metals

Article

Copper Recovery from Polluted Soils Using Acidic Washing and Bioelectrochemical Systems

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Abstract: Excavation followed by landfilling is the most common method for treating soils contaminated by metals. However, as this solution is not sustainable, alternative techniques are required. Chemical soil washing is one such alternative. The aim of this experimental lab-scale study is to develop a remediation and metal recovery method for Cu contaminated sites. The method is based on the washing of soil or ash (combusted soil/bark) with acidic waste liquids followed by electrolytic Cu recovery by means of bioelectrochemical systems (BES). The results demonstrate that a one- or two-step acidic leaching process followed by water washing removes >80 wt. % of the Cu. Copper with 99.7–99.9 wt. % purity was recovered from the acidic leachates using BES. In all experiments, electrical power was generated during the reduction of Cu. This clearly indicates that Cu can also be recovered from dilute solutions. Additionally, the method has the potential to wash co-pollutants such as polycyclic aromatic hydrocarbons (PAHs) and oxy-PAHs.

1. Introduction

Excavation followed by landfilling is the most common method for treating soils contaminated by metals. However, landfilling is not a sustainable management option, as many landfills will close in the coming decades, while new ones are not opened at the same rate. Consequently, alternative treatment methods are necessary. One interesting method is soil washing, which can be divided into physical and chemical washing, although a combination of both is often used. Physical soil washing usually aims at enriching most of the pollutants into a specific soil fraction, see e.g., [1], while chemical soil washing aims to wash out the pollutants. There is thorough lab-scale research on chemical soil washing using a variety of leaching agents, including inorganic acids, bio surfactants and complexing agents such as EDTA or its derivates [2–8]. Apart from cases where water was used as the leaching agent, not many pilot scale experiments have been conducted [9]. A reason might be that when virgin chemicals are used, recirculation or reuse of the leaching agents is essential in order to ensure an efficient and economically viable process. There are examples of recycling and reuse of the commonly used leaching agent EDTA [10,11]. However, as EDTA is non-biodegradable, it is important to ensure that any remaining EDTA does not lead to problems with the solid residues. From that perspective, an acid might be a better option. Probably the best alternative would be a waste liquid for leaching as the need for recycling is lower making the proposed method simpler and potentially less expensive. Acidic wastewater from a flue gas cleaning process has been shown to effectively (>70%) leach copper (Cu) from contaminated soils [12].

In many cases, metal-contaminated sites also contain organic pollutants; especially those at which wood preservation took place using both metal-containing and creosote-based preservers. Creosote contains high concentrations of polycyclic aromatic hydrocarbons (PAHs) that are known to be toxic, mutagenic and carcinogenic. In contaminated sites, the PAHs are degraded to oxygenated PAHs (oxy-PAHs) through chemical oxidation [13], photo oxidation [14] or biological transformation [15]. The oxy-PAHs are of great interest because they are persistent, highly toxic to both humans and the environment and more water-soluble than their corresponding PAHs [16]. When investigating treatment methods for metal-contaminated soils, it is therefore necessary to study the fate of organic pollutants.

An aspect that has not received much attention is the potential to recover the valuable metals released through soil washing processes. Conventionally, Cu is recovered from concentrated liquids (>35 g Cu/L) using large-scale energy-demanding electrolysis [17]. An interesting alternative, which would reduce the amount of electrical energy required during electrolysis, is the use of microbial bioelectrochemical systems (BES) [18]. In BES, microorganisms oxidize the organic compounds present in e.g., wastewater and use the anode as an electron acceptor, thereby transforming the chemical energy in the organic compounds into electrical energy. Recent studies on diluted Cu solutions (~1 g/L) demonstrate that the energy consumption is significantly lower with BES compared to traditional electrolysis [19–21]. At certain cathode potentials, electrical energy could even be extracted from the system together with the Cu. As in conventional electrolysis, it is possible to selectively reduce individual metals from a mixture by varying the cathode potential in the system. Modin and co-workers found that high purity Cu (99.9%) could be recovered from a simulated ash leachate containing a mixture of Cu, Cd, Pb and Zn ions (1 g/L) without energy input. In addition,

high purity Zn (>99.9%) was recovered from the mixture, although Cd and Pb needed further purification [22].

The aim of this experimental lab-scale study is to develop a remediation and metal recovery method for Cu contaminated sites. The method is based on soil washing using acidic waste liquids and BES to recover Cu. In addition, as contaminated areas often contain both metals and organic pollutants, the behavior of PAHs and oxy-PAHs during the recovery process is studied and evaluated.

2. Experimental Section

In this work, the term "soil" is defined as "the entire mantle of unconsolidated material, whatever its nature or origin", first formulated by G.P. Merrill in his book "Rocks, rock-weathering and soils" published in 1897 and used by other research groups.

2.1. Soil Samples

Soil samples with different characteristics from two sites, Köpmannebro (A) in western Sweden and Björkhult (B) in eastern Sweden, were used in this study. Both sites are highly contaminated with Cu and were previously used for wood preservation by means of $CuSO_4$ according to the Boucherie method. Based on results from chemical analyses in earlier studies on the two sites, representative samples were collected from hotspots with a high metal content. Sample A1 is a bark sample from a depth of 5–80 cm and A2 is a soil sample from the same spot but from a depth of 120–150 cm. Sample B1 is bark from a depth of 5–20 cm and B2 is a soil sample from the same spot at a depth of 40–60 cm. All samples are mixtures of several sub-samples taken from the bark and the soil, respectively.

Pre-Treatment of the Soil Samples

All samples were gently dried at 80 °C until constant weight (*i.e.*, 100% dry solids (DS)). The A1 and B1 samples (*i.e.*, bark) were cut into smaller pieces using an automatic mixer and thereafter most parts of each sample were separately incinerated to ash, while the remaining bark samples were stored for analysis. The incineration processes were performed in two ways. The bark was either incinerated in batches in a laboratory oven at 850 °C for 5 h or in a real full-scale plant (Type-D 200 using the BS Incinerator System) normally employed for the incineration and destruction of e.g., animal cadavers and hospital waste. The bark was continuously incinerated at 830 °C. This temperature was chosen to theoretically prevent vaporization of Cu compounds, thus enriching them in the collected bottom ash. Bark sample A1 was incinerated by both methods and the resulting ash (A1a) was a mixture (50/50%) of the two ashes *i.e.*, A1a$_{lab}$ incinerated in the lab and A1a$_{incin}$ incinerated in the real boiler. This mixture was used in the present study. The B1 bark was only incinerated in the laboratory oven, resulting in ash sample B1a. All samples were stored in airtight containers until use.

2.2. Leaching Experiments

Highly acidic wastewater (pH around 0) produced in the wet flue gas cleaning process during full-scale incineration of municipal solid and industrial waste was used as a leaching agent. Consequently, the wastewater contained metal ions and chlorides from the flue gases. The composition of ions in the process water varies in accordance with incineration conditions and the kind of waste used, but is dominated by Cl⁻. Representative concentrations of the most common ions are presented in Table S1. Today, acidic water is purified of toxic metal ions and small particles by means of precipitation. Thereafter, the sludge is landfilled, while the clean water is released to the recipient.

2.2.1. Optimizing Leaching Experiments

The influence of the parameters leaching time, liquid-to-solid (L/S) ratio and number of acidic leaching steps was studied to optimize the Cu leaching process. The optimization experiments were carried out on samples A1a and A2. The latter was also tested using significantly longer leaching times of 18 and 24 h. The original bark samples were not leached directly, as previous research revealed a greater leaching efficiency from the corresponding ashes as well as a higher Cu concentration in the final leachates [12]. In each experiment, 0.5–5 g of ash or soil (100% DS) was leached in airtight plastic containers using the acidic process wastewater at L/S ratios of 2, 5 or 10. The leaching times varied between 15 and 90 min, and a reciprocal shaker (SM 25, Edmund Bühler GmbH, Hechingen, Germany) was used at 140 rpm to ensure continuous agitation. After leaching, the solid-liquid-mixture was centrifuged for 15 min at 3000 G (gravity). The supernatant was transferred to a new airtight container before being stored at 4 °C until analysis. The solid residues were either leached in an additional step followed by 15 min of centrifugation at 3000 G, or washed immediately for 5 min with continuous shaking using ultrapure water (18.2 $M\Omega/cm^2$) in L/S ratios of 2 calculated on the basis of the original sample amount. In the initial ash leaching experiments, *i.e.*, one acidic leaching step, an L/S of 5 was used for washing. Finally, the sample-water mixture was centrifuged for 15 min at 3000 G and the solid residues were dried and stored in airtight containers. The leachates were also filtrated before analysis using acid resistant filters with pore size 1.6 μm. All soil samples were studied in triplicate, while the ash samples were generally investigated in duplicate due to shortage of ash.

Larger scale batch leaching experiments were performed based on the parameters identified in the optimization experiments. In the batch leaching experiments, 20–30 g (100% DS) of each sample, *i.e.*, ash (A1a, B1a) and soil (A2, B2), was used.

2.2.2. SS-EN-12457-3 Leaching Tests

The potential natural leaching from the original samples as well as from selected soil and ash residues was studied using a downscaled and somewhat modified SS-EN-12457-3 leaching test procedure, *i.e.*, L/S = 2 for 6 h and L/S = 8 for 18 h [23]. Depending on the amounts available, between 1 and 30 g was used in each experiment. The samples were continuously shaken during leaching in a reciprocal shaker (SM 25, Edmund Bühler GmbH) and then centrifuged to separate the leachates from the solids. The leachates were filtered using acid resistant filters with pore sizes varying from 1–6 μm and stored at 4 °C for further analyses.

2.3. Bioelectrochemical Experiments

The bioelectrochemical reactor consisted of cylindrical anode (2 cm diameter, 6 cm length) and cathode (2 cm diameter, 3 cm length) compartments separated by a 3.1 cm^2 anion exchange membrane (AMI-7001, Membranes International Inc., Ringwood, NJ, USA). The anode was a $5 \times 2 \times 0.2$ cm^3 carbon felt (TMIL, Tsukuba, Japan) and the cathode a 5 cm long, 0.81 mm diameter titanium wire (Sigma Aldrich). A nutrient medium containing 500 mg/L glucose, 114 mg/L NH_4Cl, 20 mg/L K_2HPO_4 and 5.6 g/L $NaHCO_3$ was circulated through the anode compartment from a 1 L glass bottle. At the start of the experiment, the anode was inoculated with sludge from an anaerobic digester. The cathode compartment was fed with either leachate A1a or a salt solution containing 2925 mg/L NaCl, 1179 mg/L $CuSO_4 \cdot 5H_2O$ and 1 mL/L 2 M HCl.

The bioelectrochemical reactor was operated for five weeks. During the first four weeks, the reactor was acclimatized with a Cu-containing salt solution in the cathode compartment. In Week 5, Cu recovery from real leachates (A1a) was investigated.

2.4. Leaching and Degradation of PAHs

The A2 soil sample was used for the leaching and degradation test of PAHs and oxy-PAHs. An undried soil sample (~2 kg) was mixed in a mortar, and bigger pieces of bark were retained, but inorganic parts such as stones were excluded. The soil sample was thereafter mixed with ~500 mL ultrapure water for 24 h to form a homogeneous soil/water slurry sample. To ensure a sufficiently high PAH content, the soil sample was spiked with additional PAHs. A sub-sample of 800 g was mixed with 1 mL of PAH-mix 3 (Supelco in 50:50 $CH_2Cl_2:CH_3OH$, Sigma-Aldrich) containing 18 specific PAHs, each with a concentration ranging from 100 to 1000 μg/mL, together with 2 mL MeOH to enable good mixing and prevent the PAHs from adsorbing to the glass surfaces of the containers. The sample was then stirred for 2 h. Thereafter, the PAH spiked sample was stored in a dark glass bottle in a refrigerator (+4 °C) for eight months. A portion of this sample was sent for external analysis of metals, minerals, PAHs, oxy-PAHs, organic (loss of ignition) and water content. Two other ~200 g portions were leached for 30 min with continuous stirring and L/S = 10 using the acidic process water as described above. The filtrates from the two samples were mixed and sent for US EPA PAH-16 and oxy-PAH-9 analysis after filtration through 0.6 μm glass-fiber filters, while the samples for metal analysis were filtered through a 0.45 μm cellulose acetate filter. It should be noted that these soil samples were not centrifuged and not washed with ultrapure water before chemical analysis.

2.5. Analytical Methods

The total metal content of the original and selected leached bark, soil and ash samples was analyzed using either ASTM D3683, *i.e.*, leaching in closed Teflon bottles heated in a microwave oven using 7 M HCl (A1a and B1a; As, Cd, Cu, Co, Hg, Ni, Pb, Sb, S, Se, Sn and Zn), HNO_3/H_2O_2 (A1, A2, B1, B2; As, Cd, Cu, Co, Hg, Ni, Pb, B, S, Sb, Se and Zn) (not Sb in A1 and B1) or ASTM D3682 *i.e.*, melting in lithium tetra borate followed by dissolution in diluted HCl (Al, Ca, Fe, K, Mg, Na, P, Si, Ti, Ba, Be, Cr, Mn, Mo Nb, Sc, Sr, V, W, Y and Zr). The solutions from the total digestion were analyzed

using ICP-MS (inductively coupled plasma mass spectrometry) or ICP-AES (inductively coupled plasma atomic emission spectrometry).

The Cu concentration in the leachates obtained from the optimized Cu leaching experiments was analyzed semi-quantitatively using an ATI UNICAM spectrophotometer with a D2/tungsten lamp. The leachates obtained from the batch leaching experiments (based on the optimized leaching parameters and larger sample volumes) and the acidic process water were analyzed for metals (Al, As, Ba, Be, Pb, Cd, Co, Cu, Cr, Li, Mn, Mo, Ni, Se, Ag, Sr, V and Zn) by means of ICP-MS. The same analytical method was also employed for the BES experiment liquids (As, Pb, Cd, Co, Cu, Cr, Ni, V and Zn). Ion chromatography (Dionex ICS-900, Thermo Scientific) was applied to analyze the K^+, Mg^{2+}, Na^+, NH_4^+, Ca^{2+}, Cl^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-} concentrations in the acidic process water. The pH was measured in some of the original samples (pH(H_2O)) using a Metrohm SM 702 pH meter. At the end of each leaching experiment, the pH was controlled to be <2 using litmus paper. To measure the influence of the various parameters on metal leaching to guarantee an accurate evaluation, analysis of variance (ANOVA) was conducted [24]. The organic content in the anode compartment of the BES was analyzed by means of a total organic carbon analyzer (TOC-V, Shimadzu, Japan). Cell potentials were logged using a data logger (USB-6008, National Instruments, USA). The amount of Cu recovered on the cathode was quantified by dissolving it in 10 mL HNO_3 (50%) and measuring the Cu^{2+} concentration using ICP-AES. The PAHs and oxy-PAHs were solvent extracted and analyzed with GC-MS by a commercial laboratory (ALS, Luleå, Sweden).

3. Results and Discussion

3.1. Characterization of Original Samples

Total Amounts

The total amounts of selected major and minor elements in the original samples (A1, A1a_oven, A1a_incin, A2, B1, B1a and B2) are presented in Table 1. For comparison purposes, the Swedish generic guideline values for sensitive and less sensitive land use are also provided [25]. Copper greatly exceeds the guidelines in all samples, while the other elements, with the exception of Ba and Zn, are below the recommended values.

The incineration temperature was chosen so as to avoid vaporization of Cu compounds as discussed above. If no Cu vaporization took place, the amount of Cu/mass unit in the collected bottom ash would have been about 10 and 3 times higher in A1a_oven and in B1a, respectively, compared to the original bark samples. The reason for the higher ash fraction in sample B1, *i.e.*, lower Cu content/mass unit, is most likely due to the non-volatile soil particles present in the bark fraction, which was not the case in the bark from site A (Figure 1). Sample A1a_incin, *i.e.*, the bark sample incinerated in a real incineration plant, resulted in less bottom ash compared to the other samples because of the continuous gas flow during the incineration procedure. In this study no fly ash was collected, in which the volatilized metal compounds are captured. However, in a real incineration situation the fly ash is collected in the flue gas cleaning system and thus interesting metals can also be recovered from that ash fraction, although this was not studied here.

Table 1. Average total amounts of selected major (oxide minerals) and minor elements in the original soil samples (A1, A1aoven, A1aincin, A2, B1, B1a and B2). The Swedish generic guidelines values for sensitive (KM) and less sensitive (MKM) land use are also shown. All amounts are shown in mg/kg DS. Measurement uncertainties vary between 20% and 25%.

Element	A1 (bark)	A1a$_{oven}$ (Bark Ash)	A1a$_{incin}$ (Bark Ash)	A2 (Soil)	B1 (Bark)	B1a (Bark Ash)	B2 (Soil)	Sensitive Land Use [a] (KM)	Less Sensitive Land Use [a] (MKM)
pH(H$_2$O)	4.9 [b]	12.1 [b]	– [c]	5.5	–	–	5.2		
wt. % DS									
SiO$_2$	1.9	54	8.4	68	26	57	76	* [d]	*
Al2O$_3$	0.7	10	4.6	12	5.3	11	13	*	*
CaO	0.8	4.5	26	1.8	0.5	1.3	0.8	*	*
Fe$_2$O$_3$	0.5	4.0	1.8	2.5	2.0	4.4	1.1	*	*
K$_2$O	0.1	2.7	6.9	2.4	1.6	3.5	4.2	*	*
MgO	0.06	0.7	1.7	0.6	0.1	0.2	0.1	*	*
MnO	0.01	0.07	0.01	0.04	0.01	0.03	0.02	*	*
Na$_2$O	0.08	2.0	7.3	2.6	1.0	2.5	2.7	*	*
P$_2$O$_5$	0.1	0.6	29	0.04	0.2	0.4	0.01	*	*
TiO$_2$	0.02	0.4	0.9	0.5	0.2	0.2	0.2	*	*
mg/kg DS									
As	2.0	11	<3	0.6	7.8	22	0.3	10	25
Ba	110	930 [e]	430	500	620	230	860	200	300
Be	0.1	1.5	<0.5	1.4	0.7	1.5	1.9	*	*
Cd	0.3	1.3	0.1	0.01	0.1	0.3	0.03	0.5	15
Co	1.2	7.5	2.3	2.2	0.9	2.2	0.3	15	35
Cr	3.9	50	71	42	9.0	24	25	80	150
Cu	11,000	130,000	19,000	1100	15,000	110,000	720	80	200
Hg	0.1	<0.01	<0.01	<0.04	0.4	<0.01	0.1	0.25	2.5
Mo	0.2	2.4	3.1	0.3	0.3	1.4	0.2	40	100
Nb	0.4	8.8	5.4	9.0	7.0	6.4	5.9	*	*
Ni	3.5	27	21	3.1	2.6	7.9	0.3	40	120
Pb	31	360	61	7.9	39	150	3.2	50	400
S	570	4900	2700	76	510	2400	<50	*	*
Sb	–	6.7	8.9	0.2	–	16	0.1	12	30
Sc	0.6	5.9	<1	7.7	1.2	2.9	1.9	*	*
Sn	–	19	33	–	–	19	–	*	*
Sr	30	230	130	190	95	260	200	*	*
V	6.7	38	12	44	7.0	15	9.7	100	200
W	0.6	<50	<50	1.2	0.6	<50	0.7	*	*
Y	2.3	19	2.9	17	6.9	8.0	5.4	*	*
Zn	44	260	1500	14	36	160	3.5	250	500
Zr	5.7	150	13	230	42	95	113	*	*

[a] [25]; [b] [12]; [c] not analyzed; [d] * no guideline values exist; [e] Italic font; above the Swedish guidelines for less sensitive land use.

(**a**)   (**b**)

Figure 1. Bark samples from (**a**) site A (Köpmannebro); and (**b**) site B (Österbybruk).

The concentrations of carcinogenic PAHs have previously been analyzed in selected spots in sites A and B [26,27]. The PAH pollution was heterogeneous at both sites. The highest presence of PAH at site A, 2.3 and 2.1 mg/kg, could be referred to two specific places; where a fire had taken place and where a small turpentine factory was previously located. At site B the highest contamination, 12 mg/kg, could not be related to any specific activity but in several places where soil samples were taken, an ash like material was present, indicating that a fire could have occurred.

3.2. Optimization of Leaching Parameters

3.2.1. Ash

In theory, a low L/S-ratio is required in order to obtain the most concentrated leachates possible. Initially, L/S = 2 was used for leaching the ash samples but the ratio turned out to be too low as more or less all the leaching agent was absorbed by the solids, making further leaching impossible. Therefore L/S ratios of 5 or 10 were used for further experiments. The L/S-ratio is more important than the leaching time (Figure 2). The Cu leaching was about twice as high when using L/S = 10 compared to L/S = 5, irrespective of leaching time. This is also confirmed by the ANOVA analysis, where the L/S ratio parameter was $p < 0.05$ (Table S2).
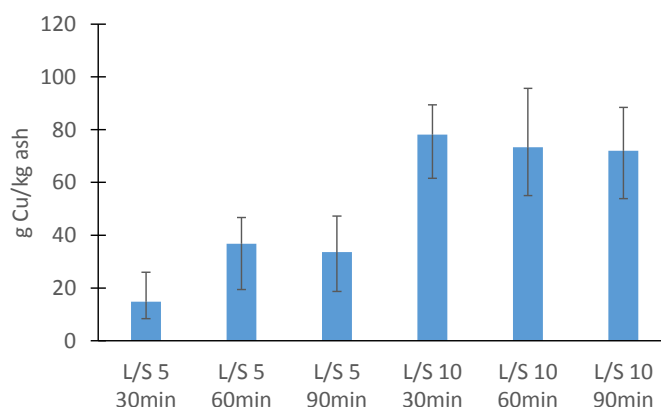

Figure 2. Cu leached from the bark-ash sample A1 with a variation in leaching time (30–90 min) and L/S-ratios (5 and 10). The columns show the average of three replicate tests. The error bars show the maximum and minimum values.

Although Cu release is very efficient when using an L/S ratio of 10, between 1 and 3 wt. % of the Cu initially present in the ash was released in the water washing step following the acidic leaching. This indicates that Cu leaching from the ash residue would exceed the legal limit for depositing it into landfills for hazardous materials (100 mg Cu/kg dry ash), despite the fact that leaching procedures are not totally comparable [28]. Consequently, several leaching steps are required to achieve an acceptable level of Cu leaching and thus a two-step leaching procedure was tested. As expected, most Cu leaching occurred in the first step; on average about 70 wt. % of the Cu, irrespective of leaching time (Figure 3). There was no statistically significant effect of time on Cu leaching (Table S3).
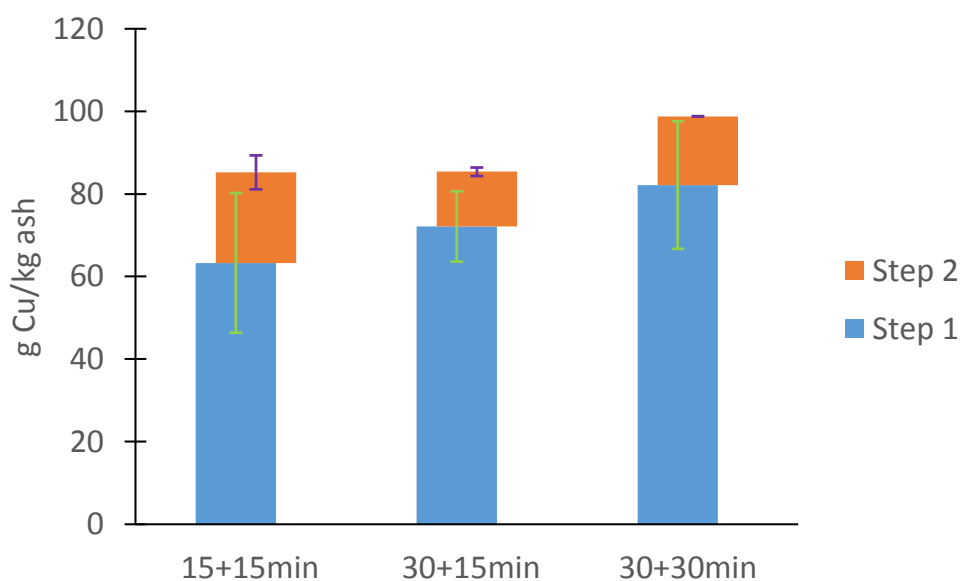

Figure 3. Cu leached from the bark-ash sample A1a using two-step leaching with different leaching times at an L/S ratio of 10. The columns show the average of duplicate tests. The error bars show the maximum and minimum values.

After two 30 min leaching steps and L/S = 10, the Cu release from the ash residue during the water washing step was <100 mg Cu/kg dry ash and thus meets the limit for depositing it into a hazardous waste landfill [28]. Therefore, these leaching parameters were chosen for further investigation, including batch leaching using a larger sample volume.

3.2.2. Soil

For the soil the L/S ratio was also found to be the most important leaching parameter and an L/S = 10 yielded the most efficient Cu leaching irrespective of time (Figure 4 and Table S4). Previous studies have indicated that longer leaching times, *i.e.*, several hours, can increase metal leaching from soils [29,30]. In the present study, the concentration of most metals detected in the leachates (>1 mg/L) after 18 and 24 h was similar to those after shorter periods (Ba, Cu, Mn, Pb and Zn). However, the Al concentration in the leachates was almost twice as high after several hours compared to 30 min leaching. This indicates that the soil matrix to some extent dissolves after several hours leaching, as anorthite was found to be one of the major minerals in soil from site A [12]. In addition, a tendency towards the opposite trend, *i.e.*, lower concentrations in leachates with longer

leaching times, was found for Zn and Pb, indicating precipitation of solid compounds or that the metal ions are adsorbed to active sites in the soil matrix. The latter is most likely in the present case, an effect also demonstrated by others [31,32]. Consequently, the soil can act as a cleaning agent for Zn and Pb ions in the process water.
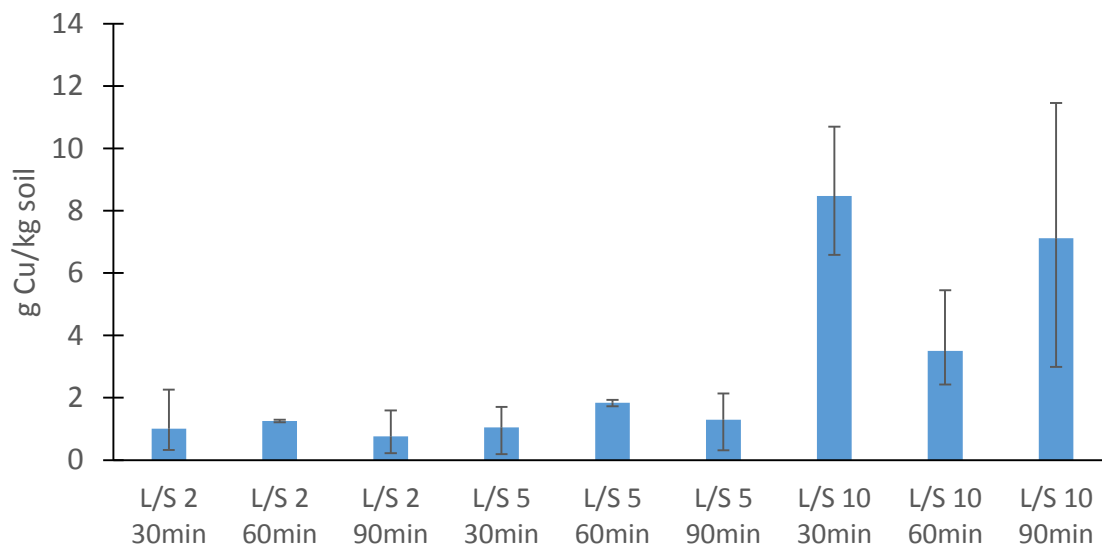

Figure 4. Cu leached from the A2 soil sample at varying leaching times (30–90 min) and L/S-ratios (2, 5 and 10). The columns show the average of three replicate tests. The error bars show the maximum and minimum values.

After one leaching step, <100 mg Cu/kg of dry soil was released in the following washing step, indicating that the soil residues can be deposited in a landfill for hazardous waste after Cu recovery. Consequently, a one-step leaching process with a leaching time of 30 min and an L/S-ratio of 10 was used for the subsequent experiments.

It should be noted that both bark and soil samples were highly heterogeneous. The concentration of Cu differed between locations at the sites and could also differ between subsamples of the collected samples. Therefore, the leached amounts are not directly comparable to the original concentrations shown in Table 1.

3.3. Batch Leaching

Batch leaching experiments were carried out on samples A1a, A2, B1a and B2, in two 30 min steps with an L/S = 10. The concentrations of selected elements in the respective leachates are presented in Table 2. It should be noted that the concentrations include the total Cu present in the leachates, *i.e.*, Cu originally present in the process water, is included (Table S1). Al, Pb and Zn were the only other measured elements present in significant amounts.

Table 2. Concentrations of selected major and minor elements in the final leachates from the ash samples A1a and B1a and from the soil samples A2 and B2. All amounts are in mg/L. Uncertainties in the analyses vary between 25% and 35%. Beryllium, Tl, U and Ag were detected in concentrations of <0.1 mg/L in all leachates.

Element	A1a (Bark Ash) [a]		B1a (Bark Ash) [a]		A2 (Soil) [a]	B2 (Soil) [a]
	Step 1 [b]	Step 2 [c]	Step 1 [b]	Step 2 [c]	Step 1 [b]	Step 1 [b]
			mg/L			
Al	820	340	96	52	150	560
As	0.7	0.3	2.5	0.4	0.2	0.2
Ba	5.2	2.1	1.3	1.5	2.0	1.7
Pb	21	12	11	11	11	9.3
Cd	0.3	0.3	0.3	0.3	0.3	0.3
Co	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cu	3400	2400	8400	1500	120	140
Cr	0.8	0.2	0.1	0.1	0.1	0.1
Li	0.6	0.08	0.06	0.04	0.06	0.0
Mn	20	5.0	6.9	4.5	4.9	5.4
Mo	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
Ni	6.6	2.5	9.4	0.7	0.1	0.1
Se	0.1	<0.1	<0.1	<0.1	0.1	<0.1
Sr	13	2.2	4.3	1.1	0.7	0.6
V	0.7	0.1	0.5	<0.1	0.2	0.1
Zn	430	90	70	60	60	50

[a] L/S = 10; [b] 30 min; [c] 30 min.

Cu leaching from B1a ash was significantly higher in the first compared to the second leaching step, while Cu leaching from A1a ash was more evenly distributed between the two steps; 85/15% and 60/40%, respectively (Table 2 and Figure 5a). This is probably due to the higher initial Cu content at site B but the properties of the original bark and the corresponding ash effect, for instance how strongly Cu is bound into the ash matrix, also play a role. It is noticeable that the A1a leaching fraction for the two steps is more evenly distributed in the batch leaching compared to the previous experiments on smaller amounts (Figures 3 and 5). This is probably due to less efficient contact between liquid and solid in larger sample volumes. Although only about 1% of the total Cu for both ashes was leached during the washing steps, it corresponds to >100 mg Cu/kg dry ash (940 mg Cu/kg and 820 mg Cu/kg dry ash for ash A1a and B1a, respectively). Consequently, leaching and washing are less effective when larger amounts of ash and process water are used. The reasons for this could be inefficient mixing or that Cu ions are temporarily adsorbed into the pore water of the particles during centrifugation and released in the following washing step instead of during leaching. In the soils, about 5% of the leached Cu was released in the washing step for both samples (Figure 5b), which corresponds to <100 mg Cu/kg dry soil, *i.e.*, below the legal limit.

As the batch leachates from A1a were more complex than those from B1a due to higher concentrations of most elements, the former were chosen for the electrolysis experiments.
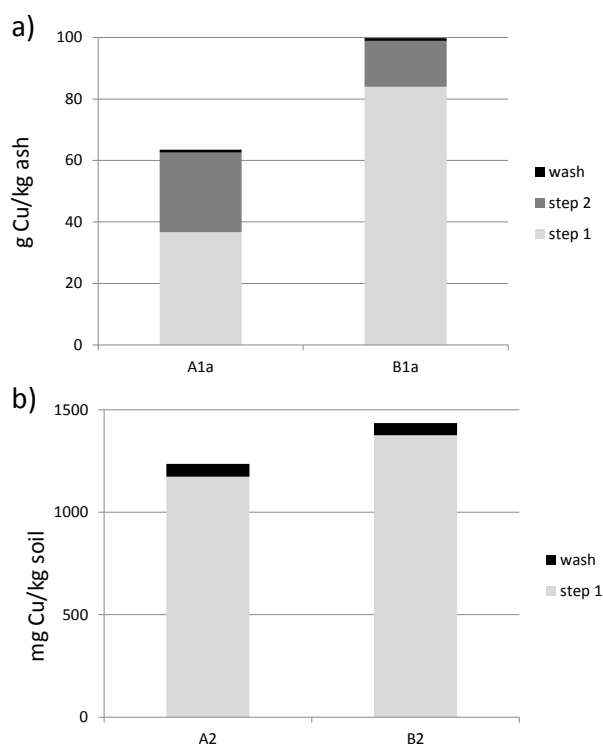
Figure 5. Amounts of Cu leached in steps 1 and 2, each 30 min, L/S = 10, followed by a washing step for (**a**) the A1a and B1a ashes; and (**b**) the A2 and B2 soils. The amounts are shown in (**a**) g Cu/kg dry ash; and (**b**) mg Cu/kg dry soil. Uncertainties in the analyses vary between 25% and 35%.

3.4. Cu Recovery Using BES

The BES was operated as a microbial fuel cell with either a 100 Ω (Ohm) or 1000 Ω resistor connected between the anode and cathode. This means that current flowed spontaneously in the reactor and no electrical energy input was needed to drive Cu reduction. After four weeks of acclimatization with a copper-containing salt solution as a catholyte, four experimental runs were carried out on real leachates. The anode of the microbial fuel cell contained 132–158 mg C/L of glucose during the experimental runs, thus the anode performance was not limited by substrate availability. Instead, the aim was to investigate the purity of the recovered Cu in the microbial fuel cell and the efficiency of Cu extraction from the A1a leachates.

A summary of the results obtained with the microbial fuel cell is presented in Table 3. In addition to Cu, As, Pb, Cd, Co, Cr, Ni, V and Zn were analyzed in the leachate. Cu made up approximately 90% of the total metal content, Zn accounted for 9.4% and Pb for 0.4%. The other metals were present in much lower concentrations. In the metal deposits recovered from the cathode, Cu made up 99.7%–99.9% of the total metal content, Zn 0.1%–0.3% and Pb 0.01%–0.03% except in Run 4 when it constituted 0.2%. This demonstrates that Cu can be selectively extracted from the leachate with only minor contamination from other metals. It is unlikely that Zn will be spontaneously reduced on the cathode in a microbial fuel cell and its presence is likely due to salt deposits or small drops of catholyte remaining on the cathode when it was removed for sampling.

Operation of the microbial fuel cells at lower resistance led to a higher current and more rapid reduction of Cu. At 100 Ω, the maximum current was 141.3 A/m^3 (catholyte volume) and at 1000 Ω 37.5 A/m^3. The currents correspond to Cu recovery rates of 167.5 and 14.0 g Cu/m^3/h, respectively, at 100% cathode efficiency. Based on the charge transfer in the microbial fuel cell, the theoretical amount of Cu reduction can be calculated for each run and compared to the actual removal of Cu from the catholyte as well as the amount recovered on the cathode surface (Table 3). Of the Cu removed from the catholyte solution, 58%–85% was recovered from the cathode surface. The remaining fraction could have been lost during sampling as not all Cu bound strongly to the cathode surface. Of the theoretical Cu reduction based on charge transfer, 73%–116% could be accounted for by the removal of Cu^{2+} ions in the catholyte. A value above 100% could mean that Cu$_2$O was formed, which only requires one electron per Cu, or precipitation of non-reduced Cu as brochantite (CuSO$_4$·3Cu(OH)$_2$) [20]. A value below 100% could indicate that oxygen on the cathode was also reduced. Of the original amount of Cu present in the catholyte, 20%–23% (at 1000 Ω resistor) and 64%–79% (at 100 Ω) were recovered on the cathode surface. Higher recovery efficiencies could probably be achieved with longer reaction times. Based on the measured current densities, the highest rate of Cu reduction that could have been obtained in this reactor was 167.5 g/m^3/h (normalized to catholyte volume). A higher reduction rate could potentially be achieved by increasing the cathode surface area per unit volume as this reactor only had 14 m^2/m^3. As the reactor was operated as a microbial fuel cell, electrical power was generated during Cu reduction. The power output ranged from 0.09–0.11 kWh/kgCu in Runs 2 and 4 (100 Ω) to 0.32–0.50 kWh/kgCu in Runs 1 and 3 (1000 Ω).

The A1a leachate was a mixture of two leaching steps. From a Cu recovery perspective, it might be more efficient to only recover Cu from the leachate with the highest Cu concentration in order to speed up the process. On the other hand, from a remediation perspective, two leaching steps are needed to release most of the Cu, which means that the less concentrated leachate still has to be taken care of, while failure to recover Cu from both steps implies that valuable Cu is lost. However, this has to be decided on a site-to-site basis, depending on the amount of Cu available and its distribution between leaching steps.

Table 3. Cu recovery from leachate in the microbial fuel cell.

Run	Duration (h)	Resistor (Ω)	Final Cu Conc. [a] (mg/L)	Theoretical Cu Recovery [b] (mg)	Cu removal from Catholyte (mg)	Measured Cu Recovery (mg)	Measured Cu Recovery [c] (%)
1	19	1000	1500	6.4	7.4	4.9	23
2	29	100	420	21	17	13	64
3	22	1000	1500	8.1	7.2	4.2	20
4	72	100	160	27	20	17	79

[a] Final Cu concentration in catholyte. The initial concentration in all runs was 2300 mg/L. This is slightly lower than the Cu concentrations measured in A1a leachate immediately after leaching (Table 2), possibly because of precipitation during storage; [b] Calculated based on charge transfer in BES; [c] Fraction of Cu recovered from the original amount in the leachate.

3.5. Characterization of Leached Soil Samples

3.5.1. Metal Content

The content of major and minor elements in the leaching residues from site A (A1a leached for 30 × 2 min and water washed for 5 min; A2 leached for 30 min) (L/S = 10), was analyzed (Table 4). Please note that the A2 residue was not washed in water after the acidic leaching and prior to metal content analyses. Apart from Cu, most elements in the solids were comparable before and after leaching. Despite the fact that the Cu leaching was efficient (>80%) in both samples, the Cu content in the ash greatly exceeded the MKM limit, which is why it has to be landfilled. However, as the Cu leaching in the EN 12457-3 test exceeded the limit for deposition in hazardous landfill, it cannot be landfilled directly (Figure 6b). The A2 soil residue was in the range of the MKM limits even without water washing and can plausibly be put back into the remediated site (Table 4). However, the Ba and Hg content in the residue exceeded the MKM limits. Barium was high in the original soil and the leaching potential low (Table 1 and Figure 6b). It is probably present as low soluble $BaSO_4$. Mercury was only identified in low concentrations in the original soil samples (Table 1). However, it is probably present in the process water and adsorbed onto the soil particles during leaching, despite the fact that the pH is acidic. Less than 0.5 mg·Hg/L in the process water can account for this phenomenon and as process water is a waste product from flue gas cleaning after waste incineration, it possibly contains such concentrations. If using this kind of leaching agent for soil remediation, it will probably require purification from Hg before utilization. Nevertheless, no water washing steps were used here; by using washing, the Hg content in the residues might fall below the MKM limit.
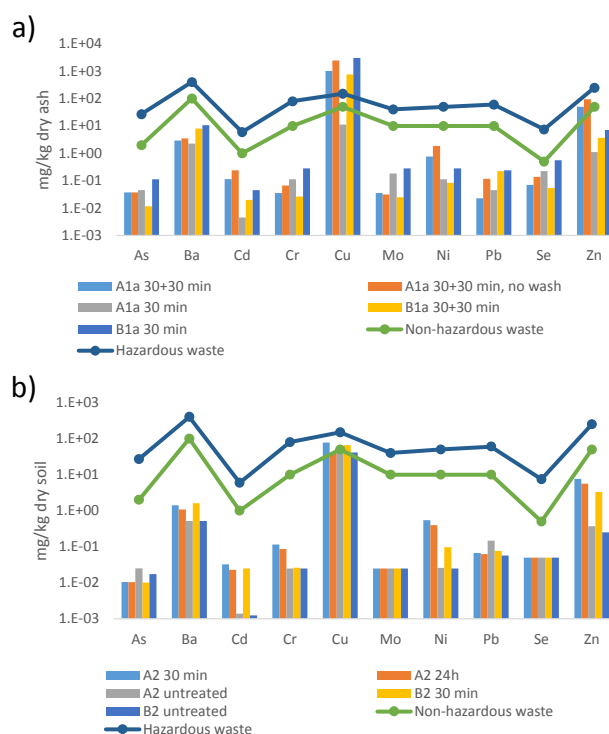

Figure 6. Metal release in the EN-12457-3 leaching test compared to the limit values for acceptance in non-hazardous and hazardous waste landfills: (**a**) treated ash samples A1a and B1a; and (**b**) original and treated soil samples A2 and B2.

The soil matrixes were stable against leaching; <5 wt. % was dissolved during leaching, while the ashes were dissolved to a greater extent. About 10 wt. % of the B1a sample was dissolved after leaching in two steps compared to 50 wt. % of the A1a sample. This difference is probably due to the presence of soil particles in the B1 sample as discussed above (Section 3.1.).

Table 4. Total amounts of selected major (calculated as oxides) and minor elements in the A1a (bark ash) and A2 (soil) residues after leaching experiments. Please note that the A2 residue was not washed in water after the acidic leaching. Uncertainties in the analyses vary between 20% and 25%.

Element	A1a Bark Ash Residue	A2 Soil Residue
	wt. % DS	
SiO_2	54	71
Al_2O_3	12	11
CaO	1.0	1.9
Fe_2O_3	5.6	2.2
K_2O	4.6	2.4
MgO	0.8	0.5
MnO	<0.1	<0.1
Na_2O	1.8	2.6
P_2O_5	1.1	<0.1
TiO_2	8.1	0.6
	mg/kg DS	
As	<6	0.8
Ba	2200	450
Be	1.9	1.3
Cd	0.7	0.1
Co	7.2	1.7
Cr	220	20
Cu	10,000	210
Hg	68	3.6
Mo	4.2	0.4
Nb	34	8.5
Ni	66	3.9
Pb	370	8.4
S	900	220
Sb	64	2.7
Sc	7.2	7.5
Sn	180	2.5
Sr	82	180
V	37	41
W	<50	1.1
Y	10	14
Zn	1000	28
Zr	140	220

3.5.2. Metal Leaching

With the exception of Cu, the leaching of all elements in the original and leached soil samples A2 and B2 was below the limits for acceptance on landfills for non-hazardous waste (Figure 6). Most elements (As, Ba, Cd, Cr, Mo and Se) also met the requirements for acceptance in an inert landfill. However, the leaching of Ba, Cd, Cr, Cu, Ni and Zn was higher from the leached soil compared to the original sample, which is most probably due to the fact that previously encapsulated metal compounds are released when the soil matrix is affected by the acid. Consequently, in this particular case, soil washing to minimize the risk of leaching is not beneficial and the total amount of a specific element is not correlated with the risk of leaching. This was also seen for the ash samples where all elements except Cu and Zn were below the non-hazardous waste limit (As, Ba, Cr and Mo were also below the inert waste limits), irrespective of the higher initial total amounts. There is no general trend as to whether a two-step acid leaching process reduces metal leaching to a greater extent in a subsequent EN-test than a one-step leaching procedure. However, water washing after leaching seems to decrease metal release during the EN-test, even if the washing period is as short as 5 min. This is probably caused by metal ions that were easily adsorbed to the ash particles being released to the first water in contact with these solids. The results also indicate that a higher L/S-ratio during the water washing step might further decrease leaching in the EN-test.

3.5.3. PAHs and Oxy-PAHs Content

The concentration of each specific PAH in the spiked soil varied from 0.25 mg/kg (DS) to 4.4 mg/kg (DS) in the unleached sample. In this sample the low-molecular weight PAH-L, *i.e.*, the sum of naphthalene, acenapthylene and acenapthene, was 10 mg/kg (DS), the mean-molecular weight PAH-M, *i.e.*, the sum of fluorene, phenanthrene, anthracene, fluoranthene and pyrene, was 2.0 mg/kg (DS) and the high-molecular weight PAH-H, *i.e.*, the sum of benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[ah]anthracene, benzo[ghi]perylene and indeno[123cd]pyrene, was 2.8 mg/kg (DS), see Figure 7. These concentrations are in the ranges of the generic Swedish guideline values for sensitive and less sensitive land use [33]. Two of the nine oxy-PAHs analyzed were also identified in this unleached sample: 9-fluorenone 0.14 mg/kg (DS), a degradation product of fluorene, and 9,10-anthraquinone 0.15 mg/kg (DS), a degradation product of anthracene, indicating that PAH oxidation may occur during storage of the spiked soil sample. This could occur, e.g., because of aerobic bacterial degradation [15] or biocatalytic activity of fungi in the soil [16]. However, it cannot be ruled out that oxy-PAHs were already present in the original samples. The calculated ratios of the sum of oxy-PAH-9/PAH-16 are 0.04, for 9-fluorenone/fluorene 0.2 and for 9,10-anthraquinone/anthracene 0.6. These ratios are much lower than reported from other sites contaminated by PAHs [16,34].

After acidic washing, the concentration of each specific PAH in the treated soil was lower and varied from 0.19 to 2.5 mg/kg (DS). These concentrations are below the guideline value for less sensitive land use, but not low enough to qualify for sensitive land use [33]. For PAH-L, the concentrations were 1.6 times lower, for PAH-M 1.3 and PAH-L 1.2 times lower, compared to the concentrations before soil washing. In the resulting leachate, the concentration of each specific

PAH varied from 0.17 to 16 µg/L. From calculations of the relative compositions of the PAHs in the soil before and after acidic washing, and in the acidic leachates, no signs of PAH degradation or volatilization could be found. If degradation had occurred, the most volatile and water-soluble PAH-L would disappear first causing a decrease in HMW/LMW PAH ratios [35,36]. None of the oxy-PAHs were found after leaching, neither in the residual soil nor in the leachate, indicating that acidic leaching may accelerate the degradation of oxy-PAHs. This may be caused by enhanced leaching of the oxy-PAHs into the water phase, *i.e.*, more exposed for degradation, caused by weathering and degradation of the soil matrix under the strong acidic washing.
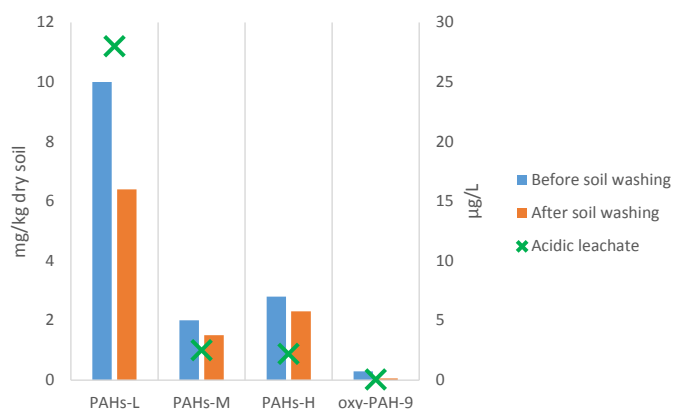

Figure 7. Concentrations of PAHs and oxy-PAHs analyzed in the A1 spiked soil sample before and after acidic washing (mg/kg), and the concentrations in the corresponding acidic leachate (µg/L).

In the leachate water, relatively more water soluble PAH-L occurred, indicating that the transport of the most water soluble PAHs into the acidic water was high. However, this transport to the water phase is expected to be very low and should not be pH dependent, but may follow the humic and fulvic acids released from the soil during mixing with acidic water. In a recent study of the distribution of organic pollutants in dissolved, colloidal and particulate form, relatively high PAH-L concentrations were detected in both the dissolved and the colloidal phases [37]. The results also suggested that dissolved organic carbon (DOC) colloids were carriers of pollutants in the colloidal phase [37,38]. PAHs are also assumed to be sorbed to Fe minerals such as goethite [39]. Iron was released during the acidic leaching (Tables 1 and 4) and in a previous study on site A, Fe minerals were identified in original soil samples but not in the acid leached residues [12]. Organic matter is known to be sorbed to iron oxides in soils [40], and therefore it is expected that the dissolution of iron oxide enhance the solubilization of DOC, and therefore could explain why PAHs are solubilized. The release of Fe minerals followed by an enhanced release of DOC can thus be important factors in the PAH leaching under strong acidic conditions. The leaching and degradation of PAHs in soils from contaminated sites may be improved by addition of a strong oxidant to achieve a Fenton-like oxidation [41], electrochemical degradation [42] or by a combination of the two techniques [43]. The addition of a strong oxidant could also affect the Cu leachability, which is something that should be studied further if this technique is used to remove PAHs.

4. Conclusions

In this study, a lab-scale method to release and recover Cu from contaminated soils has been developed and discussed. Acidic wastewater was used as a leaching agent. In a one- or two-step (depending on soil material) acidic leaching process followed by a water washing step, >80 wt. % of the Cu was leached. Although the Cu leaching efficiency was high, none of the samples are below the guidelines for less sensitive land use (MKM) or the limit values for acceptance in non-hazardous and hazardous waste landfills. Consequently, improvement of the final washing step is needed. Copper (99.7–99.9 wt. % purity) was recovered from the acidic leachates of one of the samples (A1a) using a BES operated as a microbial fuel cell. Electric power was generated, while Cu was reduced and recovered on the cathode surface. Although microbial fuel cells have been previously operated with Cu-containing catholytes, this was the first study to demonstrate recovery of high purity Cu from real soil leachate. According to predictions, there are about 30 tons of Cu in site A. Based on the results of this lab scale study, about 20 tons could potentially be recovered, corresponding to a value of approximately one million SEK (~100,000 euro). A limitation of the proposed method in full scale is the supply of acidic wastewater. Some pre-treatment is necessary in order to reduce the quantity of soil for washing. For example, physical soil washing, e.g., sieving, can concentrate the polluted material into smaller particle sizes, which efficiently reduces the amounts that require acidic washing. This study also revealed that acidic water is a good leaching agent for all PAHs; especially those with low-molecular weight. There are also indications that oxy-PAHs are fully degraded by acidic soil washing. PAH leaching mechanisms are not fully understood and the soil washing method needs to be further developed to increase efficiency.

Author Contributions

K.K.F., O.M. and A.M.S. together conceived and designed the experiments; performed the experiments; analyzed the data; and wrote the paper. K.K.F. coordinated the work.

Conflicts of Interest

The authors declare no conflict of interest.

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