

# Metals Removal from Acid Mine Water by Wood-Ash Amended Biochar

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## Abstract

The abandoned copper mine Parys Mountain has large areas of unconsolidated mine waste, lagoons of polluted water, and substantial subterranean workings. It annually discharges 34 t of metals into the Irish Sea. Wood ash amended biochar has the potential to be deployed to remediate Acid Mine Discharge (AMD). This study demonstrated that biochar can immobilise metals of concern (Zinc and Copper) from Parys Mountain AMD. Maximum measured immobilisation was  $4.1 \pm 0.4$  mg/g for zinc and  $4.1 \pm 0.0$  mg/g for copper with removal percentages up to 100%. Immobilisation mechanisms were precipitation and capture by biochar, ion exchange and co-precipitation.

**Keywords:** Metal mine waste, Biochar, Treatment, Remediation

## Introduction

Historic metal mining has led to metals of concern affecting over 2,500 km of watercourses in the UK. Acid mine drainage (AMD) from Parys Mountain has a pH of 2-3 and leaches metals including Zn (62 mg/L), Cu (42 mg/L) and Cd (148 µg/L). These concentrations are considerably above European Union Water Framework Directive (WFD) (Water Framework Directive 2015) thresholds leading to the mine discharging 10 t of Cu and 24 t of Zn into the Irish Sea annually (Morgan *et al.* 2017).

Concentrations of Zn, Cu and Fe that are above WFD thresholds can potentially harm their surrounding environment as well as human health (Yi *et al.* 2011). Depending on oxidation state, complex form and concentration these metals are associated with cancers of the lung and kidney, reduced fertility, central nervous system problems and mortality (Fosmire 1990; Beyersmann and Hartwig 2008; Morais *et al.* 2012). The use of biochar is a potential technique to remediate polluted waterways caused by acid mine drainage. Biochar is the carbon rich product obtained from the pyrolysis of biomass at temperatures generally under 900°C (Lehmann and Joseph 2009). The use of biochar in the remediation of metals

in aqueous media such as motorway runoff, industrial effluent and mine water has been discussed by previous studies (Bandara *et al.* 2020; Cairns *et al.* 2020; Gayathri *et al.* 2021). It has been highlighted as a relatively low cost, available and sustainable option in the removal of metals from water (Ahmad *et al.* 2014; Wang *et al.* 2018). Amending biochar with wood ash has been reported by Cairns *et al.* (2020, 2021) as a method to improve biochar's immobilisation of (post) transition metals. The addition of wood ash increases the pH buffering capacity, increases functional groups associated with ion exchange and promotes co-precipitation.

Acid mine drainage is a recognised global issue; this aim of this work is to investigate if wood ash amended biochar (WAS) has the potential to be scaled up and deployed as an effective remediator of acid mine waters reducing the concentration of metals of concern.

## Methodology

### Study Site

Parys Mountain, Anglesey, Wales (53°23'11"N 4°20'45"W) (Figure 1), was once the largest copper mine in the world, with both surface and subterranean

workings (Vernon 1996). At the start of the 20th century it was reduced to a one-man operation, and despite several post war efforts to reopen it, it remains abandoned. Several adits continue to drain the subterranean areas of the mine, unusually for the UK these

are acidic in nature with high concentrations of copper and iron. This pollution causes substantial deleterious effects on fauna and flora of the two watercourses that the mine discharges into (Mullinger 2004).

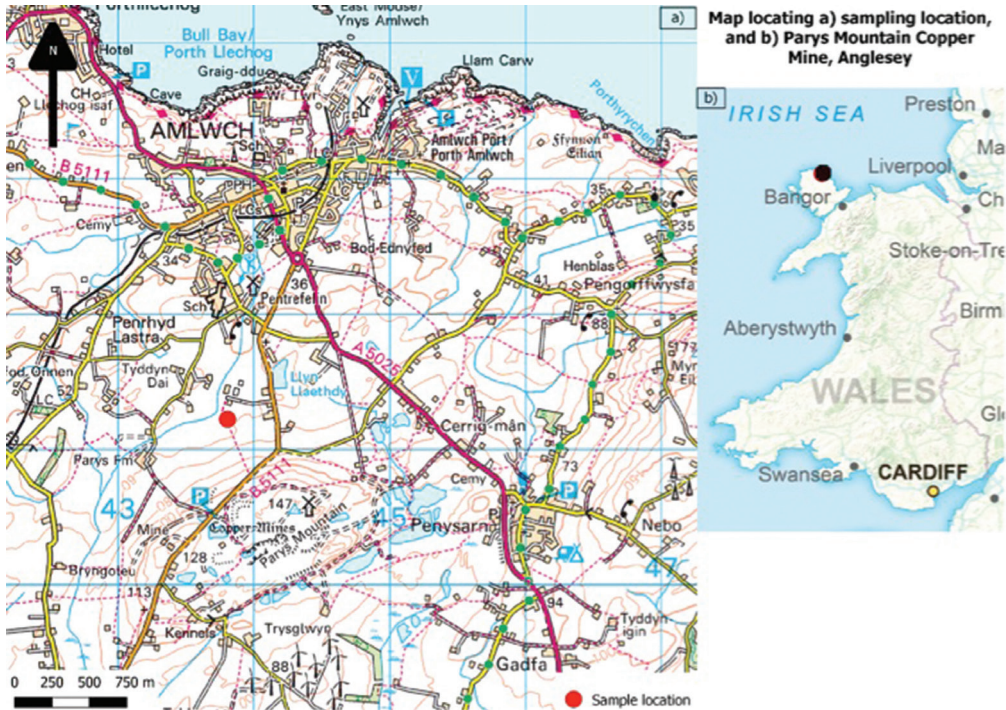


Figure 1 a) Location of sampling point (Dyffryn adit) and mined area, Parys Mountain Copper Mine; b) location of mine within Wales (Ordnance Survey 2020)

### Biochar Production

European larch (*Larix decidua* (L.) Mill.) wood chips were pyrolyzed using a pyrolysis-gasification kiln (Pyrocal BigChar-1000). Pyrolysis was undertaken at a temperature of 485–530 °C, with a retention time of ~90 s. Sustainably sourced wood ash was added to the still hot biochar at a ratio of 1:1, mixed for 15 min in a cement mixer to sinter the materials and then granulated to <3 mm using a Tria G1 granulator (Cairns *et al.* 2021). Wood ash was selected as an amendment due to its mineral fraction (specifically Ca, K, Mg, S, P and Si) and pH buffering capacity. However, the mineral fraction can potentially leach nutrients such as nitrates, phosphates

and sulphates (Liang *et al.* 2014). Cairns *et al.*; (2022) demonstrated that rinsing wood ash amended biochar with 200 mL of water per 5 g biochar removes these unbound nutrients and reduces leaching to below WFD thresholds.

### Sample Collection

Water was obtained from the Dyffryn adit at Parys Mountain Copper Mine (Figure 1) and sub-divided into five identical 1 L polyethylene terephthalate (PET) bottles. Each bottle was rinsed three times with sample water prior to filling. Samples were taken in April 2022 and were stored at 4°C in line with national guidelines (Environment Agency 2014).



### *Sorption Experiments*

Sorption batch experiments were carried out adding known quantities of WAS (0.05-2.00g) to 25 mL of Parys mine water in 40 mL polyethylene Falcon tubes. All sorbents were oven dried at 105 °C for 24 h. Agitation was achieved on a Unitwist 400 Orbital Shaker for 24 hrs at ~280 rpm to reach equilibrium. Subsequently, the mine water was separated from WAS using a Medical and Scientific Equipment. (MSE) Blue Force centrifuge at 3000 rpm for 15 minutes (OECD 2000). The supernatant was removed and acidified to < pH 2 with 1mL of 70% HNO<sub>3</sub> before being filtered with a 0.45 µm PTFE syringe filter for analysis.

Base cation and Cu, Zn, Fe, P concentrations of the acidified supernatants were measured using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES 5110, Agilent Technologies Inc., USA). Sorbent loading (q) was calculated from the difference between initial metal concentration and final metal concentrations in the aqueous phase:  $q = (c_i - c_{aq}) V / W$  where  $c_i$  is the initial concentration of metals in solution,  $c_{aq}$  is the final equilibrium concentration of metals in solution, V is the volume of solution and W is the weight of the biochar.

Two types of control experiments were included — biochar without contaminants, as well as contaminants without biochar. All experiments were performed in triplicates using a batch sorption equilibrium method (OECD 2000)

### *Biochar properties and metal speciation*

Biochar properties were determined to understand their effect on immobilisation. The release of base cations (Ca, K, Na and Mg) and nutrients (P) by biochar into the minewater were quantified and compared to review possible cation exchange and co-precipitation. Fourier transform infrared spectroscopy (FTIR) was undertaken using a Perkin Elmer Spectrum Two FTIR Spectrometer measuring in the range of 400-4000 cm<sup>-1</sup>. Absorbance measurements were used to detect changes to functional

groups and minerals associated with co-precipitation.

Speciation analysis of the mine water and biochar supernatants were carried out using the PHREEQC (pH redox equilibrium) code (version 3.7.1) and the MINTEQA4 database (Parkhurst and Appelo 1999). Prior to acidification the pH, temperature, EC, alkalinity and redox were measured using a calibrated Hanna Edge pH and EC meter, a Hanna HI-3811 alkalinity test kit and a calibrated Hanna Instruments HI98194 Multiparameter meter respectively. The pH, redox, temperature, alkalinity and concentrations of base cations, metal contaminants and nutrients were used as model inputs.

## **Results and Discussion**

### *Mine Water Chemistry*

Dyffryn adit was sampled in April 2022 and average metal concentrations were calculated. It was characterised by extremely high concentrations of Zn (68.4 mg/L), Cu (32.5 mg/L) and Fe (427.6 mg/L). Alongside these metal concentrations a low pH of 2.6 and a redox potential of 808 mV was measured. The Zn, Cu and Fe are all substantially above WFD thresholds (Water Framework Directive 2015).

### *Zn and Cu immobilisation by biochar*

Concentrations of Zn and Cu in the AMD decreased in the presence of biochar. The maximum recorded immobilisation of Zn was 4.1 ± 0.4 mg/g and of Cu was 4.1 ± 0.0mg/g. Increasing the biochar to AMD ratio increased the percentage of both Zn and Cu that was immobilised. The highest immobilisation percentage for Zn was seen with 0.5 g of biochar in 25 mL of AMD where 98% of Zn was immobilised and the highest immobilisation percentage for Cu was seen with 0.2 g of biochar in 25 mL of AMD where 100% of Cu was immobilised.

### *Aqueous Phase Chemistry*

The pH of the AMD increased in the presence of biochar from 2.7 to between 3.2 to 7.6 dependant on the quantity of biochar.

At a pH of above 6.5, 98% of Zn and 100% of Cu was immobilised and at a pH of over 3.2, 100% of Fe was immobilised. This is consistent with previously reported results for Zn, Cu and Fe (Oh and Yoon 2013). The increased immobilisation of these metals is primarily as a result of precipitation and subsequent capture on the surface of the biochar. PHREEQC modelling indicates that as the ratio of biochar to AMD increased for Zn and Cu there was a shift from divalent mobile metal species to immobile species such as  $\text{CuCO}_3$  and  $\text{ZnCO}_3$ .

P levels in the eluate change from below limit of detection (LOD) to 8.1 mg/L and 21.2 mg/L when immobilisation reduces for Zn and Cu. The most prevalent naturally occurring chemical derivative of P is phosphate which is particularly associated with the immobilisation of Zn and Cu through co-precipitation (Cairns *et al.* 2021). The retention of P whilst immobilisation is at its maximum and the release of P when immobilisation of Zn and Cu starts to wain suggests co-precipitation as an immobilisation mechanism.

### Solid Phase Analysis

FTIR was utilised to characterise the biochar and identify surface functional groups, such

as carbonyl and carboxylate, which are key to ion exchange, and minerals capable of co-precipitation with Zn and Cu. Peaks attributed to phosphate were apparent for each quantity of biochar post agitation with AMD (Uchimiya *et al.* 2010). However, these peaks shift and flatten noticeably from where 2g and 1g of biochar were used in sorption experiments and immobilisation of Zn and Cu was 100%, to where 0.1g and 0.05g of biochar were used in sorption experiments and immobilisation of Zn and Cu is negligible (figure 2). This peak shift and flattening alongside the changes in P concentrations in the batch eluate suggest that co-precipitation plays a role in the immobilisation of Zn and Cu which is consistent with previous studies of WAS (Cairns *et al.* 2021).

Peaks attributed to carboxyl surface functional groups were also evident in the FTIR spectra (Iqbal *et al.* 2009). These peaks flatten when moving from 2g and 1g of biochar used in sorption experiments to 0.1g and 0.05g of biochar used. Carboxyl groups are associated with ion exchange and a flattening of these peaks is a strong indication that ion exchange is a factor in the immobilisation of Zn and Cu (Iqbal *et al.* 2009; Cairns *et al.* 2021).

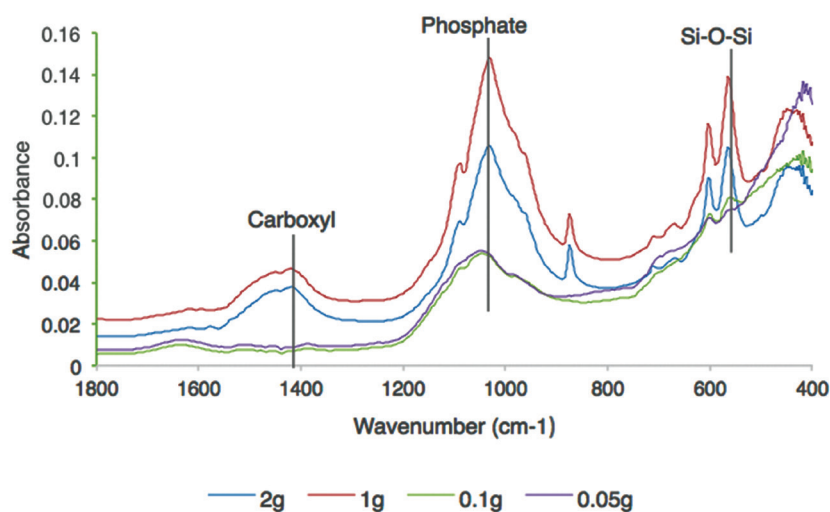


Figure 2 FTIR spectra of known quantities of larch biochar sintered with wood ash post agitation with Parys Mountain Copper Mine AMD



## Conclusion

This study assessed the application of larch biochar sintered with wood ash (WAS) to immobilise metals from Parys Mountain AMD. Parys Mountain AMD leaches large quantities of metals of concern including Zn (62 mg/L), Cu (42 mg/L) and Cd (148 µg/L) leading to the mine discharging 10 t of Cu and 24 t of Zn into the Irish Sea annually (Morgan *et al.* 2017). Larch biochar sintered with wood ash was seen to immobilise up to 100% of both Zn and Cu from Parys Mountain AMD with a maximum measured immobilisation of  $4.1 \pm 0.4$  mg/g and  $4.1 \pm 0.0$  mg/g for Zn and Cu respectively. Immobilisation was primarily as a result of precipitation with ion exchange and co-precipitation playing a role. These preliminary results demonstrate that WAS has the potential to be scaled up and used as part of a suite of techniques to remediate AMD.

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