Application of Biomass Ashes for Treatment of Acid Mine Drainage

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Abstract
Acid mine drainage (AMD) is the largest environmental problem facing the world mining and processing industry because it has low pH and can contain high concentrations of potential pollutants (e.g., Zn, Pb, Cd, Cu, As, Sb, Hg). Biomass ash (BA), which is a by-product of burning biomass in conventional power station, can be considered as a potential material for AMD treatment. The main goal of this work was to investigate potential use of BAs for AMD remediation. Four UK biomass ashes from different fuels (i.e., straw, meat and bone meal, mixed biomass) were characterised. All biomass ashes contain high concentrations of P, Ca, and K. The bulk crystalline phases in the biomass ashes include portlandite, calcite, arcanite, quartz, apatite, and other phosphates. We used a synthetic AMD which is comparable in composition to AMD from the Almasu Mare region in Romania. Batch experiments showed that a biomass ash from straw combustion (L/S = 250) can effectively neutralise the synthetic acid mine drainage (pH=2.7; Fe=310 mg/L; Zn=95 mg/L; Mn=54 mg/L), with removal of potential pollutants (pH=7.4; Fe=0.01 mg/L; Zn=0.58 mg/L; Mn=17 mg/L) in less than 1 hour. Other series of experiments were carried out on real AMDs from the Ursk Tailings of the Gold concentration plant and from the Belovo sludge pond from the Belovo zinc processing plant which have low pH (2.73-3.83) and high concentration of heavy metals. The biomass ashes from straw and mixed biomass combustion can effectively remove pollutants from the Ursk AMD at L/S = 100 and adjust pH=5.7-7.8. For the Belovo AMD, an appropriate L/S ratio is 10-30 and pH can be adjusted to 6.0-10. The metal concentrations of these treated AMDs met water quality standards. Pollutants mainly present as phosphate which usually have very low solubility product constant.

Key words: Acid mine drainage, biomass ash, AMD remediation

Introduction
Acid mine drainage is the largest environmental problem facing the world mining and processing industry (Bogush et al. 2015; GARD/INAP; Hudson-Edwards et al. 2011; Jambor et al. 2003; Lottermoser 2007; Nordstrom 2011; Nordstrom and Alpers 1999; Wolkersdorfer 2008; Younger 2002). AMDs has low pH and can contain high concentrations of potential pollutants.

Biomass ash, which is a by-product of burning biomass in conventional power station, can be considered as a potential material for AMD treatment. BA are complex alkaline inorganic-organic mixtures with polycomponent, heterogeneous and variable composition (Vassilev 2013). Biomass combustion is an important part of the global renewable energy which is growing fast worldwide (Demirbas 2005). However, approximately 480 million tons of biomass ashes could be generated worldwide annually, which is comparable to coal ash annually production (780 million tons) (Vassilev 2013). In the UK, biomass ashes are currently landfilled or used in relatively low-value applications.

The aim of the present study was to investigate, at laboratory scale, the effectiveness of biomass ashes for removing heavy metals from AMD.

Material and Methods

Four UK biomass ashes from different fuels (i.e., EBFA from straw, EPR-Gba from meat and bone meal, TBA and EBA from mixed biomass) were characterised. Figure 1 shows the appearance of the biomass ashes.

EBFA EPR-Gba TBA EBA

Figure 1 *Visual observation of UK biomass ashes.*

The Spectro XLAB2000 X-ray fluorescence (XRF) spectrometer was used for element analysis in biomass ashes. A pH value of a water leachate (L/S=10) was analysed. XRD was used to characterise the crystalline phases present in biomass ashes. The morphologies of the particles from the biomass ashes and the residue after AMD treatment were investigated by scanning electron microscopy (SEM: JEOL JSM-6480LV) with secondary electron imaging (SEI) and backscattered electron imaging (BEI) detectors.

The synthetic acid mine drainage (SAMD) was prepared with pH and element composition comparable to AMD from the Almasu Mare mining region in Romania: SAMD - pH=2.7; Fe=310 mg/L; Zn=95 mg/L; Mn=54 mg/L. The SAMD was used in the batch experiments for SAMD remediation by the biomass ash from straw combustion (EBFA). A known amount of the EBFA (0.01, 0.035, 0.05, 0.075, 0.10 and 0.25 g) was added to the SAMD (25 mL) with agitation. The pH of the solution was measured before and after EBFA addition. After 1 h, the SAMD-EBFA mixtures were filtered through the 0.45 µm membrane filters and acidified with pure HNO_3. Element concentrations (Ca, Mg, Fe, Zn and Mn) were measured by ICP-OES (Varian 730). Then, the removal efficiency was calculated.

Other series of batch experiments were carried out on the AMDs from the Ursk tailings of the Gold concentration plant and from the Belovo sludge pond from the Belovo zinc processing plant which have low pH and high concentration of heavy metals. The biomass ashes (EBFA, EPR-Gba, TBA, and EBA) were added to AMD (Ursk AMD and Belovo AMD) with agitation at different liquid to solid ratio (L/S: 10, 50, 100, 200, 500). The pH value of the solution was measured before and after BA addition. After 1 h, the AMD-BA mixtures were filtered through the 0.45 µm membrane filters and acidified. Element concentrations (Fe, Al, Zn, Cu, Cd, Ni, Cd, and Mn) were measured by AAS. Then, the removal efficiency was calculated.

Results and Discussion

Characterisation of the Biomass Ashes

The BAs contain high concentrations of P (2.2-10%) and Ca (13-37%). The bulk of the crystalline phases present in the EPR-Gba, TBA and EBA biomass ashes include calcite, portlandite, arcanite (excluding EPR-Gba), quartz, apatite and other phosphates. The biomass ash from straw combustion (EBFA) contains portlandite, arcanite, calcium sulphate hydrate, sylvite and apatite.

The biomass ashes (EPR-Gba, TBA, and EBA) mainly contain unshaped particle (up to 1 mm), aggregates and fine materials. The spherical particles were also identified in these biomass ashes. The biomass ash EBFA mainly contains fine phases (<1 µm) and unburnt straw residues (200-300 µm) with a few glassy particles.

The pH of the water-based leachates was high due to the presence of excess $Ca(OH)_2$ in BAs and varied from 12.22 to 12.78. It should be noted that a saturated solution of $Ca(OH)_2$ has a pH of about 12.4. The pH values generally correspond to the contents of $Ca(OH)_2$ and CaO (which will be hydrated in the leaching test) determined by XRD.

Synthetic Acid Mine Drainage Remediation with Biomass Ash (EBFA)

It was shown that the biomass ash EBFA efficiently treated the SAMD at L/S = 250 in 1 hour. At this L/S ratio, the concentrations of potential pollutants in treated water were below maximum permissible concentrations (MPCs) for drinking water (SanPiN 2.1.4.1074-01, 2002) and general standards for discharge of environmental pollutants (GSDEP 1993).

The solid residues after the SAMD remediation with the EBFA are mainly amorphous materials. This residue mainly contains aggregates which consist of Ca, P, Si, K, Cl, Al, S, Fe, Mn and Zn.

Acid Mine Drainage Remediation with the Biomass Ashes (EBFA, EPR-Gba, TBA and EBA)

It was shown that the biomass ash from straw and mixed biomass combustion (L/S=100) can effectively adjust pH in the Ursk AMD with removal of potential pollutants: 1) EBFA ─ pH=7.68, Fe=0.14 mg/L, Al, Zn, Cu, Ni, and Co - below the detection limit; 2) TBA ─ pH=5.69, Fe=0.27 mg/L, Zn=0.5 mg/L, Cu=0.47 mg/L, Al, Ni, and Co - below the detection limit; 3) EBA ─ pH=7.17, Fe=0.56 mg/L, Zn=1.7 mg/L, Cu=0.62 mg/L, Al, Ni, and Co - below the detection limit.

The biomass ash from straw (EBFA) and mixed biomass combustion (TBA) at L/S=10-30 can effectively adjust pH to 6.0-10 in the Belovo AMD with removal of potential pollutants. At these L/S ratios, the concentrations of potential pollutants in treated water were below the GSDEP concentrations.

Conclusions

All BAs are alkaline material and contain high concentrations of P and Ca. Mineralogical composition of investigated BAs are complex and mainly depends on biomass composition used for combustion. The bulk crystalline phases in the BAs include portlandite, arcanite, calcite, quartz, apatite, and other phosphates.

Batch experiments showed that the BA from straw combustion (L/S = 250) can effectively treat synthetic acid mine drainage (pH=2.7; Fe=310 mg/L; Zn=95 mg/L; Mn=54 mg/L), with removal of potential pollutants (pH=7.4; Fe=0.01 mg/L; Zn=0.58 mg/L; Mn=17 mg/L) in 1 hour.

It was shown that the BA from straw (EBFA) and mixed biomass (EBA and TBA) combustion can effectively remove pollutants from the Ursk AMD at L/S=100 and adjust pH=5.7-7.8. The biomass ashes EBFA and TBA at L/S ratio=10-30 are effective for Belovo AMD treatment. Pollutants mainly present as phosphate which usually have very low solubility product constant.

Therefore, biomass ashes from straw and mixed biomass (mainly contained animal residues and wood) combustion can be considered as a potential material for AMD treatment.

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