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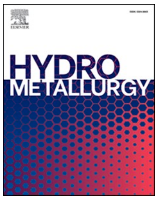

Removal and recovery of metal ions from acidic multi-metal mine water using waste digested activated sludge as biosorbent

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ABSTRACT

Highly acidic and toxic metal ion containing acid rock drainage (ARD) can cause severe environmental problems and endanger aquatic life. However, due to the high metal ion containing ARD is an auspicious source of metals for recovery and reuse. The feasibility of using waste digested activated sludge (WDAS) as a biosorbent for selective metal recovery from a highly complex mine water characterized by low pH (2.6), high sulfate concentration (80.8 g L^{-1}) and a multitude of metals (Co, Cr, Cu, Fe, Mn, Ni, Th, U, V, Y, and Zn) at concentrations from few mg L^{-1} to several g L^{-1} was investigated. The effect of pH (2.0–10.0) and WDAS concentration (3.8–22.2 g L^{-1}) on metal ion removal and the effect of several recovery solutions and their concentrations on metal recovery were explored in batch experiments. Metal removal was influenced by pH and WDAS concentration. A strong selectivity was observed in the recovery step employing 1 M Na_2CO_3 solution. The combination of a one-step removal and a two-step recovery approach enabled recovery of U (108.0 ± 6.6%), Cu (39.2 ± 2.5%), and Th (53.7 ± 7.7%) due to formation of strong carbonate complexes increasing the purity of U and Cu up to tenfold compared to the mine water. The results revealed that careful adaption of pH, WDAS concentration, and number of steps of the process according to the combination of metals present in solution is of great importance.

1. Introduction

The exposure of sulfide-containing minerals such as pyrite (FeS_2) to atmospheric oxygen and water due to mining-related activities or natural weathering causes the sulfide to be oxidized to sulfate via an acid-releasing reaction (Vera et al., 2013) and the oxidation of ferrous iron to ferric iron. Both, ferric iron and protons can enhance the oxidation of minerals, which leads to the release of metal ions into the aqueous phase (Gray, 1997). Once pH is low enough to allow for growth of acidophilic microorganisms this process is substantially accelerated by the metabolic activities of these microorganisms (Singer and Stumm, 1970). The formed acidic, metal-containing, sulfate rich water outflow is called acid rock drainage (ARD) (Akcil and Koldas, 2006) entailing environmental liabilities of billions of US$ (Tayebi-Khorami et al., 2019). The ARD often contains several different metals, depending on the minerals present at the site of formation, each at concentrations up to several grams per liter (Alegbe et al., 2019; Bhattacharya et al., 2006; Sánchez España et al., 2005; Tutu et al., 2008). Besides transition metals, radionuclides, such as uranium and thorium, and rare earth elements, such as yttrium have been detected (Villa et al., 2011; Ladeira and Gonçalves, 2007; Olías et al., 2005). Efficient removal of toxic metals from mine waters is essential, but to support environmental sustainability it should be done in a way that enables metal recycling.

Metal ions can be removed from mine waters efficiently for example via precipitation (Simate and Ndlovu, 2014), adsorption (García et al., 2014), membrane processes (Agboola, 2019), and electrochemical processes (Bejan and Bunce, 2015). However, these methods are relatively expensive due to the high chemical and/or energy demands (Bolisetty et al., 2019; Wang et al., 2005). Biosorption - the removal of substances with a material of biological origin due to various interactions including

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physisorption, chemisorption, ion-exchange, and micro/surface precipitation phenomena - offers a simple way to remove even low concentrations of metals from water (Robalds et al., 2016). Table 1 shows an overview of adsorption capacities of natural adsorbents for selected metals.

Furthermore, biosorption allows for metal recovery with a recovery agent such as an acid or base (Bashir et al., 2019). The biosorption of metals from single metal solutions (Liang et al., 2019; do Nascimento et al., 2019; Ojima et al., 2019) and synthetic water streams (Jain et al., 2018; Feisther et al., 2019; Patra et al., 2019; Kumar et al., 2019) has been reported for various metals with several biosorbents, but only few studies have addressed the biosorption of metals from real multi-metal mine waters (Hurtado et al., 2018; Fernández-González et al., 2018; Pinto et al., 2011; Chockalingam and Subramanian, 2006; Chockalingam and Subramanian, 2009). However, studying such multi-metal waters is important as they represent real life scenarios much more authentically than synthetic single-metal solutions and allow the investigation of e.g. the effect of ion competition for sorption sites. Some previous studies have investigated the use of activated sludge as a biosorbent for metal ion removal but used mostly synthetic solutions, waste streams with small number of metals, and/or solutions with low metal and sulfate concentration in the mg L^{-1} range (Ramrakhiani et al., 2017; Hughes and Gray, 2013; Guillamón and Hughes, 2014; Hughes and Gray, 2015; Ahmad et al., 2010). However, ARD waters can be significantly more complex containing varying concentrations of metals with concentrations of some metals and sulfate being in the range of several g L^{-1} (Nordstrom, 2011).

Similar to activated sludge, waste digested activated sludge (WDAS) can be used as a biosorbent. The WDAS is produced at wastewater treatment plants, where excess activated sludge is digested to produce biogas in an anaerobic digester (Appels et al., 2008). Furthermore, digestion also stabilizes the sludge as well as reduces the number of pathogens and odor problems due to removal of residual putrescible matter in the sludge (Appels et al., 2008). In addition, the properties of WDAS are reported to be less variable than those of activated sludge (Berthod et al., 2016), which would allow for a more constant adsorption performance. The remaining residue after digestion, known as digestate, consists mainly of microbial cells with a large variety of functional groups such as carboxyl, phosphoryl, hydroxyl and amine moieties on their surfaces (Jain et al., 2018) and is rich in nutrients such as nitrogen and phosphorus, but can also contain heavy metals, antibiotics, organic pollutants, or microplastics, limiting the reuse of the digestate as a fertilizer or in soil amendment (Fuchs and Drosg, 2013). Due to the complexity and toxicity of the digestate, the disposal can be a significant cost factor (Fuchs and Drosg, 2013). The WDAS is a promising biosorbent due to its high availability, low-cost and high metal uptake capability. Jain et al. (Jain et al., 2018) recently demonstrated that WDAS can adsorb 200 mg of U(VI) per g of WDAS from a synthetic U (VI)-containing solution and reported a desorption efficiency of over 95% after desorption with HCl or Na_2CO_3. Zhang et al. (Zhang et al., 2014) studied the removal of Cu(II) and Cd(II) using WDAS from single-metal solutions and obtained removal efficiencies up to 55%. Biosorption of metals from complex mine waters with WDAS has not been previously studied, although the pH and the presence of a wide range of metal ions will likely influence the adsorption of metals from complex streams such as real mine waters significantly, e.g. due to pH dependency of metal speciation and competition for sorption sites.

In this work, removal and subsequent recovery of metals from a complex acid mine water by using WDAS as the adsorbent was investigated. The objective was to evaluate whether the waste product WDAS is in principle usable in the removal and recovery of metals from complex acidic mine waters containing metals of different oxidation states at vastly differing concentrations, ranging from a few mg L^{-1} to several g L^{-1}, as opposed to the previously investigated single-metal systems (Jain et al., 2018; Zhang et al., 2014), synthetic solutions, and waste streams with low metal concentrations (Ramrakhiani et al., 2017; Hughes and Gray, 2013; Guillamón and Hughes, 2014; Hughes and Gray, 2015; Ahmad et al., 2010). The effect of both pH and WDAS concentration on metal ion removal was investigated in batch experiments. In addition, metal recovery from WDAS was studied in batch experiments to compare effectiveness and selectivity of different recovery solutions and to investigate their required amount. Furthermore, geochemical modeling was used to gain insights in the possible metal ion removal mechanism by WDAS.

2. Materials & methods

2.1. Characterization of WDAS and mine water

The WDAS was obtained from Viinikanlahti wastewater treatment plant, Tampere, Finland as described by Jain et al. (Jain et al., 2018) and was used as received without any pretreatment. A drying step was omitted to keep the required energy input and associated costs as low as possible. The concentration of total suspended solids (TSS) in the WDAS was 27.9 g L^{-1}. Analysis of the WDAS metal content revealed the presence of primarily Fe, Ca, K, and Mn but also trace amounts of U and Th (Table S1 in SI). The mine water was characterized regarding its metal content, presence of anions, pH and redox potential (Table 2).

2.2. Metal removal

Two types of metal removal experiments, where metal ion concentration in mine water was measured before and after the removal step, were performed. The general experimental procedure is summarized in Fig. 1.

In the metal removal experiment 1, WDAS and mine water were mixed at various ratios to generate different WDAS concentrations (3.6, 6.2, 8.2, 10.3, 13.4, 16.5, 18.5, 20.6 g TSS/L). In this experiment, pH was not adjusted but measured at the end of the experiment and reported as equilibrium pH (pH_{eq}). In the metal removal experiment 2, mine water and WDAS were mixed to generate WDAS concentration of 10 g L^{-1} before the pH was adjusted (2.0–10.0) and kept constant with

Table 1

Examples of adsorption capacities of different natural adsorbents for selected elements.

Element	Activated or digested sludge		Extracellular polymeric substances		Activated carbon		Algal biomass	
	pH	Adsorption mg g^{-1}	pH	Adsorption mg g^{-1}	pH	Adsorption mg g^{-1}	pH	Adsorption mg g^{-1}
Co	7.0[a]	12.34	*[d]	1.10	6.0[g]	13.88	6.0[k]	10.98
Cu	5.0[b]	65.79	*[d]	1.12	4.8[h]	50.39	5.0[l]	72.44
Mn	5.0[b]	44.84	*[e]	62.40	*[i]	9.25	*[m]	21.19
Ni	7.0[a]	12.02	*[d]	0.25	4.8[h]	26.35	5.5[l]	36.98
U	4.6[c]	200.0	7.0[f]	333.3	5.0[j]	50.34	4.0[n]	233.0
Zn	5.0[b]	64.94	*[d]	1.48	4.8[h]	56.88	5.5[l]	53.96

a = (Van Hullebusch et al., 2005), b = (Wu et al., 2012), c = (Jain et al., 2018), d = (Liu et al., 2001), e = (Pulsawat et al., 2003), f = (Wang et al., 2019), g = (Demirbaş, 2003), h = (Wilson et al., 2006), i = (Tran et al., 2018), j = (Kütahyali and Eral, 2004), k = (Vafajoo et al., 2018), l = (Sheng et al., 2004), m = (Yang et al., 2015), n = (Khani et al., 2008), * = pH not available.

Table 2

Characteristics of the mine water used for removal studies.

Cation	**Ca(II)**	**Co(II)**	**Cr(VI)**	**Cu(II)**
Concentration (mg L^{-1})	229 ± 22	44 ± 2	22 ± 6	139 ± 3
Cation	**Fe(III)**	**Mn(II)**	**Ni(II)**	**Th(IV)**
Concentration (mg L^{-1})	8527 ± 169	4364 ± 105	1952 ± 44	1.6 ± 0.2
Cation	**U(VI)**	**V(V)**	**Y(III)**	**Zn(II)**
Concentration (mg L^{-1})	14.0 ± 0.1	17.1 ± 7.8	13.3 ± 0.02	3709 ± 73
Anion	**Sulfate**	**Nitrate**	**Chloride**	**Phosphate**
Concentration (mg L^{-1})	80,800 ± 2700	107 ± 17	< LOD	< LOD

pH = 2.6, Eh = 827 mV; LOD = Limit of detection.

See table S2 in supplementary information for limits of detection and quantification.

HNO_3 (concentrations of 1.4 M and 14.4 M) or KOH (concentrations of 1 and 10 M). All experiments were performed at 27 ± 1 °C for 24 h on a rotary shaker (150 rpm) in 15 mL or 50 mL polypropylene tubes using effective volume of 10 or 20 mL, respectively. The duration of the experiment was chosen based on results by Jain et al. (Jain et al., 2018) who demonstrated rapid U removal by WDAS. Two or four mL of mine water was mixed with eight or 16 mL of ultrapure water/WDAS mixtures of different ratios, respectively, in order to achieve the desired WDAS concentration. At the end of the experiments, aqueous phase and WDAS were separated by centrifugation (10 min, 5100 g) and 1 mL of the supernatants was filtered (0.2 μm) and analyzed for metal content by X-ray fluorescence (XRF). All experiments were performed in duplicates and errors are given as standard deviations.

2.3. *Metal recovery*

Metal recovery was assessed by the amount of metals that could be recovered by the respective recovery solutions from metal-loaded WDAS. Three different recovery experiments were carried out to find most suitable metal recovery solution (Table 3). In the recovery experiment 1, metal loaded WDAS was subjected to 2 mL of different recovery solutions listed in Table 3. Recovery solutions were chosen in order to study metal recovery based on change of pH, ion-exchange and metal complexation. The used concentrations of glutamic acid were lower due to its lower solubility. In the recovery experiment 2, the metal loaded WDAS was subjected twice to 4 mL of 1 M Na_2CO_3 solution. In the metal recovery experiment 3, the effect of the WDAS concentration on metal desorption by 1 M Na_2CO_3 was studied at 82.5, 165, and 330 g L^{-1}. In this experiment metal loaded WDAS was resuspended in one, two, or four mL of 1 M Na_2CO_3 solution to achieve the desired WDAS concentrations in the recovery step. The recovery experiments were carried out for 24 h at 27 ± 1 °C and 150 rpm mixing on a rotary shaker. Solid/liquid separation was done by centrifugation at 5100 g for 10 min. The aqueous supernatant was analyzed for pH and metal content. In case of two-step recovery experiments, the recovery step was repeated by resuspending the WDAS in fresh recovery solution and the recovery step was carried out again as described above (Fig. 1). All recovery experiments were performed in duplicates and errors are given as standard deviations.

Metal loading onto WDAS was done with 10 g L^{-1} WDAS for the metal recovery experiments 1 and 2 and at 16.5 g L^{-1} WDAS for the metal recovery experiments 3 and 4. The pH was not adjusted.

2.4. *Analytical methods*

Anion analysis of the mine water was done using ion chromatograph (ICS-1600, Dionex) equipped with the Dionex IonPac AS-22 column (4 × 250 mm) and an eluent with 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ in isocratic mode. Eluent flow rate and column temperature were 1.2 mL/min and 30 °C, respectively. Dissolved organic and inorganic carbon concentration were analyzed with a Total Organic Carbon Analyzer (TOC-5000, Shimadzu) equipped with an autosampler (ASI-5000, Shimadzu). Metal analysis was done by XRF as described in Jain et al. (Jain et al., 2018). Prior to analyses all samples were filtered through 0.2 μm filters (Chromafil® Xtra PET-20/25, Machery & Nagel). The pH was

Table 3

Chemicals and concentrations used in the recovery experiments.

Recovery agent	Concentration [M]	pH_{eq}
$CaCl_2$	0.1	3.74
$CaCl_2$	1	3.58
Citric acid	0.1	2.11
Glutamate	0.06 (in 0.2 M NaOH)	4.60
Glutamate	0.1 (in 1 M NaOH)	12.4
H_2SO_4	0.1	2.57
HCl	0.1	3.23
Na_2CO_3	1	n. d.
NaCl	0.1	3.86
NaCl	1	3.75
NaOH	0.1	4.96
NaOH	1	12.6
NH_3	0.1	4.09
NH_3	1	9.19
Oxalic acid	0.1	2.98

pH_{eq} = equilibrium pH in recovery experiment, n.d. = not determined.

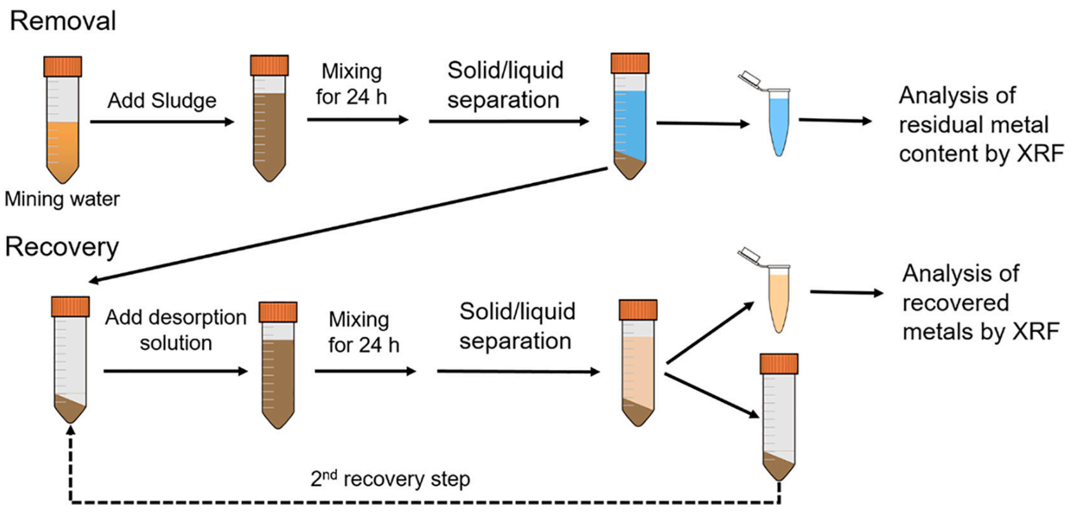

Fig. 1. Experimental scheme of metal removal and desorption experiments.

measured using a pH-meter (3110, WTW, Germany) equipped with a Hamilton Slimtrode electrode. Redox potential was measured with a pH 315i meter (WTW, Germany) and a Blue Line 31 Rx redox-electrode (Ag/AgCl, SI Analytics, Germany) and measured values were converted to SHE (+ 230 mV).

2.5. Speciation calculations

Metal ion speciation of elements in the mining water was calculated with the geochemical speciation program CHESS (Version 2.4) (van der Lee, 1998). Calculations were performed with metal ion concentrations found in the mine water in the presence of measured concentration of sulfate (80.8 g L^{-1}), CO_2 (fugacity = 3.162×10^{-4}), and O_2 (fugacity = 1.995×10^{-1}) in the pH range of 2–10 and allowing redox reactions to compute oxidation states of metals present in mine water. Thermodynamic data of U and Th were taken from the ThermoChimie database version 9 (Giffaut et al., 2014; Grivé et al., 2015). Data of all other elements were taken from the CHESS formatted version of the EQ3/6 database (van der Lee and Windt, 1999; Wolery, 1992) updated with data for copper, zinc, and nickel from Powell et al. (Powell et al., 2007; Powell et al., 2013) and Baeyens et al. (Baeyens et al., 2003) as well as data for schwertmannite ($Fe_8O_8(SO_4)(OH)_6$) from (Sánchez-España et al., 2011). For modeling of iron speciation the formation of hematite was artificially suppressed as iron precipitations in acid rock drainage systems are dominated by jarosite and schwertmannite (Nordstrom et al., 2015). For modeling of manganese speciation, the formation of several minerals of the MnO_2 type have to be considered such as pyrolusite (β-MnO_2), nsutite (γ-MnO_2), and birnessite (δ-MnO_2). In accordance with Rose et al. (Rose et al., 2003) who argue that manganese precipitates as birnessite in ARD systems, the formation of pyrolusite and nsutite was artificially suppressed during the modeling. All data used for modelling can be found in Table S3 in the supplementary information (SI).

3. Results

3.1. Metal removal

3.1.1. Effect of WDAS concentration on metal removal

Metal removal by WDAS was strongly dependent on the element (Fig. 2 and Table S4 in SI). Varying removal efficiency of U(VI), V(V), Cr(VI), Fe(III), Co(II), Cu(II), and Th(IV) (oxidation states as predicted by modeling) was observed, while no removal was observed for Mn(II), Ni(II), Zn(II), and Y(III) at any WDAS concentration. The U(VI) removal was observed for WDAS concentrations higher than 6.2 g L^{-1} and it increased with increasing WDAS concentration up to maximum removal of 67.6 ± 1.4% at 20.6 g L^{-1} of WDAS. The removal of V(V) and Cr(VI) was variable. At the lowest tested WDAS concentration, V(V) and Cr(VI) removal efficiencies were 92.9 ± 7.1% and 49.8 ± 3.6%, respectively. Complete removal of V(V) was observed at WDAS concentrations between 13.4 g L^{-1} and 18.5 g L^{-1}. The removal of Fe(III) was only observed at low WDAS concentrations and the highest Fe(III) removal of 20.0 ± 0.5% was observed at 6.2 g L^{-1} WDAS. The Co(II) removal was generally low and did not exceed 11.4 ± 2.8% (obtained at a WDAS concertation of 16.5 g L^{-1}). The Cu(II) removal was only observed for WDAS concentrations higher than 8.2 g L^{-1} and the removal increased with the increase in WDAS concentration reaching a maximum of 91.0 ± 0.2% at 20.6 g L^{-1} WDAS. However, Th(IV) removal was observed at all studied WDAS concentrations and Th(IV) was, along with V(V), the only element that demonstrated this behavior. The highest Th(IV) removal (55.6 ± 3.7%) was observed at 13.4 g L^{-1} WDAS.

Solubility calculations with CHESS software showed that the aqueous phase was supersaturated with regard to iron and manganese. Precipitation of schwertmannite ($Fe_8O_8(SO_4)(OH)_6$), cobalt ferrite ($CoFe_2O_4$), and birnessite (δ-MnO_2) according to Eqs. 1–3 was predicted showing saturation indices of 32.4, 0.004, and 0.1 respectively.

$$8\ Fe^{3+} + SO_4{}^{2-} + 14\ H_2O \rightleftharpoons Fe_8O_8(SO_4)(OH)_6 + 22\ H^+ \qquad (1)$$

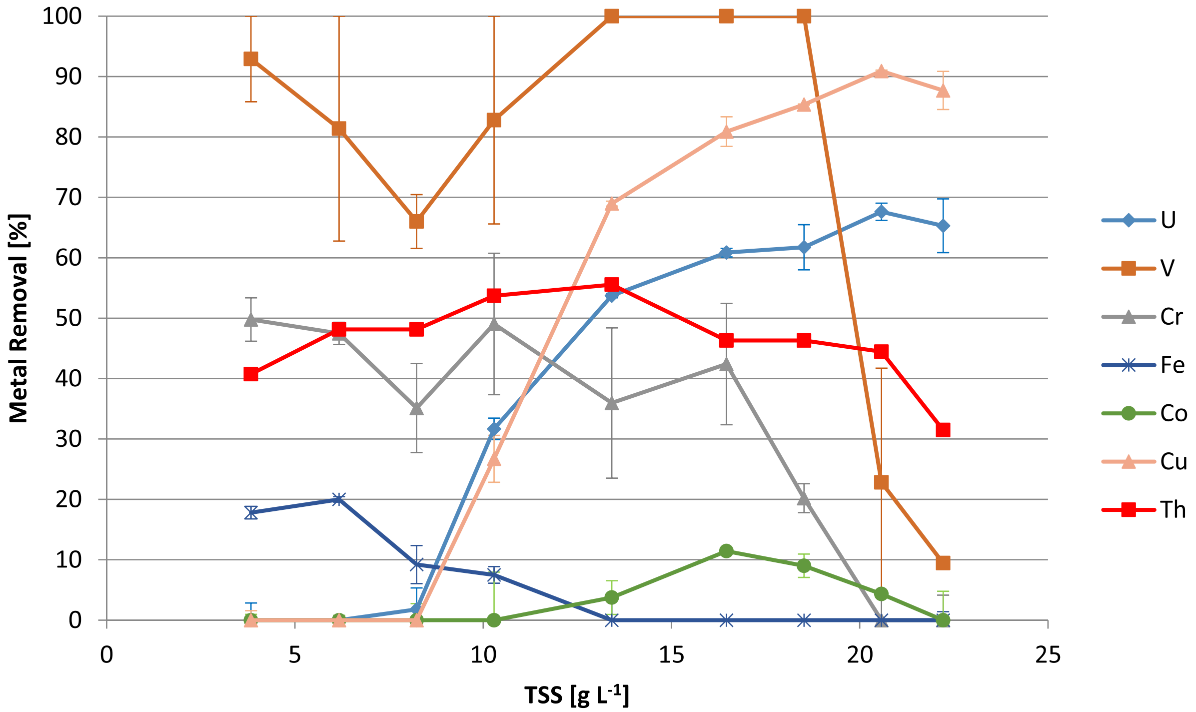

Fig. 2. Metal removal efficiency from mining wastewater as a function of waste digested activated sludge concentration measured as total suspended solids (TSS) without pH adjustment. pH_{eq} at 3.8 g/L = 2.6, pH_{eq} at 6.2 g/L = 3.2, pH_{eq} at 8.2 g/L = 3.2, pH_{eq} at 10.3 g/L = 3.7, pH_{eq} at 13.4 g/L = 3.9, pH_{eq} at 16.5 g/L = 4.0, pH_{eq} at 18.5 g/L = 4.0, pH_{eq} at 20.6 g/L = 4.1, pH_{eq} at 22.2 g/L = 4.1, initial pH of mine water = 2.6. Error bars represent standard deviations of the measurements. Data is only shown for the elements for which removal was observed.

$$Co^{2+} + 2\,Fe^{3+} + 4\,H_2O \rightleftharpoons CoFe_2O_4 + 8\,H^+ \quad (2)$$

$$Mn^{2+} + MnO_4{}^{2-} \rightleftharpoons 2\,\delta - MnO_2 \quad (3)$$

This suggests potential removal of Fe(III), Mn(II) and Co(II) from aqueous phase via (surface) precipitation reactions over a wide pH range. However, while for Mn(II) no removal was observed, removal of Fe(III) and Co(II) was observed only at certain pH values.

A strong selectivity for U(VI), Cu(II) and Th(IV) removal was observed at WDAS concentration of 20.6 g L^{-1} with removal efficiencies of 68 ± 1.4% for U(VI), 91 ± 0.2% for Cu(II), and 44 ± 0.1% for Th(IV). Elements present in the mine water at concentrations above 1 g L^{-1} (Fe(III), Mn(II), Ni(II), Zn(II)) showed removal efficiencies of less than 20% at all WDAS concentrations.

3.1.2. Effect of pH on metal removal

In order to investigate the effect of pH, a second metal removal experiment was performed at a WDAS concentration of 10 g L^{-1} at constant pH values ranging from 2.0 to 10.0. In this experiment, the metal removal generally improved with increasing pH (Fig. 3 and Table S5 in SI). The U(VI) removal started at pH 3.0 and increased to its maximum of 91.6 ± 0.9% at pH 6.5 and slightly decreased again at higher pH. The Cu(II) removal followed a similar pattern to that of U(VI) and was observed between pH 3.0 and 10.0 reaching its maximum of 99.5 ± 0.1% at pH 6.5. Even though removal could only be observed at pH > 4.0 and > 5.5, respectively, a similar trend was observed for the removal of trivalent ions Fe(III) and Y(III) and divalent ions Co(II), Ni(II), and Zn(II) all of which showed removal efficiencies of 90–100% at pH > 6.5. However, the removal of Mn(II) was only observed for pH $>$ 6.5 and in contrast to other di- and trivalent ions removal efficiencies of $>$90% were only observed at pH > 9. Interestingly, Fe(III) removal behavior differed from the previous experiment at different concentrations of WDAS where removal was observed at pH < 4.0.

Trends in removal efficiencies of V(V), Cr(VI), and Th(IV) differed from those of the other ions. For example, V(V) removal strongly varied with pH and no clear trend was observable, while complete removal efficiencies were observed at moderately acidic pH (≤4). The removal of Cr(VI) followed a similar trend but did not show the same variability as for V(V). Highest Cr(VI) removal of 84.4 ± 0.6% was observed at pH 9.5. Although Th(IV) was the only element that was removed at pH 2, the removal at higher pH values varied between 60% and 90% with no clear trend.

Speciation calculations revealed supersaturation of the aqueous phase with respect to iron phases schwertmannite ($Fe_8O_8(SO_4)(OH)_6$) (Eq. 1), cobalt ferrite ($CoFe_2O_4$) (Eq. 2), trevorite ($NiFe_2O_4$) (Eq. 4), and goethite (FeO(OH)) (Eq. 5) at pH ranges of 2.0–7.2, 2.7–10.0, 6.8–10.0, and 7.2–10.0, respectively (Fig. S1). In case of manganese the precipitation of birnessite (Eq. 3) was predicted for pH > 2.8 (Fig. S2). Brochantite ($Cu_4SO_4(OH)_6$) (Eq. 6) was found to be supersaturated between pH 5.6 and 7.4 (Fig. S4). Trevorite ($NiFe_2O_4$), hydrozincite

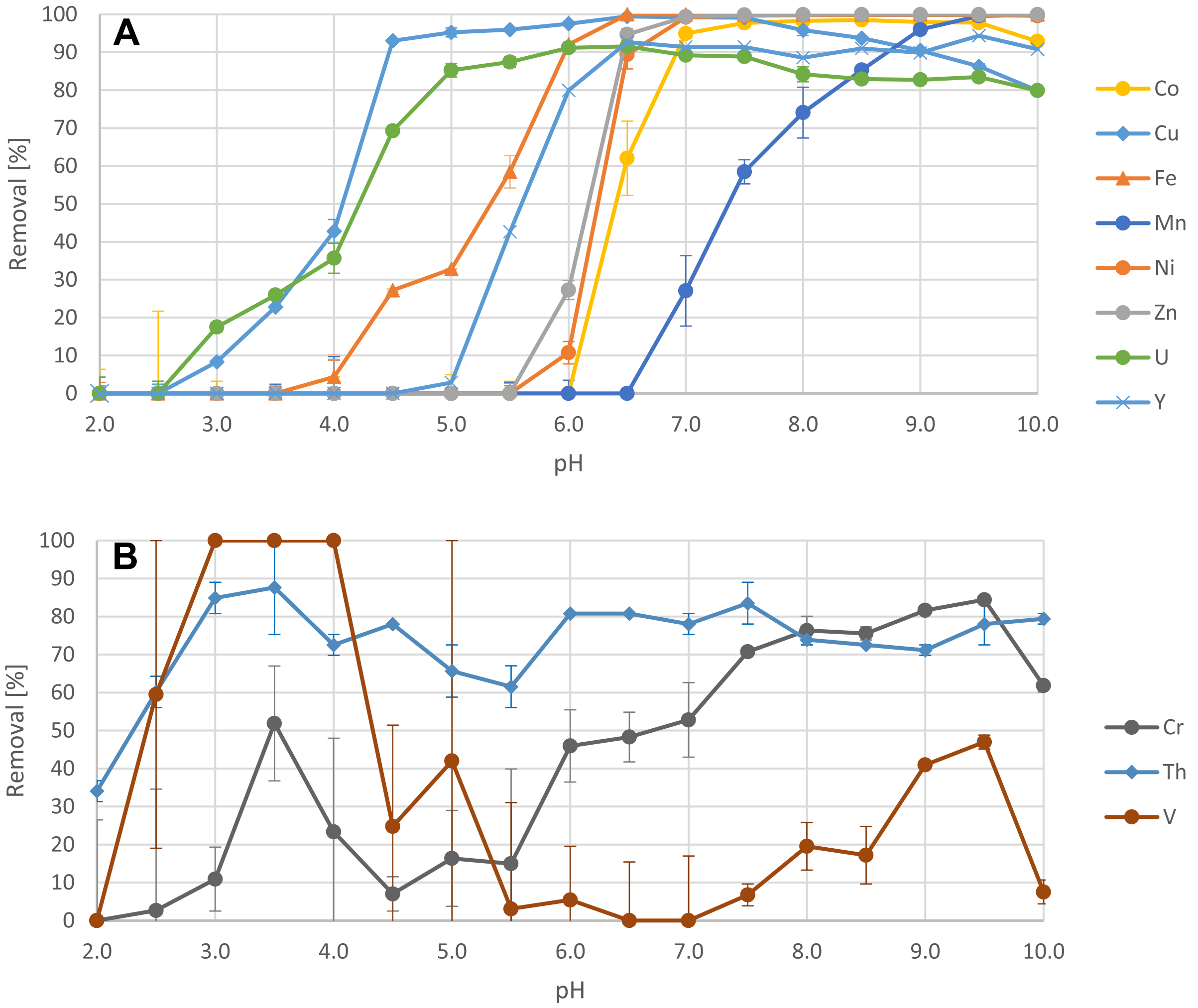

Fig. 3. Metal removal efficiency as a function of pH for A) Co, Cu. Fe, Mn, Ni, Zn, U, Y and for B) Cr, Th, V. The pH was kept constant throughout the experiment. Error bars represent standard deviations of the measurements. Waste digested activated sludge concentration measured as total suspended solids (TSS) was 10 g L^{-1} in all cases.

($Zn_5(CO_3)_2(OH)_6$) (Eq. 7), and tenorite (CuO) (Eq. 8) were supersaturated at pH > 6.1, 6.8, and 7.4, respectively (Fig. S4 – S6).

$$Ni^{2+} + 2\,Fe^{3+} + 4\,H_2O \rightleftharpoons NiFe_2O_4 + 8\,H^+ \quad (4)$$

$$Fe^{3+} + 2\,H_2O \rightleftharpoons FeO(OH) + 3\,H^+ \quad (5)$$

$$4\,Cu^{2+} + SO_4{}^{2-} + 6\,H_2O \rightleftharpoons Cu_4SO_4(OH)_6 + 6\,H^+ \quad (6)$$

$$5\,Zn^{2+} + 2\,HCO_3{}^{-} + 6\,H_2O \rightleftharpoons Zn_5(CO_3)_2(OH)_6 + 8\,H^+ \quad (7)$$

$$Cu^{2+} + H_2O \rightleftharpoons CuO + 2\,H^+ \quad (8)$$

The three ions Fe(III), Co(II), and Mn(II) are predicted to be supersaturated at a larger pH range than at which removal of these elements was observed. This might indicate that the calculations are overestimating the precipitation of Fe(III), Co(II), and Mn(II) and that the observed removal of these elements from the aqueous phase is at least partly due to (surface) precipitation instead of adsorption on WDAS. In the case of Cu(II), Ni(II), and Zn(II), the pH range at which these elements are predicted to precipitate is smaller than the pH range in which their removal was observed. This indicates that the removal of Cu(II), Ni (II), and Zn(II) is due to adsorption phenomena at pH below 5.6, 6.4, and 6.8, respectively. At higher pH, both adsorption and precipitation might be occurring.

3.2. *Metal recovery*

3.2.1. *Effect of recovery solution*

In order to optimize the recovery of metals from the metal loaded WDAS, a variety of solutions at various concentrations was studied (Table 3). Recovery of metals proceeds either via ion exchange (Eqs. 9 and 10) or complexation (Eq. 11),

$$\text{Cation exchange} :\equiv C_m + n\,X^{m+} \rightleftharpoons \equiv X_n + m\,C^{n+} \quad (9)$$

$$\text{Anion exchange} :\equiv A_m + n\,X^{m-} \rightleftharpoons \equiv X_n + m\,A^{n-} \quad (10)$$

$$\text{Complexation} :\equiv (C^{n+})_i + j\,L^{p-} \rightleftharpoons \equiv {}^{in-} + C_iL_j{}^{(in-jp)} \quad (11)$$

where m is the charge of a cation or anion X of the recovery solution and n the charge of a metal cation C or an anion A on the WDAS surface, j the number of ligands with the charge p and i the number of metal ions.

Solutions of 0.1 M NaCl and $CaCl_2$ showed recovery efficiencies below 10% for all elements except Co(II) (Fig. 4A). Similarly, the inorganic acids H_2SO_4 (0.1 M) and HCl (0.1 M) showed recoveries below 20% for all metals and no selectivity. Among the tested organic acids, oxalic acid showed recoveries around 10% with no selectivity whereas

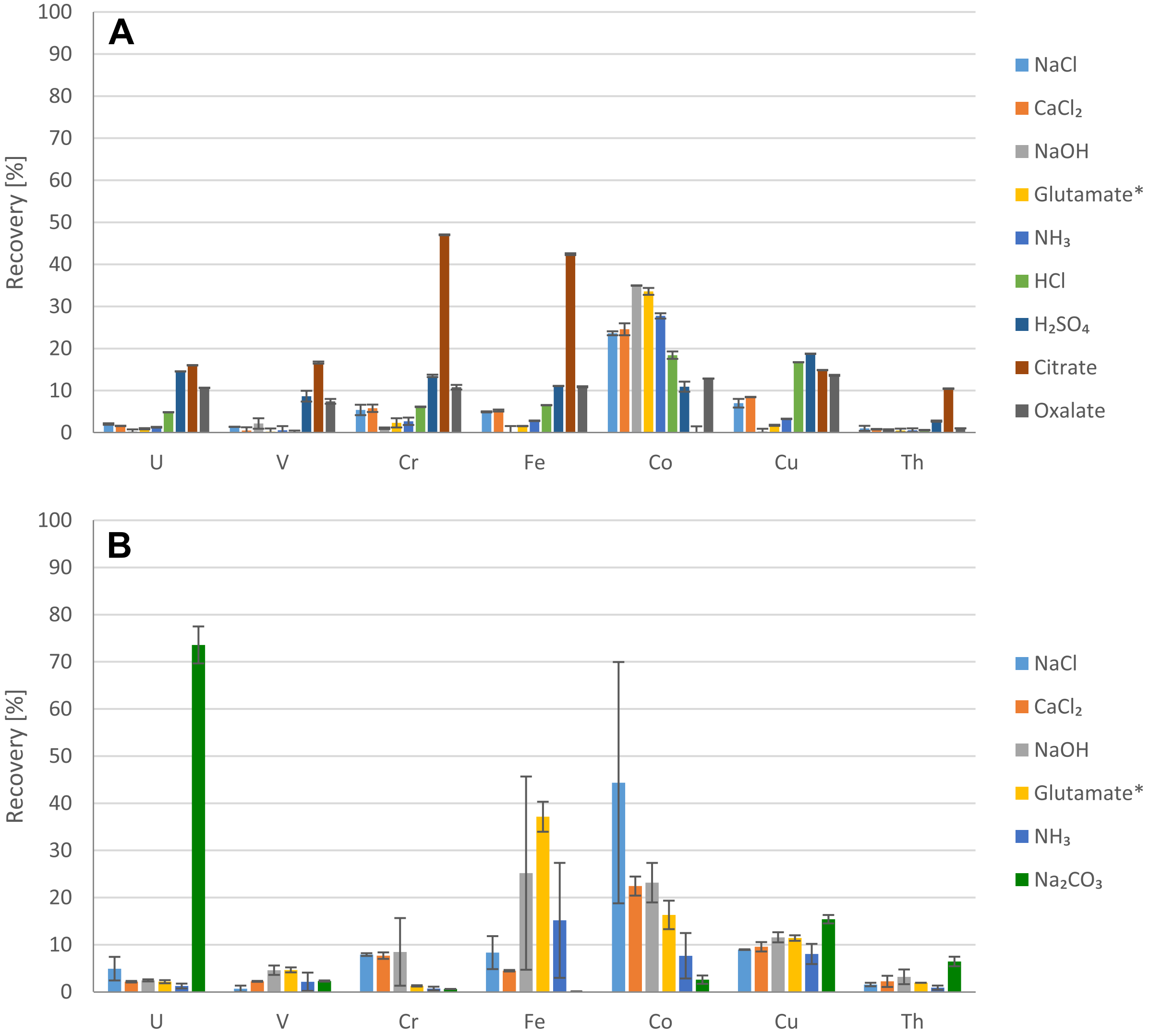

Fig. 4. Recovery efficiency obtained with the different recovery solutions at 0.1 M concentration (A) and 1 M concentration (B) except for glutamate, which was used at 0.06 M in 0.2 M NaOH (A) and 0.1 M in 1 M NaOH (B) concentration due to its low solubility.

citric acid (0.1 M) showed a comparably high recovery for Fe(III) (42.4 ± 1.5%) and Cr (47.0 ± 0.2%). Glutamic acid (0.06 M) showed very low recoveries for all elements except Co (33.6 ± 1.5%).

The alkaline recovery solutions NaOH (0.1 M) and NH_3 (0.1 M) showed recoveries of 35.0 ± 1.2% and 27.8 ± 0.1% for Co(II), whereas for the other elements the recoveries were below 5%. The inefficiency of the 0.1 M neutral and basic recovery solutions might have resulted from the low pH_{eq} during the recovery step (Table 3). However, even an increase of concentration to 1 M did not result in substantially improved recoveries with solutions of NaCl, $CaCl_2$, NaOH, glutamic acid or NH_3 (Fig. 4B). Next, Na_2CO_3 was tested since it had previously been shown to be effective of recovering U(VI) from WDAS (Jain et al., 2018) and 1 M Na_2CO_3 solution showed a high U(VI) recovery efficiency of 73.6 ± 3.9% (6.5 mg U L^{-1}) also in this study. The recovery efficiencies for Cu(II) (15.4 ± 0.9%, 30.4 mg Cu L^{-1})) and Th(VI) (6.4 ± 1.0%, 0.2 mg Th L^{-1}) were comparably low and recovery of other elements was even lower (Fig. 4). Due to the high recovery and selectivity for U(VI), further experiments were conducted only with Na_2CO_3 in order to improve U(VI) recovery.

3.2.2. *Two-step recovery*

In order to improve the U(VI) recovery from WDAS, a two-step approach in which metal-loaded WDAS was subjected twice to 1 M Na_2CO_3 solutions. The results show that with two successive recovery steps, 108.0 ± 6.6% U(VI) (4.6 mg L^{-1}) could be recovered from the WDAS (Fig. 5). In addition, 39.2 ± 2.5% Cu(II) (22.1 mg L^{-1}) and 53.7 ± 7.7% Th(IV) (0.2 mg L^{-1}) was recovered. Recovery efficiencies of V (V), Cr(VI), Fe(III), and Co(II) remained below 5% (Fig. 5).

3.2.3. *Effect of WDAS concertation on metal recovery efficiency*

The effect of WDAS concentration on recovery efficiency was investigated since a higher solid-to-liquid ratio could both decrease the volume of required solutions and lead to a higher concentration of the recovered metals. This would decrease costs and allow easier downstream processing. Three different WDAS concentrations were investigated: 82.5, 165 and 330 g L^{-1} (Fig. S12 in SI). However, an increase in the WDAS concentration during the recovery step led to a reduction of U (VI), Cu(II), and Th(IV) recovery efficiencies. An increase in WDAS concentration from 82.5 to 165 g L^{-1} in the recovery step decreased the U(VI) and Cu(II) recovery efficiencies to approximately 80% (3.4 mg L^{-1}) and 32% (18.0 mg L^{-1}) and Th(IV) recovery to approximately 19% (0.07 mg L^{-1}). Increasing WDAS concentration to 330 g L^{-1} reduced recovery to 45% (1.9 mg L^{-1}), 12% (6.8 mg L^{-1}), and 6% (0.02 mg L^{-1}) for U(VI), Cu(II), and Th(IV), respectively.

4. Discussion

4.1. *Factors influencing metal removal*

As shown in Fig. 2 Cu(II) and U(VI) removal increased with increasing WDAS concentration but no clear trend was observed for Co (II), Cr(VI), Fe(III), V(V), and Th(IV) and no removal was observed for Mn(II), Ni(II), Y(III), and Zn(II). As it was shown, due to the fact that several different functional groups such as carboxyl, hydroxyl, amino and phosphate groups are responsible for interactions with metal ions in activated and digested sludge (Jain et al., 2018; Ramrakhiani et al., 2017; Zhang et al., 2014; Pagnanelli et al., 2009; Tokcaer and Yetis, 2006), metal removal might depend on the availability of these groups for metal binding. Due to the differences in pK_a of these functional groups the interaction with these sites is pH dependent. Consequently, at low pH, the number of available sorption sites is low so that even at high concentrations of WDAS removal of Mn(II), Ni(II), and Zn(II) is not observed due to possible competitive effects with other metal ions. At higher pH other sorption sites become available, reducing competition and allowing for adsorption of Mn(II), Ni(II), and Zn(II) at pH > 6.0 (Fig. 3).

Speciation calculations showed that Cu(II), Ni(II), Zn(II), Th(IV), U (VI), and Y(III), are predominantly complexed with sulfate ions in the pH range 2–8 (see Figs. S4 – S9 in SI). This indicates that the effect of sulfate in the aqueous speciation is not a determining factor which can be used to explain the differences observed for the removal behavior. Furthermore, the observed removal of the divalent metals at constant pH follows the Irwing-Williams series (Irving and Williams, 1953) with strongest removal for Cu(II) followed by Zn(II), Ni(II), Co(II), and Mn(II) even though their concentrations decrease in the following order: Mn (II), Zn(II), Ni(II), Cu(II), and Co(II). Again, this suggests that metal ion competition plays a role in the adsorption process with WDAS. Competitive effects were also observed in the adsorption studies with other biosorbents such as tree bark (Chockalingam and Subramanian, 2009) and chitin (Pinto et al., 2011). Competitive effects could also be involved in adsorption of Fe(III) and Y(III), as both Fe(III) and Y(III) are classified as hard acids (Pearson, 1963) and, thus, have strong affinity for the hard basic functional groups such as carboxylates. Therefore, the stronger removal of Fe(III) might be due to the higher acidity of Fe(III) in comparison to Y(III) enabling preferential adsorption of Fe(III) over Y (III) (Rayner-Canham and Overton, 2010). However, this might also be simply due to high surplus of Fe(III) in comparison to Y(III). In addition, it was shown that in competitive adsorption assays at equimolar concentrations, adsorption decreased in the order: Th(IV) > U(VI) > La(III) ≈ Eu(III) ≈ Yb(III) (Andres et al., 1993), which is in accordance with the

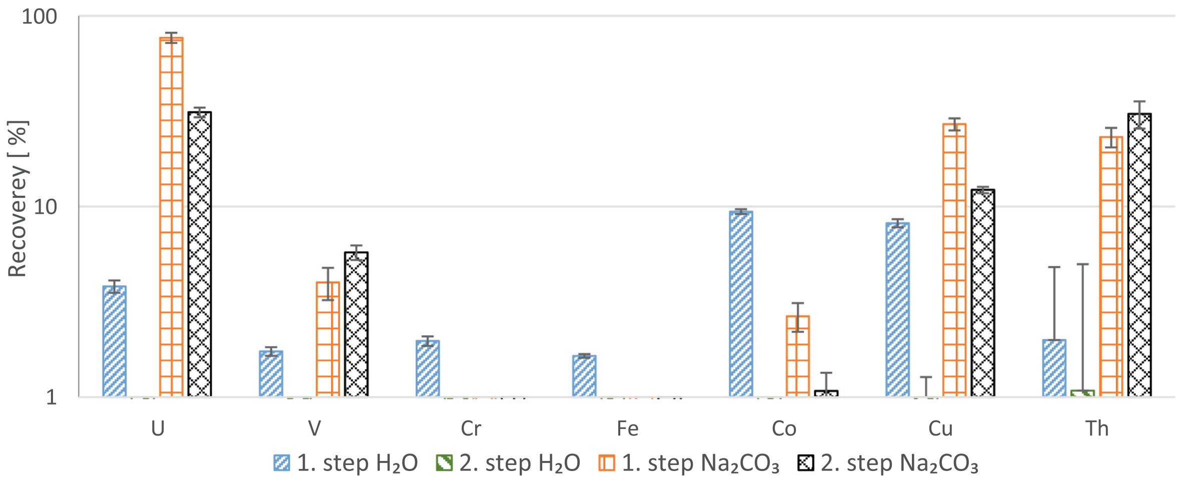

Fig. 5. Metal recovery efficiency from WDAS in two subsequent recovery steps with either 1 M Na_2CO_3 or H_2O (negative control). WDAS concentration was 82.5 g L^{-1}.

results of this study at pH < 4.5. The removal of Th(IV) was observed to be uniform over the whole pH range tested in this study. It is a result of the high charge of Th(IV) (Andres et al., 1993), enabling comparably strong electrostatic interactions with carboxylic groups shown to be present on the WDAS surface by Jain et al. (Jain et al., 2018). Only at pH < 3.0, the surplus of protons might hamper the interaction of Th(IV) with the WDAS surface due to electrostatic repulsion (Sar and D'Souza, 2002) and consequently reduce its adsorption from solution. The removal behavior of Th(IV) observed in this study contrasts with the results from Sar and D'Souza (Sar and D'Souza, 2002) reporting highest Th(IV) removal at pH 4.0. This difference in the pH dependency of Th (IV) removal might be due to the high surplus of Fe(III) (molar ratio Fe/Th = 22,190) in the mine water used for this study. The reduced Th(IV) removal due to the presence of Fe(III) was also demonstrated by Sar and D'Souza (Sar and D'Souza, 2002).

In addition to ion competition effects, redox reactions might have been involved in the interaction of metals with WDAS. For example, Cr and V are elements prone to redox reactions and depending on their oxidation state, their main species are cations or oxyanions, which have different adsorption behavior (Dzombak and Morel, 1990). However, at high redox potentials, speciation calculations suggest that Cr(VI) is mainly present as hydrogenchromate ($HCrO_4^-$) and chromate (CrO_4^{2-}) (see Fig. S10 in SI) and V(V) is mainly present as $VO_2(SO_4)^-$, HVO_4^-, and $VO_3(OH)^{2-}$ (see Fig. S11 in SI). Both hydrogenchromate and chromate compete with sulfate for sorption sites at pH < 4.5, resulting in lower Cr(VI) adsorption under acidic conditions. The increasing Cr(VI) sorption at pH > 4.5 might be due to electrostatic interactions with positively charged functional groups (e.g. $-NH_3^+$) of the WDAS. The results of this study show that Cr(VI) removal is possible by adsorption especially at pH > 7. It is an important finding, as Cr(VI) has been reported to be resistant to adsorption approaches relying only on its insolubilization via pH control (Moodley et al., 2018).

The removal of V(V) was high at pH < 4. However, it decreased at pH 4–6 with the increase in the removal of the major ions Fe(III) and Cu (II). At pH > 7, where the calculations suggest the presence of negatively charged $VO_3(OH)^-$ and HVO_4^{2-} as the predominant species, interactions with positively charged surface groups could explain the increased removal of V(V) from solution as also demonstrated by Huang et al. (Huang et al., 2020). Furthermore, it cannot be ruled out that the solid phases of iron formed at high pH may serve as an additional sorbent for V(V), as has been discussed by Weidner and Ciesielczyk (Weidner and Ciesielczyk, 2019).

As Fe(III), Mn(II), Co(II), Cu(II), Ni(II), and Zn(II) were supersaturated at some or all investigated pH values, as shown by speciation calculations, it may indicate that their removal from solution happens via precipitation on surface rather than adsorption which might hinder their recoverability. Removal of Ni(II) and Zn(II) was only observed at pH > 6 at which trevorite ($NiFe_2O_4$) and hydrozincite $Zn_5(CO_3)_2(OH)_6$ were predicted to be supersaturated and thus surface precipitation was likely contributing to their removal from the mining water (Fig. S5 and S6). Copper(II) was predicted to be supersaturated only at pH > 5.6 (Fig. S4 in SI) with the formation of brochantite ($Cu_4SO_4(OH)_6$) and tenorite (CuO). However, Cu(II) removal was observed at pH > 3 indicating that Cu(II) was removed by adsorption at pH 3–5.5. However, it has also been reported that adsorption of Cu(II) is more likely to occur instead of CuO precipitation at supersaturated conditions (Lund et al., 2008). The precipitation of Fe(III), Mn(II), and Co(II), was predicted at pH > 2 (Fig. S1 – S3). However, in pH dependent adsorption experiments (Fig. 3), Mn(II), Co(II), and Fe(III) removal could only be observed at pH 4.0, 6.5 and > 7.0, respectively, which indicates that their removal from solution involves both adsorption and precipitation mechanisms.

The results of this study demonstrate how challenging it is to selectively remove metals from complex mine waters containing a great variety of metals at different concentrations. The fact that the adsorption of some of the metal ions is susceptible to their oxidation states makes the removal even more complex. Factors such as high concentration of sulfate (Tobin et al., 1987) as measured in this study, sorption competition, and metal ion speciation, both in solution and in solid phase complicate selective removal of metal ions. Nevertheless, it is shown that the cheap biosorbent WDAS is capable of removing several metals simultaneously from a mine water sample and thus indicates the potential of WDAS in the treatment of metal containing waste streams.

4.2. Selective desorption of U(VI), Cu(II) and Th(IV)

Compared to Na_2CO_3, all the other desorption agents studied in this work performed more poorly. The low effectiveness of HCl, H_2SO_4 and oxalic acid in recovering any of the adsorbed metals might have been due the pH values not being low enough during the recovery step (HCl pH = 3.2, H_2SO_4 pH = 2.6, oxalic acid pH = 3.0), so that the precipitated solids could not be redissolved. The limited selectivity of inorganic acids observed in this study has also been reported for recovery of metals from a plant derived biosorbent (Abdolali et al., 2015) and both biochar and activated carbon (Kołodyńska et al., 2017). Cobalt(II) was the only element showing comparably high recoveries with salt solutions (20–45%) and alkaline solutions (15–35%) investigated in this study, which could indicate that Co(II) removal proceeds via an ion exchange based mechanism (Garnham et al., 1991; Kuyucak and Volesky, 1989). In addition, the increase in ionic strength of NaCl solution from 0.1 M to 1 M led to increased Co(II) recovery (Fig. 4) supporting an ion exchange based mechanism. Citric acid, in addition to Na_2CO_3, was the only desorption agent showing some level of selectivity in the metal recovery. Use of citric acid enabled recovery of mostly Fe(III) and Cr(VI) but also low levels of U(VI), V(V), and Cu(II) (Fig. 4). The slight selectivity for Fe (III) and Cr(VI) could be explained by the comparably high complex formation constants of these metal ions with citrate (Gabriel et al., 2007) under the assumption that chromate is reduced to Cr(III) as discussed by Cabatingan et al. (Cabatingan et al., 2001). The selectivity of citric acid for Fe(III) could be an interesting option as a first purification step, since Fe(III) is often the major contaminant in many mine waters and its removal might simplify recovery and further purification of other metals.

As demonstrated in a previous study (Jain et al., 2018), Na_2CO_3 allowed for high recovery of U(VI), along with the partial recovery of Cu (II) and Th(IV) from the WDAS. The observed selectivity of Na_2CO_3 is due to the formation of strong soluble metal carbonate complexes (Eqs. 12–14) as predicted in the speciation calculations (see Figs. S4, S8, and S9).

$$UO_2^{2+} + 3\,HCO_3^- \rightleftharpoons UO_2(CO_3)_3^{4-} + 3\,H^+ \; log\,K = 11.51 \tag{12}$$

$$Th^{4+} + 5\,HCO_3^{2-} \rightleftharpoons Th(CO_3)_5^{5-} + 5\,H^+ \; log\,K = -20.65 \tag{13}$$

$$Cu^{2+} + 2\,HCO_3^- \rightleftharpoons Cu(CO_3)_2^{2-} + 2\,H^+ \; og\,K = -10.48 \tag{14}$$

It becomes apparent that the recovery step, similarly to the removal step, must be adapted with regard to the type and strength of desorption solution and pH, and to the combination of metal ions present in the solution in order to achieve efficient metal recovery and, thus, is dependent on the composition of the water to be treated. The recommended conditions for removal and recovery of metal ions from the mine water used in this study are shown in Table 4. The recovery efficiency can be increased by repeating desorption steps (Fig. 5), which is, however, increasing required volumes of the desorption solution. By employing a two-step desorption approach, 40% of Cu(II), 52% of Th (IV) and all the U(VI) present on WDAS were successfully recovered to solution.

High WDAS concentrations are desirable in the desorption step to enrich the metals in recovery solutions but an increase in WDAS concentration led to reduced recovery of U(VI), Cu(II), and Th(IV) by 1 M Na_2CO_3 solution (Fig. S12 in SI). Reason for that is presumably the increased viscosity of the WDAS/recovery solution mixture leading to

Table 4
Recommended conditions for metal ion removal and recovery from acidic multi-metal mine water using WDAS as biosorbent.

Removal		
Condition	**Advantages**	**Disadvantages**
10 g L^{-1} WDAS, pH 5.0	• Removal of 95% Cu, 66% Th, and 85% U • No removal of Co, Mn, Ni, Zn, and Y	• Base addition needed • Removal of 16% Cr, 33% Fe, 42% V, and 3% Y
Recovery		
Condition	**Advantages**	**Disadvantage**
2 steps with 1 M Na_2CO_3	• Recovery of 108% U • Recovery of 39% Cu and 54% Th	• WDAS degradation at high pH • 2 steps needed

inefficient mixing and thus lower metal recovery efficiency. Consequently, an increase in concentration of the metal ions as previously reported (Jain et al., 2018) was not possible with the highly complex mine water used in this study. To avoid this WDAS could be pre-treated e.g. via a hydrolysis step to decrease the viscosity (Hii et al., 2016; Tan and Li, 2017). It could be a viable improvement of the process if a pre-treatment step would allow the use of higher WDAS concentrations in the desorption step which in turn would result in recovered metal ion solution of high concentrations.

4.3. *Practical implications*

This study demonstrated that U(VI), Cu(II) and Th(IV) can be removed and recovered from acidic mining waters using WDAS in a simple approach. It was shown that while metal ion removal from solution with WDAS is only slightly selective, with a substantially increased selectivity in the desorption step using 1 M Na_2CO_3 solution (Fig. 4). Even though no metal ion enrichment could be observed under the chosen experimental conditions, the purity (calculated as mass fraction of a metal compared to the total amont of metals) of U(VI) and Cu(II) increased from 0.07% and 0.7% in the mine water to 16.5% and 78.7%, respectively, caused by the removal with WDAS followed by desorption with Na_2CO_3. The resulting (enriched) solution could be further purified by employing ion exchange methods followed by precipitation of the different fractions as copper hydroxide and ammonium diuranate yielding CuO and U_3O_8 after calcination (Orabi et al., 2019).

Implementing a mine water treatment process as presented here would reduce environmental pollution with radiotoxic elements considerably. Assuming a relatively low average outflow of 350 L ARD min^{-1} (De Giudici et al., 2019; Lachmar et al., 2019) and uranium and thorium concentrations of 14 mg L^{-1} and 1.6 mg L^{-1} respectively, as measured in this study, over 7 kg of U(VI) and 0.8 kg of Th(IV) would be released to the environment daily if the mine water would be released untreated. In addition, such a treatment would increase the pH of the mine water, which is beneficial because it reduces activity of extremely acidophilic microorganisms accelerating the formation of ARD, favors metal ion adsorption and reduces danger to aquatic life (Akcil and Koldas, 2006). In this study it was shown that a single treatment step without pH adjustment at WDAS concentrations >14 g L^{-1} increased pH from 2.6 to 4 which is not as high as the reported increase of pH of ARD waters by commercial chitin products (pH 3 to ~8 at 2 g L^{-1}) (Pinto et al., 2011). However, it is similar to the values reported for rice husks (pH 2.3 to ~4.5 at 100 g L^{-1}) (Chockalingam and Subramanian, 2006) and tree barks (pH 2.3 to ~3.2 at 100 g L^{-1}) (Chockalingam and Subramanian, 2009) although in the present study a much lower biosorbent concentration was used.

The WDAS currently has limited applications and its disposal can be costly (Fuchs and Drosg, 2013). Therefore, it would be a cheap and widely available material for use in ARD remediation. The presented approach combines two waste streams thereby decreasing their pollution potential to the environment. This method does not require pre-treatment of WDAS or the mine water, which adds to its simplicity and cost-efficiency. However, the reusability of WDAS might be limited since organic carbon was observed to be released from WDAS at high pH resulting from the Na_2CO_3 desorption step, which might indicate WDAS degradation (Fig. S13 in SI). This is reducing the number of removal/recovery cycles that can be performed with one batch of WDAS. Therefore, used WDAS needs to be replaced with fresh WDAS after a certain number of cycles.

Furthermore, the process could be improved by either an increase in pH or a second removal step with fresh WDAS. The increase of pH could be easily achieved by the addition of a cheap base such as lime and could be fully automated; however, it would produce additional costs. The second removal step would require a two-stage mine water treatment, which would increase mine water residence time and require a larger treatment system but would also allow for increased metal ion removal. In the second stage, pH_{eq} would also increase allowing for improved metal ion adsorption but also bear the danger of precipitating solids due to saturation making them difficult to recover.

5. Conclusions

This study demonstrated the applicability of WDAS-based removal approach to recover U(VI) and Cu(II) with an up to 10-fold increase in purity. This was largely possible due to the high selectivity achieved in the two-step desorption process, which exploited the formation of strong carbonate complexes for the selective recovery of U(VI). The observed partial recovery of Cu(II) and Th(IV) was an additional benefit of the chosen approach. This study also highlighted the complexity involved in development of a single-step process for recovering metals from highly complex wastewaters. Clearly, both removal and recovery steps must be carefully designed and adapted considering whether the target metal is a major or, as U(VI) and Cu(II) in this study, a minor component of the mine water.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.hydromet.2021.105770.

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