

Sustainable Removal of Metal/loids from As-Rich Mine Waters Using Mine and Industry Waste Materials

Mari a Dolores Basallote^{1*}, Gerardo Amaya², Maira Castellanos², Carlos Ruiz Ca novas², Jose, Miguel Nieto², Rafael Pe rez-Lo pez²

¹*Department of Ecology and Coastal Management, Institute of Marine Sciences of Andalusia (ICMAN), Spanish National Research Council (CSIC), 11510 Puerto Real, Cádiz Spain*

²*Department of Earth Sciences & Research Center on Natural Resources, Health and the Environment, University of Huelva, Campus "El Carmen", 21071, Huelva, Spain.*

Abstract

Removal efficiency of metal/loids from a highly acidic (pH 2.0) and metal/loid rich waters (6111 mg/L of Fe, 906 mg/L of Al, 748 mg/L of Zn or 13 mg/L of As) from the Iberian Pyrite Belt has been evaluated using industrial and mining waste materials (i.e., biomass ashes (BA) and schwertmannite-rich wastes (SRW)) by column and batch experiments. The batch experiments evidenced a high removal efficiency for As, with values ranging from 86 to 96% using BA and from 20 to 88% using SRW, with the maximum values reached at the end of the experiment. High removal rates for Fe (72%), Cu (88%), Pb (99%) and U (98%) were also achieved using a S:L ratio 1:10 of BA. In the case of the batch experiment using SRW, up to 90% of Pb, 77% of As 22% of Cr and 14% of Fe was removed from solution. In the case of the column experiment (25 days), the removal efficiency of As ranged from 87 to 98% in the BA-column during the whole period, while in the case of the SRW, the efficiency ranged from 63 to 96%, with the maximum values observed at the beginning and end of the experiment.

Keywords: Metal/loid removal; column experiments; batch experiments; waste recycling

Introduction

Acid mine drainage (AMD) is one of the main causes of water pollution worldwide. The oxidation of sulfides can lead to the occurrence of high concentrations of a variety of contaminants in water bodies. One representative example of AMD processes is the Iberian Pyrite Belt, one of the largest polymetallic sulfide deposits in the world, with many examples of extreme pollution by AMD (Nieto *et al.*, 2013). To mitigate environmental impacts on water bodies, mining operators and environmental authorities put into practices costly measures to neutralize the acidity and reduce metal concentration in AMD generated in mining sites, generally applying alkaline raw materials (Basha *et al.*, 2008), which extraction has a negative environmental footprint. Therefore, more environmentally friendly and costly measures need to be applied, especially in orphan mines, where local or regional

authorities often assume the environmental liabilities.

Alternative options for costly alkaline raw materials are low-cost sorbents from agricultural and industrial wastes (Mohan and Pittman, 2007). Among them, biomass ash (BA) is a promising option due to their elevated alkalinity and high concentration in Ca and Mg. This material has been successfully used for the treatment of highly acid effluents from the fertilizer industry, with removal rates of 87-100% for Fe, U, F and Cr, and around 50% for Al, Zn, Cu and As (Milla n Becerro *et al.*, 2020). These ashes are generated at high volumes during biomass burning to generate electricity. Considering the current global biomass power generation market, with more than 4,500 biomass power plants by 2022 and signs that they are quickly catching up when comparing with coal power plants, the amount of ashes generated is expected to grow up in the following years.

Although the main fate of these wastes is landfilling, its application to treat acid mine waters could be a promising route of waste valorization if biomass generation is close to mine areas (Bogush *et al.*, 2020). On the other hand, Fe oxides and oxyhydroxides are materials with a high sorption capacity (Gutierrez *et al.*, 2010). Among these minerals, schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_{5,5}(\text{SO}_4)_{1,25}$), jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) and goethite (FeOOH), usually control trace metal/loid mobility in AMD systems (AMD) (Asta *et al.*, 2009). In the case of schwertmannite, this mineral precipitates naturally in the vicinity of AMD sources, the riverbanks of AMD-affected water courses and within the components of passive treatment systems. In this latter case, a decrease of 40% of initial As concentration was observed in a lagoon placed before the passive treatment plant of Mina Esperanza (SW Spain). This plant is based on the Disperse Alkaline System technology, which is basically composed of an initial lagoon, and successive tanks filled with alkaline materials such as limestone and magnesia, and settling ponds to ease the removal of metals. Thus, the Fe(II) and As rich waters are oxidized before entering to the plant, and the precipitation of schwertmannite scavenged large quantities of As by sorption processes (Orden *et al.*, 2021). Passive treatment plants like those based on DAS technology require minor maintenance, being one of them the removal of Fe precipitates accumulated along the lagoons, channels, settling ponds and tanks. This material may be removed periodically and landfilled, which obviously have economic and environmental costs. However, the use of these wastes as sorptive material to remove metal/loids from AMD-affected waters could help to solve the problems related to its management. Therefore, the main goal of this work is to assess the suitability of waste materials such as biomass ash and schwertmannite-rich wastes (SRW) as sorptive agent to treat metal/loid rich AMD waters.

Methods

Biomass ash samples (5 kg) were collected from the biomass electricity complex of ENCE at Huelva (50 MW), which generates around

56000 tonne/yr of ash, close to the main AMD sources of the IPB. Schwertmannite-rich wastes (5 kg) were collected from Mina Esperanza passive treatment plant. It worth noting that this material already accumulate high concentration of metal/loids, compared to schwertmannite precipitating from less polluted waters. In addition, 25 L of extremely metal/loid rich and acidic waters were collected from Tharsis mines. These starting materials were chemically (through ICP-MS and ICP-OES) and mineralogically characterized (through XRD and SEM-EDS) before starting the experiments. In this sense, two different experiments were performed to study the suitability of BA and SRW to be used as remediation agent of AMD waters.

Batch experiments were performed by duplicate using 4 different solid: liquid ratios (1:2, 1:5, 1:10 and 1:20). Kinetic aspects were also evaluated considering different reaction times for each experiment (15 min, 1 h, 3 h, 6 h, 12 h, 24 h, 48 h and 96 h). Samples were agitated during the experiment, and samples corresponding to each reaction time were removed, centrifuged and the supernatant was filtered through 0.45 μm cellulose nitrate filters and acidified with ultrapure HNO_3 before analysis. Physico-chemical variables (pH, ORP, electrical conductivity (EC) and temperature) were measured in each sample using a HACH multiparameter probe, previously calibrated.

Column experiments were also performed, consisting on an initial tank (5L) to store AMD waters, connected to a column with a peristaltic pump at a constant rate of 0.3 mL/min. The columns (40 cm length, 6 cm of diameter) were made of HDPE and filled with either SRW or BA mixed with wood shaving (80%:20%) to provide porosity. The column bottom was filled with 3 cm of silicic sands to enhance drainage. The column was connected to a settling pond (445 mL) to store the treated waters. Column experiments lasted 25 days, where samples were collected at a variable frequency (daily the first week and each 2-3 days the remaining time), following the same procedure as for batch experiments (measure of physico-chemical parameters, filtration and acidulation before analysis). The analysis (ICP-OES and ICP-MS) were

performed at the Central Research Services of the University of Huelva (Spain).

Results and discussion

Characterization of starting materials

The chemical composition of starting materials used in the experiments are shown in Table 1. As can be seen, SRW showed a high concentration in Fe and S, with values around 48% and 6%, which apparently coincides with the stoichiometric ratio in schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_{5,5}(\text{SO}_4)_{1,25}$). This material also showed high concentration of As (870 mg/kg), Al (867 mg/kg), P (377 mg/kg) or V (274 mg/kg). The presence of gypsum cannot be ruled out due to the high concentration of Ca found (541 mg/kg). The XRD patterns indicated that SRW are of amorphous nature, although the main peaks of schwertmannite were identified. In the case of the BA, this is mainly composed of Al, Ca, Fe and K oxides (Table 1), with high concentrations of other elements such as Na (2405 mg/kg), P (1315 mg/kg), Ti (1114 mg/kg) or Mn (840 mg/kg). The alkalinity of BA is evidenced by the high pH value (9.2), reached after a pH paste procedure. This material showed a low crystallinity, and only quartz was detected in XRD patterns. AMD samples exhibited a very low pH value (2.0) and high EC (14 mS/cm),

with high concentrations of sulfate (20814 mg/L), and metal/loids (e.g., 6664 mg/L of Fe, 910 mg/L of Al, 794 mg/L of Zn, 196 mg/L of Cu and 14 mg/L of As).

Batch experiments

The contact of AMD with BA caused a sharp increase of pH values, especially at lower rates (1:10 and 1:20), from 2.0 to 3.3 within the first hour of the experiment (Fig. 1), due to the high alkalinity of BA. The pH values exhibited an increasing tendency towards the end of the experiment (4.7 and 3.7 for rates 1:10 and 1:20 at 96h). At higher rates (1:100 and 1:200), the increase was moderate (3.4 and 2.0, respectively). In the case of the SRW, a slight increase in pH was observed (from 2.0 to 2.2) probably associated to Fe(II) oxidation.

Regarding the elimination of metal/loids, the removal of As with BA at lower ratios (1:10 and 1:20) was very high, with values of 86% (1:10) and 96% (1:20) after only 5 min of contact, reaching values close to 100% at the end of the experiment. In the case of higher ratios (1:100 and 1:200) the removal reaction was slower. However, high removal rates were also achieved at the end of the experiment (100% and 95%, respectively). In the treatment with SRW, a progressive increase

Table 1 Chemical composition of biomass ash (BA), schwertmannite-rich wastes (SRW) (in mg/kg) and AMD (in mg/L) used in the experiments

	Schwertmannite	Biomass ash	AMD
Al	867	30593	910
Ca	541	53663	210
Fe	476379	17141	6664
K	174	16813	48
Mg	439	6028	391
Mn	11	840	78
Na	74	2405	28
P	377	1315	<5
S	55201	230	6938
As	870	2,6	14
Cr	8,8	29	0,6
Cu	112	77	196
Co	<1	5,5	1,1
Pb	31	8	0,5
Sr	<1	5,5	1,1
Ti	25	1114	0,04
V	274	127	0,7
Zn	80	50	794

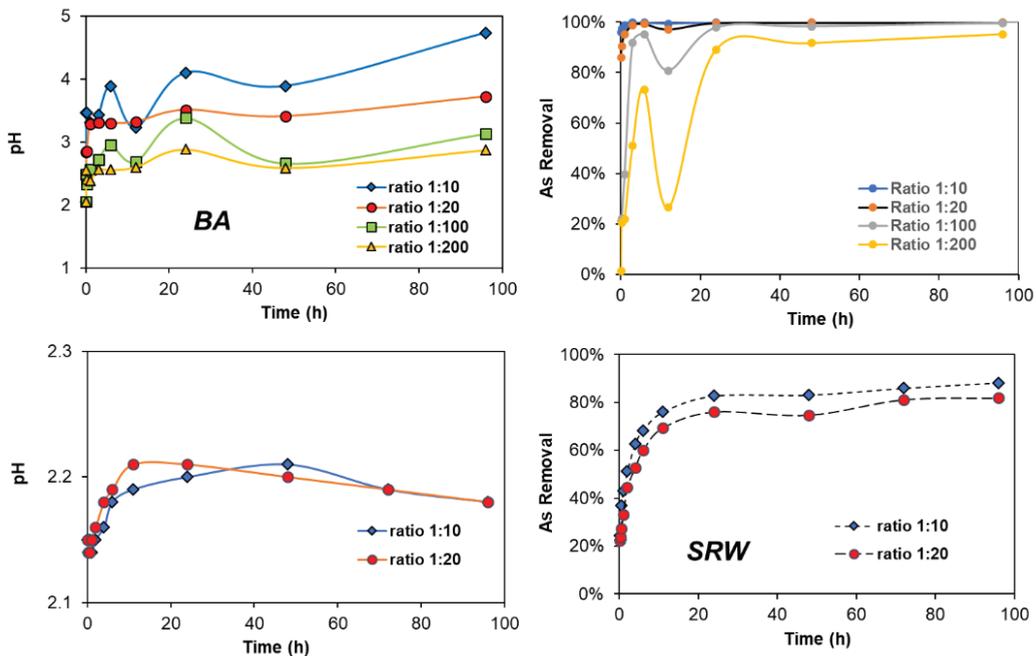


Figure 1 Evolution of pH and As removal during the batch experiments with biomass ash (BA, top) and schwertmannite rich wastes (SRW, bottom).

in As removal was observed, with final values of 88% (1:10) and 82% (1:20). During the experiments with BA, the removal of other contaminants was observed; up to 72% of Fe, 85% of Cu or 98% of U was removed at a ratio 1:10, with moderate removal rates for the rest of ratios ($< 40\%$ and 20%). In the case of V and Pb, the removal ranged from 88% to 98% and from 56% to 100% respectively. Lower values were observed for sulfate and Zn with removal rates of 24-48%, and 13-26%. Higher removal rates were also observed during the batch experiments with SRW, with values of up to 90% of removal for Pb, 69-77% for Cs or 22% for Cr. However, due to the contact of the acidic waters with BA and SRW some elements were released to the solution. On the one hand, the dissolution of BA increased the concentration of Ca, Mg, K or Mn. Conversely, the competitive sorption processes with As, caused the released back to solution of some elements such as V or U.

Column experiments

The alkalinity contained in BA caused a sharp increase of pH values (a maximum of 4.8), although temporarily until the depletion of the reagent, recovering the initial values at the

end of the experiments (Fig. 2). In the case of the SRW column, the pH values increased slightly until a value of 2.2, remaining afterwards as the initial values. Regarding the removal of contaminants, the elimination of As in both columns was successful with removal rates of 60-100%, although with a different evolution in both columns (Fig. 2). The removal rate was above 98% in the BA column most of the experiment, decreasing progressively until a final value of 87%, while in the SRW column higher rates were observed at the beginning and the end of the experiment ($>90\%$), with lower rates during the intermediate period (60–80%).

As in the batch experiments, a remarkable removal of other pollutants was observed. For example, 60-73% of Fe, 58-100% of Al, 58-64% of sulfate, or 49-60% of Mn (Fig. 2) was removed from the initial solution, decreasing progressively until the end of the experiment. These concentrations were even higher than initials for Al, Mn and Si in the case of BA due to the dissolution of oxides contained in this material, and for Fe and sulfate in the case of SRW, due probably to re-dissolution processes of Fe oxyhydroxysulfates. The columns were also efficient to remove Pb and U. In the case

of SRW column, the removal of Pb was very high (75–93%) and constant through the time, while for BA column higher values were observed at the beginning and the end of the experiment (76–96%). For U, a high removal was initially observed (66–99%), decreasing progressively through the experiment, and reaching values even higher than initials.

A high retention of V and Cr was also observed during the first days of the experiment, with values ranging from 53–99% and 70–99%, respectively. However, a progressive decrease is observed afterwards, reaching in the SRW column V concentrations higher than initials, probably due to competence with other oxyanions for sorption sites of schwertmannite. A similar behavior was observed for Cu and Zn, initially removed from solution at high rates (58–99% and 60–64%), and a progressive decrease afterwards. As in the case of the batch experiments, a remarkable increase in concentration of elements such as Ca and Si was observed, associated to the dissolution of oxides in the BA column. In this sense, it is remarkable the solubility differences between Ca and Si oxides, evidenced by a high initial increase of Ca and a latter increase of Si.

Conclusions

This work evaluates the removal efficiency of metal/loids from a highly acidic (pH 2.0) and metal/loid rich (6111 mg/L of Fe, 906 mg/L of Al, 748 mg/L of Zn or 13 mg/L of As) waters using industrial and mining waste materials. Column and batch experiments were performed. The batch experiments evidenced a high removal efficiency for As, with values ranging from 86 to 96% using BA and from 20 to 88% using SRW, with the maximum values reached at the end of the experiment. In the case of the batch experiment using SRW, up to 90% of Pb, 77% of As 22% of Cr and 14% of Fe was removed from solution. In the case of the 25-days-column experiment, the removal efficiency of As ranged from 87 to 98% in the BA-column during the whole period, while in the case of the SRW, the efficiency ranged from 63 to 96%, with the maximum values observed at the beginning and end of the experiment. Both in batch and column experiments, high removal rates were also observed for other pollutants such as Fe,

Cu, Pb, Al, Mn, sulfate, or U, evidencing the suitability of these materials to treat AMD waters. Increased concentrations of some elements (e.g., Ca, Al, K for BA and sulfate, Fe, or V for SRW) were observed during the experiments due to dissolution of oxides contained in BA or desorption processes and re-dissolution of Fe minerals in SRW. Deeper research is needed to evaluate the reactivity of the solids after the treatments, especially the potential release back of pollutants, and about the binding mechanisms behind the metal/loid removal in these materials.

This investigation emerges as a collaboration with the company ATLANTIC COPPER. In this context, the shown results are essential for the development of appropriate, environmentally friendly and economically rational waste management. Our results have also shown potential for being scaled up and used as the base of modeling studies with other industrial by-products.

Acknowledgements

The authors thank all co-organisers for hosting the IMWA2023 Conference. This work has been funded by the supported by the Spanish Ministry of Economic and Competitiveness through the project TRAMPA (PID2020–119196RB-C21) and the ATLANTIC COPPER Cátedra through the ARCHENICAL project.

References

- Asta MP, Cama J, Martí nez M, Gime nez J (2009) Arsenic removal by goethite and jarosite in acidic conditions and its environmental implications. *J Hazard Materials* 171, 965-972, doi.org/10.1016/j.jhazmat.2009.06.097
- Basha CA, Selvi SJ, Ramasamy E, Chellammal S (2008) Removal of arsenic and sulphate from the copper smelting industrial effluent. *J. Chem. Eng* 141, 89– 98, doi.org/10.1016/j.cej.2007.10.027
- Bogush AA, Dabu C, Tikhova VD, Kim JK, Campos L (2020). Biomass Ashes for Acid Mine Drainage Remediation. *Waste Biomass Valor* 11, 4977–4989, doi.org/10.1007/s12649-019-00804-9
- Gutierrez C, Hansen HK, Nuñez P, Jensen PE, Ottosen LM (2010) Electro-chemical peroxidation as a tool to remove arsenic and copper from smelter wastewater. *J. Appl.*

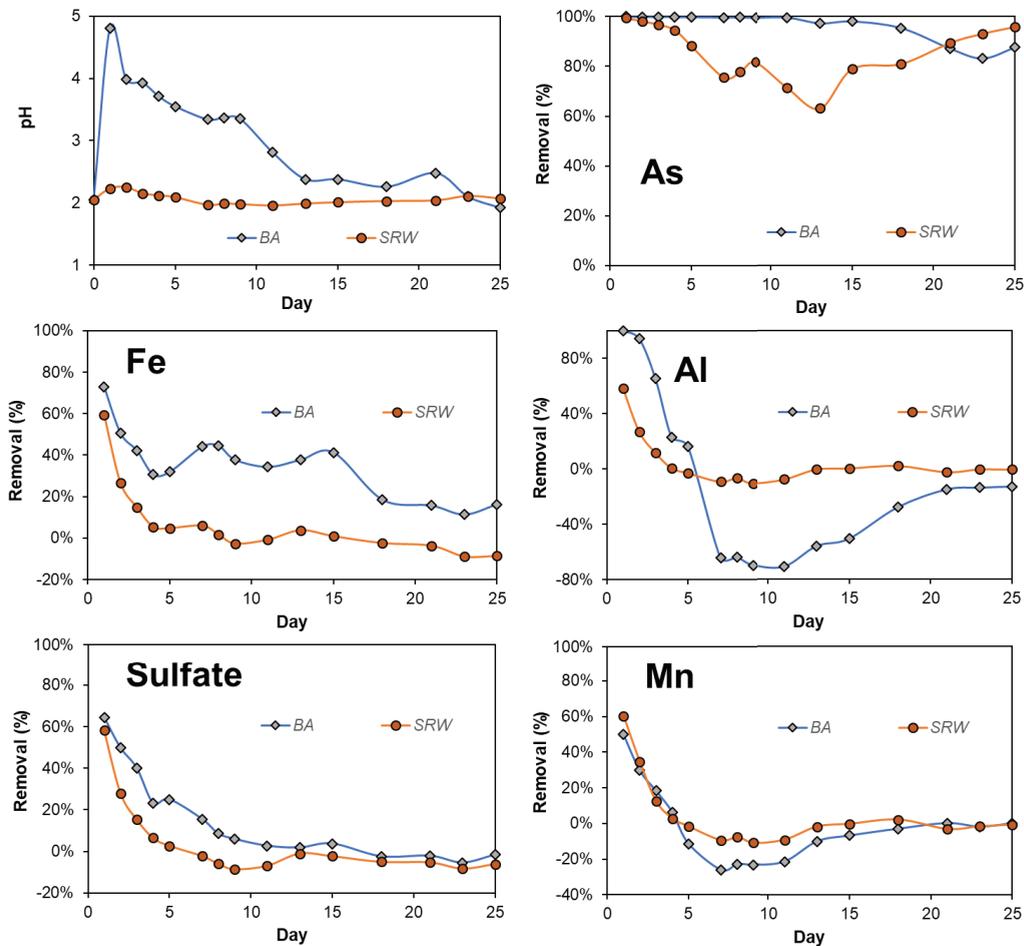


Figure 2 Evolution of the pH and removal rates for different contaminants during the column experiments with biomass ash (BA) and schwertmannite rich wastes (SRW).

Electrochem. 40, 1031-1038, doi.org/10.1007/s10800-009-0045-6

Milla n-Becerro R, Pe rez-Lo pez R, Mací as F, Ca novas CR (2020) Design and optimization of sustainable passive treatment systems for phosphogypsum leachates in an orphan disposal site. J. Environ. Manage. 275, 111251, doi.org/10.1016/j.jenvman.2020.111251

Nieto JM, Sarmiento AM, Canovas CR, Olias M, Ayora C (2013) Acid mine drainage in

the Iberian Pyrite Belt: 1. Hydrochemical characteristics and pollutant load of the Tinto and Odiel rivers. Environ. Sci. Pollut. Res. 20 (11), 7509–7519, doi.org/10.1007/s11356-013-1634-9

Orden S, Mací as F, Ca novas CR, Nieto JM, Pe rez-Lo pez R, Ayora C (2021) Eco-sustainable passive treatment for mine waters: full-scale and long-term demonstration. J. Environ. Manage. 111699, doi.org/10.1016/j.jenvman.2020.111699