The concentration of suspended solids (SS) was determined gravimetrically, following the Chinese standard "Water quality-Determination of suspended substance-Gravimetric method GB 11901-1989." Sulfate (SO_4^{2-}) was measured gravimetrically according to the Chinese standard of "Water quality-Determination of sulfate-Gravimetric method GB 11899–1989". The concentration of Mn (II) was assessed using potassium periodate spectrophotometric methods as per to the Chinese standard of "Water quality-Determination of manganese-Potassium periodate

spectrophotometric method GB 11906-1989". The concentration of Fe (II) was measured by ortho phenanthroline spectrophotometry following to the standard of "Environmental Protection Industry Standards of China" HJ/T 345-2007.

Pretreatment Experiments

The raw AMD water pretreatment experiment conditions: the flowrate of raw AMD water was controlled by an inlet valve, maintaining a hydraulic retention time (HRT) of 45 min in the coagulation reactor. The mixer speed was set to 150 r/min, and the dosage of coagulant PAC and flocculants PAM were 12.0 mg/L and 0.5 mg/L respectively. The filtering speeds of the quartz sand filter and manganese sand filter were controlled at 8.0 m/h.

Results and Discussion

Pretreatment Experiments

Figure 4 shows the removal effects of impurity contents, including SS, Fe (II) ions, and Mn (II) ions in the raw AMD water by the pretreatment process. The removal rates for suspended solids (SS) averaged 87.0% when the SS concentration fluctuated between 80 to 120 mg/L in the influent during the pretreatment period. For Fe (II) ions, the removal rates averaged 90% when the concentration of Fe (II) ions fluctuated from 120 to 350 mg/L. Similarly, for Mn (II) ions, the removal rates averaged 86.0% when the concentration of Mn (II) ions fluctuated from 8.0 to 12.0 mg/L. These pretreatment experiment results showed that the pretreatment met the expected requirements.

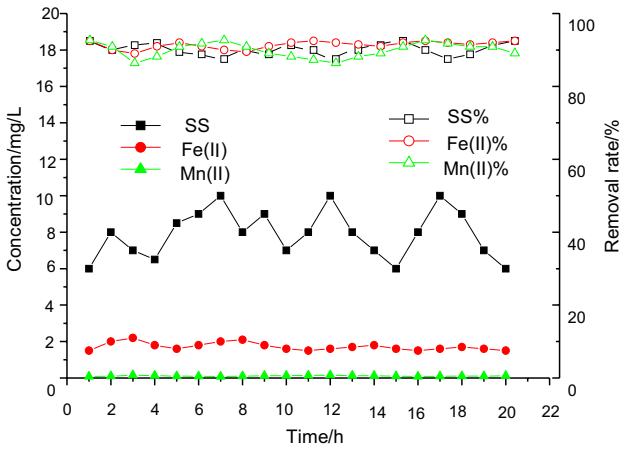


Fig. 4 Pretreatment effect for SS, Fe (II), and Mn (II)

Sulfate Adsorption Experiments

(1) Influence of AMD pH values on sulfate adsorption.

The influence of initial AMD pH values on the sulfate adsorption effect was investigated by adjusting its pH to 2.0, 3.0, and 4.0 in the adsorption reactor at a sulfate concentration of 3,500 mg/L and an adsorbent dosage of nano zirconia hydroxide of 30.0 g/L. The influence of AMD pH on sulfate adsorption is shown in Fig. 5. The sulfate adsorption rates reached 80% after 30 min when the initial AMD pH was 2.0. While the adsorption rate continued to increase, the rate of increase slowed down, and the adsorption curve gradually flattened over time.

When the initial AMD pH was 3.0, the sulfate adsorption rates reached 50.0% after 35 min. Similar to the previous case, the rate of adsorption continued to increase but at a slower pace, and the curve flattened gradually over time.

At an initial AMD pH of 4.0, the sulfate adsorption rate only reached 35% after 40 min, indicating a slower increase in the adsorption rate. The experiment results showed that the sulfate adsorption rates decreased gradually as the initial AMD pH increased.

(2) Relationship between sulfate adsorption rate and time.

The variation of sulfate adsorption rate with adsorption time was investigated at an AMD pH of 2.5 and a sulfate concentration of 3,500 mg/L. The experiment examined the sulfate adsorption rate over time with different dosages of nano zirconia hydroxide: 10.0 g/L, 20.0 g/L, and 30.0 g/L. The results showed that the sulfate adsorption rates increased with higher dosages of nano zirconia hydroxide. At a dosage of 30.0 g/L, the sulfate adsorption rate reached 64.2% after 30 min, and 78.5% after 60 min. The sulfate adsorption rate

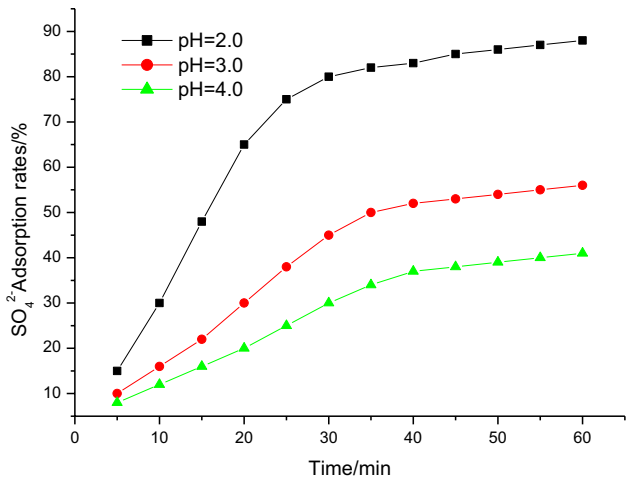


Fig. 5 Influence of the AMD pH on sulfate adsorption

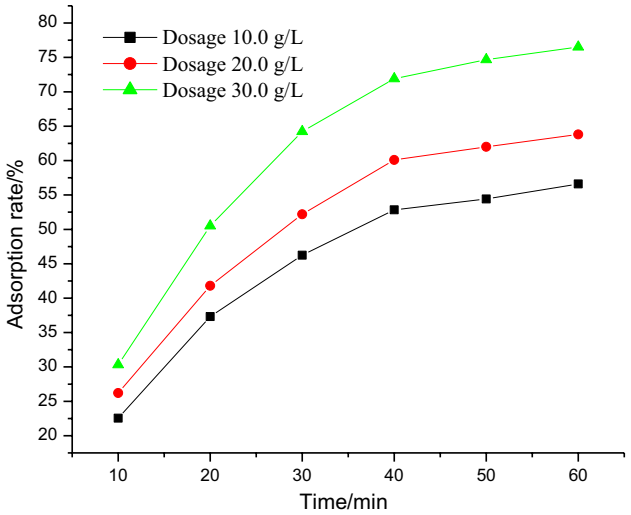


Fig. 6 Relationship between sulfate adsorption rate and adsorption time

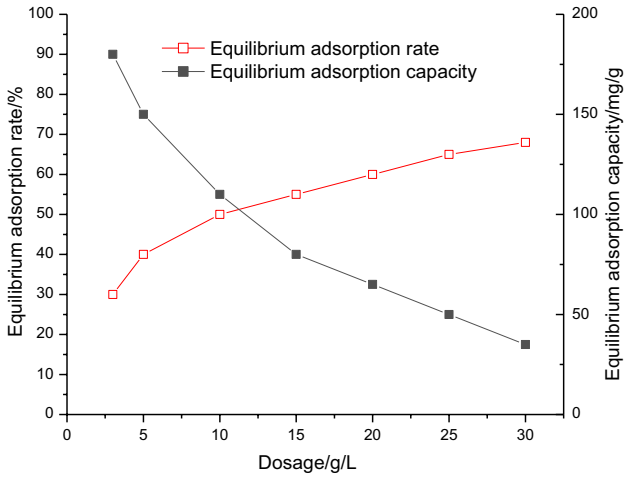


Fig. 7 Relationship between adsorption capacity and dosage

increased rapidly in the first 30 min and could achieve a maximum adsorption rate over 80.0%. However, the growth rate of adsorption began to slow down approximately 40 min after the adsorption began, even though the adsorption rate continued to increase (Fig. 6).

(3) Equilibrium adsorption capacity and equilibrium adsorption rate.

Adsorption capacity refers to the amount of adsorbate adsorbed per unit of adsorbent when equilibrium is reached, characterizing the ability of an adsorbent to adsorb a particular substance. The relationship between the adsorption capacity of nano zirconia hydroxide and its dosage was investigated by adjusting the adsorbent dosage under the condition of an initial AMD pH of 2.5 and a sulfate concentration of 3,500 mg/L. The adsorption capacity was determined by measuring the sulfate concentration after an adsorption duration of 60 min. The test results are shown in Fig. 7.

The adsorbent dosage of nano zirconia hydroxide influences both the equilibrium adsorption capacity and equilibrium adsorption rate. When the dosage was 3.0 g/L, the sulfate adsorption rate only reached 30.0%, and the equilibrium adsorption capacity peaked at 115.0 mg/g. At a dosage of 30.0 g/L, the sulfate adsorption rate peaked at 70.0%, while the equilibrium adsorption capacity was 35.0 mg/g.

As the sulfate adsorption rate increased, the sulfate adsorption rate increased, whereas the equilibrium adsorption capacity gradually decreased. However, a crossing point was observed on the equilibrium adsorption capacity curve and the equilibrium adsorption rate curve, indicating the optimal adsorbent dosage. At this point, with a dosage of 11.0 g/L, the sulfate adsorption rate was 55.0% and the equilibrium adsorption capacity was 98.0 mg/g. The result of the equilibrium adsorption capacity experiment results indicate the existence of an optimal, economically efficient adsorbent dosage.

Adsorbent Regeneration Experiments

(1) Influence of the regenerant dosage on the regeneration of the adsorbent.

The dosage of regenerant (sodium hydroxide solution) influences the regeneration effectiveness of the saturated adsorbent (nano zirconia hydroxide) to a certain extent. Investigating the optimum or economic dosage is therefore meaningful. The dosage ratio, defined as the ratio of actual dosage to theoretical dosage, was used to assess the optimum dosage. The theoretical regenerant dosage was calculated to be 1.20 mol/L when the adsorbent equilibrium adsorption capacity was 98.0 mg/g.

The influence of regenerant dosage on the adsorbent regeneration effect was investigated at dosage ratios of 1.0, 1.5, and 2.0, corresponding to regenerant concentrations of 1.2, 1.8, and 2.4 mol/L, respectively. The regeneration experiment yielded the following results (Fig. 8):

- With a regenerant dosage ratio of 1.0, the sulfate desorption rate of the saturated adsorbent reached 37.0% after 30 min and 44.0% after 60 min of regeneration.
- With a regenerant dosage ratio of 1.5, the sulfate desorption rate reached 53.0% after 30 min and 62.0% after 60 min of regeneration.
- With a regenerant dosage ratio of 2.0, the sulfate desorption rate reached 82.0% after 30 min and 95.0% after 60 min of regeneration.

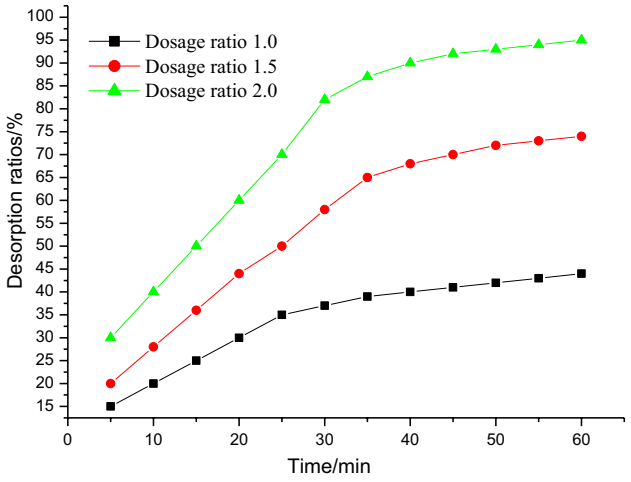


Fig. 8 Influence of the regenerant concentration on the regeneration of the adsorbent

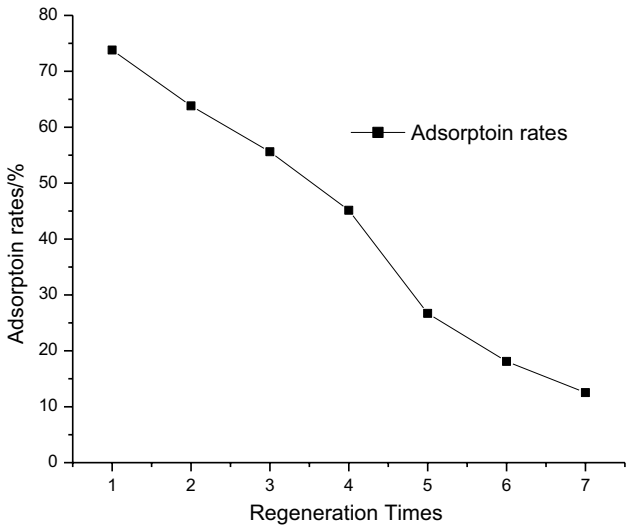


Fig. 9 Influence of regeneration times on the adsorption rates

- The experimental results indicate that the concentration of the regenerant influences the regeneration of the saturated adsorbent. Higher regenerant concentrations result in higher sulfate desorption rates and improved regeneration effectiveness. The experimental results also suggest that the sulfate desorption rates nearly reached equilibrium after 30 min of regeneration, with only a slow increase in desorption rates after that.

(2) Useful life of the adsorbent.

The nano zirconia hydroxide adsorbent can be reused and recycled multiple times for sulfuric acid extraction from AMD, and its useful life influences performance parameters. The useful life of the adsorbent was investigated through adsorption and desorption experiments to evaluate its re-adsorption capability. Experimental conditions: the regenerant (sodium hydroxide) concentration was 60.0 g/L, and the adsorbent solution temperature was 20 ℃.

The initial adsorption rate of fresh adsorbent of nano zirconia hydroxide was 73.8%, but its adsorption performance gradually decreased with each regeneration. The readsorption rates dropped to 45.0% after four cycles of reuse and to 26.7% after seven cycles (Fig. 9). There was a rapid decline in performance after the fourth cycle, indicating that while nano zirconia hydroxide is an effective selective adsorbent for sulfate from AMD and can be recycled several times, its adsorption efficiency decreases with repeated regeneration.

Generation of Sulfuric Acid and Energy Consumption

A BMED device was used to electrolyze sodium sulfate solution to generate sulfuric acid. After comparing different experimental schemes, the equivalent current method was selected for setting the BMED parameters. The operational parameters of the BMED device was as follows: the membrane stack voltage was 50.0 V, the limit current density was1530.0 A/m^2, the concentration of raw sodium sulfate solution in the salt chamber was 0.56 mol/L, and the circulating flowrate in each chambers was 100 L/h. The energy consumption of sulfuric acid production by BMED was investigated with 15 membrane couples. The results showed that the energy consumption increased with both electrolysis time and sulfuric acid concentration. The current efficiency equation of BMED is shown as Eq. 7:

$$\eta = \frac{Fz\left(c_t V_t - c_0 V_0\right)}{n_t I t} \times 100\% \tag{7}$$

where: η = the average current efficiency during the time of 0-t; F = Faraday's constant (96,485 C/mol); z = the number of charges carried by migrating ions; c_t = the solution concentration at time t, mol/L; V_t = the solution volume at time t, L; c_0 = the initial solution concentration, mol/L; V_0 = the initial solution volume, L; n_t = the membrane couples; I = the electric current, A; and t = the time, s.

The energy consumption equation of generated sulfuric acid is shown as Eq. 8:

$$E = \int_0^t \frac{UIdt}{3600 \times 10^3 \times m} \quad (8)$$

where: E the energy consumption per unit mass of generated sulfuric acid, kW.h/kg; U = the voltage, V; I electric current, A; m the mass of sulfuric acid generated, kg; and t = the time, s.

During the electrolysis process, the sulfuric acid concentration increased rapidly in the first 120 min but continued to increase slowly after that. In contrast, energy consumption increased slowly during the first 120 min, but then increased rapidly as the electrolysis continued.

At 120 min, the sulfuric acid concentration reached 0.38 mol/L. Approximately 85.0% of the 0.45 mol/L concentration was achieved at 150 min. Similarly, energy consumption reached 4.6 kWh at 120 min, about 56% of the 8.2 kWh consumed at 150 min. The average current efficiency during the electrolysis process was calculated to be 65.4% for the alkali chamber and 54.3% for the acid chamber. The energy consumption for sulfuric acid generation was 0.25 kWh/kg (Fig. 10).

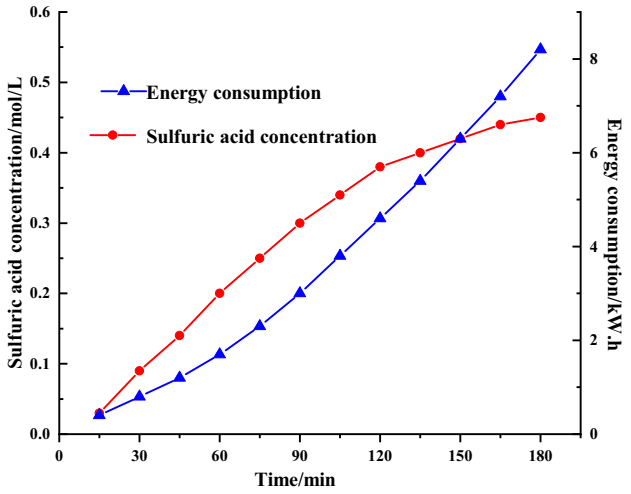


Fig. 10 Influence of energy consumption on the sulfuric acid concentration

Techno-Economic Analysis

A preliminary cost model has been developed for the proposed technology, allowing for a comparison of its economic benefits with those of competing technologies. The model includes a levelized cost of target sulfuric acid (LCS) recovery (Eq. 9).

$$LCS = \frac{\text{Total annualized cost of recovered sulfuric acid}\left(\frac{\$}{kg_{\text{recovered}}}\right)}{\text{Annual yield of recovered sulfuric acid}\left(\frac{kg_{\text{recovered}}}{kg_{\text{Total}}}\right)} \quad (9)$$

The total annualized cost of recovered sulfuric acid was determined by summing the process costs and dividing by the mass of recovered sulfuric acid per year. Process costs comprise the capital cost (Capex) multiplied by a capital recovery factor (CRF) for a 15-year operating life, along with annual operating costs (Opex). A techno-economic analysis (TEA) was conducted, considering the influencing factors shown in Table 2.

Considering the average concentration of sulfate (SO_4^{2-}) in AMD was 3500 mg/L, and assuming a 75.0% extraction rate for concentrated sulfuric acid recovery, the LCS of sulfuric acid can be calculated as 0.83 $/kg.

Operational costs for acid wastewater treatment using the acid–base neutralization method typically range from 7.7 to

Table 2 Levelized cost of target sulfuric acid (LCS)

Categories	Influence factors	Indicators	Units	Values
Pre-treatment cost	Cost of pre-treatment processes	C_{A0}	$/kg	0.08
Adsorption- regeneration cost	Adsorption capacity of the adsorbent	C_{A1}	g/kg	230
	Regeneration capacity of the adsorbent	C_{A2}	g/kg	160
	Cost of the adsorbent	C_{A3}	$/kg	0.26
	Cost of the regenerant	C_{A4}	$/kg	0.16
Electrochemical cost	Energy intensity of the process	C_{E1}	$/kg	0.12
	Cathode and anode materials expected lifetime	C_{E2}	year	5.00
	Cost of other materials	C_{E3}		0.006
	Cost of any pre or post treatment	C_{E4}	$/kg	0.05
	Recovered sulfuric acid yield and the value	C_{E5}	$/kg	0.36
	Recovered sodium hydroxide yield and the value	C_{E6}	$/kg	0.15
Capex and Opex cost	Capex mainly contains equipment cost	Capex	$/kg	0.03
	Opex mainly contains the process and maintenance cost	Opex	$/kg	0.12
LCS			$/kg	0.83

16 $/m^3, depending on factors such as sulfuric acid concentration and the presence of other metals in the AMD (Aydin et al. 2019). Energy consumption for sulfuric acid recovery via bipolar membrane (BPMED) for reuse in the ammonium sulfate scrubber ranges from 7.1 MJ/ kg (SO_4^{2-}) to 9.5 MJ/ kg (SO_4^{2-}) (Narayen et al. 2024). In this study, the LCS was calculated as 0.83 $/kg, encompassing various costs incurred during the recovery process, with an average sulfate concentration of 3500 mg/L in the AMD. While this approach can potentially reduce operating costs for AMD treatment, it may not entirely offset the treatment expenses. However, if the concentration of sulfate ions in AMD is high enough, the cost-effectiveness of sulfuric acid extraction becomes more pronounced, offering greater cost reductions in AMD treatment.

Conclusion

A productive experiment of sulfuric acid extraction from AMD was conducted on-site, based on an analysis of basic principles and technical approach options.

(1) Sulfuric acid was successfully extracted from AMD through a process involving pre-treatment, sulfate adsorption, and sodium sulfate solution electrolyzation.
(2) Pre-treatment experiments demonstrated that the process effectively removed suspended solids (SS), iron ions (Fe I)), and manganese ions (Mn II) from raw AMD, with removal rates averaging 87%, 90%, and 86%, respectively, confirming the feasibility of the pre-treatment process.
(3) The sulfate adsorption experiments revealed that the nano zirconia hydroxide served as a selective adsorbent, effectively adsorbing sulfate from the AMD at low pH conditions. However, its adsorption performance gradually declined with increasing pH. The maximum adsorptive capacity of the adsorbent was 115.0 mg/g, while the equilibrium adsorption capacity was 85.0 mg/g, indicating an economically viable dosage. Moreover, the sulfate adsorption rate exceeded 80.0%.
(4) The experiments showed that the nano zirconia hydroxide could be regenerated and reused after reaching saturation. The regeneration effect was influenced by the regenerant dosage, with higher concentrations resulting in a better desorption rate and improved regeneration effectiveness. At a regenerant dosage ratio of 2.0, the saturated adsorbent's sulfate desorption rate reached 95.0% within 60 min. Nevertheless, the useful life experiment showed a gradual decline in adsorption performance with regeneration cycles.
(5) The electrolysis experiment demonstrated an increase in sulfuric acid concentration with electrolysis time using BMED membrane couples. With 20 membrane couples, the average current efficiency during the electrolysis was 65.4% for the alkali chamber and 54.3% for the acid chamber, with an energy consumption of 0.25 kW·h/kg for sulfuric acid generation.
(6) Techno-economic analysis revealed a LCS of sulfuric acid at 0.83 $/kg.

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Data availability The data supporting the findings of this study are available from the corresponding author upon reasonable request. The authors agree to the journal's use and dissemination of the data in accordance with its publication policies.

Declarations

Ethical statement We are committed to upholding the highest standards of ethical conduct in our research on the extraction of sulfuric acid from acid mine drainage (AMD). In line with the guidelines of the Committee on Publication Ethics (COPE), we ensure the integrity and transparency of our work by adhering to the following ethical principles:

1. Originality and Non-Simultaneous Submission: This manuscript presents original research and has not been submitted for simultaneous consideration to any other journal. It also has not been published elsewhere, in part or in full, and we have ensured that no previous work has been inappropriately reused without proper citation.
2. Integrity of Results: We have presented our research results clearly and honestly, avoiding any form of fabrication, falsification, or inappropriate data manipulation. The experimental procedures, including the use of nano-zirconia hydroxide particles for sulfate adsorption and the subsequent electrolysis process, were conducted according to rigorous standards, with all data and methodologies accurately reported.
3. Avoidance of Salami-Slicing/publishing: We have not divided our study into multiple parts to increase the quantity of submissions. Our research is presented as a complete study, encompassing the pre-treatment, sulfate extraction, and electrolysis stages.
4. Plagiarism and Acknowledgement: All data, theories, and text from other sources have been properly acknowledged. We have ensured that quotations are clearly marked, and permissions for copyrighted materials have been secured. No data or text have been presented as if they were our own, and proper citation practices have been followed throughout.
5. Ethical Implications: Our study aims to address the environmental challenges associated with AMD and to provide a sustainable pathway for resource recovery. We have carefully considered the ethical implications of our research, including its impact on environmental management and commercial viability.

We believe that our adherence to these ethical principles ensures the trustworthiness and quality of our research, contributing positively to the scientific community and advancing knowledge in this field.

Statement of Novelty Conventional treatments for acid mine drainage (AMD) focus on neutralizing sulfate as a harmful byproduct, often overlooking its potential as a valuable resource. We introduce a novel approach to AMD treatment that prioritizes sulfate recovery and commercial valorization. By employing a three-stage process—AMD pretreatment, sulfate extraction, and electrolysis of sodium sulfate solution to produce sulfuric acid—we demonstrate a significant shift from traditional practices. Our field experiments show that nano-zirconia hydroxide particles achieve an 80% sulfate adsorption rate under low pH conditions, with an energy consumption of 0.25 kW.h/kg for sulfuric acid generation. Our techno-economic analysis reveals a competitive Levelized Cost of Sulfuric Acid (LCS) of $0.825/kg, underscoring the economic feasibility of this innovative technique. This approach not only mitigates environmental impacts of AMD but also provides a sustainable and economically viable pathway for resource recovery and commercial utilization.

References

Aydin MI, Yuzer B, Hasancebi B, Selcuk H (2019) Application of electrodialysis membrane process to recovery sulfuric acid and wastewater in the chalcopyrite mining industry. Desalin Water Treat 172:206–211. https://doi.org/10.5004/dwt.2019.25051

Azizi S, Beauclair N, Maaza M, Mokrani T, Ambushe AA, Seopela MP, Msagati ATM (2024) Acid mine drainage treatment and metals recovery by means of selective precipitation using magnesium oxide (MgO): an experimental study. Ground Water Sustain Dev 25:101151. https://doi.org/10.1016/j.gsd.2024.101151

Geoffrey S, Simate Ndlovu S (2014) Acid mine drainage: challenges and opportunities. J Environ Chem Eng 2:1785–1803. https://doi.org/10.1016/j.jece.2014.07.021

Guo X, Fu S, Di J, Dong Y, Jiang G (2021) Study on the treatment of acid mine drainage containing Fe^{2+} and Mn(II) using modified spontaneous combustion gangue. J Renew Mater 9:541–555. https://doi.org/10.32604/jrm.2021.012335

Han F, Wang M, Liu W, Song W (2024) Recovery of sulfuric acid and iron from titanium dioxide waste acid by membrane electrolysis combined with selective electrodialysis. Sep Purif Technol 344:127199. https://doi.org/10.1016/j.seppur.2024.127199

Houssem E, Alia B, Neculitaa CM, Molsonb JW, Maqsouda A, Zaguryc GJ (2019) Performance of passive systems for mine drainage treatment at low temperature and high salinity: a review. Miner Eng 34:325–344. https://doi.org/10.1016/j.mineng.2019.02.010

Kaur G, Couperthwaite SJ, Hatton-Jones BW, Millar GJ (2018) Alternative neutralisation materials for acid mine drainage treatment. J Water Proc Eng 22:46–58. https://doi.org/10.1016/j.jwpe.2018.01.004

Kefeni KK, Msagati TAM, Mamba BB (2017) Acid mine drainage: prevention, treatment options, and resource recovery: a review. J Clean Prod 151:475–493. https://doi.org/10.1016/j.jclepro.2017.03.082

Kefeni KK, Msagati TAM, Nkambule TTI, Mamba BB (2018) Synthesis and application of hematite nanoparticles for acid mine drainage treatment. J Environ Chem Eng 6:1865–1874. https://doi.org/10.1016/j.jece.2018.02.037

Li N, Bao J, Hong Y, Zhou F (2013) Study of sulfate adsorption onto magnetic nano-zirconium hydroxide. Environ Sci Technol 36:47–52. https://doi.org/10.3969/j.issn.1003-6504.2013.06.010[inChinese]

Lopez J, Reig M, Gibert O, Cortina JL (2019) Recovery of sulphuric acid and added value metals (Zn, Cu and rare earths) from acidic mine waters using nanofiltration membranes. Sep Purif Technol 212:180–190. https://doi.org/10.1016/j.seppur.2018.11.022

Lu YP (2006) Study on preparation of zirconium hydroxide nano-particles and adsorption of sulfate radical. Tianjin Univ, PhD Diss (**[in Chinese]**)

Narayen D, Berlo EV, Lier JB, Spanjers H (2024) Recovery of sulfuric acid and ammonia from scrubber effluents using bipolar membrane electrodialysis: Effect of pH and temperature. Sep Purif Technol 338:126605. https://doi.org/10.1016/j.seppur.2024.126605

Park SM, Yoo JC, Ji SW, Yang JS, Baek K (2013) Selective recovery of Cu, Zn, and Ni from acid mine drainage. Environ Geochem Hlth 35:735–743. https://doi.org/10.1007/s10653-013-9531-1

Park I, Tabelin CB, Jeon S, Li X, Seno K, Ito M, Hiroyoshi N (2018) A review of recent strategies for acid mine drainage prevention and mine tailings recycling. Chemosphere 219:588–606. https://doi.org/10.1016/j.chemosphere.2018.11.053

Patel M, Jade RK, Dewangan PK, Dash AK, Kaushik AK (2021) Removal of iron and sulphate during acid mine drainage treatment using laboratory successive alkalinity producing system and its behavioural relationship. Int J Chem React Eng 20:1–7. https://doi.org/10.1515/ijcre-2021-0120

Peng Y, Azeem M, Li R, Xing L, Li Y, Zhang Y, Guo Z, Wang Q, Ngo HH (2022) Zirconium hydroxide nanoparticle encapsulated magnetic biochar composite derived from rice residue: application for As(III) and As(V) polluted water purification. J Hazard Mater 423(127081):1–12. https://doi.org/10.1016/j.jhazmat.2021.127081

Roa A, Lopez J, Cortina J (2024) Recovery of rare earth elements from acidic mine waters: a circular treatment scheme utilizing selective precipitation and ion exchange. Sep Purif Technol 338:126525. https://doi.org/10.1016/j.seppur.2024.126525

Rodriguez GM, Baena MFM, Vazquez S, Arroyo TF, Vilches LF, Zhang Z (2019) Remediation of acid mine drainage. Environ Chem Lett 17(4):1529–1538. https://doi.org/10.1007/s10311-019-00894-w

Simate GS, Ndlovu S (2014) Acid mine drainage: challenges and opportunities. J Environ Chem Eng 2:1785–1803. https://doi.org/10.1016/j.jece.2014.07.021

Singh J, Mukherjee A, Sengupta SK, Im J, Peterson GW, Whitten JE (2012) Sulfur dioxide and nitrogen dioxide adsorption on zinc oxide and zirconium hydroxide nanoparticles and the effect on photoluminescence. App Surf Sci 258:5778–5785. https://doi.org/10.1016/j.apsusc.2012.02.093

Tong L, Fan R, Yang S, Li C (2021) Development and status of the treatment technology for acid mine drainage. Min Metall Explor 38:315–327. https://doi.org/10.1007/s42461-020-00298-3