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Article

Environmental Science
Advances

Accepted Manuscript

Environmental Science
Advances

rsc.li/esadvances

Volume 1
Number 1
January 2022

ISSN 2754-7000

ROYAL SOCIETY
OF CHEMISTRY

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OF CHEMISTRY

rsc.li/esadvances

Environmental Significance

The anthropogenic effect of mining on the aquatic environment is a global issue and has led to contamination of waters by up to 1000 times water quality thresholds for Zn and Pb. Larch biochar with the novel amendment of wood ash (WAS), was studied to determine if it was an effective remediator of contaminated mine water. Results demonstrated that WAS removed 97% of Zn and 86% of Pb within one minute of contact, with a maximum measured removal of 14.8 mg/g and 23.7 mg/g, due to precipitation and ion exchange. This shows that WAS is a viable, sustainable and cost-effective option to remediate (post)-transition metals in mine water and other polluted waters such as motorway runoff and industrially polluted rivers.

Environmental Science: Advances Accepted Manuscript

1   **<u>Treatment of Mine Water for the Fast Removal of Zinc and Lead by Wood Ash Amended</u>**

2   **<u>Biochar</u>**

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15

16   **Abstract**

17   Lead and zinc mines are a primary source of environmental (post)-transition metal

18   contamination resulting in major water pollution. In this study, the use of biochar amended with

19   wood ash (WAS) was evaluated as a method to remediate zinc and lead contaminated mine water.

20   Water from Nantymwyn lead mine, with zinc and lead concentrations as high as 12.1 mg/L and

21   1.7 mg/L respectively was used. The contact time for WAS to immobilise zinc and lead (1 min to

22   24 h), immobilisation mechanisms and maximum measured removal of lead and zinc were

23   studied. FTIR spectroscopy and XPS was used to characterise WAS and the aqueous modelling

24   program PHREEQC (pH redox equilibrium) was used to analyse mine water speciation. The fast

25   removal performance of a biochar is a key indicator of its viability to be used as a green

26   remediator. If the required contact time to remediate contaminated water is too long the sorbent

27   becomes impractical. This study demonstrated that WAS removed 97% of zinc and 86% of lead

28   within the first minute of contact with the mine water (0.5 g of WAS per 20 mL of mine water),

29   with a maximum measured removal of 14.8 mg/g for zinc and 23.7 mg/g for lead (using 0.1g –

30   0.002 g of WAS per 40 mL of mine water). Fast removal was primarily a result of precipitation,

31   and subsequent capture by WAS, and ion exchange. These findings show that WAS has the

32   potential to be scaled up and deployed at mine sites to remediate contaminated water.

33

34

35   **Keywords:** biochar, mine water, metals, remediation, treatment, contact time

36

37   **1.   Introduction**

38   Active and abandoned mines are a major source of contamination for both terrestrial and aquatic

39   environments [1]. Water pollution from these mines can originate from point sources such as mine

40   adits, or diffuse sources such as spoil heaps [2]. In the UK, the potential contamination by mines is

41   compounded by the fact that owners of mines abandoned before 1999 bear no responsibility for

42   their impacts. In Wales, there are over 1300 such mines affecting over 700km of river all of which

2

43 were abandoned before 1999 [3,4]. Pb / Zn mining and smelting are seen as some of the primary

44 sources of environmental (post)-transition metal contamination with Pb and Zn mines having

45 resulted in major water contamination [5].

46 Both Zn and Pb concentrations that are above European Union Water Framework Directive

47 (WFD) standards have the potential to cause harm to the environment and to human health.

48 Current WFD thresholds are 0.0129 mg/L for Zn and up to 0.014 mg/L for Pb[6]. Metals such as Zn

49 and Pb can enter the food chain harming plants, herbivores, carnivores and humans [7,8]. High

50 concentrations of Pb can have effects on the central nervous system and kidneys, interfere with

51 brain development and adversely affect both male and female reproduction with blood

52 concentrations above 60 μg/dl [9]. Exposure to Zn at concentrations ~6.5 mg/L can cause nausea,

53 vomiting, epigastric pain, lethargy, and fatigue [10,11].

54 Where polluted mine water is present remediation is important not just to improve the quality of

55 the water but also to improve the surrounding environment; mine impacted water can

56 bioaccumulate in flora, fauna and soils adjacent to the mine impacted water. As a result

57 improvements in water quality can also improve environmental quality in the area surrounding

58 the watercourse[12]. Indirectly this improvement in water quality can improve usable farmland and

59 restrict the intake of metals into plants, animals, and eventually humans. Currently there are

60 three basic methods of water remediation or improving water quality: (i) diversion of the water

61 away from the mine so that metals are not leached into rivers and streams; (ii) active treatment

62 of the polluted water e.g. with chemical dosing or electrical coagulation; and (iii) passive

63 treatment e.g. with settling ponds or reed beds [13]. As each site has different issues due to water

64 chemistry, underground workings, physical space and access, remediation should be tailored on

65 an individual site basis. Current remediation of metal mines in the UK has been limited due to the

66 regulatory framework as no one holds direct responsibility for the mines and resultant pollution

67 and where it does occur it is often expensive, requires significant maintenance and creates

68 potentially toxic waste products [14,15].

69 Water diversion is one of the remediation techniques that can be seen at Frongoch Mine, Wales,

70 UK, an abandoned Pb-Zn mine with subterranean connections to Wemyss Pb-Zn mine.

71 Frongoch has a large area of spoil mounds suitable for reprofiling and capping, and a single

72 entry point for the majority of the water flowing into the mine. These site conditions make it

73 possible for water in Frongoch to be diverted from entering the mine. The channel the diverted

74 water follows has been lined with concrete cloth to reduce contact with spoil, and the largest spoil

75 heaps have been recontoured and capped with either 300+ mm of clay or a geotechnical clay liner,

76 covered with 100 mm of topsoil [16]. While the mine continues to fail environmental quality

77 standards, the Zn load in the stream was reduced from 23.0 t p.a. to 7.4 t p.a. [16]. This approach

78 will however only be possible where site conditions allow stream diversion.

79 An example of a passive mine water treatment scheme can be seen at Force Crag Mine in

80 Cumbria, a Zn / Pb mine that was abandoned in 1991, which adversely affects 60 km of

81 river. Since 2014 the mine effluent has been captured by two parallel Vertical Flow Pond compost

82 bioreactors followed by a small wetland, removing 95-99% of the Zn [17]. It is estimated however

83 that the substrate will require replacing after 10 years of use, and the disposal alone of this is

84 almost the same as the capital expenditure for building the system [17]. A similar but larger system

85 has been in use in West Fork Pb mine in Missouri, treating 76 L/s of water and reducing the Zn

86 concentration by 75%, with a design life of 12 years [18].

87 Active treatment systems, such as those employed at Wheal Jane in Cornwall, require less land

88 area for the system, but ongoing dosing of chemicals; 2,000 t of hydrated lime and 7 t of anionic

89 flocculant, averaging £1.5M annually [14]. The Wheal Jane active treatment system removes up to

90 99.2% of the metals, resulting in 600 t of metal contaminated sludge to dispose of annually.

91 A cost-effective alternative to these remediation techniques is the use of biochar to remove

92 environmental contaminants from aqueous media. The use of biochar has been highlighted as a

93 cost effective remediation technique particularly in comparison to other removal techniques such

94 as anionic liquid ion exchange (ALIX) process, activated carbon or packed bed filtration [19-22].

95 Biochar is a porous, carbonaceous material produced by biomass pyrolysis at temperatures

4

96   ranging from 350–1000 °C under limited oxygen conditions [23]. In addition to the removal of

97   contaminants from aqueous media studies have also highlighted several other benefits of biochar

98   including carbon sequestration and enhancing soil fertility [19,24]. Its appeal is heightened as a

99   result of its relatively low cost, simple production process and the ability to use a vast number of

100 locally sourced feedstocks including sustainable and waste materials [23,25–29].

101 Biochar has six key immobilization mechanisms for inorganic contaminants in aqueous media

102 namely: cation exchange, complexation, electrostatic attraction, cation π bonding, reduction and

103 subsequent sorption, and precipitation[30] (Figure 1). Several mechanisms can be relevant in any

104 given biochar and these mechanisms can remove contaminants at different rates. Initial fast

105 stage adsorption can be attributed to mechanisms such as electrostatic attraction and ion

106 exchange whereas rate limiting steps have been seen to mainly involve chemical processes such

107 as inner sphere complexation and co-precipitation [31]. The fast removal performance of biochar

108 has been highlighted as a necessity for a successful adsorbent [32]; if the required contact time

109 between sorbent and sorbate to remediate a contaminated water is too long then the use of that

110 sorbent becomes impractical. This is particularly true in systems with a continuous flow where

111 contact time between biochar and contaminant is limited.

112 Wood ash, a waste product of biomass power plants, has been used as a novel amendment to

113 biochar to improve immobilisation of metals [33]. The use of a waste product rather than chemical

114 activation to improve immobilisation not only increases the sustainability of biochar but prevents

115 costs associated with chemical activation being incurred[34]. The increased rates of immobilisation

116 are as a result of the wood ash mineral fraction and pH buffering capacity [35]. The alkali and

117 alkaline earth metals added are central to ion exchange as well as increasing the pH of its

118 environment inducing changes in metal speciation favourable to the immobilisation of Zn and Pb

119 [36,37]. Minerals including P and Si added to the biochar by the wood ash are also key in the

120 formation of phosphates and silicates important in forming co-precipitates.
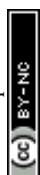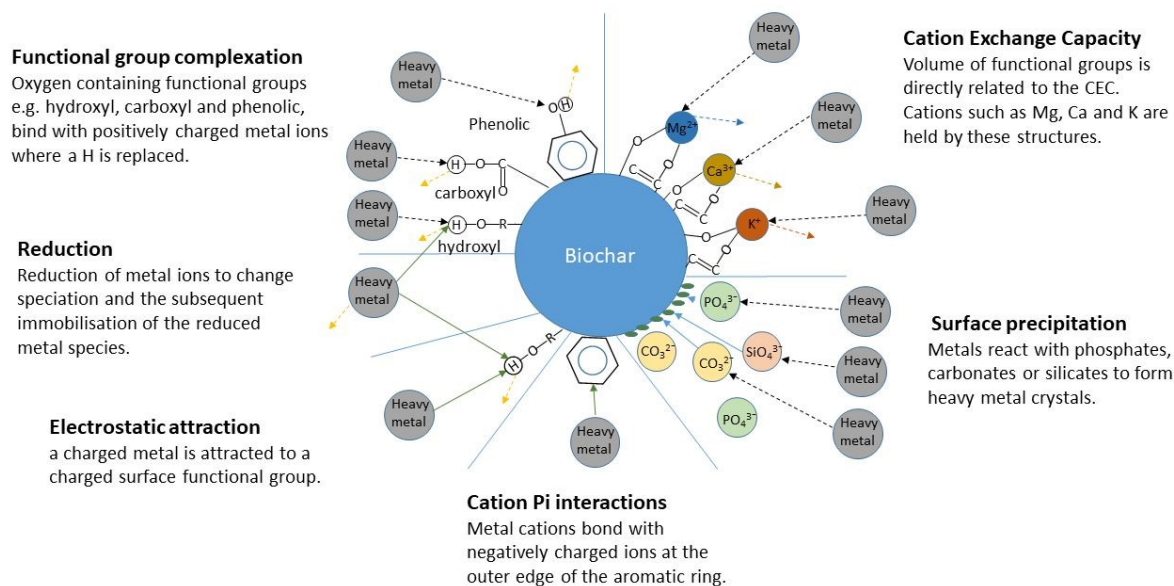
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122   Figure 1 - immobilisation mechanisms of inorganic contaminants in aqueous media [30]

123

124   Research has demonstrated that biochar can be successful in the removal of key mine water

125   contaminants such as Zn and Pb from aqueous solution [33]. Most existing biochar studies do not

126   focus on the scalability and practicality of the use of biochar which are essential considerations

127   in moving to the end goal of industry-scale application. The required contact time for remediation

128   is often overlooked. When considering practical use of biochar in a field setting the minimum

129   contact time in which biochar can reach equilibrium is an important factor. This factor is

130   particularly relevant in systems with continual flow, such as streams or rivers, where contact time

131   between aqueous contaminant and sorbent is much shorter than in stagnant systems, such as

132   ponds. Synthetic single contaminant solutions are often used rather than complex waters such as

133   mine water. The adoption of single contaminant solutions neglects the fact that contaminants like

134   Zn or Pb often co-exist with other pollutants, such as Fe, Al or SO_4^{2-} causing competition for

135   sorption sites effecting sorption [38,39]. Furthermore, the biochars studied are often produced on a

136   laboratory scale rather than on a large or industrial scale putting further steps in the process to

137   move toward scaled up production [40,41].

138   The overall aim of this study is to determine if the use of wood ash amended biochar is a viable

139   option to remediate mine water contaminated with Zn and Pb. The following objectives have been

140   devised to meet this aim using wood ash amended biochar produced by an industry scale

141   pyrolysis gasification kiln: (i) to quantify the contact time required for WAS to immobilise Zn and

142   Pb (ii) to quantify the maximum measured removal of Zn and Pb by WAS (iii) to identify the

143   mechanisms key to Zn and Pb immobilisation.

144

145   **2. Methods**

146

147   **2.1 Study site**

148

149   Nantymwyn Pb mine is one of a number of mines accessing the mineral veins of Mid Wales which

150   cross the site in a north easterly direction carrying galena (PbS) and sphalerite (ZnS) [42]. The mine

151   (Figure 2) (52°5'12'' N; 3°46'20'' W) was worked sporadically over centuries by a variety of

152   methods as technologies progressed, leaving a complex hydrogeological system, scarcely mapped

153   when in operation and now complicated further by 90 years of degradation since

154   closure [43]. Records detailing quantities of ore recovered are limited, but in the final four months

155   of full scale operation in 1930, 168 t of Pb and 548 t of Zn concentrates were recovered [43].

156   Nantymwyn causes the River Tywi to fail European Union Water Framework Directive (WFD)

157   standards for Zn for up to 69 km [4]. The River Tywi also provides drinking water to Swansea and

158   Carmarthen from an intake at Nantgaredig. However, the substantially larger flow of the River

159   Tywi means that metals from Nantymwyn are diluted [44,45]. Much of the mine site is now a

160   forestry plantation, but the main spoil heaps remain bare. The site is intersected by two streams;

161   firstly, to the north the Nant y Bai flows through the main Nantymwyn spoil heaps and areas

162   where the more recent surface operations were carried out [46]. The Nant y Bai receives diffuse

163   polluted water from spoil run off, including over 30% of its Zn load from Tributary 1, which flows

164   through spoil and tailings before joining the Nant y Bai, as well as subterranean sources [47]. The

165   second stream to the south is the smaller Nant y Mwyn, which does not flow through any visible

166   surface spoil but receives point source input from the Pannau adit and the Deep Boat Level, both

167   of which drain the mine workings. Zn and Pb WFD standards of 0.0129 mg/L and 0.014 mg/L

168   respectively are both widely exceeded at Nantymwyn; this is apparent at both the Deep Boat Level

169   and Tributary 1 [48,49].

170
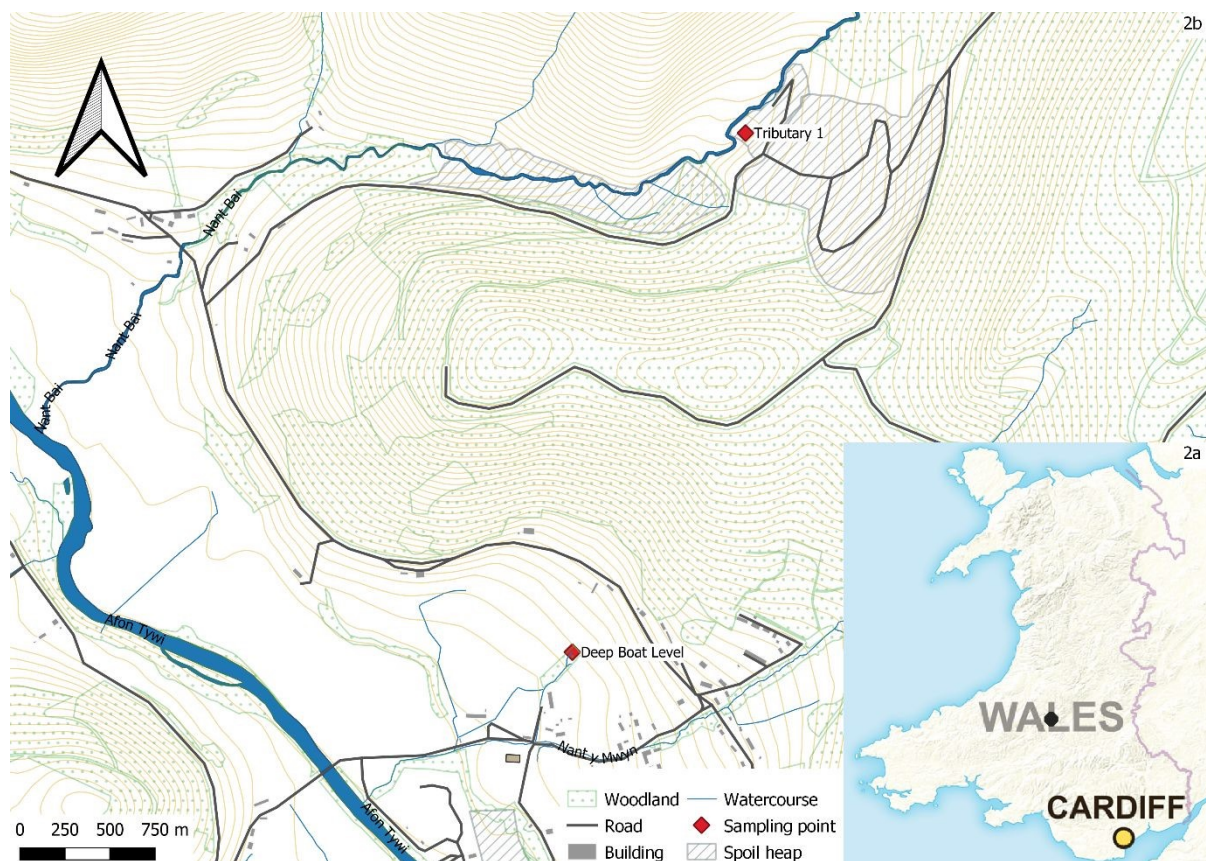
172   Figure 2 – (a) Nantymwyn within Wales, (b) sample point locations (Ordnance Survey 2013,

173   2020)

174

175

176   **2.2 Biochar production**

177   European larch (*Larix decidua* (L.) Mill.) wood chips were pyrolyzed in a Pyrocal BigChar-1000

178   pyrolysis-gasification kiln at a temperature of 485–530 °C, with a retention time of ~90 s. Wood

179   ash, originating from a renewable energy plant in the UK, was added to the still hot biochar at a
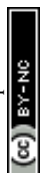
180   ratio of 1:1 and mixed for 15 min in a cement mixer to sinter the materials and then granulated

181   to <3 mm with a Tria G1 granulator [35]. Wood ash was selected as an amendment to the pristine

182   biochar because of its mineral fraction (specifically Ca, K, Mg, S, P and Si) and pH buffering

183   capacity. However, as a result of the mineral fraction the wood ash amended biochar (WAS) can

184   potentially leach nutrients such as nitrates, phosphates and sulphates [50]. Cairns et al. [51]

185   demonstrated that rinsing wood ash amended biochar with 200 mL of water per 5 g biochar

186   removes these unbound nutrients and reduces leaching to below water framework directive

187   thresholds. To remove these unbound nutrients every 15 g of biochar was rinsed with 600 mL of

188   deionised water. To rinse, the biochar was added to an open-ended polypropylene column with

189   an internal diameter of 31 mm, a wall thickness of 1 mm and a length of 500 mm. An 80 μm mesh

190   was used to stabilise the column content and further prevent loss of biomass [33].

191

192   **2.3 Sample collection and mine water characterisation**

193   Water was obtained from the Deep Boat Level adit and Tributary 1 at Nantymwyn lead

194   mine (Figure 2b) and sub-divided into five identical 1 L polyethylene terephthalate (PET) bottles.

195   These bottles were each rinsed with sample water three times before filling, and stored at 4 °C, in

196   accordance with national guidelines [52]. The pH, electrical conductivity, temperature, redox and

197   dissolved oxygen levels were taken concurrently at each site with a calibrated Hanna

198   Instruments HI98194 Multiparameter meter following national guidelines [52].

199

200   **2.4 Sorption Experiments**

201   Batch sorption experiments were carried out to determine the effect of contact time on

202   immobilisation using the Deep Boat Level adit and Tributary 1 water and to determine the

203   maximum measured removal of Zn and Pb by biochar using Tributary 1 water. For both sorption

204   batch experiments the sorbent was oven dried at 105 °C for 24 h. To determine the effect of

205   contact time on immobilisation, biochar (0.5 g with a particle size of <3 mm) was added to 5 mL

206   of deionised water in 50 mL polyethylene Falcon tubes and shaken for one hour to saturate the

207 sorbent thus reducing the time needed for the mine water to saturate WAS. 0.5g biochar was a

208 larger quantity than previous studies to take into account the reduced immobilisation capacity of

209 mine water compared to synthetic contaminated water [35]. Mine water was then added (20 mL) to

210 the biochar slurry and shaken for a known amount of time (1 min, 5 min, 15 min, 30 min, 1 h and

211 24 h). To determine the maximum measured removal of Zn and Pb by biochar a known amount

212 of biochar (0.1 g, 0.05 g, 0.03 g, 0.02 g, 0.01 g, 0.006 g, 0.003 g and 0.002 g) was added to 40 mL

213 of Tributary 1 mine water in 50 mL polyethylene Falcon tubes and shaken for 24 h. For both

214 sorption batch experiments agitation was achieved on a Unitwist 400 Orbital Shaker at ~280

215 rpm. The solution was subsequently separated from the sorbent using an MSE Centaur 2

216 centrifuge at 3000 rpm for 15 min [53]. The supernatant was then acidified to < pH 2 with 1 mL of

217 70% HNO_3 before being filtered with a 0.45 μm PTFE syringe filter for analysis. All experiments

218 were performed in triplicates using a batch sorption equilibrium method with biochar without

219 mine water and mine water without biochar used as controls [53].

220 Zn and Pb concentrations of the acidified supernatants were measured using Microwave Plasma

221 Atomic Emission Spectroscopy (MP-AES 4200, Agilent Technologies Inc., USA). For contact time

222 sorption batch experiments the percentage of sorbent removal was calculated from the difference

223 between initial metal concentration and final metal concentrations in the aqueous phase:

224 $$\% \text{ removal} = \left(\frac{c_i}{c_{aq}}\right) \times 100$$

225 where Ci is the initial concentration of metals in solution and Caq is the final equilibrium

226 concentration of metals in solution. For maximum measured removal experiments removal in

227 mg/g was calculated as the difference between initial metal concentration and the final metal
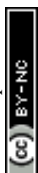
228 concentration in the aqueous phase:

229 $$q = (c_i - c_{aq})V/W$$

230 where q is the maximum measured removal, V is the volume of solution and W is the weight of

231 the biochar.

232

233 **2.5 Biochar properties**

234 A range of biochar properties were determined to understand how they effected immobilisation.

235 The release of base cations (Ca, K, Na and Mg) by the biochar were measured for biochar that had

236 been agitated with deionised water and for biochar that had been agitated with mine water and

237 compared to review possible cation exchange. The pH, EC and alkalinity of the biochar

238 supernatant from the sorption experiments were measured prior to acidification using a

239 calibrated Voltcraft pH Meter, a calibrated Whatman CDM 400 Conductivity Meter and a Hanna

240 HI-3811 Alkalinity test kit respectively. Fourier transform infrared spectroscopy (FTIR) was

241 undertaken using a Perkin Elmer Spectrum Two FTIR Spectrometer. Measurements in the range

242 400-4000 cm^{-1} were determined to compare possible changes to functional groups, minerals

243 capable of precipitation and aromatic structures. Comparisons of the spectra were made for

244 biochar before sorbent loading and at each timed stage of the sorption experiment. X-ray

245 photoelectron spectroscopy (XPS) analysis was carried out on a Kratos Axis Supra instrument

246 using a monochromatic Al Kα X-Ray source at 225W, with a 15mA emission current. Each sample

247 had multiple wide scans at pass energy of 160eV over the binding energy range of 1200-0eV to

248 identify all possible elements present, with a step size of 1eV. High resolution spectra were

249 scanned with a pass energy of 40eV, a step size of 0.01eV and a multi sweep dwell time of 2000ms

250 to improve the signal to noise ratios for the lower concentration elements of interest. The binding

251 energy axis was charge correct to the C-C component of the carbon peak at 284.8eV. Casa XPS

252 (2.3.22PR1.0) was used to quantify the data using the Kratos sensitivity factor library, standard

253 Shirley backgrounds and Gauss-Lorentz peak models. XPS analysis was conducted to identify the

254 change in biochar characteristics, especially in composite compounds, before and after sorption.

255

256 **2.6 Metal speciation**

257 Speciation analysis of the mine water and biochar supernatants were carried out using the pH

258 redox equilibrium (PHREEQC) program (version 3.7.1) and the MINTEQV4 database [54]. The pH,

259 redox, temperature and concentrations of base cations, metal contaminants, alkalinity and

260 nutrients were used as model inputs. To confirm the PHREEQC modelling, the proportion of

261 mobile Zn and Pb species in Tributary 1 were further investigated by comparing acidified and

262 non-acidified Tributary 1 samples. One set of mine water samples were acidified to < pH 2 with 1

263 mL of 70% HNO_3 before being filtered with a 0.22 μm PTFE syringe filter, a further set was not

264 acidified and filtered with a 0.22 μm PTFE syringe filter. All experiments were performed in

265 triplicates and measured using Microwave Plasma Atomic Emission Spectroscopy (MP-AES 4200,

266 Agilent Technologies Inc., USA).

267

268

269 **3. Results and Discussion**

270

271 **3.1 Mine water chemistry**

272 The Deep Boat Level was sampled 12 times during 2019-2020 and average metal concentration

273 were calculated[47]. It was characterised by a high Zn concentration of 12.7 mg/L, a Pb

274 concentration of 0.2 mg/L, a pH of 7.0 and a flow of 24 L/s [48].Tributary 1 had Zn concentrations

275 of 9.8 mg/L, Pb concentrations of 3.8 mg/L, a pH of 6.4 and a flow of 3.4 L/s, again from 12

276 samples taken 2019-2020 [48]. The Zn and Pb concentrations for both Deep Boat Level and

277 Tributary 1 are substantially above the WFD standards for dissolved Zn and Pb in the River Tywi

278 which are 0.0129 mg/L and 0.014 mg/L respectively [49].

279

280 **3.2 Contaminant removal time-scales**

281 The time in which biochar can immobilise contaminants from aqueous media is an important

282 aspect of remediation with flowing water, as contaminant contact time with any sorbent is limited

283 [32,55]. Mechanisms such as precipitation and ion exchange have been demonstrated to be

284 important in early stage immobilisation whereas mechanisms such as co-precipitation can take

285 longer and as such be seen as rate limiting factors [31].

286   The immobilisation of Zn from both the Deep Boat Level and Tributary 1 was a relatively fast

287   process with 97% of mine water Zn removed in the first minute and equilibrium and complete

288   removal achieved around 1 h (Figure 3a and b). The immobilisation of Pb from Tributary 1 was

289   also a relatively fast process with 86% of mine water Pb removed in the first minute and an

290   equilibrium of 92% removal again achieved around 1 h. Pb concentration in the Deep Boat Level

291   mine water was below the limit of detection (<0.1 mg/L) and as such removal was not quantified.
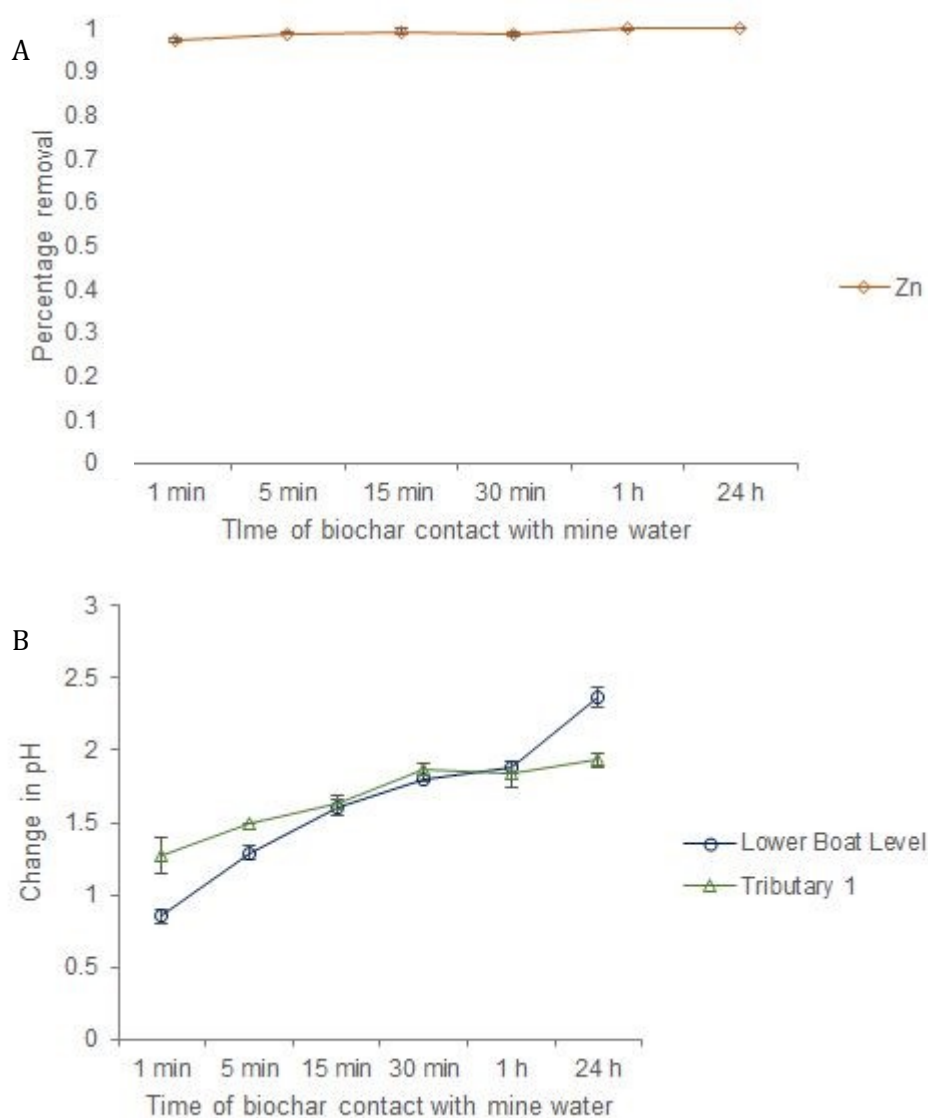
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293

294   Figure 3 - (a) percentage of zinc removed from the Deep Boat Level mine water by contact time

295   with wood ash amended biochar. Lead concentrations in the Deep Boat Level being below

296   detection limits (<0.1 mg/L); (b) percentage of zinc and lead removed from Tributary 1 mine

297   water by contact time with wood ash amended biochar

13

298

3.3 Immobilization mechanisms

300 The pH of both the Deep Boat Level and Tributary 1 mine water was increased as a result of

301 contact with the wood ash amended biochar (WAS) (Figure 4 a) leading to early stage Zn and Pb

302 immobilisation and capture via precipitation (Figure 4 b). An increase in media pH can be

303 instrumental to changes in metal speciation that are favourable for the immobilisation of metals

304 such as Zn and Pb [33]. After a contact time of 1 min with WAS the Deep Boat Level mine water

305 increased in pH to 8.2 and after 1 h increased to a pH of 9.2 where equilibrium was reached. After

306 a contact time of 1 min with the WAS the Tributary 1 mine water pH increased to 8.9 and after 1

307 h it increased to a pH of 9.4 at which point equilibrium was reached.

308 Speciation modelling of Zn and Pb ions was conducted using PHREEQC software [56]. According to

309 the PHREEQC calculations with the environmental conditions and pH observed in the mine water

310 of Tributary 1 before the addition of WAS, 92% of Zn would be in mobile divalent forms (figure 4

311 b). This proportion of mobile Zn was confirmed by a comparison of Tributary 1 acidified (pH <2)

312 and non-acidified samples. Mobile species were captured in the filtered eluate whereas immobile

313 species were filtered out of the eluate. Once WAS had been applied for 1 min, the PHREEQC

314 modelling demonstrated that Zn mobile divalent forms only constitute 3% of Zn species present

315 (Figure 3b). This change was caused by WAS promoting the formation of immobile carbonates

316 and hydroxides, such as $ZnCO_3$. Divalent forms of Zn dropped to close to 0% when WAS had been

317 added between 15 min and 24 h. The distribution shifts from divalent Zn to immobile zinc

318 carbonate and hydroxide forms, forming mineral precipitates which were captured on the surface

319 of WAS. The capture of $ZnCO_3$ on the surface of the biochar was confirmed by XPS analyses where

320 peaks attributed to $ZnCO_3$ were observed only when WAS had been in contact with the Tributary

321 1 mine water (FIGURE 5 a and b).

322   PHREEQC results also showed that before the addition of WAS, 44% of the Pb in the mine water

323 of Tributary 1 would be in mobile divalent forms (figure 4 c). Again, that a proportion of Pb was

324 mobile was confirmed by the comparison of filtered acidified and non-acidified Tributary 1 mine

325   water. According to PHREEQC modelling, once WAS had been applied to the mine water for 1 min,

326   the divalent Pb concentration was reduced to close to 0%; this proportion remained constant for

327   the 24 h period of this study. Mobile divalent Pb species shift to immobile lead carbonate and

328   hydroxide forms which dominate speciation causing Pb precipitation and capture by WAS. The

329   formation of lead carbonates, such as $Pb(CO_3)$ modelled by PHREEQC, have been seen to be

330   related to the high alkalinity of the biochar and soluble carbonate, sulphate and phosphate anions

331   [57,58]. Regular sampling of Nantymywn has shown sulphate concentration to be as high as 11 mg/L

332   adding substantially more anions into the system possibly playing a role in Zn and Pb speciation

333   and further increasing the formation of precipitates [48,59]. Given the right conditions, as the

334   addition of WAS to the Nantymwyn system provides, precipitation is a rapid process. This, in part,

335   explains the speed of Zn and Pb removal by WAS.

336

A

337

B

338

C

339

16

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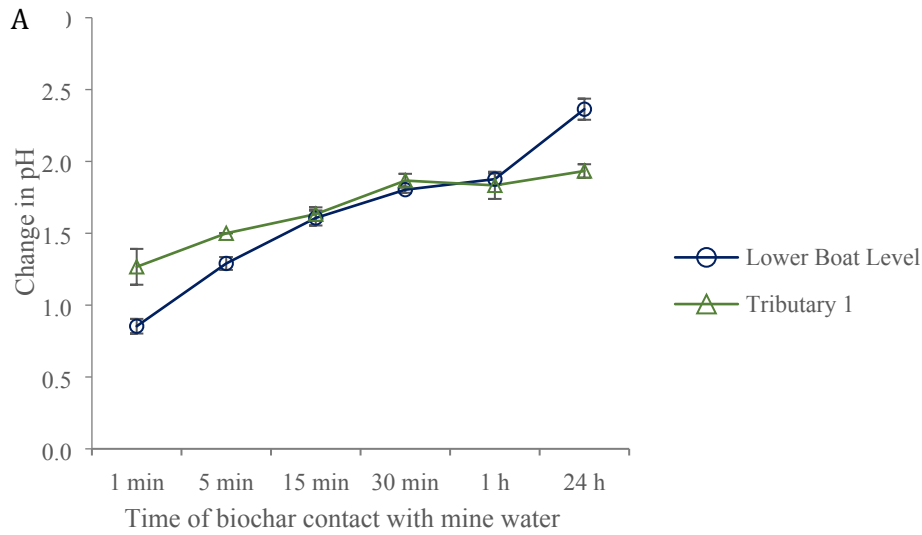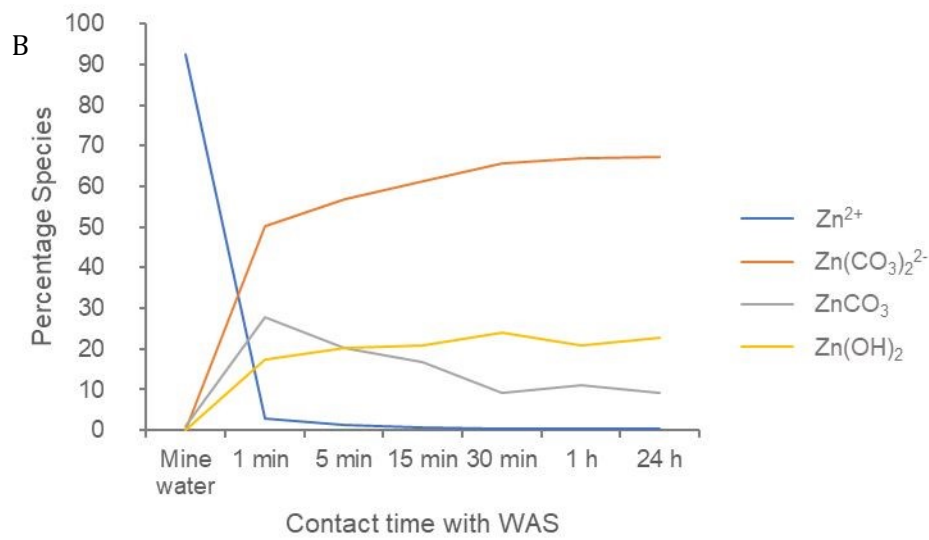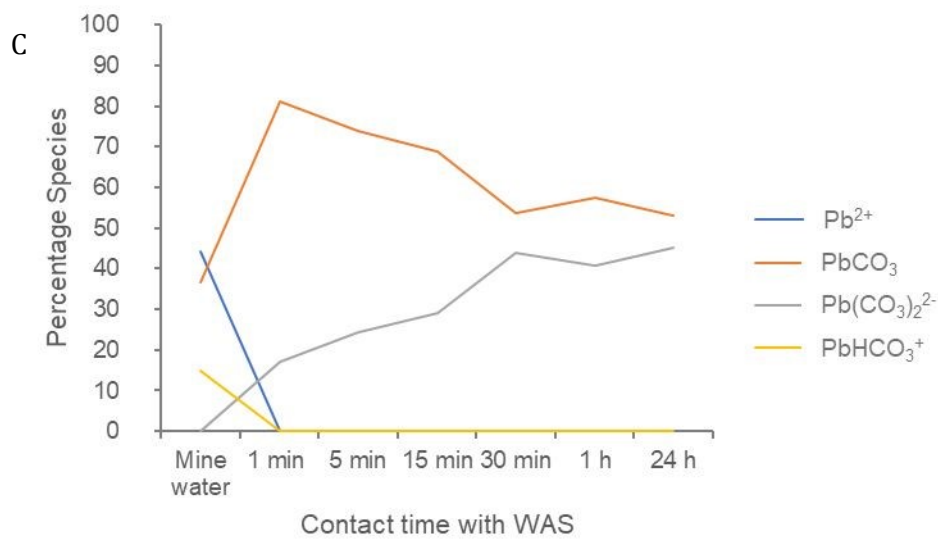
341   Figure 4 - (a) change in Deep Boat Level and Tributary 1 mine water pH by contact time with

342   wood ash amended biochar; (b) speciation plots of Zn in Tributary 1 mine water across contact

343   time with wood ash amended biochar; (c) speciation plots of Pb in Tributary 1 mine water across

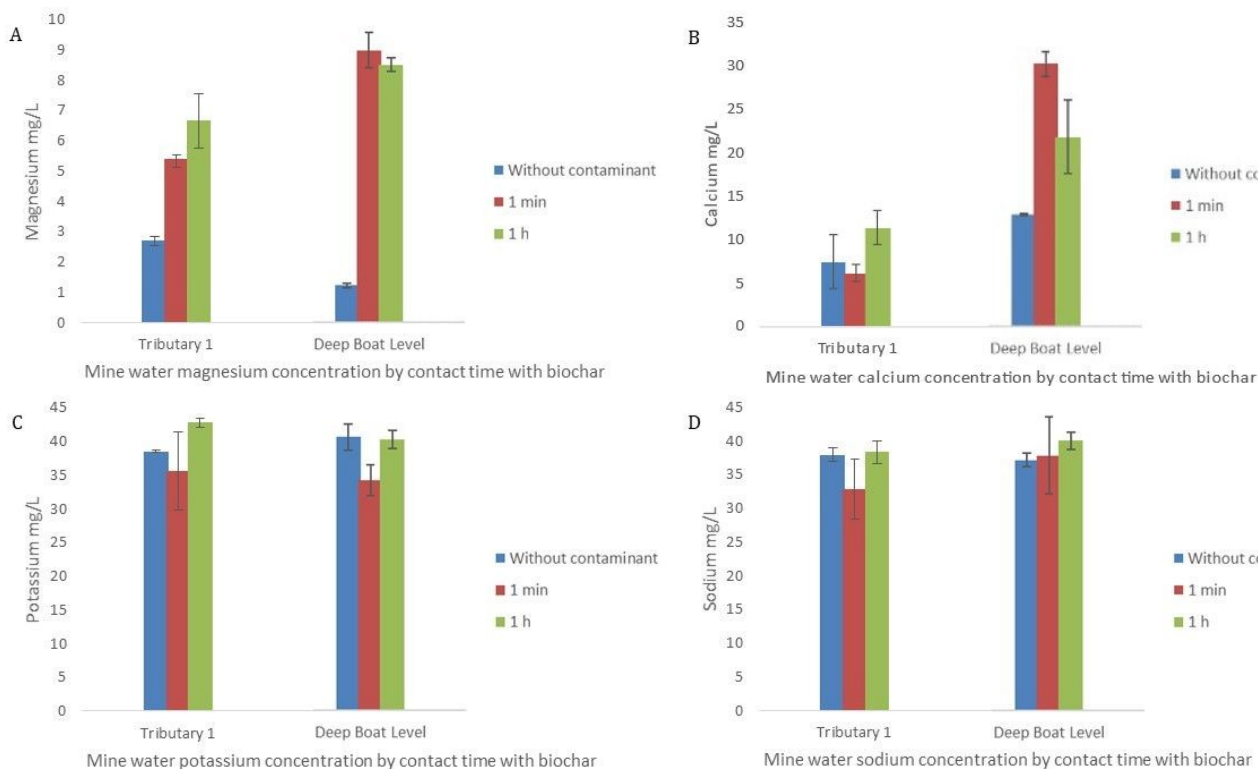344   contact time with wood ash amended biochar

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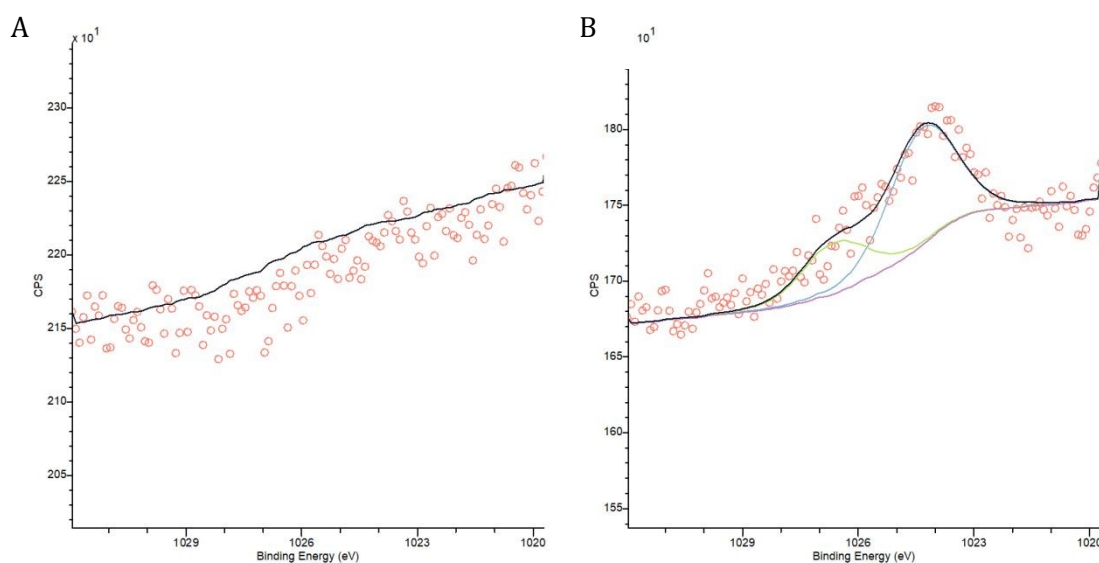
347

348   Figure 5 – X-ray photoelectron spectroscopy (XPS) region scans and peak fitting for wood ash

349   amended biochar (a) Zn peaks prior to contact with Tributary 1 mine water (b) Zn peaks after 24

350   hours contact time with Tributary 1 mine water

351

352   Ion exchange was also seen to play a role in early stage sorption of Zn and Pb by WAS. A rise in

353   base cation release in the presence of metals can signify ion exchange on the surface of the biochar

354   as the divalent contaminants replace the divalent cations such as Ca^{2+} and Mg^{2+} [60]. In this study

355   concentrations of Ca and / or Mg in solution increased within the first minute of the experiment

356   and remained broadly steady for the 24 h sampling period indicating that cation exchange played

357   an early role in sorption of Zn and Pb and continued to be of importance for the duration of the

358   study (Figure 6 a and b). Early stage sorption of Zn and Pb have been ascribed to ion exchange in

17

359   several previous studies often alongside electrostatic attraction, with Ca and Mg being cited as

360   the ions most important in the exchange, which is consistent with the findings of this study [31,61].

361

362

363   Figure 6 – (a) changes in magnesium concentrations by contact time with wood ash amended

364   biochar for Tributary 1 and Deep Boat Level (b) changes in calcium concentrations by contact

365   time with wood ash amended biochar for Tributary 1 and Deep Boat Level (c) changes in

366   potassium concentrations by contact time with wood ash amended biochar for Tributary 1 and

367   Deep Boat Level (d) changes in sodium concentrations by contact time with wood ash amended

368   biochar for Tributary 1 and Deep Boat Level

369

370   **3.4 Maximum measured Zn and Pb removal and late stage immobilisation mechanisms**

371   The maximum measured removal of Zn and Pb by wood ash amended biochar (WAS) was 14.8

372   mg/g and 23.7 mg/g respectively. Maximum immobilisation of Zn was seen with 0.5 mg of

373   adsorbent per L of mine water and maximum immobilisation of Pb was seen with 0.05 mg of
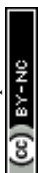
374   adsorbent per L of mine water. Immobilisation of Pb continued at 84% even as the proportion of

375   Zn immobilised dropped to 3% demonstrating that WAS affinity with Pb is stronger than with Zn

376   and that Pb removal can continue even once the capacity of WAS to remove Zn is exhausted. The

377   key mechanisms that drive the removal of Zn and Pb through to maximum measured removal

378   remained precipitation, and subsequent capture by WAS, and ion exchange.

379   PHREEQC modelling demonstrated that as the proportion of immobile Zn species reduced so too

380   did the proportion of Zn immobilised by WAS with a strong correlation ($r = 0.91$; $p<0.01$)

381   illustrating the importance of precipitation to Zn removal (SI 2). The modelling also shows that

382   immobile Pb species remains as high as 92% even when Zn immobile species reduces to 20%.

383   This partly explains why WAS continues to remove Pb beyond Zn exhaustion.

384   Cation exchange with Ca and Mg is also a relevant mechanism in the ongoing removal of the

385   metals of concern by WAS. As the removal of Zn decreases the concentration of Ca, and to a lesser

386   extent Mg, also decrease indicating that these base cations have been replaced by Zn and reducing

387   the sites left available for Zn (Figure 7a). There is a strong correlation between Ca concentration

388   and Zn removal ($r = 0.85$; $p<0.01$) as well as a strong correlation between Mg concentration and

389   Zn removal ($r = 0.77$; $p<0.01$). FTIR analysis further demonstrates the importance of ion exchange

390   in the removal of metals of concern (Figure 7b). The FTIR peak at 1418 is assigned to the carboxyl

391   surface functional group [35,62]; when immobilisation of Zn by WAS is as high as 99% this peak is

392   strong. However, as immobilisation of Zn decreases to exhaustion this peak diminishes

393   considerably. This, in conjunction with the correlation between Zn immobilisation and Ca and Mg

394   concentrations, shows that ion exchange plays an important role in the immobilisation of metals

395   of concern from the mine water from initial immobilisation to exhaustion.

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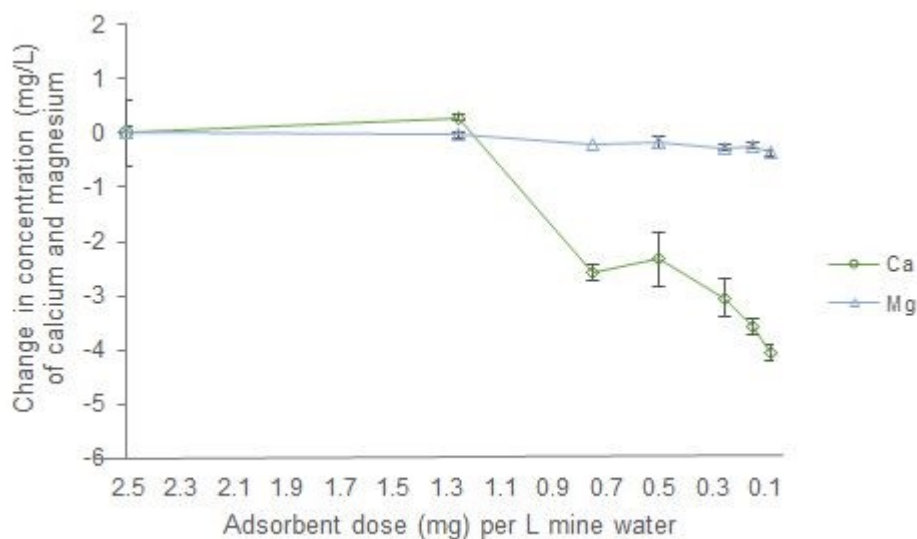
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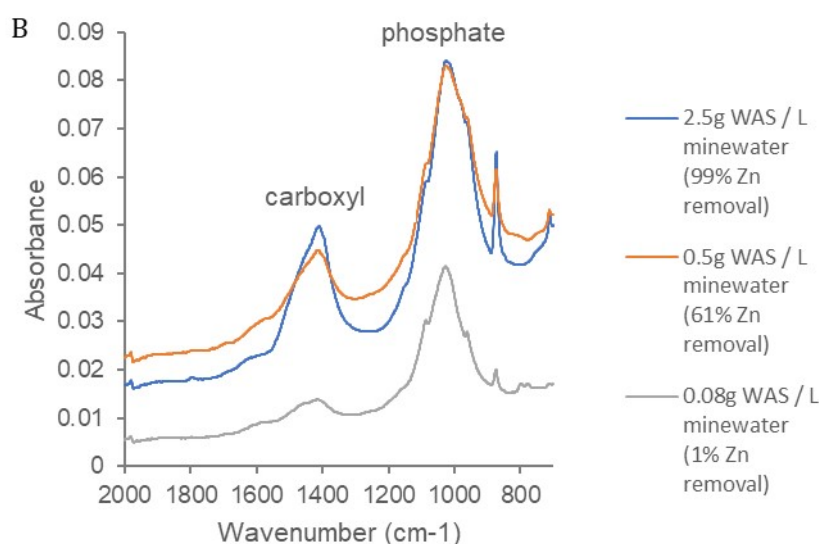
398

399 Figure 7 – (A) The change in concentration (mg/L) of calcium and magnesium in the presence of

400 different quantities of wood ash amended biochar (WAS) in a litre of mine water. (B) FTIR spectra

401 of wood ash amended biochar (WAS) before maximum measured removal of Zn (2.5 mg WAS / L

402 mine water), maximum measured removal of Zn (0.5 g WAS / L mine water) and at exhaustion of

403 Zn (0.08 g WAS / L mine water)

404

405

406 **4. <u>Conclusion</u>**

20
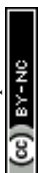
407   On a global scale, mine sites are a major source of contamination of aqueous environments.

408   This study investigated if wood ash amended biochar (WAS) could immobilise Zn and Pb with

409   a short enough contact time to be viable as a green remediator using mine impacted waters

410   from the Deep Boat Level and Tributary 1 areas of the Nantymwyn. These waterways

411   displayed Zn concentrations as high as 12.1 mg/L and Pb concentrations as high as 1.7 mg/L,

412   both considerably above WFD standards for the River Tywi (0.0129 mg/L for Zn and 0.014

413   mg/L for Pb). WAS removed 97% of Zn and 86% of Pb within the first minute of contact time

414   with the mine water, with a maximum measured removal of 14.8 mg/g for Zn and 23.7 mg/g

415   for Pb. The removal of these metals of concern was primarily caused by precipitation, and

416   subsequent capture by WAS, and ion exchange; both processes were key to early stage

417   immobilisation. Elevated pH and the presence of minerals shifted metal species to carbonates,

418   such as $Pb(CO_3)$ and $Zn(CO_3)$ and hydroxides such as $Zn(OH)_2$. Under such conditions, these

419   metal species are more susceptible to precipitation. The resultant capture of the species

420   modelled by PHREEQC on the surface of the biochar was observed by XPS. Ion exchange was

421   demonstrated between the metal contaminants and base cations specifically Ca and Mg. The

422   fast removal performance due to these mechanisms demonstrates the potential for WAS to

423   remove pollutants from aqueous environments.

424

425

426   **Acknowledgements**

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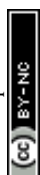
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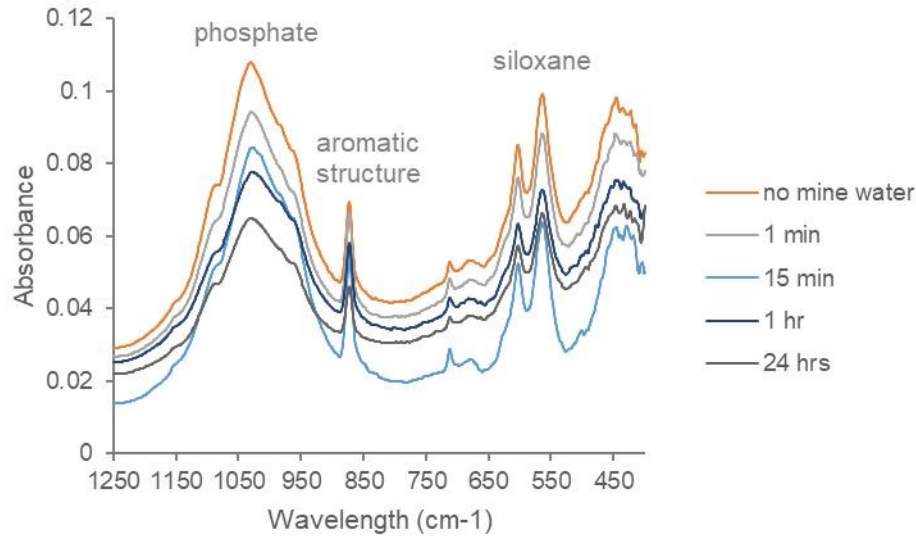
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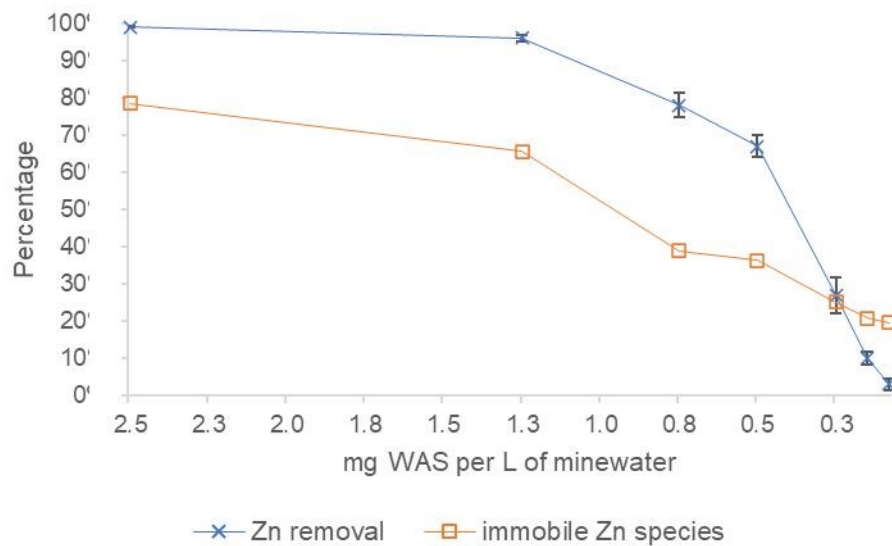642   Appendix A

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646   SI 1: FTIR spectra of wood ash amended biochar pre immobilisation of Zn and Pb during

647   immobilisation at 1 min, 15 min, 1 h and 24 h

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650   SI 2: Reduction in Zn removal by WAS as the proportion of Zn immobile species reduces

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