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Removal and potential recovery of dissolved metals from acid sulfate soil drainage by spent coffee-grounds and dissolved organic carbon

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ABSTRACT

This study explores the reuse of spent coffee-grounds (SCGs) and the use of dissolved humic acid (DHA) to remediate acid sulfate (AS) soil drainage using adsorption and precipitation experiments, with changing pH, weight/volume, and concentrations (mg/L of dissolved organic carbon). In addition, this study aims to extend the usability of the SCGs, after being reacted with AS soil drainage, by identifying the potential recovery of incinerated SCGs from the ash of the SCGs produced incineration. As compared to DHA, the SCGs had greater efficiency in removing metals, such as Al (98%), Ca (96%), Co (94%), Fe (88%), Mn (100%), Ni (93%), and Zn (96%). However, the removal of Fe was significantly reduced when higher weight/volume of SCGs were introduced. In addition, SCGs could not bind sulfur, while DHA had removed up to 25% of S from the solution. This suggests the simultaneous use of SCGs and DHA could restrict the formation of problematic Fe(III) secondary compounds (e.g., schwertmannite/akaganeite) which are problematic in some AS soil settings. The results show that Co (69%), Ni (58%), Mn (60%), Fe (59%), Zn (55%), and Al (34%) had the highest recovery percentage by sequential chemical extraction, respectively. The recovery of metals, as well as the removal of dissolved metals from the drainage water, illustrates the effectiveness of the proposed approach for SCGs reuse.

Introduction

Biosubstances, such as spent coffee-grounds (SCGs), tea, rice hulls (Utomo and Hunter 2006; Kaikake et al. 2007; Kyzas 2012; Nam et al. 2017), and dissolved organic carbon (DOC) such as humic acid (Klučáková and Pavlíková 2017) have been used to remove metals from metal-rich solutions. In addition, SCGs have a broad range of applications, such as removal of dyes (Kyzas et al. 2012; Sartape et al. 2017) and metals (Nam et al. 2017) from solutions, and used as sources of energy (Kim and Oh 2021), bio-oil (Yang et al. 2016), biochar (Maree et al. 2020), biocrude production (Yang et al. 2019; Zhang et al. 2021), substitute for coking coal (Maree et al. 2020) and provides adsorption sites for soluble metals and, therefore, be used for water treatment (Utomo and Hunter 2006; Kyzas 2012; Nam et al. 2017). Furthermore, with the worldwide coffee consumption reported to be over 11 billion tons/year (Jagdale et al. 2019), SCGs have great potential for being used as alternative biosorbents for remediation (McNutt and He 2019). In Europe, the most common trend to deal with organic waste, such as

SCGs, is incineration (Kaikake et al. 2007; Šyc et al. 2020) of combustible waste to produce electricity (McNutt and He 2019). In addition, the use of bottom ash from general (mixed) waste for metal recovery has been previously studied (Šyc et al. 2020). Previous studies have used sequential chemical extraction (SCE) experiments to extract metals from incinerated waste, bottom ash (Chaudhary and Banerjee 2007; Xiong et al. 2014; Šyc et al. 2020). With these two properties of SCGs, the usable lifespan of the SCGs is expected to extend by its' reuse to remediate contaminated waterways and finally recover metals from the incineration processes. To the best of our knowledge, the use of SCGs has never been investigated previously for remediating AS soil drainage waters. Also, the potential recovery of metals from SCGs ash has not been evaluated.

Pollutants are introduced into natural and managed environments by direct and indirect human activities (Masindi and Muedi 2018). Potential toxic elements (e.g., toxic metals) can enter water bodies or neighboring environments (lakes, wetlands, and estuaries) from Acid Sulfate (AS) soils drainage systems (Karimian et al. 2017; Shahabi-Ghahfarokhi

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et al. 2022). AS soils occur mainly along coastlines and consist primarily of marine sulfidic sediments, e.g., deposited during the last sea-level highstand. The main sulfidic components in these materials are iron sulfides (Boman et al. 2008). Under reduced conditions (e.g., below the groundwater table), these materials are harmless (Mattbäck et al. 2022). However, post-glacial uplifts, common in Northern Europe, causes relative sea levels to fall and exposes sulfidic sediments to oxygen into the vadose zone, leading to oxidation of iron sulfides and formation of sulfuric acid (Boman et al. 2008; Shahabi-Ghahfarokhi et al. 2022). In addition, climate change will increase the amplitude of seasonal groundwater table variations in boreal settings and expose more parent material of AS soils into the vadose zone (Jarsjö et al. 2020). All these processes eventually contribute to the formation of AS soils and associated leaching of acidic ($\text{pH} < 4$) and metal-rich solutions from the soils (Gröger et al. 2011; Vithana et al. 2021). In general, the drainage waters from AS soils are rich in many metals, such as cadmium (Cd), zinc (Zn), nickel (Ni), aluminum (Al), iron (Fe) (Gröger et al. 2011; Shahabi-Ghahfarokhi et al. 2022) and reactive non-metals such as sulfur (S). Aluminum is the most toxic element for the environments under influence of AS soils and has been implicated in extensive fish kills (Powell and Martens 2005; Toivonen et al. 2020). Iron is another metal with environmental threats, because it has suffocating effects for vegetations by producing secondary Fe(III) precipitates on the surrounding recipient wetland and coastland planes of the AS soil drainage (Sullivan and Bush 2004; Shahabi-Ghahfarokhi et al. 2022). Manganese, Ni, Zn, and Co are trace elements usually reported from AS soil drainage (Åström and Corin 2000) that contribute to diseases if concentrations are over threshold values (Blust 2011; Röllin 2011; Rajput et al. 2018; Genchi et al. 2020). To reduce the risk of contamination and to take advantage of AS soil drainage, removing the metals and S from the solution and eventually recovering would be the most favorable approach for an environmentally friendly (Kaikake et al. 2007) and circular economy (Pires and Martinho 2019) perception.

Therefore, this study investigates the potential of SCGs and DHA for remediating metal-contaminated waterways associated with drained AS soil through adsorption and precipitation reactions. In addition, the results from the adsorption (SCGs) and the precipitation (DHA) experiments are also compared to evaluate the highest uptake of metals from the solution. Furthermore, the interaction of SCGs wastewater with dissolved metals of the drainage is studied. Finally, this study investigates the potential metal recovery after incineration of the metals-sorbed SCGs through an SCE scheme.

Methods

Study site and AS soil drain water collection

This study uses water samples collected in an artificial drainage system in southern Sweden (Skåne), north of the Kristianstad municipality (Fig. 1). AS soils and metal mobilization (Fe, Al, Ni, Co, Mn) in associated artificial drainage systems have been reported in the area (Shahabi-Ghahfarokhi et al. 2022). Over time, the discharge of drained water from AS soils onto the north wetland area has caused environmental degradation by multiple metals (Shahabi-Ghahfarokhi et al. 2022). The AS soils' water is drained and meets in the central drainage system (Fig. 1). On two separate occasions (September 2020 and April 2021), water samples were collected in 10 L water containers and stored at 4 °C. On-site, the pH (pH/mV/°C Meter, Handheld, pH 1100 H, pHEnominal®) values were immediately measured from the central drainage. The first water sample collected was used for the pre-test (small scale experiments under similar settings of this study), and the second water sample was used for the main experiment of this research. The water samples collected (without treatment) from the drain were directly employed to simulate natural conditions. From both samples, dissolved metal contents were also measured (Section 2.4).

Fig. 1. Illustrating the study site and the view of the drainage system.

SCGs preparation

The SCGs were collected from Linnaeus University vending machines (Selecta® coffee vending machines and Pelican Rouge® Amor coffee beans). The wet and fresh SCGs were collected on the same day and treated according to the following steps: The SCGs were pre-treated (Utomo and Hunter 2006) with 0.01 M NaOH (Sigma-Aldrich) and mixed with a weight to volume ratio (W/V) of 1/10 (dry SCGs to water), and washed with deionized water. The washing was repeated until achieving a non-color supernatant with a TOC < 5 mg L⁻¹. During the washing process DOC (measured with LCK 380 and 381, HACH® kits) and pH values (pH/mV/°C Meter, Handheld, pH 1100 H, pHenom-enal®) were measured. The SCGs were then washed with Milli-Q water until a pH of ≈6 was achieved (Utomo and Hunter 2006). Finally, the SCGs were air-dried (30 °C) for 24 h, and the dried grains were sieved via a plastic sieve (to avoid metal contamination) into two separated fractions of 500 and 250 µm (the 500- and 250- µm fractions consist of 1000-500 µm and 500-250 µm fractions, respectively). These separated fractions were used to understand the effect of grain size on the adsorption of elements onto SCGs particles.

Adsorption experiment

For the experimental adsorption setup, five weights of 0.05, 0.1, 0.5, 1.0, and 1.5 g SCGs added to a constant volume of 40 mL were used to estimate the adsorption capacity of the two different fractions (500 and 250 µm) under altering pH values of 4.5 and 6.5 (Table 1). After weighing the SCGs into the 50 mL falcon tubes, the water collected in the field was added to each sample with a dispenser (Poulsen & Graf GmbH FORTUNA™ OPTIFIX™ Safety S Dispenser) at a constant volume of 40 mL. The prepared tubes were fixed in racks and shaken (Heavy Duty Shaker, OHAUS™) at 4 °C (average winter season temperature present in the study region) for 18 h under dark conditions. The samples were then filtered (cellulose acetate membrane, 0.45 µm, Whatman) and stored for total metal concentration measurement (Section 2.5). In addition, 6 extra adsorption batch experiments with 500 mm SCGs under pH of 6.5 were conducted using the highest W/V ratio (300 gr/800 mL, batch 5, Table 1) in 1L bottles (Pyrex™ Borosilicate Glass Reagent Bottle). Samples with a higher W/V ratio were prepared to have enough material for incineration and the potential metal recovery experiment.

After the adsorption experiments, the contaminated SCGs were merged into 2 groups by mixing the material from 3 of the experiments (after filtration) to further perform the sequential extraction on duplicates. Later, each compiled sample was air-dried and incinerated into ash at 750 °C (Ghosh et al. 2020) for 5 h (Heiri et al. 2001).

Precipitation experiment

For the precipitation experiments, two different reactants were added to the collected water sample under varying pH of 4.5 and 6.5. The first reactant, dissolved humic acid (DHA), was made by dissolving 2.5 g of dry humic acid (HUMIN-P 775, Humintech, Germany) in 5 L of water, leading to 700 mg L⁻¹ DOC (Zhou et al. 2019). For the second reactant, the extract was taken from the 1st step (1st Batch) of washing the SCGs (Table 1), coffee DOC, which leads to a DOC concentration of 1440 mg/L (Table A1). Based on target DOC concentrations and liquid volumes (Table 1), the addition from DOC stock solutions took place (Table A1). The same pH values employed in the adsorption experiment were used for the precipitation experiment. A 20-80 mg L⁻¹ DOC range was chosen for the DHA as intervals for the precipitation experiment. The proposed range of DOC final concentrations were chosen for natural processes based on typical DOC leaching values of 40 mg/L from forest soil (Scheel et al. 2007). To study the lower and higher inputs of DOC, ±40 mg/L DOC was applied to our center value (40 mg/L) to study the extent of precipitation in the covering range. Since the aromaticity (Fig A1) of the coffee DOC is almost half of the DHA, it was decided not to use the same volumes added from DHA to keep the volume constant, which leads to double DOC concentrations used (Table 1). All samples were prepared in 50 mL Falcon tubes, fixed on racks, and shaken at 4 °C for 18 h. After filtration (cellulose acetate circles membrane, 0.45 µm, Whatman®), the DOC was measured (LCK 380 and 381, HACH®), and the remaining samples were stored for total metal concentration measurement (Section 2.5).

Trace element analysis and sequential chemical extraction

The filtered liquid supernatant samples were acidified to a pH below 2 with 1% HNO₃. The samples were then analyzed for concentrations of Fe, Al, Mn, Ni, Zn, Co, Ca, Na and S (Table A2-11) with ICP-OES (Thermo Scientific Inc., ICP-OES spectrometry iCAP7000, University of Latvia). The detection limit was 1–10 ppb for Al, Ca, and Fe, 0.1–1 ppb for Na, and 0.1 ppb for all other elements.

To evaluate the potential for metal recovery after incineration, a sequential extraction scheme modified from Tessier and Campbell, (1987) was applied to the incinerated samples (Xiong et al. 2014, See Table 2). Since the material consists of mostly organic matter, the last two steps of the scheme (bound to organic matter and residual fraction) were not included.

- Step 1: Fraction of water-soluble and easily exchangeable compounds. A sample (1.0000±0.0050 g) was extracted by 1 M MgCl₂ in deionized water in a glass beaker for 1 h on a mechanical shaker (Tachometer RPM PSU-20, Biosan).
- Step 2: Fraction of weak acid-soluble compounds (e.g., carbonates). Sample left from the 1st step of sequential extraction were carefully

Table 1

The variables (pH, grain size, and DOC) and loads were used for the adsorption and precipitation experiment.

Experiment	Variables						
Adsorption	Grain-Size µm	pH	Weight (g) of SCGs*				
			Batch1	Batch2	Batch3	Batch4	Batch5
	500	4.5	0.05	0.1	0.5	1	1.5
	250						
Precipitation	500	6.5	0.05	0.1	0.5	1	1.5
	250						
	DOC	pH	DOC mg L ^{-1**}				
			Batch1	Batch2	Batch3	Batch4	Batch5
	DHA	4.5	20	30	40	60	80
		6.5					
	Coffee1st extract	4.5	40	60	80	120	160
		6.5					

*Each weight of coffee is reacted with 40 mL of liquid sample **From each stock, DHA, and coffee extract, volumes were added to reach 40 mL and the target DOC value (Appendix 1). The terms used are: spent coffee-grounds (SCGs), dissolved organic carbon (DOC), and dissolved humic acid (DHA).

Table 2

The sequential extraction scheme used for this study.

Fraction	Fraction Name	Agent	Conditions	V (mL)	Changes made by Xiong et al., (2019)	
			Mixing time (hour)		V (mL)	Time (hour)
1	Water soluble and Exchangeable	1 M MgCl ₂	1	8	18	2
2	Bound to carbonates	1 M NaOAc	Until necessary	8	15	5
3	Bound to Fe and Mn oxides	0.04 M NH ₂ OH·HCl in 25 % HOAc	Until necessary	20	30	6

collected into a glass beaker and extracted with 40 mL of 1 M NaOOCCH₃ for 16 h on a mechanical shaker (Tachometer RPM PSU-20, Biosan).

- Step 3: Fraction of reducible compounds. Sample left from the 2nd step of sequential extraction were collected into a glass beaker and extracted with 20 mL of 0.5M NH₂OH × HCl for 16 h on a mechanical shaker.

After each step, double filtration of extracts using a paper filter and a membrane filter (0.45 µm, Simplepure) were done; the extracts were put into polypropylene tubes and diluted with deionized water to 50 mL and acidified with 0.7M HNO₃. Each analytical solution was made in triplicate and, at each step, blank samples were prepared in the same manner. All obtained extracts were stored until analyses in a cool place (+4 °C). The quality of the analytical measurements was ensured by the analysis of certified reference material IAEA-336 Lichen containing reference values on wide spectra of major and minor elements.

Results and discussion

AS soil drain water pH and metal concentration

Records show the different pH values (4.5 and 6.5) and element concentrations measured from the drain system (Table 3). From the measured pH, the two values were included as the minimum and maximum pH variables in the adsorption and precipitation experiments. In case of the low pH event, during the water sampling in 2020, the water was pumped out of the drain system, allowing more drainage and potentially exposing the parent material to oxidation and lowering the pH. This is supported by the fact that the concentrations of metals, in particular, Al and Fe, were higher during the low pH events. The low pH and higher soluble metal values correlate with the AS soils being drained. The same feature was also seen in other AS soil settings, where higher concentrations of elements were observed in the drain waters during active drainage and low pH (Dang et al., 2018). Comparing the available threshold values of the Swedish EPA (Swedish EPA 2000), Zn and Ni on different occasions show concentrations above EPA threshold values. For Zn, in low and high pH values in drainage water, concentrations are high and very high (class IV and V, Table 3), respectively, when compared to Swedish EPA threshold values (Swedish EPA 2000). In addition, under low and high pH events, Ni shows low and very high concentrations (class II and V, Table 3), respectively, when compared to threshold values of the Swedish EPA (Swedish EPA 2000). Class II is

classified as a slight risk for biological effects (Swedish EPA 2000), whereas classes 4 and 5 are classified as increasing risks for biological effects. The most significant are the effects of class 5 metal contaminations, where even short-term exposure affects organisms (Swedish EPA 2000).

Monitoring of SCGs washing steps and NaOH treatment

Two parameters, including pH and DOC and visually observed color changes, were used to control the SCGs washing procedure (Fig. 2). The supernatant in each washing step (batch 1-13) shows a decreasing DOC concentration, increasing pH, and changing color from brown to transparent (Fig. 2). Previous research (Utomo and Hunter 2006) has used visual recognition (transparent watercolor) to judge the final step of the SCGs washes. However, as illustrated in Fig. 2, from washing step number 10, it will be challenging to identify the final wash even though the solutions still contain high levels of DOC (<100 mg L⁻¹). This study shows that TOC and pH are more appropriate parameters for identifying the final washing step. Also, ensuring close to zero DOC concentrations coming from the SCGs will reduce the spontaneous formations of precipitates, metal-DOC complexes, and aid in distinguishing between the adsorption and precipitation processes. The pH also could indicate the solution has reached a stable condition when the washing NaOH solution (pH 11.8) shows the extracted DOC has reached its minimum (Fig. 2).

From the washing steps, it is evident that Na has been adsorbed onto the washed SCGs (Table A3-10). The increasing Na concentration released into solution after the 18 h adsorption experiment (Fig. 3) might indicate a weak bond of Na from the pre-treatment washing step onto the SCGs. Also, confirming that even with the after wash with distilled water, the Na is still adsorbed. In addition, it is evident that with different volumes of SCGs added, the Na introduced into solution is increased. This increasing concentration of Na could affect the adsorption processes by altering the ionic strength, which is discussed in the next chapter (chapter 3.3). Because of the known Na toxicity effects in aquatic systems and water quality (Corsi et al. 2010), the increase of Na by SCGs addition shall be considered for the application in the field.

Adsorption

Aluminum, Ca, Co, and Mn show an overall higher adsorption (91-98%, 95-96%, 92-94%, and 99-100%, respectively) onto SCGs in the pH = 6.5 than in pH = 4.5 with no relation to grain sizes (Fig. 4). For Ca, the

Table 3

Element concentration of Al, Fe, Mn, Co, Zn, S, Ca, Ni and Na in two different dates sampled from the drain system which are influenced by the pH. When available, the class of metal contamination from the Swedish EPA (Swedish EPA 2000) values are also mentioned for comparison. Values missing from the Swedish EPA are mentioned as no data (n.d).

Value	pH	Elements (µg/mL)								
		Al	Fe	Mn	Co	Zn	S	Ca	Ni	Na
Drain water-2020	4.5	29	31	5.3	0.11	0.58	-	177	0.7	27
Drain water-2021	6.5	0.04	0.4	1.6	0.02	0.12	94	148	0.02	22
EPA classes		Range of values (µg/mL)								
I		n.d	n.d	n.d	n.d	≤ 0.0005	n.d	n.d	≤ 0.0007	n.d
II		n.d	n.d	n.d	n.d	0.0005-0.003	n.d	n.d	0.0007-0.015	n.d
III		n.d	n.d	n.d	n.d	0.003-0.009	n.d	n.d	0.015-0.045	n.d
IV		n.d	n.d	n.d	n.d	0.009-0.045	n.d	n.d	0.045-0.225	n.d
V		n.d	n.d	n.d	n.d	>0.045	n.d	n.d	>0.225	n.d

Fig. 2. Inverse relation of pH and dissolved organic carbon (DOC) is 13 steps of washed the spent coffee-grounds (SCGs) water and the color change of each sequence.

Fig. 3. Sodium (Na) concentrations were released into solution over the adsorption (left graph) and precipitation experiment (right graph). For batch information refer to Table 1. The dissolved humic acid (DHA) and coffee DOC are used in the precipitation experiment.

adsorption equilibrium was not reached even though the uptake is close to 100% (Fig. 4), indicating the affinity of dissolved calcium interacting with SCGs. Comparing Al to Fe (75–88% adsorbed), the latter shows a slightly higher adsorption capacity and removal rates with smaller grain sizes. For Ni and Zn, the lower pH values have increased the adsorption capacity (93% and 95–96%, respectively) of SCGs when compared to pH 6.5 (81–82% and 74%, respectively), without the grain size affecting the percentage of adsorbed Co, Ni, and Zn. For most elements, with an increasing weight of SCGs (>0.05/40 W/V), the competition over adsorption seems to be smaller, and hence less adsorbed elements were observed (Fig. 4). This decreasing trend of adsorption with addition of SCGs is also evident in normalized values (mass of adsorbed metal normalized by mass of SCG, Fig A2 and Table A12). The most substantial decrease of adsorption is for Fe (Fig. 4 and A2). SCGs adsorbs close to 90% of Fe in the solution of batch 1 and almost 30–45% in the last batch 13 (1.5/40 W/V). In addition, the SCGs does not show any affinity for S; therefore, the results were not included in the adsorption experiment. Multiple mechanisms could explain the decreasing adsorption of soluble Fe with higher SCGs addition. The adsorption times used in this study

are higher than in previous SCGs adsorption studies (Lavecchia et al. 2016; Nam et al. 2017; Sukhbaatar et al. 2021), which could cause desorption. However, Kyzas et al. (2012) reports the adsorption of soluble metals onto SCGs under experimental adsorption times up to 24 h, which do not indicate desorption of soluble metals from the SCGs. In addition, with increasing adsorbers, the aggregation of bio-adsorbers is probable, thus reducing the adsorption sites (Sartape et al. 2017; Mashkoor et al. 2018). That mechanism is also unlikely because our samples were agitated during the experiment. Finally, the soluble Na released into solution with increasing addition of SCGs (Fig. 3), increases the ionic strength of the solution and might reduce the pH, which causes desorption or reduce the adsorption of soluble metals onto SCGs. Although the pH and ionic strength of solutions during and after the experiment were not measured, this mechanism is likely to decrease the adsorption of soluble elements with increasing SCGs.

The results show that the tested grain sizes don't affect the adsorption capacity, while the pH of the solution plays a more critical role in the uptake of these metals. The methods to brew, bean type, and the growing conditions of coffee beans are variables that can change the

Fig. 4. Aluminum, Ca, Co, Fe, Mn, Ni and Zn from the adsorption experiment with pH (4.5 and 6.5) and spent coffee-grounds (SCGs) grain size (500 and 250 mm) as variables. For batch information please refer to Table 1.

adsorption properties of SCGs (Blinová et al. 2017; McNutt and He 2019). For Al, Co, Ni, and Zn (Fig. 4) at higher pH values, the adsorption slightly decreases even with increasing the amount of SCGs added to the solution. This has also been observed previously by Utomo & Hunter (2006) for Zn, in which 60% (from 1 mL L⁻¹ and pH 5) is adsorbed by SCGs. Chromium also had previously shown affinity (45 mg/g) to SCGs and weak adsorption when solutions were acidic, pH < 6 (Kyzas 2012). Calcium might not be problematic, however, in acidic settings with large quantities of CaCO₃ additions to increase the pH of soils (Åström 1998), the dissolved Ca can cause a color change and can precipitate to cause white surfaces (Lydersen et al. 2002). With the effects of Ca known (Åström 1998), removing this metal from AS soil drainage waters could improve local environmental statuses by removing the dissolved Ca.

Precipitation

The precipitation results show that DHA, with higher aromatic content (Fig. A1), has higher metal removal than coffee DOC (Fig. 5a). The role of pH is more prominent for Al, Ca, Co, Mn, and S. For Al, like adsorption, the precipitation reaches the highest value at the pH = 6.5, for both DHA and coffee DOC additions (87–92 % and 70–93%, respectively). Overall, the coffee DOC additions were only effective for Al, and all other elements have smaller precipitation values when compared to DHA additions. However, in pH = 6.5, the coffee DOC shows slightly higher precipitation rates when compared to a solution with pH = 4.5. Calcium, Co, and Mn show a higher precipitation for DHA under the pH = 6.5 (4–28%, 20–70%, and 7–43%, respectively), and slightly lower (2–24%, 3–62%, and 4–33%, respectively) for pH = 4.5. When looking at Fe and Ni removed percentages by precipitation, it is evident that with fewer DOC concentrations (Fig. 5a), higher precipitation occurs at pH = 4.5 rather than at pH = 6.5. The Fe and Ni removed by precipitation is 28–79% and 8–56% at pH 4.5 and 36–74% and 30–50% at pH = 6.5, respectively. In the case of Zn, the addition of DHA or coffee DOC has almost the same effect (Figs. 5a and b), with lower pH giving higher precipitation percentage (9–72% and 5–65%, respectively) at lower DOC concentrations (batch 1–3) when compared to pH = 6.5 (26–61% and 30–48%, respectively). Overall, for most elements, this shows the effectiveness of DHA under different changing pH environments with slightly less precipitation under acidic conditions.

Sulfur precipitation and adsorption results show a higher affinity for DOC in forming complexes in precipitates rather than SCGs adsorption

(Fig. 4–5). Under the two pH conditions, DHA and coffee DOC have very similar abilities in precipitating S complexes (up to 25%). The formation of Fe/Al (hydroxide)-DOC complexes during the addition of DHA or coffee DOC could provide adsorption sites for sulfate (Tamrat et al. 2019; Sadeghalvad et al. 2021), which are dominant in AS soil drainage (Green et al. 2007) and counted as total S measurements in solution. In addition, the removal of S and Fe, restricts the formation of problematic Fe species such as schwertmannite (Fitzpatrick et al. 2017) and akaganeite (Shahabi-Ghahfarokhi et al. 2022) in acidic settings. Schwertmannite is reported to form a suffocating media as it precipitates on plants in adjacent AS soil drainage areas (Fitzpatrick et al. 2017). Coffee DOC is not recommended since its environmental-related issues, related to high nutrient and DOC load that could lead to the formation of anoxic zones in aquatic environments, having previously been reported by Campos et al. (2021). In acidic settings, with available sulfate and Fe, the formation of schwertmannite is highly probable (Fitzpatrick et al. 2017). These iron sulfate species in Mediterranean (Fitzpatrick et al. 2017), tropical (Johnston et al. 2010; Keene et al. 2011; Johnston et al. 2016), and subtropical (Ahern et al. 2004; Claff et al. 2010) regions have caused severe vegetation degradation by forming schwertmannite and/or akaganeite, two poorly crystalline Secondary Fe(III) phases (Shahabi-Ghahfarokhi et al. 2022). Therefore, by using SCGs and HA, the formation of these problematic secondary iron species are potentially restricted by limiting the Fe and sulfate to form schwertmannite/akaganeite, often seen in sulfuric rich, acidic settings (Burton et al. 2021; Shahabi-Ghahfarokhi et al. 2022). However, the effects of simultaneous addition of SCGs and DHA should be further studied.

SCE of metals in ash and the overall approach

From the SCE ($\sum 3$ steps), it could be seen that Co, Ni, Mn, Fe, Zn, and Al present the highest percentage of recovery, respectively (Table 4). However, the overall highest extractions from the $\sum$ SCE belongs to Zn, Al, Co, Fe, Mn, and Ni. Looking at the separate steps of the contaminated SCE results for Al, Co, Fe, and Mn, the highest percentage of SEC recovery is obtained from the Fe and Mn oxides phases (Fig. 6).

In addition, Ni and Zn also show an increased percentage in the SCE fraction bound to carbonates (Fig. 6).

An essential part of solid waste management is incineration (Šyc et al. 2020). The obtained ash also contains high Al, Fe, Mn, Ni, and Zn (Silva et al. 2019; Šyc et al. 2020) concentrations. Zinc, compared to Ni,

Fig. 5. (a) Aluminum, Ca, Co, Fe, Mn, Ni and Zn from the adsorption experiment with pH (4.5 and 6.5) and spent coffee-grounds (SCGs) grain size (500 and 250 mm) as variables (b) precipitation results of metals with dissolved humic acid (DHA) and SCGs extract (Coffee DOC) from washing, under varying pH (4.5 and 6.5) is illustrated.

Table 4

Percentage and standard deviation of recovered elements from ash spent coffee-grounds (SCGs). The standard deviation (SD) for Zn is not provided since a duplicate sample provided no value.

Variables	Element	Al	Co	Fe	Mn	Ni	Zn
Coffee Recovery %		34	69	59	60	68	55
SD		2.16	13	0.214	28	5.59	-

has also shown to have the highest percentage of the Σ SCE, and both were found in easily accessible fractions (Lukowski, 2022). For Mn (Bruder-Hubscher et al., 2002), Co (Nurmesniemi et al., 2008), Al, and Fe (Haberl and Schuster, 2019), previous research have also indicated the low potential of these elements to be removed from bottom ash and mainly present in the reducible phases (Bruder-Hubscher et al. 2002; Nurmesniemi et al. 2008). In this study, the proposed strategy for reusing SCGs in AS soil drainage waters or acid mine tailings is presented in Fig. 7. The initial usage of SCGs, for remediation of metal contaminated waters, is followed by the recovery of metals from the incinerated waste (SCGs), which can further extend its lifespan (Fig. 7). In addition,

other valuable compounds such as rare earth elements (REEs) (Mondal et al. 2019) should also be studied, and their potential recovery from SCGs used in AS soil drainage could be evaluated. This is due to the nature of AS soil settings that contain up to several mg kg⁻¹ of REEs in their recipients (Astrom et al. 2020).

Conclusion

The element uptake (Al (98%), Ca (96%), Co (94%), Fe (88%), Mn (100%), Ni (93%), and Zn (96%)) for SCGs has higher percentage compared to the precipitated with DHA (Al (92%), Ca (28%), Co (70%), Fe (79%), Mn (43%), Ni (56%), and Zn (72%)). However, the spent coffee-grounds did not show any affinity towards S adsorption. In contrast, DHA and coffee DOC forms complex with S and removes up to 25% of the soluble S. The coffee DOC extract also shows affinity towards Al (93% adsorption). However, with the known environmental impact of SCGs wastewater, the usage of this extract is not recommended. Therefore, combining SCGs and dissolved DHA in AS soil drainage settings is recommended to restrict the formation of Fe(III) secondary minerals such as schwertmannite and/or akaganeite, which can cause environmental degradation. In addition, for SCGs, the effect of grain size on adsorption of studied elements is negligible. However, pH has

Fig. 6. Sequential extraction for the ash spent coffee-ground (SCGs) before and after the adsorption experiment. Extraction A, B and C refer to as the Exchangeable, bound to carbonates and bound to Fe and Mn oxides, respectively (Table 2). Total concentrations (µg) from the three extractions are mentioned at the bottom of each sample.

Fig. 7. The overall approach chosen for the re-use of the spent coffee-grounds (SCGs) to remediate acid sulfate (AS) soil drainage water and the potential recovery of Al, Mn, Zn, Fe, Ni, and Co from the loaded SCGs.

opposite effects on the removal of different metals, that is, Al, Co and Ca had higher adsorption efficiency in the high pH (pH=6.5) experiment, whereas, Zn and Ni were removed more efficiently in the low pH (pH=4.5) experiment.

The washing steps of the SCGs could affect the obtained results in single and combined methods for element adsorption, because the DOC could affect the adsorption by precipitation with the DOC of the SCGs. The Na released into the solution from treated SCGs could be additionally decreased by washing the SCGs further with Milli-Q water. However, this washing technique is recommended to separate the

adsorption from precipitation in experiments. In the real-world scenarios, additional washing steps SCGs will increase the processing costs of SCGs and produce additional wastewater. Therefore, other cost-effective techniques for treating SCGs should be studied/tested in the future.

The lifespan of the loaded/contaminated SCGs can be extended by potential element recovery from the incinerated ash product. The results show that Co (69%), Ni (58%), Mn (60%), Fe (59%), Zn (55%), and Al (34%) had the highest recovery percentage by sequential chemical extraction, respectively. Therefore, the reuse of SCGs for remediation and their application for metals recovery after incineration in municipal waste is beneficial. Furthermore, with the impact of climate change on the groundwater recharges in the boreal landscapes, the leached metals from the drained AS soil could be a potential source for metal recovery by using substances such as the SCGs. In addition to the application of SCGs for the remediation of AS soil drainage waters and metal recovery from the remaining SCGs, other similar environments such as acid mine drainage might also be suitable environments for such treatments. This is due to the low pH and consequently the high metal concentrations of the acid mine drainage.

CRediT authorship contribution statement

Sina Shahabi-Ghahfarokhi: Conceptualization, Methodology, Validation, Software, Formal analysis, Writing – original draft, Visualization. **Mahboubeh Rahmati-Abkenar:** Methodology, Validation, Investigation, Writing – review & editing. **Johan Glenn Matson:** Investigation, Writing – review & editing. **Hadi Karimi:** Software, Writing – review & editing, Visualization. **Changxun Yu:** Validation, Writing – review & editing. **William Hogland:** Resources, Writing – review & editing. **Maris Klavins:** Resources, Writing – review & editing. **Marcelo Ketzer:** Resources, Writing – review & editing, Supervision.

Declaration of Competing Interests

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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