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EXTRACTION OF HEAVY METALS FROM CCA CONTAMINATED SOIL USING BIO-DEGRADABLE CHELATING ORGANIC ACIDS

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ABSTRACT

This study examined the efficiency of biodegradable chelating organic acids; oxalic acid and malonic acid enhanced extraction for the remediation of soil sample taken from an active wood preservation site in Benin City containing elevated levels of As ($39.55 \pm 0.21 mg.kg^{-1}$), Cr ($313.97 \pm 1.00 mg.kg^{-1}$) and Cu ($200.00 \pm 0.14 mg.kg^{-1}$). Sequential extraction procedures used to assess the distribution of the metal forms in the soil showed that As was predominantly associated as mobile pools; 28% exchangeable, 16% carbonate bound and 14% water soluble, whereas Cr and Cu were mainly associated as non-labile pools; 61% and 57% respectively in the residual fraction, and 14% and 19% respectively in the organic bound fraction of the soil. Batch extraction (washings) experiments were carried out on 1g portions of the contaminated soil using constant soil:liquid ratio of 1:25 and concentration of extracting solution (0.05M) for various (2, 4 and 6hr) contact periods. Extraction efficiency increased with contact time but were generally ineffective in reducing the environmental burden of the metals, was generally higher for malonic acid than oxalic acid and was of the order Cu > Cr >As. It was found that the mobile metal pools in the post-chelate extracted soils was markedly higher for Cr and Cu than in the unwashed soil sample and suggested that extraction of labile metal pools occurred simultaneously with dissolution and re-distribution of the non-labile residual fractions among the operationally defined mobile metals pools.

Keywords: Soil contamination, Heavy metals, Washing, Organic acids

INTRODUCTION

Contamination of soil and sediment with organic and inorganic pollutants is a by-product of industrialization and urbanization. Although a small proportion of heavy metals in soils is derived from natural processes, a much higher proportion originates from anthropogenic sources such as mining and smelting industry, use of mineral fertilizers and pesticides, sewage sludge and animal husbandry manure application, etc (Bolan *et al.*, 2004). Unlike organic contaminants, heavy metals do not undergo microbial or chemical degradation and therefore total concentrations and ecotoxicological effects persist for very long periods after their introduction to the soil (Zhou and Haynes, 2010). Remediation of metal contaminated soils is geared towards achieving three broad objectives: reduce metal leaching, reduce metal bioavailability to human and ecological receptors, and re-establish vegetation.

Soil washing is a viable treatment option for metal contaminated sites. In *ex situ* soil washing technology, undesirable contaminants in soil are removed by dissolving or suspending then in a washing solution. In the case of heavy metals contaminated soil, the washing solution is generally an aqueous solution of chelating agent. The advantages of using chelating agents in soil washing are high efficiency of metal extraction, high thermodynamic stabilities of the metal complexes formed, good solubilities of metal complexes and normally low adsorption of chelating agents and their metal complexes on soils (Fischer *et al.*, 1998).

The objective of this study is to assess the effectiveness of organic chelating acids; oxalic acid and malonic acid to clean-up soil from an active wood contaminated site containing elevated levels of As, Cr and Cu. Oxalic acid ($C_2H_4O_4$, m.p. 189°C; pka_1 1.46; $pka_2$4.40) and malonic acid ($C_3H_4O_4$, m.p. 135°C, pka$_1$ 2.80, pka$_2$5.85) are naturally occurring and therefore biodegradable crystalline solids. Application of these low molecular weight chelating organic acids in the remediation of contaminated soil is considered environmentally benign in contrast to treatment of contaminated soils with strong acids and non-biodegradable polyaminocarboxylic acids.

MATERIALS AND METHODS

The study soil was composited from subsurface (0-10cm) samples collected from ten randomly selected locations within the wood preservation site. The soil was air-dried and sieved (< 2nm) prior to use. Table 1 summarizes the geochemical properties and total levels of As, Cr and Cu in the test soil. Particle size analysis on the soils was carried out using the method described by Bouyoucos (Bouyoucos, 1962; Day, 1965; Asagba, 2007). The soil pH was determined using a 1:2 soil weight/water volume ratio (Folsom, 1981) by a Suntex digital pH-meter. The Cation Exchange Capacity (CEC) was determined by the buffered ammonium acetate method (Thomas, 1982). CEC estimated by summing the exchangeable cations (Na^+ and K^+, determined by flame photometric method and Ca^{2+} and Mg^{2+} determined by Buck scientific atomic absorption spectrophotometer). Total organic carbon was determined by the Walkley-Black rapid oxidation method (Nelson and Sommers, 1982). In order to ensure the accuracy and reliability of results, analytical grades (BDH or Sigma) reagents were used in preparing standard solutions and analysis. All glasses and plastic were acid-washed. Buck scientific standard solutions were used to calibrate the Atomic Absorption Spectrophotometer. Procedural blank samples were subjected to similar extraction method using the same amounts of reagents. The analyses were carried out in triplicates (Uwumarongie *et al.*, 2008).

Table 1: Geochemical properties of CCA contaminated soil

pH (1:1 soil:water)	5.91 ± 0.19
Electrical conductivity (µs.cm^{-1})	0.011 ± 0.01
K (meq/100g)	0.20 ± 0. 01
Na (meq/100g)	0.07 ± 0. 01
Mg (meq/100g)	19.17 ± 0.05
Ca (meq/100g)	28.40 ± 0.40
Clay (%)	26.08 ± 0.50
Sand (%)	71.62 ± 1.00
Silt (%)	2.30 ± 0.04
P (mg/kg)	46.78 ± 0.70
CEC (meq/100g)	47.84 ± 0.10
As (mg.kg^{-1})	39.55 ± 0.21
Cr (mg.kg^{-1})	313.97 ± 1.00
Cu (mg.kg^{-1})	200.00 ± 0.14

Heavy metal fractionation in the soil sample

The heavy metal fractionation in the contaminated soil sample was determined using the sequential extraction procedure described by Salbu and Oughton (1998). The protocol for the sequential extraction procedure employed in this study is given in Table 2. The protocol operationally defined the heavy metal distribution in the contaminated soil into the following fractions: F_1, water soluble, F_2, exchangeable; F_3, carbonate bound; F_4, Fe-Mn oxides bound (reducible); F_5, organic matter bound (oxidisable) and R, residual fractions. The results given in Table 2 indicate that As was predominantly bound to the exchangeable fraction (11.0 ± 0.1 mg.kg^{-1}; 28.28 %) and could be the most mobile among the three metals. Although the contaminated soil contained the highest level of Cr (313.97 ± 1.00 mg.kg^{-1}) it was mostly associated with the organic matter (14.98 %) and residual (61.78 %) fractions of the soil, while the proportions of Cu within the intransigent soil phases were 14.03 % reducible, 19.54 % oxidisable and 57.17 % residual fractions of the soil. Based on the fractionation data of the heavy metals, the mobility or lability of the three metals followed the sequence As > Cr > Cu.

Table 2: Fractionation of As, Cr and Cu in CCA contaminated soil sample

Fractions	Extraction method and condition	As (%)	Cr (%)	Cu (%)
F_1 Water-soluble	Distilled water 1hr	14.91	17.83	0.83
F_2 Exchangeable	1M NH_4OAc (pH 7), 2hr	28.28	7.66	1.56
F_3 Carbonate bound	1M NH_4OAc (pH 5), 2hr	16.45	6.36	6.86
F_4 Fe-Mn oxides – bound (Reducible)	0.04M $NH_2OH.HCl$, 6hr at 60°C	11.83	3.35	14.03
F_5 Organic matter - bound (oxidisable)	30% H_2O_2 (pH 2), 5.5hr 80°C + 3.2M NH_4OAc, 30min	4.11	14.98	19.54
R Residual	Conc. HNO_3, 6hr	24.42	61.78	57.17

Heavy metal extractions with chelating agents

Batch extractions of heavy metal contaminants were carried out with 0.05 M aqueous solutions of oxalic acid and malonic acid following the procedure reported by Khodadoust *et al*. (2008) using a soil : liquid ratio of 1: 25. One gram of the contaminated soil sample was placed in a 50mL flask and 25mL of the extracting solution were added and the flask was sealed with a Teflon cork. The flask was shaken by hand for about a minute to ensure full saturation of the soil with solution and then the flask was shaken on a multipurpose flask shaker (model TT12F, Techmel & Techmel, US) for various periods of time (2, 4 and 6h). The resulting slurry was centrifuged at 2000 rpm using a digitally operated high speed centrifuge (model TGL 16 G). The supernatant was carefully decanted through a glass funnel.

The amounts of As, Cr and Cu in the filtrate and residue (air-dried to touch and then oven-dried at 70°C for 8h) were determined by AAS (Buck Scientific; model VGP210) using oxy-acetylene gas. Duplicate, blank and reagent determinations were carried out as part of quality control/assurance measures.

Post-extractive decontaminated redistribution of metals in soil

To investigate the redistribution of mobilized metals in the decontaminated soil, the sequential extraction protocol described above for the untreated soil was carried out on the chelating agent-washed soil samples.

RESULTS AND DISCUSSION

Contamination status of soil.

The pseudo-total levels of As, Cr and Cu given in Table 1 were used to estimate their intervention levels in the contaminated soil via the Department of Petroleum Resources method (DPR, 2002) which considers the organic matter and clay contents of the soil. Intervention levels of metal contaminant in soil give indications of the quality for which the functionality of the soil for human, animal and plant life is considered to be impaired. The intervention levels of As, Cr and Cu in the contaminated soil are given in Table 3. The results show that the pseudo-total levels of As, Cr and Cu are markedly higher than the intervention values and these values correspond to moderate (with respect to As) and high (with respect to Cr and Cu) levels of contamination of the soil (Hakanson, 1980). The contamination factor, C_f, a ratio of metal concentration in the contaminated soil to that in uncontaminated soil, degree of contamination, C_D, and the contamination/pollution index, C/P index, given as the ratio of metal concentration in contaminated soil to statutory target values of the metals (M_{contam}/M_{Target}) also given in Table 3, suggest that the soil from the wood preservation site may be classified as slightly contaminated with respect to As, moderately polluted with respect to Cr, and severely polluted with respect to Cu (Hakanson, 1980).

Table 3: Contaminated status of soil sample from active wood treatment site

Metal	Intervention values (mg.kg^{-1})	Contamination factor (M_{contam}/M_{ref})	Contamination/Pollution index (M_{Target})
As	8.81 ± 1.26	90.57^a; 21.13^b	1.09
Cr	90.52 ± 9.28	689.71^a; 2.41^b	2.41
Cu	76.51 ± 6.08	16.09^a; 3.06	4.25
C_D = degree of contamination = $\sum C_f$		796.39^a; 26.60^b	

$C_f = M_{contam}/M_{ref}$; a is with reference to control soil sample (0.35mg.kg^{-1} As, 0.35mg.kg^{-1} Cr and 9.50mg.kg^{-1} Cu) and b is with reference to uncontaminated soil (1.50mg.kg^{-1} As, 100.0mg.kg^{-1} Cr and 50.0mg.kg^{-1} Cu [12], M_{Target}; As = 29.00mg.kg^{-1}, Cr= 100.00 mg.kg^{-1}, Cu = 36.00 mg.kg^{-1})

Extraction efficiency of chelating organic acids

Table 4 gives the residual amounts of As, Cr and Cu removed from the contaminated soil by aqueous solutions of oxalic and malonic acids, together with the corresponding extraction efficiencies. The results showed that extraction efficiency increased with contact time and was generally about the same order of magnitude but tended to be higher for extractions with malonic acid that with oxalic acid. The efficiency of a chelating agent in the extraction of metals is usually related to the stability constant of the chelant-metal complexes. According to Schowanek *et al.* (1997), complexing agents can be divided into three categories depending on their complex formation constants: weak (e.g. zeolites polycarboxylates), moderate and high (e.g. ethylenediaminetetraacetic acid). Oxalic acid and malonic acid can both be classified as weak complexing agents and the observed extraction efficiencies (Table 4) suggest that soil washing with organic chelating agents provides an environmentally benign remediation technology for metal contaminated soil.

Table 4: Extractive decontamination of CCA contaminated soil with aqueous solutions of oxalic and malonic acids

Duration of extraction (hr)	Extraction with oxalic acid			Extraction with malonic acid		
	Amount of metal removed (mg.kg^{-1})			Amount of metal removed (mg.kg^{-1})		
	As	Cr	Cu	As	Cr	Cu
2	1.22±0.04 (3.08%)	5.92±0.31 (1.88%)	12.47±0.86 (6.24%)	1.23±0.02 (3.11%)	6.75±0.038 (2.15%)	23.67±0.64 (11.84%)
4	6.25±0.12 (15.80%)	72.71±1.06 (23.16%)	63.30±1.24 (31.65%)	7.68±0.16 (19.42%)	105.03±1.22 (33.45%)	83.00±1.64 (41.50%)
6	11.53±0.41 (29.15%)	112.27±2.01 (35.76%)	67.00±1.68 (33.50%)	12.95±0.46 (32.74%)	135.10±2.01 (43.03%)	95.40±2.06 (47.70%)

Table 5 provides a comparison of the residual amounts of As, Cr and Cu in the contaminated soil after extraction with oxalic and malonic acids with the statutory target values provided in national regulatory guidelines and standards (DPR, 2002). The results in Table 5 suggest that although extraction with aqueous oxalic acid and malonic acid solution for up to 6hr markedly alleviated the environmental risk presented by the elevated levels of As, Cr and Cu in the soil and improving the quality profile of the soil, it did not provide remediation endpoint, particularly with regards to residual levels Cr and Cu, sufficient to meet national regulatory limits.

Table 5: Comparison of residual amounts of As, Cr and Cu in oxalic acid- and malonic acid-extracted soil with Statutory Target values (M$_{Target}$). Contact time 6hr

Metal	M$_{Target}$ (mg.kg^{-1})	Residual amount in organic acid extracted soil (mg.kg^{-1})	
		Oxalic acid	Malonic acid
As	29.00	28.02±0.81	26.60±0.66
Cr	100.00	201.70±2.14	178.87±1.22
Cu	36.00	133.00±2.41	104.60±1.38

Post-extraction redistribution of metals in soil

A major concern in chelant-assisted soil washing of contaminated soil is the relative proportion of mobilized pools of metals that are not extracted from the soil. Prolonged mobilization of heavy metals may result ultimately in groundwater pollution. To examine the redistribution of metals among the operationally defined pools in the extracted soil samples, sequential extraction procedures were applied. The redistribution patterns of As, Cr and Cu are given in Tables 6 and 7 for oxalic acid- and malonic acid-extracted soil samples respectively.

Table 6: As, Cr and Cu extraction yields (mg.kg^{-1}) and standard deviation (n=3) for oxalic acid washing of CCA contaminated soil for 2hrs

Fractions	Extraction yields of metals (mg.kg^{-1})		
	As	Cr	Cu
F$_1$ Water-soluble	4.49±0.01; 3.85±0.06[a] (2.21±0.10)	11.59±1.11; 15.83±1.17[a] (14.54±0.91)	20.53±0.55; 14.81±1.00[a] (13.88±0.56)
F$_2$ Exchangeable	13.56±0.08; 12.55±0.70[a] (11.33±0.10)	31.81±2.69; 31.65±0.59[a] (26.06±0.45)	20.81±0.04; 16.81±1.00[a] (16.24±0.23)
F$_3$ Carbonate bound	6.02±0.17; 4.19±0.40[a] (3.08±0.40)	28.13±0.51; 27.66±2.90[a] (21.99±0.91)	25.81±0.04; 20.63±0.40[a] (19.41±0.21)
F$_4$ Reducible	3.50±0.10; 2.71±0.01[a] (2.66±0.06)	10.28±0.48; 9.03±0.86[a] (8.37±1.36)	25.65±0.98; 21.11±0.42[a] (18.53±0.98)
F$_5$ Oxidisable	1.68±0.40; 1.62±0.01[a] (1.50±0.10)	40.71±2.13; 39.42±0.72[a] (37.26±0.89)	28.63±0.51; 22.42±0.86[a] (21.70±0.14)
R Residual	8.58±0.11; 7.56±0.07[a] (6.83±0.10)	176.67±1.02; 109.26±1.66[a] (87.12±3.03)	59.20±0.34; 40.00±0.82[a] (39.74±0.95)
Σ (Sum of fractions)	37.83±0.16; 32.48±0.04[a] (27.61±0.40)	304.17±0.97; 232.85±0.81[a] (195.33±3.01)	180.63±0.96; 135.78±0.91[a] (129.50±0.49)
Pseudo-total	38.33±0.01; 33.30±0.01[a] (28.02±0.01)	308.05±0.01; 241.26±0.04[a] (201.70±0.01)	187.53±0.66; 136.70±0.01[a] (133.00±0.10)

a= contact time of 4hr
Values in parentheses are for contact time of 6hr

Table 7: As, Cr and Cu extraction yields (mg.kg^{-1}) and standard deviation (n=3) for malonic acid washing of CCA contaminated soil for 2hrs

Fractions	Extraction yields of metals (mg.kg^{-1})		
	As	Cr	Cu
F$_1$ Water-soluble	4.40±0.01; 3.23±0.40[a] (1.80±0.01)	17.29±1.83; 15.31±0.10[a] (14.24±0.54)	18.06±0.01; 13.30±0.42[a] (13.00±0.10)
F$_2$ Exchangeable	13.90±0.14; 12.52±0.20[a] (11.00±0.01)	30.35±1.30; 27.46±0.11[a] (27.02±0.38)	20.50±0.10; 11.53±0.13[a] (14.07±0.13)
F$_3$ Carbonate bound	5.90±0.06; 4.10±0.10[a] (3.04±0.01)	28.38±0.50; 24.22±0.18[a] (23.78±0.26)	24.63±0.10; 20.99±0.13[a] (11.88±0.10)
F$_4$ Reducible	3.43±0.06; 2.65±0.60[a] (2.51±0.06)	9.95±0.33; 8.69±0.38[a] (8.02±0.14)	25.51±0.31; 14.00±0.10[a] (13.31±0.25)
F$_5$ Oxidisable	1.60±0.14; 1.52±0.40[a] (1.49±0.10)	45.54±0.23; 132.96±0.88[a] (37.26±0.89)	26.52±0.40; 15.08±0.88[a] (14.98±0.10)
R Residual	8.47±0.14; 6.92±0.11[a] (5.49±0.10)	170.80±1.13; 87.82±0.35[a] (69.79±0.27)	59.20±0.16; 34.10±0.38[a] (29.82±0.36)
Σ (Sum of fractions)	37.70±0.40; 30.94±0.50[a] (25.33±0.33)	302.28±3.02; 186.02±2.8[a] (17449±1.35)	174.42±1.75; 111.10±4.28[a] (101.87±2.36)
Pseudo-total	38.32±0.45; 31.87±0.01[a] (26.60±0.01)	307.22±0.31; 191.05±1.34[a] (178.87±0.01)	176.33±0.01; 117.00±1.41[a] (104.60±0.01)

a= contact time of 4hr
Values in parentheses are for contact time of 6hr

The redistribution patterns of As, Cr and Cu in the chelant-extracted soil samples are constituent with the suggestion that extraction of non-residual, labile pools of metals and dissolution of non-labile residual pools occurred simultaneously. It would appear that a large proportion of the residual metal pools solubilized by the chelant washing solutions were distributed among the labile pools, predominantly as exchangeable and carbonate-bound. Redistribution of non-labile pools of metals (reducible + oxidisable + residual) as mobile pools (water soluble + exchangeable + carbonate bound) has environmental risk implications. The mobile and potentially bioavailable fractions of As, Cr and Cu in the untreated and chelant-extracted soil samples are given in Table 8.

The results indicate extraction of the contaminated soil with aqueous solutions of oxalic acid and malonic acids appeared in the contaminated soil. These results suggest that total levels of metals removed from contaminate soil may not be an adequately sufficient index for evaluating the effectiveness of chelant-enhanced-soil washing for the remediation of contaminated soil. It should be combined with the potential of the chelant to solubilize and re-distribute non-labile metal pools amongst labile, mobile and potentially bioavailable pools. The ability of oxalic acid and malonic acid to solubilize and subsequently re-distribute the residual metal pools among the operationally defined mobile pools can be exploited in chelate-enhanced phytoextraction of metals in contaminated soil with the added advantage of the biodegradability.

Table 8: Mobile fraction (F_1+F_2+F_3) (mg.kg^{-1}) of As, Cr and Cu in oxalic acid extracted CCA contaminated soil

Contact time (hr)	Mobile metal pools (F_1+F_2+F_3) (mg.kg^{-1})		
	As	Cr	Cu
0	23.30±0.70	60.52±0.60	17.80±0.80
2	24.07±0.26	71.53±4.31	67.15±0.63
	(24.20±0.21	(76.34±3.63)	(63.19±0.21
4	20.59±1.16	75.14±4.66	52.25±0.97
	(19.85±0.70)	(66.99±0.39)	(45.82±0.68)
6	16.62±0.60	62.59±2.27	49.53±0.97
	(15.84±0.03)	(65.04±1.18)	(43.95±0.33)

Values in parenthesis are for malonic acid extracted soil

CONCLUSION

This study examined the effectiveness of oxalic acid- and malonic acid-enhanced washing for the remediation of CCA contaminated soil. Contaminated soil washing with oxalic acid and malonic acid solutions appeared relatively effective in reducing the environmental load of As, Cr and Cu, but inadequate under the experimental conditions described here in ameliorating the environmental risk presented by the metals. The need for assessment criteria for chelate-assisted soil washing/extractive decontamination of contaminated soil to include re-distribution of metals amongst the operationally defined pools in post-extraction soil is highlighted from the results of this study.

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