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TECHNICAL ARTICLE

Removal of Trace Metals from Acid Mine Drainage Using a Sequential Combination of Coal Ash-Based Adsorbents and Phytoremediation by Bunchgrass (Vetiver [*Vetiveria zizanioides* L])

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Abstract Potentially scalable low-cost treatment methods for acid mine drainage (AMD) are very limited. We used a sequential combination of adsorption and phytoremediation by bunchgrass (Vetiver [*Vetiveria zizanioides* L]) in a semi-batch system to remove Zn, Mn, Ni, and Cu from AMD. The objectives were: (1) to compare the removal of these metals by raw and NaOH-activated coal ash (NaOH-CA); and (2) to determine the effect of sequencing adsorption and phytoextraction on metal removal. The NaOH-CA adsorbed significantly more metals than raw coal ash (RCA) in both batch and semi-batch fixed column experiments, demonstrating the effectiveness of NaOH hydrothermal activation, which forms zeolites. Adsorption by NaOH-CA removed 59.1, 95.7, 67.6, and 77.9% of the Zn, Mn, Ni, and Cu, respectively, compared to 50.6, 95.1, 30.2, and 60.5% for the RCA. Metal removal by phytoremediation was generally less than that by adsorption, accounting for between 3.4 and 54.6% for both adsorbents. Phytoremediation following adsorption by NaOH-CA removed 89.2–99.9% of the metals compared to 70.8–98.5% when phytoremediation followed adsorption by RCA. Overall, relatively high metal removal efficiencies were attained, considering the acidic conditions ($pH < 4$), at hydraulic residence times of 1 to 5 days. Using coal ash to treat AMD is potentially a low-cost and environmentally friendly option for minimizing the adverse public health and environmental risks associated with both wastes.

Keywords Adsorption · Batch · Hydrothermal activation · Semi-batch system · Zeolites

Introduction

Mining and mineral processing can produce acid mine drainage (AMD) when coal seams and other pyritic rocks are exposed to air and water. AMD is characterized by a pH as low as 2 (Feng et al. 2000) and can contain high concentrations of metals, making it potentially toxic to aquatic organisms. Earlier studies have shown that several biomaterials can be used as low-cost adsorbents for metal removal in aqueous solutions. For example, biochar derived from sawdust and water hyacinth removes 94 to 100% of Zn and Ni from aqueous solutions (Gwenzi et al. 2014), and sulphonated waste polystyrene can remove Pb^{2+} and Zn^{2+} (Ruziwa et al. 2015).

The formation of zeolites from coal ash generated by the combustion of coal in thermal power stations and their subsequent use for environmental remediation has also received substantial attention (Murayama et al. 2003; Musyoka et al. 2013; Prasad and Kumar 2015). Zeolites can be synthesized by hydrothermal treatment of coal ash with hot NaOH or KOH (Murayama et al. 2003; Prasad and Kumar 2015), as well as AMD or circumneutral or alkaline mine wastewater (Musyoka et al. 2013). NaOH-activated coal ash (NaOH-CA) has been shown to remove 92, 60, and 89% of Zn, Mn, and Ni respectively from wastewaters (Sahoo et al. 2012). In other studies, the percentage metal

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removal using NaOH-CA ranged from 78.6 to 96% (Wang and Zhu 2007).

Phytoremediation has also been reported as a promising technology for metal removal. Most studies conducted to date have focused on metal uptake by various plant species (e.g. Danh et al. 2009; Evangelou et al. 2007). Several species, including Indian mustard (*Brassica juncea*), water hyacinth (Shim et al. 2003), sunflower (*Helianthus annuus*; Evangelou et al. 2007), and vetiver (*Vetiveria zizaionides*; Danh et al. 2009) have high capacities for metal uptake. Vetiver is highly tolerant to a wide range of extreme chemical conditions, including acidic and alkaline pH, salinity, sodicity, and Al and Mn toxicity (Danh et al. 2009). In pot experiments, 71–90% of metals were removed by water hyacinth and vetiver grass (Shim et al. 2003; Truong 1999; Truong and Baker 1996). Most research on the use of vetiver for phytoremediation has focused on metal-contaminated soils.

These studies focused on removal of metals using either adsorption or phytoremediation, and most of them used batch systems under laboratory conditions and synthetic single or multiple ion solutions. However, using adsorption or phytoremediation alone for metal removal from AMD is potentially problematic. First, while adsorption of metals tends to be high in neutral to alkaline pH, it decreases at extremely low pH due to competition with protons. Second, highly acidic conditions and high concentrations of phytotoxic elements such as Mn and Zn can constrain plant growth and survival. The potential exists to overcome these challenges and enhance metal removal by the sequential combination of inherently alkaline adsorbents such as raw coal ash (RCA) and NaOH-CA in tandem with phytoremediation. However, little attention has been paid to the sequential combination of the two processes. Therefore, the specific objectives of our batch and semi-batch fixed-bed column experiments were: (1) to compare removal of metals from AMD by NaOH-CA to that by RCA; and (2) to determine the effect of sequencing adsorption and phytoextraction on metal removal from AMD.

Materials and Methods

Chemical Characterization of Acid Mine Drainage

AMD was obtained from a storage pond at a pyrite mining company in Mazowe about 30 km northeast of Harare, the capital city of Zimbabwe. The metal concentrations in the AMD from the study site have been described in an earlier study (Mapanda et al. 2007). The AMD was filtered through a Whatman 540 # 1 to remove sediments and the other suspended particles. The pH and electrical conductivity (EC) were measured using the Eutech ION 700 and Eijkelkamp 18.21 pH and EC electrodes, respectively. Mn, Ni, Cu, Zn, Fe, Pb, and Cd were determined using an atomic absorption (AA) spectrophotometer (Model: MSE SpectraAA50).

Preparation of Adsorbents

The two adsorbents (RCA and NaOH-CA) were initially prepared and evaluated in batch experiments. Coal ash was collected from the Zimbabwe Power Company thermal power station in Harare. The coal ash was oven-dried at 70 °C for 24 h. The NaOH-CA was prepared following published procedures for hydrothermal synthesis of zeolites (Chang and Shih 1998; Höller and Wirsching 1985). Since the pioneering work of Höller and Wirsching (1985), hydrothermal treatment of coal ash with strong alkali solutions (e.g. NaOH, KOH) has been widely used for zeolite synthesis (Chang and Shih 1998; Murayama et al. 2003; Querol et al. 2002). In this study, the oven-dried coal ash and NaOH pellets were mixed in a weight ratio of 1:1.2, ground in a mechanical mortar, and thoroughly mixed. The mixture was then fused at 550 °C for 1 h in a muffle furnace to convert the insoluble ash mineral phase to a soluble sodium alumino-silicate phase. The resultant fused mixture was then cooled and milled again. The powder thus obtained was mixed with 43 mL of distilled water and stirred overnight at room temperature. Thereafter, the solution was incubated at 55 °C for 4 days. The long incubation period is necessitated by the zeolite's low temperature of crystallization (Chang and Shih 1998). The solid part was then separated from the liquid phase using a MSE Centaur 2 centrifuge. The resulting zeolitic coal ash was rinsed thoroughly with distilled water and then oven-dried at 80 °C for 12 h (Chang and Shih 1998).

Batch Evaluation of Adsorbents

Selection of the adsorbent to be used in the adsorption-phytoextraction semi-batch system was based on metal adsorption data from batch experiments, which were conducted using duplicate dosages of 2.5, 5, 8, 12, and 15 g of the adsorbents added to 100 mL of AMD. The mixtures were agitated on a mechanical shaker at 120 rpm for 3 h at ambient temperature (27 ± 2 °C) and then filtered using Whatman 540 #1 filter paper (Sahoo et al. 2012). The equilibrium concentrations of the Mn, Zn, Ni, and Cu in the filtrate were determined using AA. The pH and EC were also measured using a calibrated pH and EC meter, respectively. The experiments were carried out in duplicate to ensure reproducibility (Sahoo et al. 2012). The removal efficiency (*RE*) of the adsorbents was calculated using Eq. [1]:

$$RE = \left(\frac{c_i - c_f}{c_i}\right) \times 100 \tag{1}$$

where c_i and c_f are the concentrations of metals in the initial and final solutions, respectively.

Semi-batch Adsorption and Phytoextraction

Based on the metal adsorption capacity from the batch experiments, only RCA and NaOH-CA were used in the semi-batch adsorption-phytoextraction system. The semi-batch system consisted of two components: a fixed-bed adsorption column and a vetiver phytoremediation chamber (Fig. 1). The adsorption system was fabricated from a PVC column (internal diameter: 200 mm and length: 300 mm). Glass wool was placed at the bottom of the column to prevent outflow of the adsorbent and clogging of the outlet. The column was packed with 75 g of sand and adsorbent, mixed in a 3:7 ratio. Given the fine texture of both the RCA and NaOH-CA, the 30% sand was incorporated to facilitate flow through the system. Sand filters were put at the top and bottom of the packed columns to ensure uniform distribution of the AMD through the adsorbent while maintaining a constant flow rate. The vetiver phytoextraction chamber consisted of a PVC column (internal diameter: 180 mm diameter and length: 170 mm) packed with 1.5 kg of clean sand. Glass wool was also placed at the bottom of the column to retain the sand. Three uniform clumps of vetiver grass, each with three actively growing tillers, were planted in each pot and kept active until used for phytoremediation. To minimize the effects of dilution on metal concentrations and pH, sand was used as a growth medium to facilitate rapid drainage. Moreover, the vetiver phytoextraction chambers were allowed to drain for three days after irrigation before being charged with AMD from the adsorption unit. Therefore, dilution effects on metal concentrations and pH were considered negligible.

The effect of hydraulic residence times (HRT) of 1 to 5 days in the adsorption columns was assessed by collecting treated AMD samples at the outlet of the adsorption columns. For each residence time, 3 L of AMD was poured into the adsorption column to attain an adsorbent: liquid ratio of 1 g: 40 mL, similar to the lowest ratio used in batch evaluation. The adsorption column was operated in a downflow mode. After a day, the outlet valve was opened and three 100 mL aliquots representing replicates were taken at one min intervals. The remaining effluent was then passed into the vetiver phytoextraction chamber where it remained for 7 days. Thereafter, the outlet valve was opened and three 100 mL aliquots were collected at one min intervals to serve as replicates. The same procedure was followed for day 2, 3, 4, and 5 in the adsorption column.

Laboratory Chemical Analyses

Mn, Zn, Cu, and Ni concentrations in the leachate from the adsorption and phytoextraction chambers were determined using AA. The differences between the initial concentration of metals in the AMD and after adsorption and phytoextraction were calculated to determine the contribution of each process to metal removal. The leachate pH from both the adsorption and phytoextraction columns was also measured, as described earlier.

Data Analysis

Data were first tested for parametric assumptions of normality and homogeneity of variance. Analysis of variance and t-test were used to evaluate the effects of adsorbents and HRT on metal removal. Data failing to conform to parametric assumptions were either transformed or analysed using non-parametric statistical tests. All statistical

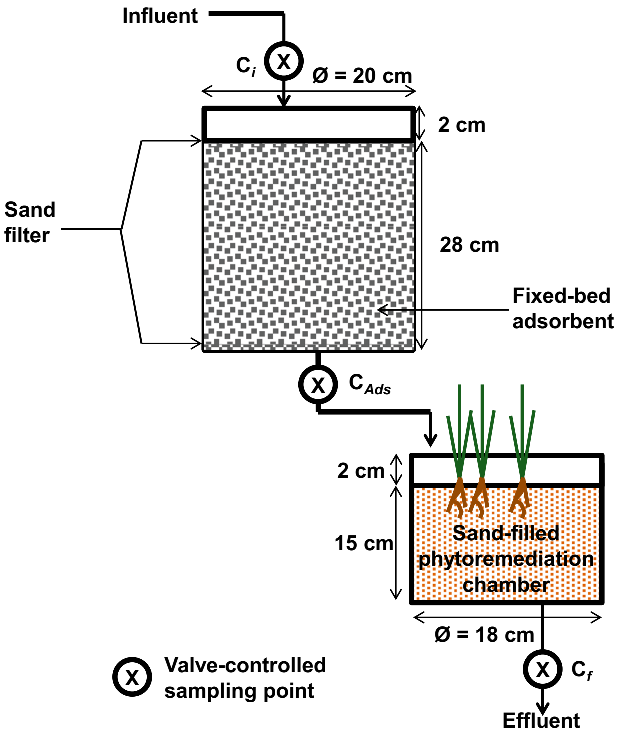


Fig. 1 Schematic of the semi-batch system for sequential removal of metals by adsorption and phytoextraction. C_i, C_Ads and C_f denote initial concentration, concentrations after adsorption and final concentration after phytoremediation, respectively

analyses were done using Minitab software version 16 at probability level $p = 0.05$.

Results

Chemical Properties of the Acid Mine Drainage

The AMD had an extremely acidic pH (1.7). The EC was also very high (38.5 dS/m), indicating a high concentration of soluble salts. Table 1 shows that the concentrations of metals in AMD decreased in the order: Fe (2562 mg/L) > Mn (214.0 mg/L) > Zn (11.8 mg/L) > Ni (6.65 mg/L) > Cu (1.96 mg/L) > Pb (0.97 mg/L) > Cd (0.08 mg/L). Subsequent batch and column experiments focused on Mn, Zn, Ni, and Cu due to their potential toxicity, while Pb and Cd were excluded because their concentrations in the leachate were generally below the AA detection limit of 0.001 mg/L. Fe was excluded because it is less toxic than the other metals and is very ubiquitous in the study area, which has predominantly red clayey soils rich in Fe (Nyamapfene 1991).

Batch Evaluation of Adsorbents

The NaOH-CA was highly alkaline (pH 11.3 ± 0.01) while the RCA had a near-neutral pH. As expected, the effluent pH for both adsorbents (Fig. 2a) was higher than that of the influent AMD. The NaOH-CA had significantly ($p < 0.001$) higher metal removal than the RCA (Fig. 3). The NaOH-CA had higher percentage removal for Zn (53.8%), Mn (93.1%), and Cu (96.6%), but its Ni removal (18.9%) was less than that of the RCA (35.1%). For both adsorbents, removal was highest for Mn, averaging 89.5% for the RCA and 93.1% for the NaOH-CA. At all doses, NaOH-CA had remarkably better Cu removal than the RCA, while the opposite trend was observed for Ni. Except for Ni, NaOH-CA was generally a better adsorbent than RCA.

For the dosage range of 2.5–15 g/100 mL, metal adsorption was generally independent of adsorbent dose. An exception was the initial linear increase in Ni adsorption by NaOH-CA in the range of 2.5–8 g/100 mL, followed by a plateau at 12–15 g/100 mL. Based on these findings, subsequent semi-batch fixed-bed adsorption columns were packed with either NaOH-CA or RCA, at a uniform dosage of 6 g/100 mL, equivalent to 60 g/L.

Semi-batch Adsorption and Phytoremediation

As observed in the batch experiments, the pH of the effluent from the NaOH-CA adsorption chamber was above that of the RCA for all residence times, though the difference between the two decreased over time (Fig. 2b). The vetiver phytoextraction unit did not meaningfully affect effluent pH. The adsorption-phytoextraction system incorporating NaOH-CA had significantly ($p < 0.001$) higher Ni removal than the RCA (Figs. 4, 5). However, for Mn, Zn, and Cu, there was no significant difference between the various HRT, with p values of 0.105, 0.104, and 0.051, respectively. The NaOH-CA system had higher percentage removals for Zn, Mn, Cu, and Ni than the RCA. In both cases, the greatest removal was with Mn. Overall, the metal removal capacity of the NaOH-CA system was consistently higher than that of the RCA system for all metals except for Mn, which were similar. Across the various HRT, the NaOH-CA system maintained more metal removal capacity than the RCA system (Figs. 4, 5). In general, the NaOH-CA maintained high metal removal for the first four days, followed by a gradual decline on the final day. On the other hand, removal of metals dropped slightly after day 3 for both RCA and NaOH-CA, probably due to desorption associated with the decrease in pH (Fig. 2b).

Phytoextraction increased metal removal from the AMD (Fig. 6). Combining adsorption by NaOH-CA and phytoextraction increased metal removal from 59.1, 95.7, 77.9, and 67.6% to 99.1, 99.9, 89.2, and 99.5% for Zn, Mn, Cu, and Ni, respectively, which was significantly ($p < 0.001$) higher than for each process alone. Solution pH is one of the key factors controlling the release and adsorption of metals. The mean pH of the effluent from the NaOH-CA adsorption chamber ranged from 2.2 to 3.7 compared to 2.2–3.5 from the phytoremediation chamber. The mean pH of the effluent from the RCA adsorption chamber ranged from 2.0 to 2.5 compared to 1.9–2.2 from the phytoremediation chamber. Notably, the pH of the effluent from both the adsorption and phytoremediation chambers for the NaOH-CA was about 0.5–2.0 above the initial pH of the AMD. Effluent from treating with the RCA-based system had a pH 0.2–0.8 SU above the initial pH of the AMD. For both systems, pH increases were greater in the adsoption than the phytoremediation chambers.

Partitioning of metal removal between adsorption and phytoremediation showed that the contributions of the

Table 1 Initial concentration (mg/ L) of Mn, Ni, Cu, Zn, Fe, Pb and Cd in acid mine drainage

	Mn	Ni	Cu	Zn	Fe	Pb	Cd
Concentration (mg/L)	214.00	6.65	1.96	11.80	2562.00	0.97	0.08

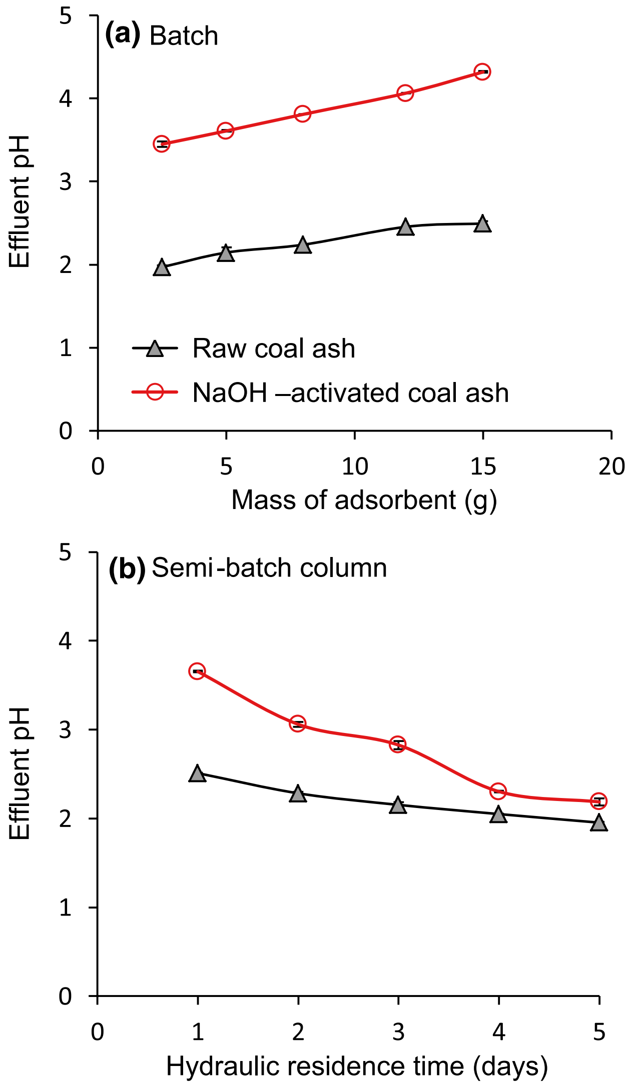


Fig. 2 The pH of the effluent from batch (**a**) and semi-batch column (**b**) experiments for the coal ash and NaOH-activated coal ash

two processes were dependent on the adsorbent and the metal (Fig. 6). Zn and Ni removal dominated phytoremediation and adsorption in the RCA and NaOH-CA systems, respectively (Fig. 6a–d). The high contribution of adsorption to Zn and Ni removal in a system with NaOH-CA further demonstrated its superiority compared to RCA. Adsorption was the key removal mechanism for Mn and Cu for both systems using the RCA and NaOH-CA as adsorbents (Fig. 6e–h).

Discussion

The current study provides insights into the potential to enhance metal removal by sequentially combining adsorption using coal ash-based adsorbents and phytoremediation by an acid- and metal-tolerant vetiver. As expected, the AMD was extremely acidic, and had high concentrations of metals that exceeded local and international guidelines for effluent disposal except for Cu, which was below 2 mg/L. The high concentration of metals in the AMD is attributed to the extremely acidic pH, which enhanced dissolution of metal-bearing waste rock (Mapanda et al. 2007; Musyoka et al. 2013). Discharge of the AMD without prior treatment could potentially lead to soil pollution, public health risks through contamination of surface and groundwater resources, and severe impacts on ecosystems. Batch and semi-batch fixed column experiments revealed three key findings: (1) metal adsorption capacity of the NaOH-CA was either similar to or significantly ($p < 0.05$) greater than that of the RCA; (2) For both, metal removal by adsorption was consistently greater than that of phytoremediation by vetiver; and (3) sequential combination of adsorption and phytoremediation achieved more metal removal than either of the two processes alone, corroborating the need to combine the two processes.

The generally high adsorption capacity of the NaOH-CA and RCA is attributed to non-pH dependent adsorption, including formation of insoluble precipitates and coordination complexes (Rahimi et al. 2014). The high removal of metals by the NaOH-CA demonstrated effective activation by NaOH and the formation of zeolites, which have high surface area and cation exchange capacity (Musyoka et al. 2012; Prasad and Kumar 2015). Isomorphic substitution of Si^{4+} by Al^{3+} in the three-dimensional lattice of the zeolite contributes to the net negative charge, which is counterbalanced by exchangeable cations, i.e. metal ions (Wingenfelder et al. 2005). However, the two adsorbents exhibited contrasting Cu and Ni adsorption; NaOH-CA adsorbed more Cu than Ni, while RCA exhibited the opposite trend. The results suggest mutual inhibition or contrasting adsorption affinities between the two metal ions. Higher adsorption of Cu than Ni on NaOH-CA conformed to the Irving-Williams (1948) series on stability of metal complexes (Stumm and Morgan 1996).

Contrary to the results observed in the semi-batch column experiment, RCA had higher Ni removal than NaOH-CA in the batch experiments. The reasons for this are unclear, but it could reflect mechanistic differences between the experiments.

The NaOH-CA in this study removed less Zn and Ni and more Mn than was observed in a previous study (Sahoo et al. 2012). This could be due to the different methods used for the synthesis of the zeolites. NaOH-CA was still better than RCA and can therefore be used as a low-cost adsorbent in AMD treatment. Based on a coal ash: NaOH ratio of 1: 1.2, 1.2 t of NaOH is required to produce a metric tonne (t) of NaOH-CA. Considering the current market

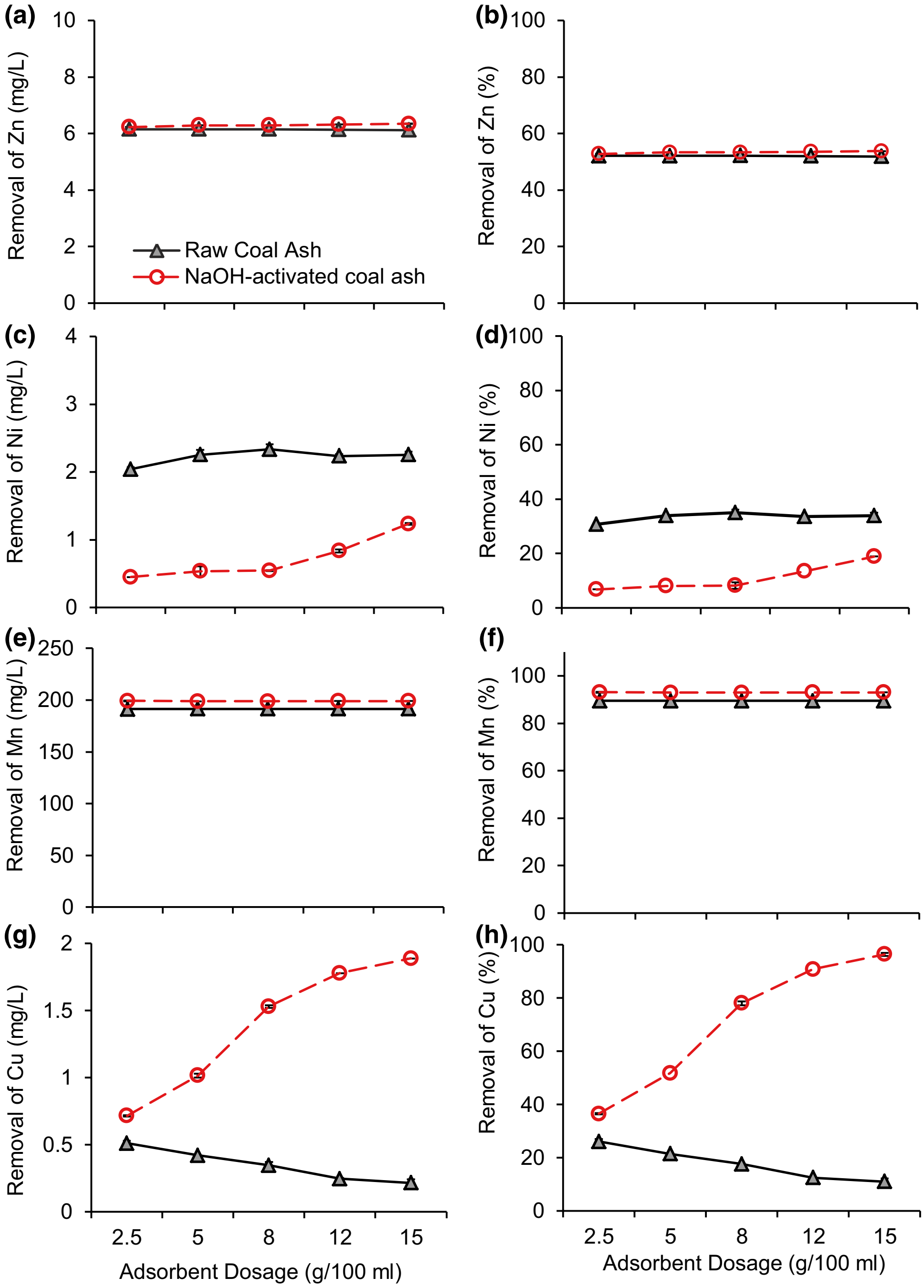
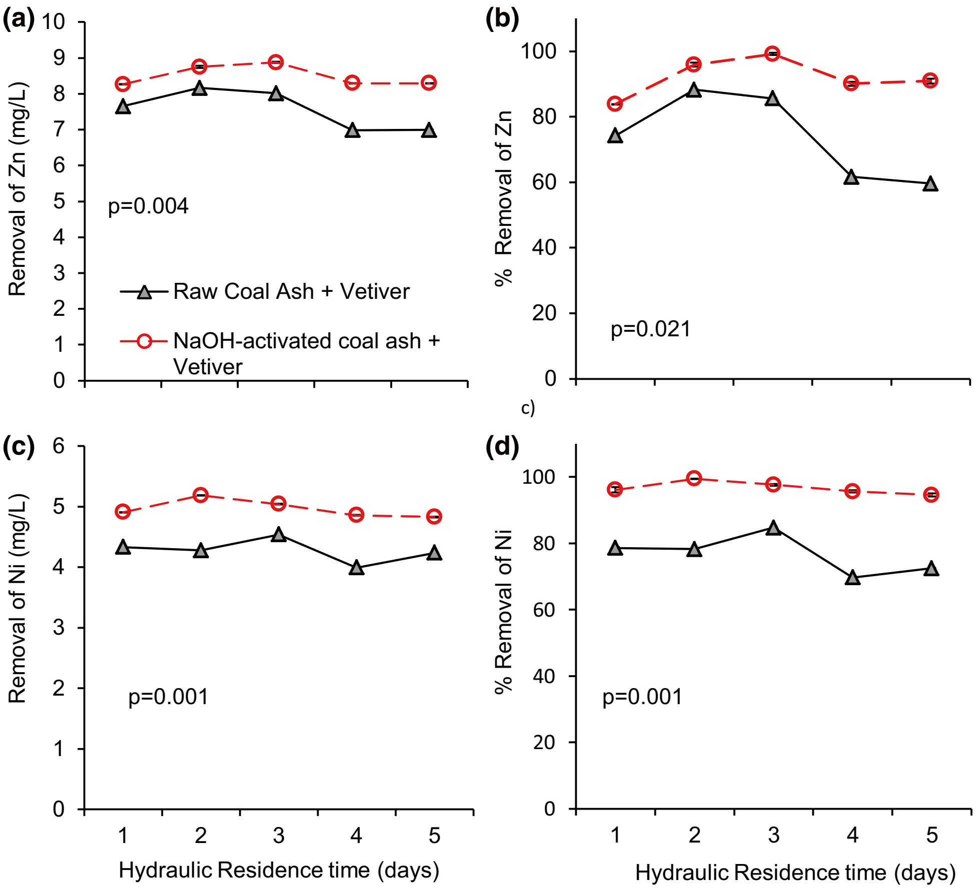


Fig. 3 Adsorptive removal of Zn (**a, b**), Ni (**c, d**), Mn (**e, f**) and Cu (**g, h**) by coal ash and NaOH-activated coal ash at various adsorbent doses. Data shown are concentrations removed (*left*) and per cent removal (*right*)

price of US$300/t for industrial NaOH, and that coal ash is a waste available for free, this yields a cost of approximately US$ 0.36/kg NaOH-CA. This unit price of NaOH-CA is on the lower end of the range reported for low-cost adsorbents (US$ 0.02–2.20), and is more than an order of magnitude less than that of commercial activated carbon (US$ 21.00) and chitosan (US$16.00) (Grassi et al. 2012).

The high metal removal capacity of the NaOH-CA system was more pronounced in the semi-batch adsorption-phytoremediation system than in the batch experiments, probably because agitation tends to even out differences in adsorption properties among the adsorbents. Moreover, this could also explain the synergistic effects of combining adsorption and phytoremediation. The removal trends of Zn, Ni, and Cu over time suggests that the NaOH-CA adsorption sites might have become saturated after about five days compared to three days for the RCA, suggesting less adsorption capacity for the RCA, consistent with the batch adsorption data. Mn removal remained high throughout the five day period, suggesting preferential adsorption of Mn for both adsorbents (Fig. 5). The initial low removal of Cu and Zn by RCA suggests that short contact times

Fig. 4 Adsorption of Zn (**a, b**) and Ni (**c, d**) by sequential adsorption using coal ash, NaOH-activated coal ash and phytoextraction by vetiver. Data shown are concentrations removed (*left*) and per cent removal (*right*)



may limit the exposure of the metals to adsorption sites, while reduced removal after 3 days could be due to saturated adsorption sites.

Overall, adsorption accounted for 70–80% of metal removal while phytoremediation accounted for the rest. The low contribution of phytoremediation could be due to the extremely acidic pH and exclusion of metals by the plants. Earlier studies have shown that exclusion is one of the mechanisms used by plants to grow and survive in conditions with high metal concentrations (Baker 1981; Ernst 2006). Even so, sequential combination of adsorption and phytoremediation resulted in higher metal removal than the two processes operating alone. Adsorption has the capacity to remove metals, even at low concentrations, while phytoremediation polishes the effluent through root extraction of the metals. Literature on metal removal in AMD is dominated by adsorption studies (Ahmaruzzaman 2010; Cetin and Pehlivan 2007; Chenxi 2008; Sahoo et al. 2012), while those based on phytoremediation, or a sequential combination of adsorption and phytoremediation are scarce. The total removal observed in the current study (≈90–100%) was higher than that reported in previous studies based on adsorption alone (Ahmaruzzaman 2010; Cetin and Pehlivan 2007; Chenxi 2008; Sahoo et al. 2012). Besides the collective contribution of the two processes, contrasting results observed between the current and earlier studies (e.g. Chenxi 2008; Motsi et al. 2009) could also be due to differences in the initial metal concentrations, adsorption capacity of the adsorbents, and the initial pH of the AMD, all of which influence the adsorption process.

Partitioning of metal removal between adsorption and phytoremediation revealed contrasting patterns among metals attributed to preferential removal by the two processes. Mechanisms accounting for metal removal by phytoremediation may include phytostabilization, where plants minimize metal mobility in contaminated media through accumulation by roots, precipitation and complexation within the rhizosphere (Nascimento et al. 2006), and adsorption on root surfaces and the solid phase. In addition, phytoextraction or direct root uptake may also contribute to removal of essential metals, particularly Zn (Kuzovkina and Volk 2009).

Solution pH is one of the factors influencing adsorption and bioavailability of metals. The pH of the effluents from the adsorption chamber was above that of the initial AMD, suggesting that the adsorbents had acid-neutralizing capacity or a putative pH buffering capacity. This is consistent

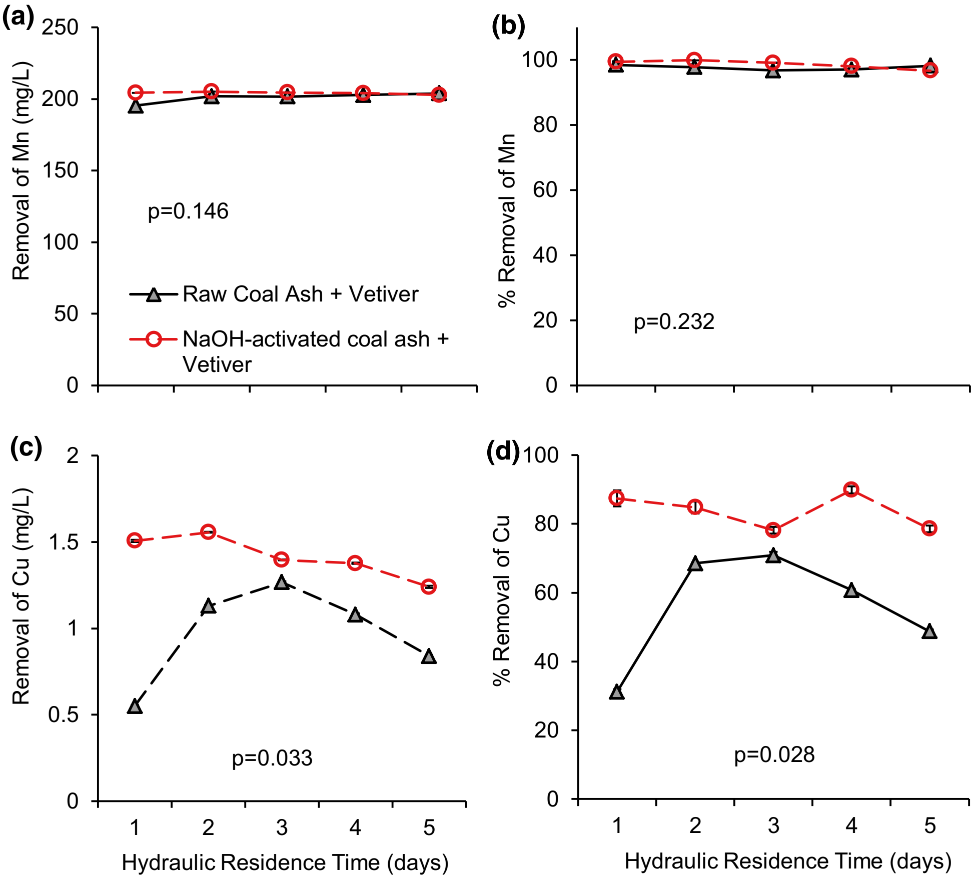


Fig. 5 Adsorption of Mn (**a, b**) and Cu (**c, d**) by sequential adsorption using coal ash, NaOH-activated coal ash and phytoremediation by vetiver. Data shown are concentrations removed (*left*) and per cent removal (*right*)

with the near-neutral to alkaline pH of the RCA and NaOH-CA, suggesting the possible contribution of precipitation to metal removal. In contrast, no remarkable change in effluent pH was observed between the adsorption and phytoremediation chambers. Partitioning metal removal by adsorption on solid phase and roots surfaces, and phytoextraction or direct plant uptake by vetiver was beyond the scope of the current study. However, acidic conditions in the phytoremediation chamber may enhance bioavailability (Salomons 1995) and uptake of metals by vetiver, which could lead to phytotoxicity. Phytotoxicity potentially poses a threat to the long-term efficiency and sustainability of phytoremediation technology on metalliferous mine wastes and wastewaters.

The bulk of previous studies on treatment of AMD focused on a single process, such as adsorption (Mohan and Chander 2006; Motsi et al. 2009) or phytoremediation (Nyquist and Greger 2009; Sheoran and Sheoran 2006). Using sequential combination of adsorption and phytoremediation to enhance metal removal appeared to be beneficial. First, high removal efficiencies were attained for all metals, suggesting limited or no preferential removal, in contrast to some earlier studies that reported strong preferential removal of certain metals to others. Second, the high removal efficiencies occurred under highly acidic conditions ($pH < 4$) and HRT of 1–5 days compared to those reported for similar treatment systems with longer HRT (e.g. Uster et al. 2015). Under comparable pH conditions, some studies have reported lower (<40%) metal removal efficiencies (e.g. Lee et al. 2002). In cases where metal removal is pH-dependent, higher values occurred under alkaline conditions due to co-precipitation with insoluble carbonates, phosphates, and hydroxides of Fe, Al, and Mn (Gwenzi and Mupatsi 2016; Lee et al. 2002; Robinson-Lora and Brennan 2009). This demonstrates that, besides precipitation, multiple mechanisms (e.g. filtration, sedimentation) contribute to metal removal. Moreover, the current system used lower HRT than those (>10 days) often reported (e.g. Cheong et al. 2010; Uster et al. 2015), pointing to a potentially high throughout and low land/capacity requirements.

Literature on metal removal from AMD shows that results vary among studies (Table 2). For example, Mn removals close to 100% were reported for adsorbents such as crab-shell chitin and mussel shells high in carbonates and phosphates (Robinson-Lora and Brennan 2009; Uster et al. 2015). The percent metal removal of Zn, Ni, Mn, and Cu by adsorption observed in this study was higher than those reported for natural and thermally-pre-treated zeolites (Motsi et al. 2009), but were generally similar to those for RCA and its zeolites (Prasad and

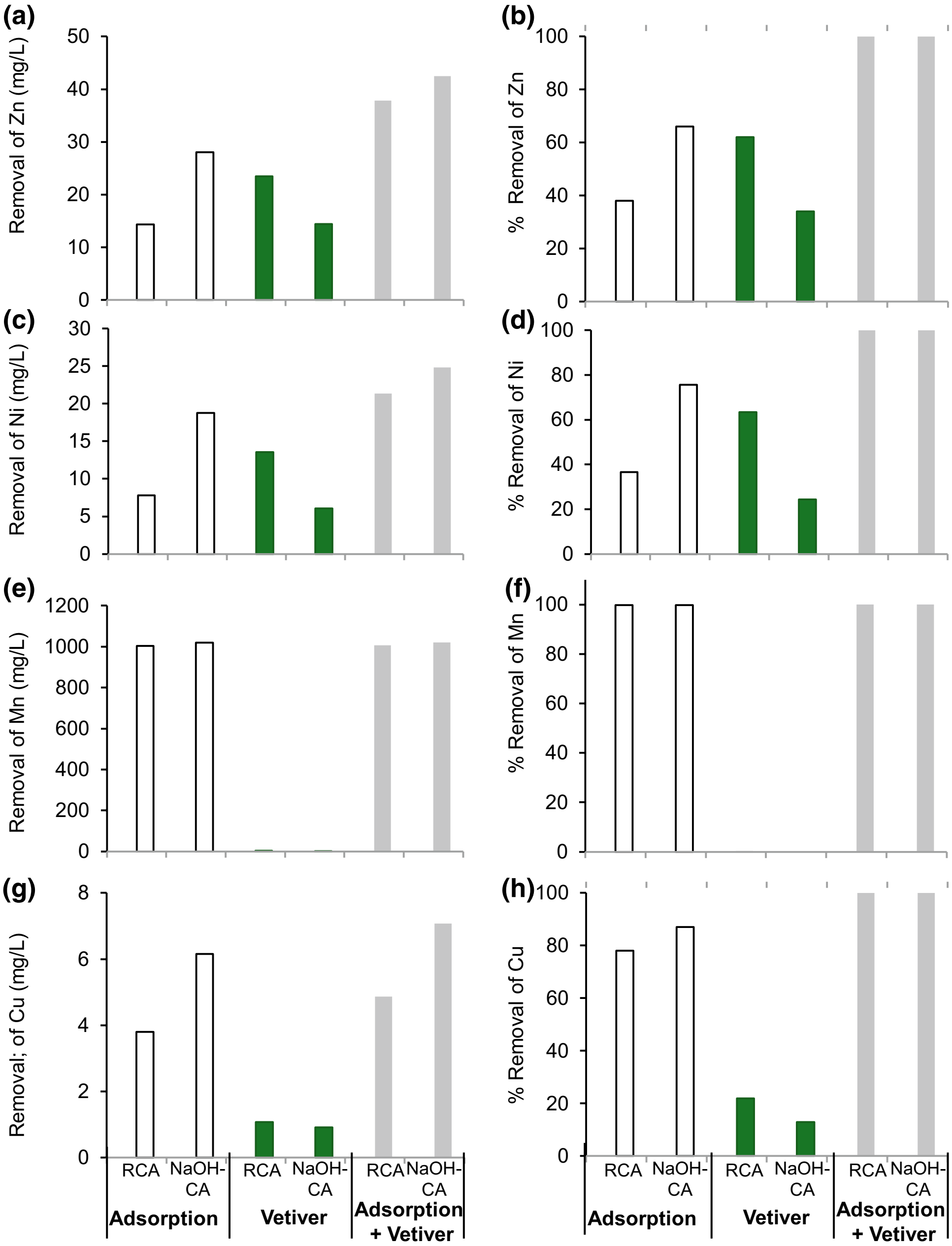


Fig. 6 Contribution of adsorbents, vetiver phytoremediation and their combination on cumulative removal of Zn (**a, b**), Ni (**c, d**), Mn (**e, f**) and Cu (**g, h**) in acid mine drainage over the 5-day experimental period. Data shown are concentrations removed (*left*) and per cent removal (*right*)

Mortimer 2011). Notably, besides the adsorption capacity of the adsorbents, percent removal also depends on the amount of metals adsorbed, which were often not reported. However, the observed combined total removal percentages for the two processes were about approximately 100% higher than those reported for either adsorption or phytoremediation alone, demonstrating the superiority of sequencing the two processes.

Studies investigating metal removal in AMD by wetlands have also yielded inconsistent results. For example, Mn removal efficiencies ranged from 23 to 86% (Sheoran and Sheoran 2006), presumably due to preferential removal of iron and varying mine water acidity and wetland design. Similarly, metal removal efficiencies by artificial and natural wetlands range from low removal, 33–40% (Sheoran and Sheoran 2006), to as high as 88–94%. For example, passing AMD with a pH of 2.65 through a wetland with and without plants removed 50–57% and 36% of Cu, respectively, but had no effect on Zn and pH, causing Nyquist and Greger (2009) to conclude that emergent plants and wetlands could not treat very harsh AMD. Variations between studies reflect contrasting AMD characteristics, treatment methods, and operating conditions (Neculita et al. 2011), and point to the need to select the correct passive treatment method. Consequently, comparison of our observed removal efficiencies and those in the literature yield mixed results (Table 2): (1) removal efficiencies for adsorption, and adsorption combined with phytoremediation, were generally greater than those reported for artificial and natural wetlands; (2) The overall removal efficiencies (70.8–99.9) observed in this study are similar to or greater than those in single or multiple process (bio)-reactor systems based on strongly alkaline adsorbents, oxidation, and sulphate-reducing bacteria. However, there is need for caution when comparing and interpreting removal efficiencies across studies due to differences in scale (e.g. small-scale laboratory vs. large scale field studies), initial pH, concentration of metals, and HRT. Note that, while this study used actual AMD, which is multi-component system, some literature is based on synthetic AMD (e.g. Cheong et al. 2010). Multi-component AMD is expected to have more pronounced interference effects than synthetic ones with one or only a few metal ions. Another drawback associated with most wetland-based treatment literature is that data are not reported on adsorption capacities of the growth media and, in some cases, HRT.

Conclusion and Outlook

We investigated the potential of sequencing adsorption by coal-ash based adsorbents and phytoremediation by vetiver

Table 2 Comparison of removal efficiencies for Cu, Zn, Ni and Mn in semi-batch adsorption—phytoremediation system in the current study to those in literature

Removal method	Pollutant	pH	Removal efficiency (%)	References
Peat biofilter	Cu, Ni, Zn	Influent: 4.2–6.1 Effluent: 4.9–5.5	34, 27, 12	Clyde et al. (2016)
Mussel shells HRT: 3 and 10 days	Zn, Mn, Cu, Ni	Influent: 2.9 Effluent: 6.49–6.79	29.6–99.6	Uster et al. (2015)
Limestone HRT: 3 and 10 days	Zn, Mn, Cu, Ni	Influent: 2.9 Effluent: 6.36–6.49	19.8–99.1	Uster et al. (2015)
Natural and artificial wetlands	Zn, Cu	Influent: 2.65 Effluent: 2.60–2.81	−3.4-57.1	Nyquist and Greger (2009)
Mushroom, cow manure, rice straw and sawdust HRT: 4 days	Mn	Influent: 2.65 Effluent: 6.1–7.8	49–61	Song et al. (2012)
Natural wetland	Cu, Zn	Influent: 2.7 Effluent: 5.5	83–94	Dean et al. (2013)
Artificial wetland	Cu	-	36–88	Sheoran and Sheoran (2006)
Co-precipitation with Fe, Al and Mn	Zn, Cu, Ni	Influent: 2.2–3.4 Effluent: 2–8.5	<40 (pH <4) 40–95 (pH 4–8.5)	Lee et al. (2002)
Oxidising system	Mn	Influent: 5.8–7.6 Effluent: 6.8–7.7	10	Trumm and Pope (2015)
Slag leaching bed	Mn	Influent: 5.8–7.6 Effluent: 6.8–7.7	90	Trumm and Pope (2015)
Spent mushroom and limestone	Cu, Mn	Influent: 2.31 Effluent: 6.3	88–92.9	Cheong et al. (2010)
Waste gas sludge	Cu, Zn, Mn	Influent: 2.7–2.9	100, 97, 94	Jafaripour et al. (2015)
South African bentonite clay	Mn	Influent: <3 Effluent: 7	90	Masindi et al. (2015)
Immobilised sulphate reducing bacteria	Cu, Zn, Mn	Influent: 2.8 Effluent: 7.8–8.3	<99.9, >99.9, 42.1–99.3	Zhang and Wang (2014)
Raw coal ash (CA)	Zn, Mn, Ni, Cu	Influent: 1.7 Effluent: 2–2.51	30.2–95.1	Present work
NaOH-activated coal ash (NaOH-CA)	Zn, Mn, Ni, Cu	Influent: 1.7 Effluent: 2.13–3.67	59.1–95.7	Present work
Vetiver phytoremediation	Zn, Mn, Ni, Cu	Influent: 1.7 Effluent: 2.0-3.5	3.4–54.6	Present work
Raw coal ash + phytoremediation	Zn, Mn, Ni, Cu	Influent: 1.7 Effluent: 2.0-2.2	70.8–98.5	Present work
NaOH-CA + phytoremediation	Zn, Mn, Ni, Cu	Influent: 1.7 Effluent: 2.2–3.5	89.2–99.9	Present work

HRT hydraulic residence time

grass to enhance metal removal from AMD. NaOH-CA was a more effective adsorbent than RCA due to putative formation of zeolites with high metal adsorption capacity. Relatively high removal efficiencies were attained for all metals under highly acidic conditions ($pH < 4$) and HRT of 1 to 5 days. The metal removal efficiencies of adsorption and adsorption combined with phytoremediation were generally better than those of wetlands, though of course this may only have been due to the small scale of these experiments. The overall removal efficiencies (70.8–99.9%) were also similar to or better than those for bioreactors using strongly alkaline adsorbents and/or sulphate reducing bacteria.

Besides reducing the concentrations of metals in solution, the use of vetiver can also contribute to dewatering by root water uptake and subsequent evapotranspiration. In addition, plants enhance the aesthetic values of waste/wastewater disposal facilities.

Given the prevalence of AMD and the availability of large quantities of coal ash, the potential exists for large-scale application of this technology. Using coal ash as an adsorbent could simultaneously reduce the public health and environmental risks associated with both AMD and the ash. Such industrial symbiosis could represent a low-cost and environmentally friendly win–win option for the management of AMD and coal ash, especially in developing countries. However, like other adsorbents, RCA and NaOH-CA transfer metals from aqueous solution (AMD) to a solid phase, raising operational questions about the fate of contaminants in spent adsorbents. Possible options to overcome this could entail regenerating the spent adsorbents and recovering the metals. Once the RCA and NaOH-CA cannot be regenerated further, scope exists to solidify/stabilize them using cement. The stabilized adsorbents could then be used as aggregates in construction applications such as concrete and road surfacing. However, further research on risk assessment and life cycle analysis is warranted to understand the fate and environmental impacts of such practices.

Besides NaOH hydrothermal activation, other studies report that zeolites can also be synthesized from coal ash using circumneutral or acidic mine wastewaters (Musyoka et al. 2013). This could potentially generate large amounts of zeolites for large-scale applications at relatively low cost. Overall, use of coal ash as an adsorbent potentially represents a low-cost and environmentally friendly win–win option for simultaneously minimizing the adverse public health and environmental risks associated with both AMD and coal ash. Although the current study provides insight on the potential value of combining adsorption and phytoremediation, further research is clearly required to address key knowledge gaps pertaining to the technology. Based on the results of this short-term study, it is unclear whether uptake by vetiver will persist in the long-term, given the acidic pH and the possibility that metals will bioaccumulate in the vetiver to potentially toxic levels. This calls for further research to optimize the system with respect to loading rates, regeneration of adsorbents, determining of optimal residence times, and uptake of metals by plants in the phytoremediation chamber. Long-term research under field conditions is also required to evaluate the sustainability of the approach. Moreover, considering the highly acidic conditions and relatively short HRT in the current study, there may be scope to further increase the removal efficiencies by incorporating a separate pH neutralization unit and increasing the HRT.

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