Acid Mine Drainage Remediation with Waste Products: Laboratory Findings and Field Model Applications

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Abstract

Industrial byproducts were tested for acid mine drainage (AMD) treatment in the Iberian Pyrite Belt. Bench-scale experiments evaluated paper sludge and biochar at different AMD: material ratios (1:50, 1:100, 1:200) under oxic/anoxic conditions. Paper sludge raised pH from 1.64 to 6.23 (1:50), promoting Fe removal (100%). Biochar effectively adsorbed Cu (98%) at pH 5. A geochemical model simulated a field-scale treatment using a downflow pond with paper sludge and a biochar barrier. Results suggest these materials effectively neutralize AMD and retain potentially toxic elements, supporting their use in passive remediation.

Keywords: Passive Treatment, Industrial Byproducts Solutions, Geochemical Modeling, Iberian Pyrite Belt

Introduction

The Caveira polymetallic sulfide mine, in the northwest Iberian Pyrite Belt (IPB), faces significant environmental challenges due to historical mining. Its geology consists of an N-S-oriented antiform with a core of phyllites and quartzites (Middle-Superior Famenian) and flanks of sedimentary and volcanic sequences from the volcano-sedimentary complex (VSC). Sulfide mineralization, mainly pyrite with minor chalcopyrite, galena, and sphalerite, occurs in the VSC (Matos & Martins, 2006; Reis *et al.*, 2012). Despite its small size, the site contains extensive heap leach areas and ~2 Mt of waste (Reis *et al.*, 2012). Mining began in Roman times, initially for Au and Ag, later shifting to Cu, S, and pyrite until its abandonment in the 1960s, leaving uncontrolled acid mine drainage (AMD) that flows into the Grândola stream, dispersing potentially toxic elements (PTE) such as Cu, Pb, Zn, As, Mo, Se, Cd, Fe, and Hg (Matos & Martins, 2006; Reis *et al.*, 2012).

AMD treatment in abandoned IPB mines could involve industrial byproducts, reducing environmental impact and supporting a circular economy. The paper industry produces alkaline residues rich in lime and organic compounds, often landfilled, but capable of neutralizing AMD and facilitating metal attenuation. The most common paper sludge, from the kraft pulping process, consists primarily of organic residue with mineral impurities plus residual Ca and Na carbonates or oxides (Simão, 2018; Haile *et al.*, 2021). Likewise, biochar, which is charcoal produced from oxygen-limited biomass combustion (e.g., vineyard prunings, forestry waste, sewage sludge), has shown adsorptive potential for AMD remediation (Hu *et al.*, 2020; Qiu *et al.*, 2022). Bench-scale tests are crucial to assess these materials' feasibility. Simulating pond conditions with varying material-to-AMD ratios provides insights into their effectiveness, optimizing pH neutralization and metal attenuation. Integrating industrial byproducts into AMD treatment aligns with sustainable waste management, offering a viable alternative to conventional methods. This study investigates the effectiveness for paper sludge and biochar to be used for neutralizing AMD, with potential application in the IPB and beyond.

Methods

Bench-scale experiments evaluated the potential of industrial byproducts – paper sludge and biochar – for AMD. The study assessed their capacity to neutralize AMD and attenuate metal contaminants under controlled conditions. Batch tests were conducted in parallel under oxic or anoxic conditions to simulate a downflow pond. The pond experiments used 200ml AMD sample with material-to-AMD ratios of 1:50, 1:100, and 1:200 over 10 days, without agitation. The initial AMD had pH 1.68, SO_4 15000 mg/L, Fe 2830 mg/L, Al 583 mg/L, and Mn 63.7 mg/L, plus elevated concentrations of As (17.6 mg/L), Cd (0.528 mg/L), Co (1.01 mg/L), Cr (0.31 mg/L), Cu (33.1 mg/L), Ni (1.22 mg/L), Pb (2.29 mg/L), and Zn (146 mg/L). Effluent pH and electrical conductivity (EC) were monitored daily, while final effluent samples were analyzed by ICP-OES for metal concentrations. Solid-phase materials that accumulated in the ponds were dried at 40°C, ground, digested with *Aqua Regia*, and then analyzed by ICP-OES. Kinetic adsorption tests at pH 5 assessed metal retention by biochar and paper sludge. Using 0.4g of each material in 40ml of single-element solution, samples were shaken at 225 rpm at room temperature, with collection at intervals (5 min–24 h), followed by filtration and ICP-OES analysis.

A preliminary geochemical model was developed using PHREEQC (Parkhurst and Appelo, 2013) and the PHREEQ-N-AMDTreat+REYs water-quality tools with the wateq4fREYsKinetics.data database (Cravotta, 2022) to simulate the observed chemical changes during bench experiments. Subsequently, the model was applied to simulate a field-scale downflow pond system. Paper sludge served as a base layer to increase pH and precipitate Fe, followed by a biochar-based barrier for Cu and other metals.

Results

Kinetic Adsorption Tests

The kinetic adsorption tests assessed the adsorption rate and capacity of excess metals in Caveira mine water using the studied materials. Results revealed distinct behaviors due to their differing physicochemical properties: carbonate-rich paper sludge exhibited a different adsorption profile than highly porous, carbon-rich biochar. Copper (Cu) (Fig. 1) demonstrated similarly high retention rates for both materials, with paper sludge achieving 99.9% retention and biochar 98.3%. However, paper sludge removed nearly all Cu within 15 minutes, whereas biochar adsorbed it more slowly. Mercury (Hg) (Fig. 1) was rapidly retained by biochar (99.6% in 5 min), while paper sludge showed slower retention, reaching only 50.6% after 24 hours. Manganese (Mn) (Fig. 1) behaved differently: biochar retained just 18.4%, while paper sludge achieved complete removal (100%) within 15 minutes. Zinc (Zn) (Fig. 1) followed a similar trend, with paper sludge reaching 100% retention in 5 minutes, whereas biochar initially retained some Zn, then released it entirely after 10 hours, ending with only 21% retention after 24 hours.

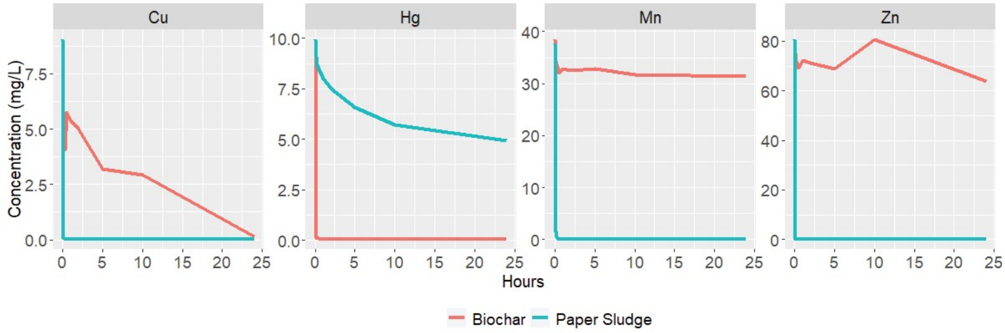

Figure 1 *Adsorption kinetics of biochar and paper sludge for the studied metals over time.*

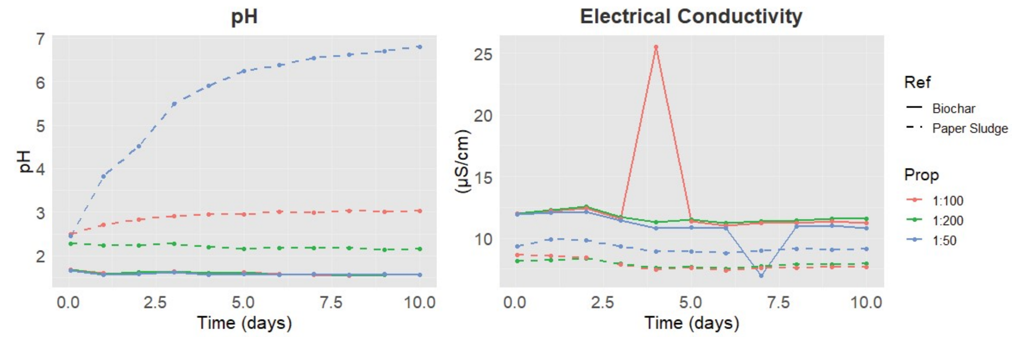

Figure 2 *pH and electrical conductivity recorded in ponds under anoxic conditions over time.*

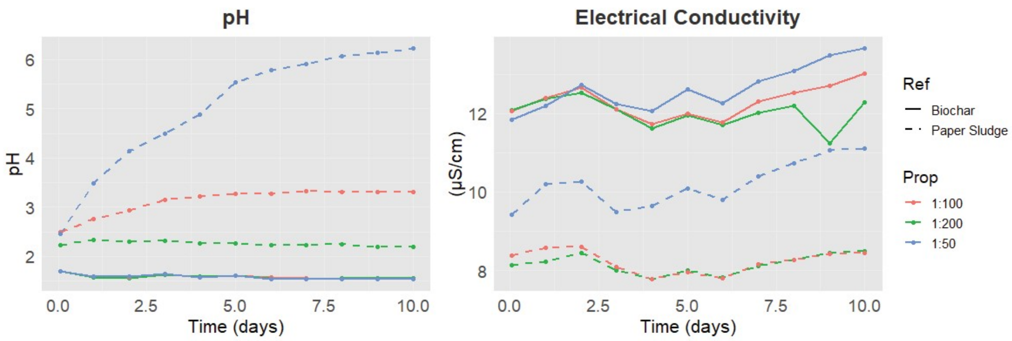

Figure 3 *pH and electrical conductivity recorded in ponds under oxic conditions over time.*

Pond Simulation Experiments

The primary objective of the bench-scale pond simulation experiment was to identify the optimal conditions for increasing the initial water pH (1.64) to enhance the retention capacity of metallic elements, which typically occurs at pH levels above 5–5.5. Additionally, the study aimed to assess the retention capacity of the materials for each element. The initial water EC was 11.67 mS/cm.

In biochar ponds, the initial pH (1.64) remained stable under both anoxic (Fig. 2) and oxic conditions (Fig. 3). In contrast, paper sludge ponds showed an important pH rise, especially at a 1:50 ratio, reaching 6.80 (anoxic) and 6.23 (oxic) after 10 days. Lower ratios were pH, around 3 (1:100) and 2 (1:200).

Table 1 PTE and Alcaline Metals Removal after 10 days, ((C0-Ct)/C0 in %) in Anoxic Ponds water columns.

	P. Sludge 1:200	P. Sludge 1:100	P. Sludge 1:50	Biochar 1:200	Biochar 1:100	Biochar 1:50
Al	-20,9	10,6	**100**	-12,4	-14,4	-12,9
As	**76,1**	**100**	**100**	**21,1**	**23,6**	**26,0**
Ca	-425,4	-277,1	-286,6	13,8	7,5	1,4
Cd	**49,5**	**66,4**	**97,1**	15,9	18,0	20,8
Co	5,0	-7,9	**86,3**	2,2	3,9	7,4
Cr	-1,5	58,2	**64,7**	-0,6	-0,5	4,4
Cu	28,2	31,8	**99,7**	**42,5**	**41,3**	**43,2**
Fe	23,2	**100**	**100**	-14,2	-16,5	-14,2
K	-2693	-11503	-23208	-2127	-2349	-6223
Mg	-196,1	-289,9	-512,7	0,5	0,5	-0,3
Mn	-23,9	-57,5	25,2	**20,6**	**19,7**	**22,8**
Na	-724,5	-1219	-2397	-24,2	-24,7	-25,8
Ni	3,9	7,6	**90,9**	10,3	10,5	15,1
Pb	**67,6**	**86,8**	**96,3**	-1,0	-12,7	-2,0
Zn	-26,2	-3,4	**98,7**	-5,2	-7,5	-6,0

In anoxic conditions (Fig. 2), paper sludge maintained stable EC (7–8 mS/cm), lower than the original water. In oxic ponds (Fig. 3), only the 1:50 ratio showed similar value (11.11 mS/cm after 10 days). Biochar conductivity in anoxic ponds (Fig. 2) was generally stable, except for peaks at 1:100 (day 4) and 1:50 (day 7). In oxic conditions (Fig. 3), this parameter increased gradually, peaking at 13.66 mS/cm for the 1:50 ratio.

PTE removal efficiencies were similar in both conditions (Tabs. 1 and 2). Biochar, particularly at the 1:50 ratio, had the lowest retention rates, while the most effective system was the 1:50 paper sludge pond with oxygenation.

The As exhibited the highest retention rates among all elements, with values ranging from 21.1% to 100% in anoxic ponds (Tab. 1) and from 0.6% to 100% in oxic ponds (Tab. 2), with

Table 2 PTE and Alcaline Metals Removal after 10 days, ((C0-Ct)/C0 in %) in Oxic Ponds water columns.

	P. Sludge 1:200	P. Sludge 1:100	P. Sludge 1:50	Biochar 1:200	Biochar 1:100	Biochar 1:50
Al	-81,7	-3,1	**99,9**	-19,9	-29,9	-46,8
As	**78,9**	**100**	**100**	**7,8**	**10,6**	**0,6**
Ca	-619,0	-301,2	-268,7	2,8	0,8	-26,6
Cd	**44,7**	**64,0**	**95,3**	13,6	9,2	3,2
Co	-2,3	-17,3	**93,6**	4,6	-2,8	-9,4
Cr	-3,6	60,8	**63,7**	0,5	-3,8	-8,7
Cu	24,1	30,2	**99,6**	**29,8**	**24,5**	**17,5**
Fe	20,8	**99,8**	**100**	-20,6	-30,9	-46,2
K	-2859	-10891	-27615	-2453	-5404	-8363
Mg	-346,8	-397,0	-665,2	-5,2	-14,6	-33,0
Mn	-32,6	-72,3	45,1	**9,1**	**2,5**	**-5,7**
Na	-1144	-1551	-3227	-30,6	-41,0	-67,9
Ni	-2,7	-18,0	**95,3**	11,7	3,3	2,8
Pb	**72,2**	**88,9**	**97,2**	-17,3	-14,3	-10,0
Zn	-88,8	-26,4	**99,5**	-11,5	-21,1	-38,9

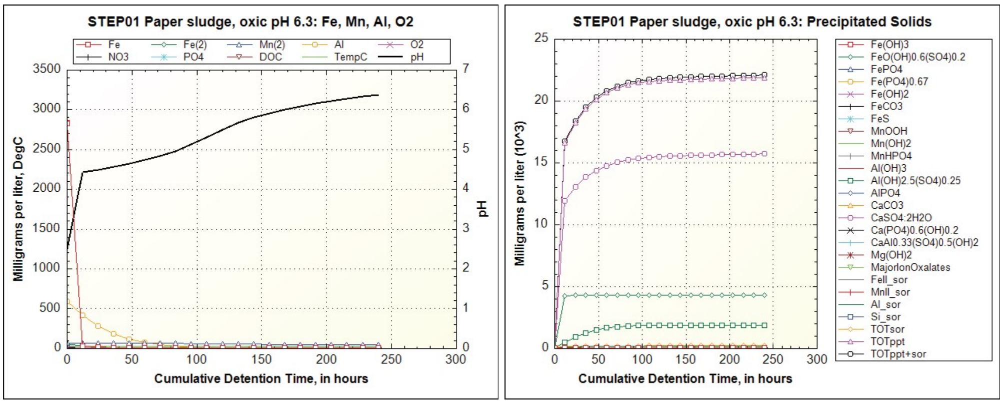

Figure 4 *Major Elements in solution (left) and precipitated solids (right) vs time, modeled in PHREEQ-N-AMDTreat + REYs for paper sludge pond.*

the highest retention observed in paper sludge systems. K and Na were the only elements not retained; instead, they were released into the environment, as indicated by their negative retention values. In the case of paper sludge, As retention was the most successful, with removal rates between 76.1% and 100% in anoxic ponds (Tab. 1) and between 78.9% and 100% in oxic ponds (Tab. 2). For biochar, the highest retention was observed for Cu, with retention rates ranging from 41.3% to 43.2% in anoxic ponds (Tab. 1) and from 17.5% to 29.8% in oxic ponds (Tab. 2).

Geochemical Modeling

To simulate remediation with paper sludge, the PHREEQ-N-AMDTreat+REYs kinetics models, TreatTrainMix2_wateq.exe and TreatTrainMix2REYs.exe were used to simulate the progressive dissolution of limestone over 240 hours combined with an excess of solid organic carbon (SOC 20 mol) under oxidizing conditions. To account for the removal of the trace elements by adsorption, a specified mass of sorbent (1000 mg) having Fe, Mn, and Al concentrations of 81.4wt%, 1.8wt%, 16.8wt%, consistent with the mass fractions in the starting solution, was assumed to be present for the duration. Fig. 4 shows an equilibrium trend for basaluminite ($Al(OH)_{2.5}(SO_4)_{0.25}$) and schwertmannite ($FeO(OH)_{0.6}(SO_4)_{0.2}$). However, it also indicated that various metal-bearing species remain in solution, leading to increased precipitation of these and other alkaline solids, with gypsum ($CaSO_4 \cdot 2H_2O$) being the most predominant.

Discussion

In the kinetic assays, biochar exhibited approximately 100% retention for Cu and Hg (Fig. 1). According to Kılıç *et al.* (2008), adsorption occurs on the biomass surface, where the release of protons and basic metal ions (Ca^{2+}, Na^+, and K^+) happens during Cu^{2+} or Hg^{2+} adsorption. This mechanism may explain the low retention rates in both oxic and anoxic biochar ponds (Tabs. 1 and 2). Biochar has a high affinity for Cu, evidenced by the kinetic assays (Fig. 1) and by Cu being the most adsorbed metal in the pond experiment (Tabs. 1 and 2). This reaction is pH-dependent (Padilla *et al.*, 2024). Mn and Zn showed approximately 20% retention in biochar assays (Fig. 1). Zn likely relies on ion exchange or electrostatic attraction, while Mn retention is hindered by high H^+ ion concentrations. Paper sludge demonstrated about 50% retention for Hg in kinetic tests (Fig. 1). Hg adsorption on cellulosic surfaces is pH-dependent, with higher pH favoring $HgOH^+$ formation and increased metal retention (Min & Ray, 2024). In contrast, Cu, Mn, and Zn retention by paper sludge reached nearly 100%. This efficiency is attributed to Ca^{2+} and Mg^{2+} release, facilitating ion exchange and promoting metal precipitation (Méndez *et al.*, 2009). Negative retention values (Tabs. 1 and 2) further suggest this. pH, a key parameter influencing adsorption interactions, was not measured during this experiment. Future studies will address this limitation.

Biochar, in the pond experiment, exhibited higher EC in both oxic and anoxic conditions (Figs. 2 and 3), indicating a higher concentration of dissolved metals, supported by Tables 2 and 3. This outcome is likely due to biochar's limited ability to increase pH, as its adsorption capacity is pH-dependent and more effective at higher values (Padilla *et al.*, 2024). However, EC was higher in oxic ponds, suggesting greater metal retention in anoxic conditions, likely due to enhanced ion reduction and metal immobilization on biochar (Zhao *et al.*, 2024). Paper sludge in the 1:50 ratio showed higher EC in an oxidizing environment (Figs. 2 and 3), indicating a greater concentration of metal ions. Higher levels of K, Na, and Mg were observed in oxic conditions (Tab. 2), likely due to oxidation reactions that accelerate organic matter breakdown and cation release (Bastviken *et al.*, 2001). This may explain why paper sludge ponds in oxygenated conditions performed slightly better than in anoxic environments (Tabs. 2 and 3).

The geochemical model generated by PHREEQ-N-AMDTreat+REYs (Fig. 4), showed that although most of the Fe precipitated at pH <3, the specified sorbent indicates this hydrous ferric oxide, as well as hydrous aluminum oxide and hydrous manganese oxide that form at higher pH, continues to be available when the pH increases to values sufficiently high for the elements to sorb. The model results are consistent with observed changes in the pH, Fe, Al, Mn, and trace elements, including nearly complete removal of Fe, Al, and most trace elements, but incomplete removal of Mn and Zn. Extrapolating the experimental results to a field model, Padilla *et al.* (2024) suggest that biochar exhibits higher retention ability at pH levels above 6.5. This supports the use of a paper sludge pond for initial mine drainage treatment, where it could effectively increase pH and retain elements. Following this, a biochar-based reactive barrier could further enhance metal adsorption by targeting the remaining dissolved elements, capitalizing on biochar's increased retention efficiency at higher pH levels.

Conclusions

Biochar and paper sludge demonstrated promising potential for AMD treatment, each exhibiting distinct adsorption behaviors for different elements. Biochar proved particularly effective in adsorbing Cu and Hg, with its performance being pH-dependent, while paper sludge showed high retention rates for Cu, Mn, and Zn, likely due to ion exchange mechanisms and its ability to raise pH. The pond experiments highlighted the importance of environmental conditions, such as oxygen availability, in influencing metal retention and conductivity. Extrapolating to a field model, biochar's increased efficiency at pH levels above 6.5 supports its potential role in a two-stage treatment system, where paper sludge could initially raise pH and retain PTE, followed by a reactive biochar barrier for further metal adsorption.

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