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Comparative Evaluation and Kinetics of Active, Passive, and Hybrid Treatment for Acid Mine Drainage Neutralization and Fe–Mn Precipitation Using Goat Manure as Organic Substrate

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Abstract: Acid Mine Drainage (AMD) from sulfide-mineral oxidation poses an urgent threat to receiving water bodies due to its low pH and dissolved-metal load, making efficient, sustainable neutralization a priority for small- to medium-scale mines. This study comparatively evaluated active treatment ($Ca(OH)_2$), passive treatment (goat manure as an SRB substrate), and a hybrid combination for AMD neutralization and Fe–Mn removal, using a 15-day laboratory batch experiment monitoring pH, TSS, Fe, and Mn against an untreated control, analyzed via effectiveness calculations and Two-Way ANOVA. All treatments raised pH toward neutral, with passive treatment achieving the highest effectiveness (75% pH improvement, 52% Fe removal, 67% Mn removal); pH improvement plateaued near this level once added alkalinity reached equilibrium with residual acidity from ongoing pyrite oxidation. TSS rose in all treatments most in the hybrid system because effective metal removal itself generates suspended Fe/Mn-hydroxide flocs and SRB biomass, though values stayed within the regulatory limit (400 mg/L). These results position goat manure-based passive and hybrid treatments as low-cost, mechanistically distinct alternatives for net-acid, low-metal AMD management. Given the single-reactor, non-replicated design, further research with biological replicates, controlled temperature/DO/ORP monitoring, and field-scale validation is recommended, particularly to optimize passive-system design for TSS mitigation.

Keywords: Acid Mine Drainage, Calcium Hydroxide Neutralization, Goat Manure Bioremediation, Heavy Metal Precipitation, Sulfate-Reducing Bacteria.

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1. Introduction

Mining is essential for meeting the demand for raw materials and energy required for present-day human development; however, it is also one of the human activities with the greatest potential to pollute the environment [1]. Based on water-quality testing at the Mitra Void of PT Gorby Putra Utama, a pH value of 2.61 was obtained. This value indicates that the Acid Mine Drainage (AMD) at the study site falls into the net-acid category, namely water with a high level of acidity. This condition indicates that the AMD has considerable potential to degrade the quality of receiving water bodies if it is discharged without adequate treatment. The very low pH can increase the solubility of heavy metals, potentially causing toxicity to aquatic organisms, disturbing the balance of aquatic ecosystems, and lowering overall environmental quality.[2] Therefore, the management of acid mine drainage is a very important aspect of mining activities.

AMD must be treated before being discharged into the environment so that it complies with the quality standards stipulated in the Regulation of the Minister of Environment and Forestry (MoEF) No. 5 of 2022 on Wastewater Treatment for Mining Businesses and/or Activities[3][4]. The active method using calcium hydroxide ($Ca(OH)_2$) was selected because it can rapidly neutralize acidity through chemical neutralization, thereby raising the pH of AMD within a relatively short time and meeting the required quality standards. However, this method requires the continuous use of chemicals and relatively high operating costs [5] [6].

As a comparison, the passive method using goat manure was selected because it offers a more sustainable and economical treatment alternative. The organic-matter content of goat manure supports the activity of microorganisms, particularly sulfate-reducing bacteria (SRB), which play a role in increasing alkalinity and lowering dissolved-metal concentrations through biogeochemical processes [7]. In addition, using livestock waste as a treatment medium adds value in terms of sustainability, operational-cost efficiency, and the application of circular-economy principles in the management of mining waste.

The determination of treatment doses in this study was based on previous studies and the working mechanism of each treatment medium. A dose of 2 g $Ca(OH)_2$ was chosen with reference to Sari et al.[8], who showed that this dose can provide sufficient alkalinity to neutralize free H^+ ions through neutralization reactions, thereby raising the pH and triggering the precipitation of dissolved metals in AMD. The combination of $Ca(OH)_2$ and goat manure is expected to raise the pH rapidly in the early stage, while goat manure maintains alkaline conditions through the biological activity of sulfate-reducing bacteria. This combination also aims to reduce chemical requirements, increase treatment-cost efficiency, and produce effluent that meets environmental quality standards[9].

Previous research on AMD bioremediation shows three specific, unresolved limitations that this study directly targets. First, studies generally test a single organic substrate in isolation without benchmarking it against chemical treatment or other substrates within one controlled experimental framework; Wang et al. showed that single-substrate systems fail to sustain sulfate-reduction efficiency over time compared with mixed carbon sources, yet no study has placed a single livestock-manure substrate in direct, simultaneous comparison with an active chemical method under identical AMD conditions. Second, substrate performance is rarely attributed to specific biochemical drivers: poultry manure, despite high dissolved organic carbon, has been shown to yield the *lowest* sulfate- and metal-reduction efficiency among tested manures demonstrating that dissolved organic carbon content alone is a poor predictor of SRB performance, and that decomposition kinetics and C:N ratio are the more relevant explanatory variables. Third, goat manure specifically has not been evaluated as a sole SRB substrate under a net-acid, *low*-metal-load AMD profile; existing Indonesian AMD literature has focused on alternative media such as coal fly ash or oil-palm empty fruit bunches, and international substrate studies are dominated by fungal compost, wood chips, or poultry/cattle manure tested under high-metal-load conditions. Goat manure's comparatively high C:N ratio and slower decomposition rate relative to simple liquid substrates suggest it may act as a more stable, medium-term electron-donor source for SRB a hypothesis that has not been mechanistically tested.

These limitations point to a broader, unresolved scientific challenge: the absence of a comparative framework explaining the trade-off between neutralization *rate* (the strength of active chemical methods) and long-term alkalinity *stability* (the strength of SRB-based passive methods using locally available organic waste) a trade-off with direct relevance to small- and medium-scale mining regions

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where livestock waste is abundant but has not been systematically evaluated as a treatment substrate. Addressing this gap, rather than resolving an operational issue at a single site, is the central scientific contribution of this study; the site-specific dataset instead serves as a representative case for testing the generalizability of the proposed active–passive trade-off mechanism to net-acid, low-metal AMD systems more broadly.

Based on this framework, the working hypotheses are: (1) the active method ($Ca(OH)_2$) achieves faster pH neutralization but is more susceptible to short-term fluctuation; (2) the passive method (goat manure) achieves greater medium-term stability and higher Fe–Mn removal via the SRB biogeochemical pathway; and (3) the hybrid method produces a synergistic effect that combines rapid initial neutralization with sustained stability, offering higher technical efficiency than either method alone. Testing these hypotheses carries practical significance for AMD management in resource-limited mining operations, where continuous chemical supply is often logistically constrained: confirming hypothesis (3), in particular, would establish a lower-cost, more operationally resilient treatment pathway than active treatment alone.

The objectives of this study are: (1) to analyze the effectiveness of AMD neutralization using the active and passive methods; (2) to identify the most effective treatment method for improving AMD quality; and (3) to evaluate the effectiveness of the active, passive, and combined methods on changes in the water-quality parameters pH, TSS, Fe, and Mn after treatment.

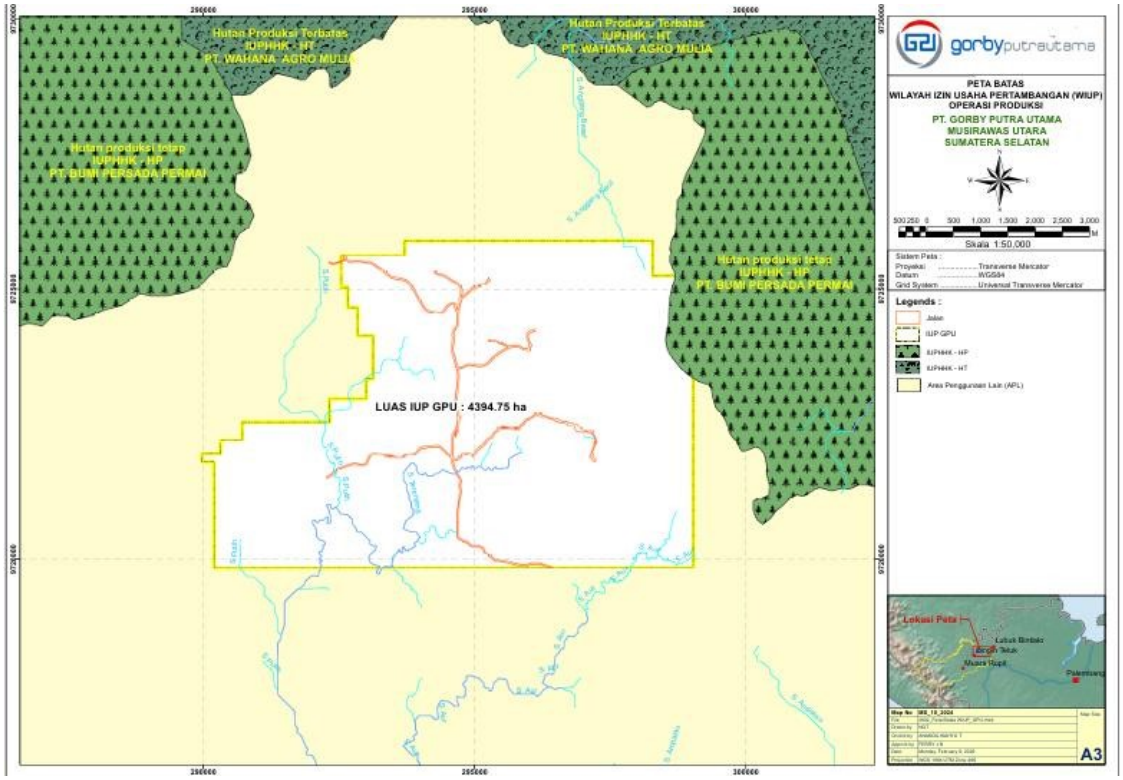

Figure 1. Research Location Map

2. Literature Review

This review is structured to move from general to specific: it first establishes the geochemical basis of AMD formation, then interrogates how this basis manifests at the study site, and finally critically evaluates whether existing active and passive treatment mechanisms are actually suited to the site's specific geochemical profile rather than assuming their effectiveness reported elsewhere is directly transferable. This funnel structure is intended to demonstrate that the research gap and hypotheses arise directly from unresolved tensions in the literature, not from a generic absence of prior comparative studies.

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2.1. Geochemical Characteristics of AMD and Their Relevance to the Study Site

Acid Mine Drainage (AMD) forms through the oxidation of sulfide minerals (primarily pyrite, FeS_2) exposed to air and water within mine waste materials. This process yields Fe^{2+}, SO_4^{2-}, and H^+ ions as primary products, resulting in typical pH levels of 3.4–4.8 and high sulfate concentrations. While reactions (1) - (4) outline the general mechanism, the specific oxidation products depend heavily on the type of mine waste and local hydrogeological conditions factors accounted for by the Potential Acid Forming (PAF) and Non-Acid Forming (NAF) classification approach commonly used in South Sumatra coal mines to predict acid generation potential prior to discharge into the environment.

Reaction 1:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (1)$$

Reaction 2:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (2)$$

Reaction 3:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (3)$$

Reaction 4:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

Preliminary characterization of the PT Gorby Putra Utama "Mitra Void" reveals a noteworthy pattern: despite a very low pH (2.61), concentrations of Fe (0.33 mg/L) and Mn (1.13 mg/L) remain below the limits set by MoEF Regulation No. 5/2022. This scenario differs from the "classic" AMD profile typically reported in coal mine geochemical studies including those from other mines in South Sumatra which usually exhibit low pH alongside high dissolved metal loads. Consequently, the primary geochemical issue at this site is not a high metal load, but rather a deficit in water alkalinity or buffering capacity. This distinction is crucial for determining appropriate treatment success criteria: the selected method must be evaluated primarily on its ability to raise and maintain pH levels, rather than solely on metal removal efficiency an emphasis rarely addressed in general AMD literature but which serves as the logical basis for selecting the evaluation parameters in this study. Reactions (1) - (4) remain relevant for explaining the source of these H^+ ions, but they must be interpreted within the context described above: the continued oxidation of residual pyrite (Reaction 4) has the potential to keep generating H^+ even when the current dissolved Fe load is low; consequently, without the addition of alkalinity, acidic conditions in the Mitra Void could persist, even if dissolved metal levels appear "safe" according to quality standards.

Because the site's core deficiency is alkalinity rather than metal load, the following subsections evaluate active and passive methods specifically against their capacity to generate and *sustain* alkalinity not merely their general capacity to remove metals, which is the criterion most commonly emphasized in the broader AMD literature.

2.2. Critical Evaluation of Active Methods

The active method using $Ca(OH)_2$ works through the dissociation of $Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$, in which hydroxide ions rapidly raise the pH and, at higher pH levels, trigger the precipitation of $Fe(OH)_3$ and $Mn(OH)_2$. Given that the main problem at Mitra Void is alkalinity deficiency (rather than high metal loads), this method should theoretically be highly suitable because it directly addresses the root cause rapidly raising the pH. However, previous studies using $Ca(OH)_2$ or similar lime-based materials were generally conducted on AMD with high metal loads; thus, its effectiveness under conditions of low metal load but highly acidic pH as at this study site has not yet been extensively confirmed. On the other hand, this method’s reliance on a sustainable supply of chemicals poses a significant operational challenge for small- to medium-scale mining sites with limited logistical access; therefore, its long-term relevance must be weighed against alternatives that are more operationally self-sufficient.

This chemical-supply dependency motivates a critical examination of passive, substrate-based alternatives that could, in principle, sustain alkalinity generation without continuous reagent input the subject of the following subsection.

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2.3. Critical Evaluation of Organic Substrate-Based Passive Methods

Passive methods utilize the activity of sulfate-reducing bacteria (SRB), which employ organic matter as an electron donor to reduce sulfate to sulfide; this process simultaneously generates bicarbonate a byproduct of organic matter mineralization that directly contributes to increased alkalinity. This characteristic is particularly relevant to the Mitra Void site, as the SRB mechanism not only precipitates metals but, crucially, generates sustained alkalinity a factor more critical at this location than mere metal removal capacity.

However, the literature indicates that the effectiveness of this method depends heavily on the type of organic substrate employed, and not all animal manure-based substrates yield comparable performance. Studies characterizing organic substrates for SRB have shown that poultry manure used as a sole substrate actually results in the lowest sulfate and metal reduction efficiencies among tested materials despite its high dissolved organic carbon content whereas other studies report that combining livestock manure with lignocellulosic materials yields significantly higher and more stable sulfate reduction efficiencies than single substrates. Existing literature on Acid Mine Drainage (AMD) in Indonesia has largely focused on testing alternative media such as coal fly ash and oil palm empty fruit bunches for pH stabilization and Fe–Mn removal; conversely, the use of goat manure as a sole SRB substrate under conditions of net-acid AMD with low metal loads a profile that specifically mirrors the conditions at Mitra Void has not yet been extensively characterized. It is this research gap that directly underpins the selection and testing of goat manure in the present study, rather than considerations of local availability alone.

Because substrate-dependent alkalinity generation may introduce side effects not captured by pH alone (e.g., particulate release from biomass or precipitate formation), the evaluation framework must extend beyond pH to a broader set of water-quality indicators, as outlined below.

2.4. Water Quality Parameters and Evaluation Criteria

With reference to the geochemical characteristics of the site described in Section 2.1 where pH is the most critical parameter compared to Fe and Mn the parameters of pH, TSS, Fe, and Mn are still measured comprehensively to ensure that pH correction does not cause side effects such as an increase in TSS or the re-release of bound metals, while also maintaining comparability with MoEF Quality Standard No. 5 of 2022

Table 1. Wastewater Quality Standards for Coal-Mining Activities

Parameter	Unit	Standard
pH	–	6–9
TSS	mg/L	400
Iron (Fe) total	mg/L	7
Manganese (Mn) total	mg/L	4

Synthesizing Sections 2.1 - 2.4 makes clear that no existing study has evaluated whether the rate advantage of active methods and the stability advantage of passive, substrate-specific methods can be reconciled for a net-acid, low-metal AMD profile the precise gap this study is designed to close.

2.5. Synthesis and Research Gaps

AMD management continues to develop through active, passive, and combined approaches. For the active method, Zhao et al.[10], Sari et al. [11], and Yolanda et al. [12] showed that adding alkaline materials such as CaO, soda ash (Na_2CO_3), and $Ca(OH)_2$, or combinations with alum, can significantly raise pH and reduce Fe and Mn concentrations. For the passive method, Sasaoka et al. [13] reduced Fe, Mn, and Zn below quality standards using constructed wetlands and limestone channels, while Xu et al.[14] and Chen et al.[15] developed innovative materials a red-mud-based geopolymer and an attapulgite–soda-residue adsorbent that removed heavy metals close to 100% while neutralizing acidity. Several studies developed hybrid systems: An et al. [16] showed that combining bio-oxidation with carbonate-rock neutralization gave higher efficiency than carbonate rock alone, Hu et al.[17] used a reducing-barrier system that removed more than 99% Cu and 100% Zn, and the review of Mosai et al.[18] concluded that combining treatment technologies increases metal and sulfate removal

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while opening opportunities for resource recovery. Pocaan et al. [19] further demonstrated a locally available mixed-media passive system reaching 98–99% removal for several metals.

The novelty of this study lies in comparing three methods (active, passive, and combined) within a single study framework, using goat manure as the main substrate for the passive system, combining slaked lime with goat manure as a pure bioremediation pairing, and utilizing locally accessible livestock waste. Based on the identified problem, the hypothesis is that active management using $Ca(OH)_2$ is more effective in neutralizing pH, while passive management using an organic substrate is more efficient for long-term use owing to its simpler operational aspects, and the combination of active and passive methods significantly increases pH and optimizes the concentrations of Fe, Mn, and TSS so that the AMD meets environmental quality standards.

A synthesis of Sections 2.1–2.3 highlights three interrelated points: (1) the primary geochemical issue with the Void Partner is an alkalinity deficit rather than a high metal load; (2) active methods excel at rapidly raising pH but rely on continuous chemical inputs; and (3) SRB-based passive methods offer the potential for sustained, autonomous alkalinity generation, though their performance depends heavily on the type of organic substrate which varies across different types of livestock manure. These findings logically point to the need to test three schemes active treatment, passive treatment using goat manure, and a combination of the two directly on AMD characterized by a net-acid profile and low metal loading.

These synthesized limitations directly justify the three working hypotheses introduced, that active treatment offers superior neutralization rate, passive treatment offers superior medium-term stability and metal selectivity, and their combination can reconcile this rate–stability trade-off a reconciliation not yet mechanistically tested for goat manure-based passive systems under net-acid, low-metal AMD conditions.

3. Methodology

This study was conducted as a laboratory-scale experiment using a closed 10 L batch reactor (Figure 2), operated at ambient laboratory conditions without active control or systematic recording of temperature, dissolved oxygen (DO), or redox potential (ORP) over the 15-day observation period. These limitations are explicitly acknowledged as methodological constraints, given that temperature, DO, and ORP directly influence the metabolic rate of sulfate-reducing bacteria (SRB) in Treatments 2 and 3; consequently, unmeasured environmental variations could contribute to result variability that is not fully explained by the time (day) or treatment factors in the Two-Way ANOVA analysis.

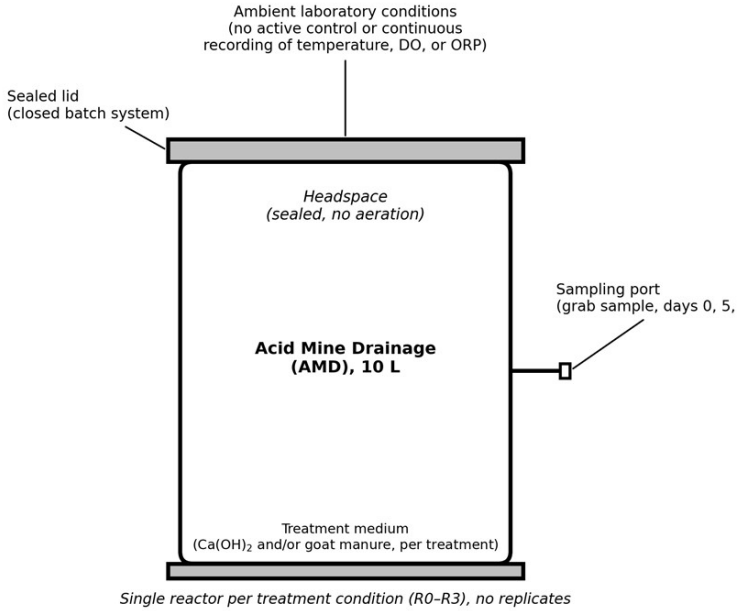

Figure 2. Schematic of the closed 10 L batch reactor

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Each treatment condition (R0–R3) was carried out using a single reactor without biological or technical replicates, with the observation days (0, 5, 10, and 15) serving as the repeated factor in the Two-Way ANOVA design. While this type of design is common in preliminary or screening laboratory-scale studies regarding Acid Mine Drainage (AMD), the absence of true replicates limits the statistical test's ability to distinguish treatment-induced variability from random variability inherent to a single reactor (pseudoreplication). Therefore, the ANOVA results in this study are interpreted as indicative of initial trends rather than definitive conclusions; verification through replicated designs in subsequent pilot or field scale studies incorporating continuous monitoring of temperature, DO, and ORP is recommended.

The dosage determination for the two-treatment media combined stoichiometric calculation for the chemical component with literature-informed practical dosing for the organic component, rather than a direct, unjustified adoption of values from reference studies. The $Ca(OH)_2$ dosage (2 g/10 L) was stoichiometrically validated based on initial AMD characterization results (Table 2): total acidity was calculated from the free H^+ ion concentration at an initial pH of 2.61 ($[H^+] \approx 2.45\times10^{-3}$ mol/L, equivalent to 0.0245 mol H^+ in 10 L), plus the latent acidity contribution from the hydrolysis of dissolved Fe (0.33 mg/L) and Mn (1.13 mg/L). This resulted in an estimated total base requirement of ±0.0251 mol H^+ equivalents, or ±0.93 g $Ca(OH)_2$ at the theoretical stoichiometric neutralization point. The actual dosage (2 g, or ±2.1 times the minimum stoichiometric value) was established to account for the limited solubility of $Ca(OH)_2$, the need to raise the pH beyond the neutral point into the regulatory target range (6–9), and potential acidity generation from residual sulfide oxidation over the 15-day observation period, consistent with recommended dosage practices reported in previous studies [20] [21].

In contrast, the goat-manure dosage (1 kg per 10 L, corresponding to an organic-loading rate of 100 g/L) was determined using a practical dosing rationale informed by organic-loading rates commonly reported for sulfate-reducing bacteria (SRB)-based passive AMD treatment systems, in which the organic substrate is typically supplied in excess of the minimum electron-donor demand in order to sustain a continuous release of biodegradable carbon over the treatment period and to compensate for the fraction of organic matter that remains structurally bound and not readily bioavailable during short-term incubation [22]. Unlike the $Ca(OH)_2$ dosage, this value was not derived from a substrate-specific stoichiometric calculation, since the carbon-to-nitrogen (C:N) ratio and biodegradable-carbon fraction of the goat manure used in this study were not independently characterized. The 15-day observation period was selected based on typical acclimation kinetics reported for SRB-based AMD bioreactors, in which measurable sulfate-reduction and alkalinity-generation activity generally requires a lag phase before stabilizing after day 5–7 [23]; a 15-day window was therefore considered the minimum duration needed to capture both the initial neutralization response (active treatment) and the onset of biologically mediated stabilization (passive and hybrid treatments) within the operational constraints of a laboratory-scale screening study. This is acknowledged as a limitation of the present dosing approach, and future studies should incorporate substrate characterization (e.g., C:N ratio analysis or preliminary sulfate-reduction assays) to refine and quantitatively validate the organic-substrate dosage.

Sampling was carried out on 16 February 2026 using the grab-sampling method following SNI 6989.59:2008 on wastewater sampling. Goat manure was collected directly from a goat farm. Each treatment used 10 L of AMD. Four conditions were observed: an untreated control (AMD only); Treatment 1 (AMD + 2 g $Ca(OH)_2$) as the active method; Treatment 2 (AMD + 1 kg goat manure) as the passive method; and Treatment 3 (AMD + 1 g $Ca(OH)_2$ + 0.5 kg goat manure) as the combined method. Laboratory testing of pH, TSS, Fe, and Mn was carried out on days 0, 5, 10, and 15 at the Center for Environmental Health Engineering and Disease Control (BTKLPP), Palembang, South Sumatra.

Data were analyzed descriptively (tables and bar charts) and through an effectiveness analysis and a Two-Way ANOVA. The effectiveness of the reduction of heavy metals (TSS, Fe, and Mn) was calculated using Equation (5) [24]:

$$E = [(C_{in} - C_{out}) / C_{in}] \times 100\% \quad (5)$$

where E is the effectiveness (%), C_{in} is the initial concentration, and C_{out} is the concentration after treatment. The Two-Way ANOVA was used to determine variation in water quality (pH, TSS, Fe,

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Mn) arising from the treatment factor and the residence-time (day) factor, using the hypothesis rule that if $F_e < F_t$ then H_0 is accepted, and if $F_e > F_t$ then H_0 is rejected and H_1 is accepted. The overall research procedure is shown in Figure 3.

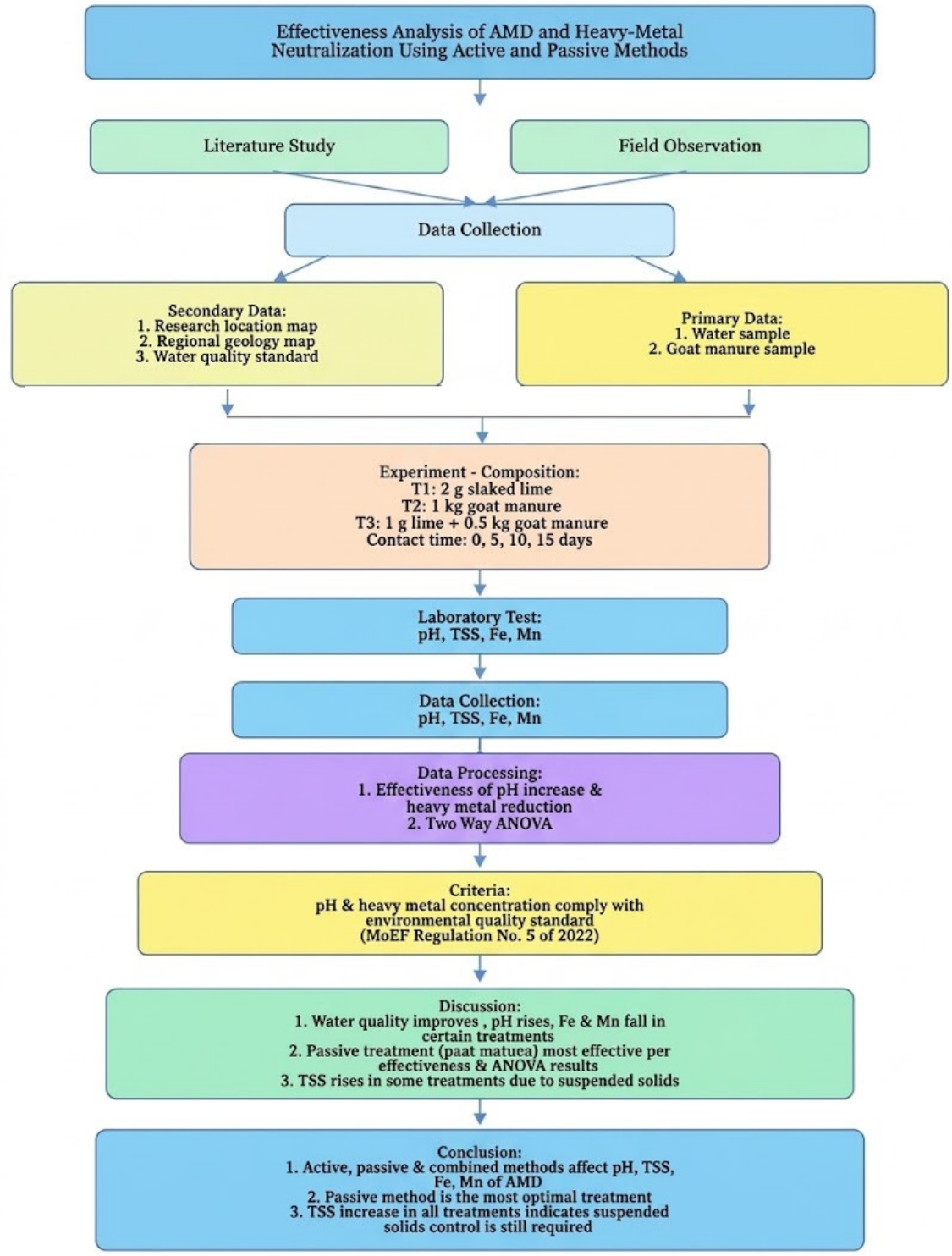

Figure 3. Research Procedure

In summary, this study's design carries three explicit methodological limitations that constrain the interpretability of its results: (1) the absence of biological or technical replicates, which limits the ANOVA's ability to distinguish treatment effects from single-reactor variability (pseudoreplication);

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(2) the absence of active control or continuous monitoring of temperature, DO, and ORP, all of which directly influence SRB metabolic activity and may account for unexplained variability between observation days; and (3) the goat-manure dosage being based on practical organic-loading-rate rationale rather than substrate-specific stoichiometric calculation, due to the C:N ratio and biodegradable-carbon fraction not being independently characterized. These limitations mean the findings should be interpreted as indicative screening-level trends rather than definitive, generalizable conclusions, pending verification through replicated, environmentally controlled, and field-scale studies.

4. Finding and Discussion

4.1. Finding

The characteristics of the AMD at the study site were determined through an initial characterization test, presented in Table 2. The results show that the pH at the Mitra Void was very low (2.61), classifying the water as a net-acid-type AMD (pH < 4.5) [25]. The low pH is associated with dissolved metals such as Fe (0.33 mg/L) and Mn (1.13 mg/L). The initial TSS (21 mg/L), Fe, and Mn values were already below the quality standard, whereas the pH did not yet meet the standard, so treatment was required.

Table 2. Initial characterization of AMD at the Mitra Void

Parameter	Standard	Result
pH	6–9	2.61
TSS (mg/L)	400	21
Fe (mg/L)	7	0.33
Mn (mg/L)	4	1.13

1) pH

The pH values for all conditions on days 0, 5, 10, and 15 are compared in Figure 4. In the untreated control the pH remained essentially stable in the acidic range (2.61 → 2.58).

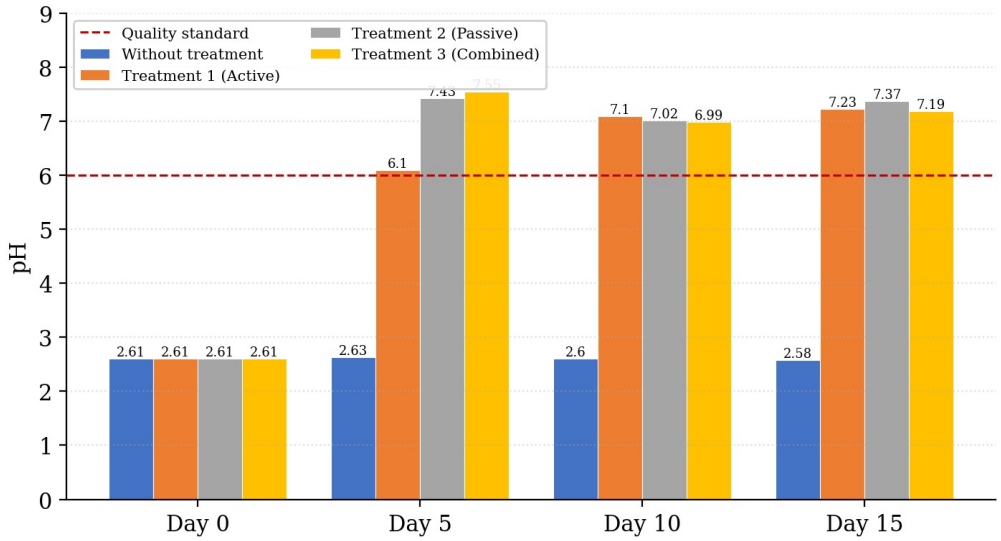

Figure 4. Comparison of pH Changes Across Treatments

In Treatment 1 ($Ca(OH)_2$), the pH rose from 2.61 to 6.10 on day 5, 7.10 on day 10, and 7.23 on day 15, because the strong base dissociates ($Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$) and the hydroxide ions neutralize the H^+ responsible for acidity. In Treatment 2 (goat manure), the pH rose sharply to 7.43 on day 5, decreased slightly to 7.02 on day 10, and increased again to 7.37 on day 15; the increase results from

organic-matter decomposition producing bicarbonate (HCO_3^-) and from SRB consuming H^+, while the small day-10 decrease is linked to the temporary formation of organic acids during mineralization. In Treatment 3 (combined), the pH rose to 7.55 on day 5, decreased to 6.99 on day 10, and recovered to 7.19 on day 15, reflecting the rapid neutralization by lime together with the gradual alkalinity release and buffering from organic-matter decomposition. Overall, Treatments 1–3 raised the pH into the neutral range and maintained it, whereas the control remained acidic.

2) Total Suspended Solids

Figure 5 compares Total Suspended Solids (TSS) across treatments. The control maintained low TSS (21 → 18 mg/L). In Treatment 1, TSS fell to 15 mg/L on day 5 but rose sharply to 188 mg/L on day 10 before declining to 165 mg/L on day 15; the increase is linked to metal-precipitation, in which lime addition forms insoluble metal hydroxides that appear as flocs before settling. In Treatment 2, TSS was 20 mg/L on day 5, rose to 198 mg/L on day 10, then fell markedly to 89 mg/L on day 15, driven by the dispersion of organic material, biofilm formation by SRB, and microbial biomass, followed by sedimentation. Treatment 3 showed the highest TSS (210 mg/L on day 10, then 195 mg/L on day 15) because it combines two solid sources chemical metal-hydroxide precipitates and organic particles/biomass. Although TSS increased, all values remained below the 400 mg/L standard.

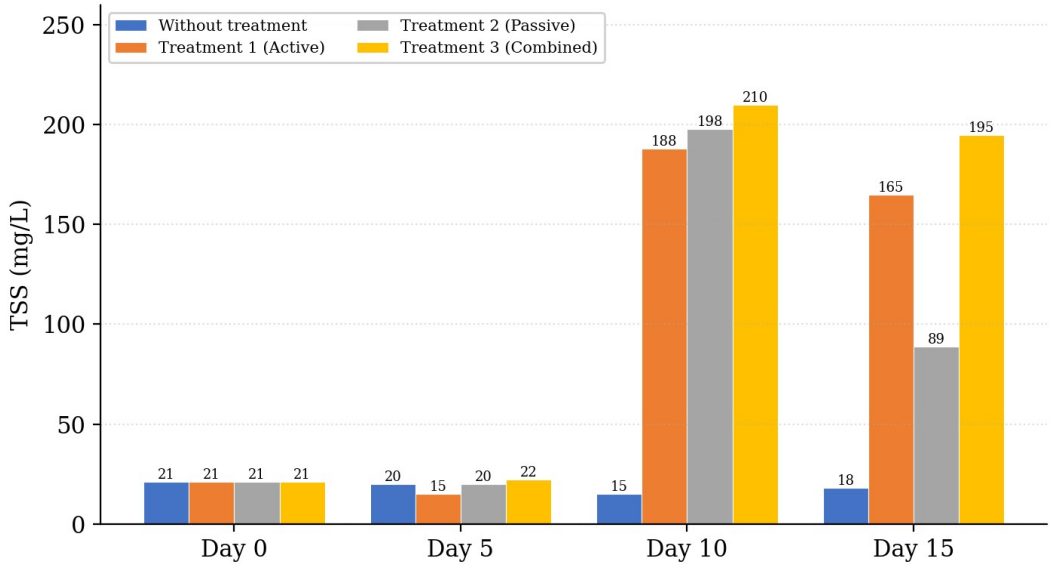

Figure 5. Comparison of TSS Changes Across Treatments

3) Iron

Figure 6 compares Iron (Fe) concentrations. In the control, Fe increased (0.33 → 0.76 → 0.79 mg/L) owing to continuing sulfide oxidation and leaching, then decreased slightly to 0.65 mg/L on day 15. In Treatment 1, Fe dropped sharply to 0.006 mg/L on day 5 through hydroxide precipitation ($Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$), rose to 0.54 mg/L on day 10 due to temporary redissolution, and fell to 0.03 mg/L on day 15 — the lowest final value. In Treatment 2, Fe decreased to a minimum of 0.01 mg/L on day 10 through adsorption and SRB-mediated metal-sulfide precipitation, then rose to 0.27 mg/L on day 15 as further organic decomposition released bound Fe. In Treatment 3, Fe fell to 0.01 mg/L on day 5, rose to 0.29 mg/L on day 10, and settled at 0.09 mg/L on day 15, reflecting the interplay between rapid hydroxide precipitation and slower organic decomposition. The lowest final Fe was obtained in Treatment 1.

4) Manganese (Mn)

Figure 7 compares Mn concentrations. In the control, Mn remained essentially stable (1.13 → 1.17 mg/L), confirming that Mn is difficult to reduce without treatment because it requires oxidation or a

higher pH to precipitate. In Treatment 1, Mn decreased steadily (0.84 → 0.26 → 0.16 mg/L) through hydroxide precipitation ($Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$) as the pH rose. In Treatment 2, Mn fell sharply to 0.01 mg/L on day 5 through adsorption and SRB activity, then rose gradually to 0.07 mg/L (day 10) and 0.27 mg/L (day 15) as organic decomposition released bound Mn. In Treatment 3, Mn dropped to 0.12 mg/L and remained stable to day 10, then rose to 0.28 mg/L on day 15. All treatments reduced Mn far below the initial concentration.

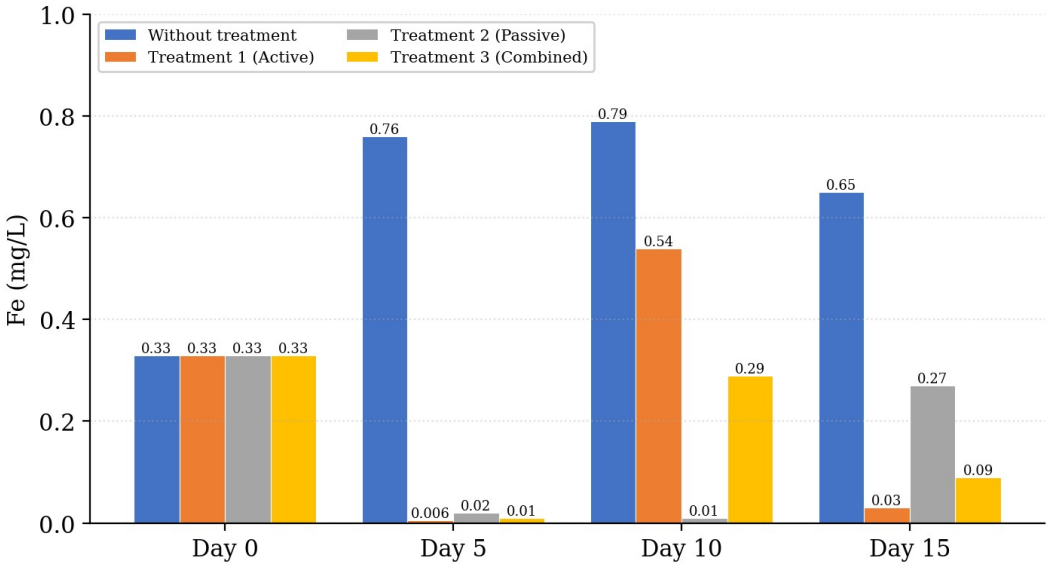

Figure 6. Comparison of Fe Changes Across Treatments

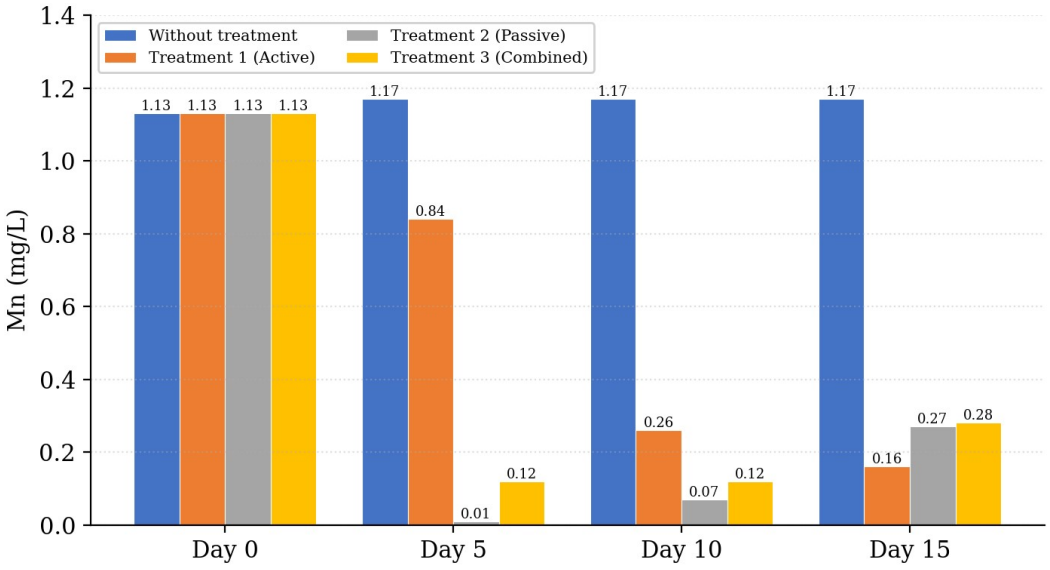

Figure 7. Comparison of Mn Changes Across Treatments

The average effectiveness of each treatment is presented in Table 3. The passive method (Treatment 2) produced the highest effectiveness, particularly in raising pH and reducing Fe and Mn, followed by the combined method for long-term stability, while all treatments showed negative TSS effectiveness because suspended solids increased during treatment.

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Table 3. Average effectiveness of each treatment (%)

Parameter	Without Treatment	Treatment 1	Treatment 2	Treatment 3
pH	−1.36	74.9	75	75
TSS	12	−363	−261	−433
Fe	−43	31	52	46
Mn	−3	47	67	64
Classification	Not effective	Fairly effective	Highly effective	Effective

A Two-Way ANOVA was performed to determine the influence of the day factor and the treatment factor on water-quality changes. The results for the day factor and the treatment factor are summarized in Tbale 4 and Table 5.

Table 4. ANOVA Results for The Day Factor

Parameter	$F_e - F_t$	Hypothesis
pH	8.225 > 3.86	H_0 rejected
TSS	6.833 > 3.86	H_0 rejected
Fe	0.753 < 3.86	H_0 accepted
Mn	4.911 > 3.86	H_0 rejected

Table 5. ANOVA results for the treatment factor

Parameter	$F_e - F_t$	Hypothesis
pH	8.313 > 3.86	H_0 rejected
TSS	2.518 < 3.86	H_0 accepted
Fe	4.675 > 3.86	H_0 rejected
Mn	5.814 > 3.86	H_0 rejected

For the day factor, pH, TSS, and Mn gave $F_e > F_t$ (H_0 rejected), meaning the day factor significantly affects these parameters, whereas Fe gave $F_e < F_t$ (H_0 accepted). For the treatment factor, pH, Fe, and Mn gave $F_e > F_t$ (H_0 rejected), showing a significant treatment effect, whereas TSS gave $F_e < F_t$ (H_0 accepted), indicating that treatment did not significantly affect TSS.

4.2. Discussion

The findings indicate that all three methods have the potential to improve AMD quality, each with different strengths; however, given the single-reactor design without biological or technical replicates described in Section 3, these findings should be interpreted as indicative trends rather than confirmed effects. The active method using $Ca(OH)_2$ raises pH rapidly and produces the lowest final Fe, consistent with the hydroxide-precipitation mechanism. However, the passive method using goat manure and the combined method provide better effectiveness in maintaining pH stability and optimizing Fe and Mn, owing to the buffering capacity of decomposing organic matter and the metal-binding activity of sulfate-reducing bacteria. Based on the effectiveness values (Table 3), the statistical results, and operational considerations, the passive method (Treatment 2) appears to be the most promising treatment among those tested, achieving the highest effectiveness for Fe (52%) and Mn (67%) and a pH-increase effectiveness of 75% [26] [27].

The increase in TSS across all treatments is a consequence of floc and precipitate formation from neutralization and biological activity; although TSS rose, it remained below the standard, and the non-significant ANOVA result for the treatment factor indicates that this increase is an inherent by-product of the reactions rather than a treatment-specific effect. These preliminary results are broadly consistent with the working hypotheses: active management with $Ca(OH)_2$ appears to neutralize pH quickly, passive management with an organic substrate appears more efficient for long-term use, and the combination appears to improve pH while optimizing Fe and Mn, suggesting that the AMD has the potential to meet the environmental quality standards of MoEF Regulation No. 5 of 2022.

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However, given the absence of biological or technical replicates (Section 3) and the lack of active control over temperature, DO, and ORP, these findings should be regarded as indicative trends that require verification through replicated and field-scale studies rather than as definitive conclusions. With this caveat in mind, the results are broadly consistent with previous work reporting that combined and passive approaches can provide reliable, low-cost, and sustainable AMD treatment [28] [29] [30].

1) Metal Dissolution Kinetics

The Fe and Mn profiles in Treatments 2 and 3 exhibit a characteristic "precipitation–redissolution" pattern (sharp decline by day 5–10, followed by partial rebound by day 15) that reflects competing first-order processes rather than steady, monotonic removal. Initial removal is dominated by rapid adsorption and sulfide/hydroxide precipitation ($Fe^{2+} + S^{2-} \rightarrow FeS$; $Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$), which proceeds quickly once SRB activity or lime dissociation raises local alkalinity. The subsequent rebound in dissolved Fe and Mn (day 10–15) is consistent with a slower, competing desorption/redissolution kinetic pathway: as goat manure continues to decompose, previously bound Fe and Mn are re-released into solution either through ligand-exchange with newly generated organic acids and dissolved organic matter, or through partial re-oxidation of freshly precipitated FeS at the reactor's air–water interface. In Treatment 1, the smaller day-10 Fe rebound (0.03→0.54→0.03 mg/L) is instead attributable to transient supersaturation and incomplete $Fe(OH)_3$ floc settling rather than biogeochemical redissolution, since no organic decomposition pathway is present. This distinction is significant: it indicates that passive and hybrid systems face a *kinetic trade-off* between precipitation rate and re-release risk that active treatment does not, and that a 15-day window may be insufficient to reach true steady-state removal a hypothesis directly testable in future studies with more frequent sampling (e.g., daily) around days 8–15.

2) Flocculation Dynamics and the TSS Spike (Days 10–15)

The sharp TSS increase common to all treatments, and most pronounced in Treatment 3 (up to 210 mg/L on day 10), reflects at least three concurrent solid-generation mechanisms rather than a single cause. First, in Treatment 1, rapid $Ca(OH)_2$ dissociation generates supersaturated conditions for $Fe(OH)_3$ and $Mn(OH)_2$, producing fine colloidal flocs with low settling velocity (consistent with Stokes' law for particles in the sub-10 μm range); these flocs remain suspended for several days before aggregating into larger, faster-settling particles, explaining the day-10 peak followed by partial day-15 decline. Second, in Treatment 2, goat manure itself directly contributes suspended solids through the physical dispersion of fine particulate organic matter and the release of dissolved/colloidal organic compounds during hydrolysis independent of any biological activity. Third, and specific to the passive and hybrid systems, active SRB metabolism generates microbial biomass and extracellular polymeric substances (EPS) that both add particulate mass and promote bioflocculation, which can transiently increase turbidity before biofilm-bound aggregates settle. Treatment 3's higher TSS (relative to Treatments 1 and 2 individually) is therefore not a design flaw but an expected additive outcome of combining chemical floc formation with organic particulate/biomass generation from a single reactor highlighting that TSS management, not neutralization or metal removal, is the key engineering bottleneck for scaling passive and hybrid systems.

3) Reasons Behind the Hybrid Method's Failure to Outperform Initial Hypotheses

Contrary to hypothesis (3), Treatment 3 did not exceed Treatment 2 in Fe (46% vs. 52%) or Mn removal (64% vs. 67%), despite combining both mechanisms. This apparent lack of synergy is mechanistically explainable rather than anomalous: halving each treatment's dose (1 g $Ca(OH)_2$ + 0.5 kg goat manure, versus 2 g or 1 kg individually) proportionally reduces the alkalinity and electron-donor supply available from each pathway. The rapid pH rise from the chemical component may also transiently suppress SRB activity, since sulfate-reducing bacteria typically show optimal activity near circumneutral pH and can experience short-term metabolic stress from abrupt pH shifts rather than gradual biological buffering; this would explain why Treatment 3's Fe/Mn trajectories (Section 4.1(3)–4.1(4)) mirror Treatment 1's early-stage kinetics more closely than Treatment 2's. Rather than a true synergistic effect, Treatment 3 appears to represent a *dose-diluted average* of the two individual

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mechanisms, with its main advantage being pH stability (less day-10 dip than Treatment 2) rather than superior metal removal. This finding refines, rather than confirms, the original hypothesis: combining active and passive methods at full (not halved) individual doses, or introducing the chemical and organic components sequentially rather than simultaneously, may be necessary to realize true synergy a design variable this study did not test and that future work should isolate.

4) Integrating ANOVA Results with Physicochemical Mechanisms

The ANOVA results (Tables 4–5) are consistent with, and help substantiate, the mechanisms proposed above. The non-significant treatment effect on TSS ($F_e = 2.518 < F_t = 3.86$) supports the interpretation in Section 4.2.2 that TSS generation is an inherent by-product of *all* neutralization pathways rather than a treatment-specific artifact i.e., every treatment generates solids through precipitation or biomass, just via different chemical routes. Conversely, the significant treatment effect on Fe ($F_e = 4.675 > F_t$) and Mn ($F_e = 5.814 > F_t$) confirms that the choice of neutralization pathway (chemical vs. biological vs. combined) measurably alters metal-removal outcomes, consistent with the distinct precipitation/redissolution kinetics described in Section 4.2.1. The non-significant day effect on Fe ($F_e = 0.753 < F_t$) is notable: despite the visible day-to-day fluctuation described in Section 4.1(3), this fluctuation is not large enough, relative to inter-treatment variability, to register as a statistically distinguishable time trend reinforcing that Fe dynamics in this system are governed more strongly by treatment-specific mechanisms than by simple elapsed time, unlike pH and Mn, whose significant day effects reflect their more gradual, cumulative response to ongoing neutralization and biogeochemical activity.

5) Comparison with International Regulatory Thresholds

Evaluated solely against MoEF Regulation No. 5/2022 (TSS ≤ 400 mg/L), all treatments in this study "pass" despite their substantial TSS increases. However, benchmarked against stricter international effluent standards such as the U.S. EPA's Coal Mining Effluent Limitations Guidelines (40 CFR Part 434), which set a maximum instantaneous TSS limit of 70 mg/L and a 30-day average of 35 mg/L, alongside Fe (7.0/3.5 mg/L) and Mn (4.0/2.0 mg/L) limits the day-10 and day-15 TSS values observed here (89–210 mg/L across treatments) would exceed the international discharge threshold by a factor of 1.3–3×, even though final Fe and Mn concentrations in Treatments 1–3 remain comfortably within both the Indonesian and U.S. limits. This comparison reframes the study's central engineering challenge: pH and dissolved-metal control are readily achievable at laboratory scale by all three methods, but suspended-solids management the parameter most likely to fail under internationally recognized discharge standards remains the critical unresolved constraint for translating any of these treatments, especially the hybrid method, into a globally applicable AMD management technology.

5. Conclusion

This study demonstrates that active, passive, and hybrid AMD treatments provide different pathways for balancing rapid neutralization and biogeochemical stability. Active treatment with $Ca(OH)_2$ provides rapid pH correction and effective iron removal, while the goat-manure-based passive treatment shows stronger overall performance for Fe and Mn removal through organic-mediated and sulfate-reducing processes. The hybrid treatment did not produce the expected synergistic effect at the tested half-dose ratio, indicating that treatment sequence and dosing proportion are important design variables.

The findings have theoretical implications for AMD treatment by showing that treatment effectiveness should be assessed not only from pH correction and dissolved-metal removal but also from secondary effects such as suspended-solids generation. Practically, goat-manure-based passive treatment is a promising low-cost option for AMD with a manageable acidity and metal load, provided that downstream solids management is incorporated into system design.

The conclusions remain preliminary because the experiment used a single non-replicated reactor and did not continuously monitor temperature, dissolved oxygen, or redox potential. Future research should therefore use replicated reactors, characterize the organic substrate, optimize chemical organic dosing and sequencing, and validate the treatment at pilot or field scale with a dedicated TSS-control stage.

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