

*Full Length Research Paper*

# Extractive decontamination of heavy metals from CCA contaminated soil using organic acids

Uwumarongie-Ilori E. G.<sup>1\*</sup> and F. E. Okieimen<sup>2</sup>

<sup>1</sup>Chemistry Division, Nigerian Institute for Oil Palm Research, P. M. B. 1030, Benin City, Nigeria.

<sup>2</sup>GeoEnvironmental Research Laboratory, Department of Chemistry, University of Benin, P. M. B. 1154, Benin City, Nigeria.

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In this paper, the mobilization and extraction of As, Cr and Cu from chromated copper arsenate (CCA) contaminated soil obtained from a wood treatment factory site by four organic acids are presented and discussed. The CCA contaminated soil (pH = 5.91, carbon = 0.32, CEC = 47.84 meq/100 g) was found to contain 39.55 mg/kg As, 313.97 mg/kg Cr and 200.00 mg/kg Cu with a contamination factor greater than 6 for As, 3.14 for Cr and 4 for Cu; thus classifying the soil as very highly contaminated for As and considerably contaminated with Cr and Cu. However, speciation studies on the contaminated soil sample showed that 59% As, 19% Cr and 5% Cu were potentially bio-available and mobile. Chemical wash test using four chelating agents: oxalic, malonic, succinic and citric acid were performed at 1:10 solid/liquid ratio, 0.05M chelant concentration and at 2, 4 and 6 h contact time, respectively. At the investigated operating conditions, oxalic acid extracted the lowest amount of As, Cr and Cu from the contaminated soil and the extraction efficiency depended on the solid/liquid contact time. The amount of metal extracted at the contact time of 6 h were 10.41, 12.50, 17.71 and 18.75 mg/kg As using oxalic, malonic, citric and succinic acid, respectively; 97.05, 123.69, 140.05 and 147.28 mg/kg Cr using oxalic, malonic, citric and succinic acid, respectively; 64.00, 94.10, 106.00 and 118.00 mg/kg Cu using oxalic, malonic, citric and succinic acid, respectively. Chromium (47%) was the least to be removed of the three metals after 6 h of washing. The contamination factor of the contaminated soil was affected by the extraction test. Levels of the metals in the decontaminated soil after 6 h of washing were found to be below the target value for all metals, which is somewhat higher for Sparks in respect of As and higher than the control values for As, Cr and Cu. After the 6 h extraction test, 15.84 – 16.62 mg/kg (60 - 63%) As, 59.35 - 65.04 mg/kg (32 - 38%) Cr and 37.10 - 49.53 mg/kg (38 - 50%) Cu was found in the bio-available fraction of the soil treated with the four different organic acid chelants.

**Key words:** CCA contaminated soil, decontamination, organic acids, extraction.

## INTRODUCTION

Soils are the major sink for heavy metal contaminants released into the environment by anthropogenic activities (Kirpichtchikova et al., 2006). Ecotoxicological studies show that soil contamination, resulting in heavy metals, is still a major and growing public health and environmental concern owing to their ability to impair human life and the environment (D'Amore et al., 2005). Heavy metal contamination results from several activities including mining, smelting, vehicle emission and deposition or leakage of industrial waste (Papassiopi et al., 1999). One of such

potential industrial source of heavy metals is the wood preservative treatment factory, in which salts of As, Cr and Cu in mixed soluble formulations have been used extensively to treat wood since 1933 (Rahman et al., 2004; Ndiokwere, 1985).

Soil and waste contaminated with CCA wood preservatives have been found in many former and active wood treating plants, resulting from past practices and accidental spillage (Uwumarongie et al., 2008; Ndiokwere, 1985).

Heavy metals cannot be destroyed by biogeochemical processes and site restoration relies on their removal (Kirpichtchikova et al., 2006). Numerous *in situ* and *ex situ* soil remediation technologies such as incineration,

\*Corresponding author. E-mail: [esohe\\_grc@yahoo.com](mailto:esohe_grc@yahoo.com).

**Table 1.** Physico-chemical characteristics and levels of As, Cr and Cu in CCA contaminated soil.

Parameter	
pH	5.91 ± 0.10
Clay (%)	26.08 ± 1.00
Silt (%)	2.30 ± 0.00
Sand (%)	71.62 ± 1.00
Soil texture	Sandy loam
Carbon (%)	0.32 ± 0.04
CEC (meq/100 g)	47.84 ± 0.70
Copper (mg/kg)	200.0 ± 0.14
Chromium (mg/kg)	313.97 ± 1.00
Arsenic (mg/kg)	39.55 ± 0.21

\*Values expressed on dry weight of soil.

disposal in landfill, flotation, electro-remediation, bioleaching, phytoremediation and chemical soil washing, developed for the treatment of heavy metal contaminated soils (Kirpichtchikova et al., 2006; Benschoten et al., 1997; Peters, 1999; Mulligan et al., 2001; Irene and Yang, 1999), are based on two principles: immobilization, by increasing the retention of metal on soil or decreasing the mass transfer rate of metal; and mobilization, by the removal of metal from the soil matrix (Irene and Yang, 1999).

Incineration and landfill techniques are incompatible with sustainable development precepts as the soil resource is irretrievably lost and they are not environmentally acceptable when large volumes of contaminated soils are to be treated. Electro-remediation and flotation are generally used to treat clayey and organic soils of low permeability (Mulligan et al., 2001). However, bioleaching and phytoremediation have major obstacle of treatment time (Kirpichtchikova et al., 2006; Cunningham and Berti, 1993; Tichy et al., 1998). Soil washing is efficient in terms of metal solubilisation and it is performed *ex situ* in reactors with strong acids and bases. However, the treatment with aggressive chemical alters the original soil texture and biogeochemistry, thereby leaving an inorganic matrix that may not support re-vegetation (Kirpichtchikova et al., 2006; Peters, 1999). The use of chelating agents to remove heavy metals from contaminated soil is a more attractive alternative. Chelating agents have been used for analytical purposes to displace metals from soils and sediments, but more recently, they have been studied as reagents for decontaminating metal-polluted soils. Organic ligands with amino and carboxylic functional groups are reported as potential metal extracting reagents (Elliott and Shastri, 1999).

Chelating agent has a high affinity for heavy metals, and may be used as remedial chemical treatment or in adjunct to another process. The efficiency of chelating agent in metal solubilization is high with less undesirable effects on the soil physicochemical properties. In

addition, extraction agents are thought to enhance the bioavailability of metals in soil and thereby influence their uptake by plants (Kirpichtchikova et al., 2006, Peters, 1999). Although many chelating agents for mobilizing heavy metals have been evaluated, the problem of optimum process conditions for full-scale application still remains. In soil, the most labile species dominates the short term solubilization of metals, while the replenishment of the labile pool from more recalcitrant species determines the long term removal of metals. Therefore, the identification and quantification of coexisting solid metal species in the soil before and after treatment are important to design and assess the efficiency of appropriate remediation technology (Kirpichtchikova et al., 2006).

Although, CCA has been restricted since 2004, in wood meant for domestic application in the USA and prohibited by the European Union, it remains the main chemical cocktail used in the preservation of wood in Nigeria and has been in use in the wood treatment facility under study since the 1970's.

In this paper, experimental tests of metal extraction from contaminated soil are presented and discussed. Soils were collected from the vicinity of a chromated copper arsenate wood treatment factory where significant As, Cr and Cu contents have been observed (Uwumarongie et al., 2008).

The aim of the experimentation was to determine the potential of four organic acid extractants namely; oxalic, malonic, succinic and citric acid, in remediation of heavy metal contaminated soil.

## MATERIALS AND METHODS

### Soil characterisation

Ten grab samples were collected from ten different locations within the vicinity of the wood treatment factory at the topsoil depth of 0 – 10 cm from the vicinity of a wood treatment factory in Benin City, Nigeria. Ten soil samples were air-dried at ambient temperature (28 - 31 °C) in the laboratory, crushed in a porcelain mortar and sieved through a 2-mm sieve. The experimental tests were performed on aggregate samples prepared by mixing thoroughly equal amount of each of the 10 soil samples collected by coning to make three replicate samples.

The physicochemical properties and total concentration of As, Cr and Cu of the aggregate sample were determined according to standard methods (IITA, 1982) and are given in Table 1. Cation exchange capacity was estimated by summing the exchangeable cations determined by flame photometric method with the exchangeable acidity determined by titration method (Jackson, 1960). The soil pH was determined using a 1:2 soil weight/water volume ratio by a Sontex digital pH meter (Folson and Lee, 1981), whereas the particle size was done according to Bouyoucos method (Bouyoucos, 1962). Total organic carbon was determined by the Walkley-Black rapid oxidation method (Nelson and Sommer, 1982), while available phosphorus was determined by the Bray and Kurtz method (1945). Total concentration of As, Cr and Cu in the contaminated soil was determined by digesting 1g sample with 5mL concentrated nitric acid and 1mL perchloric acid. The resultant supernatant was then analysed by Buck scientific VGP 210 atomic

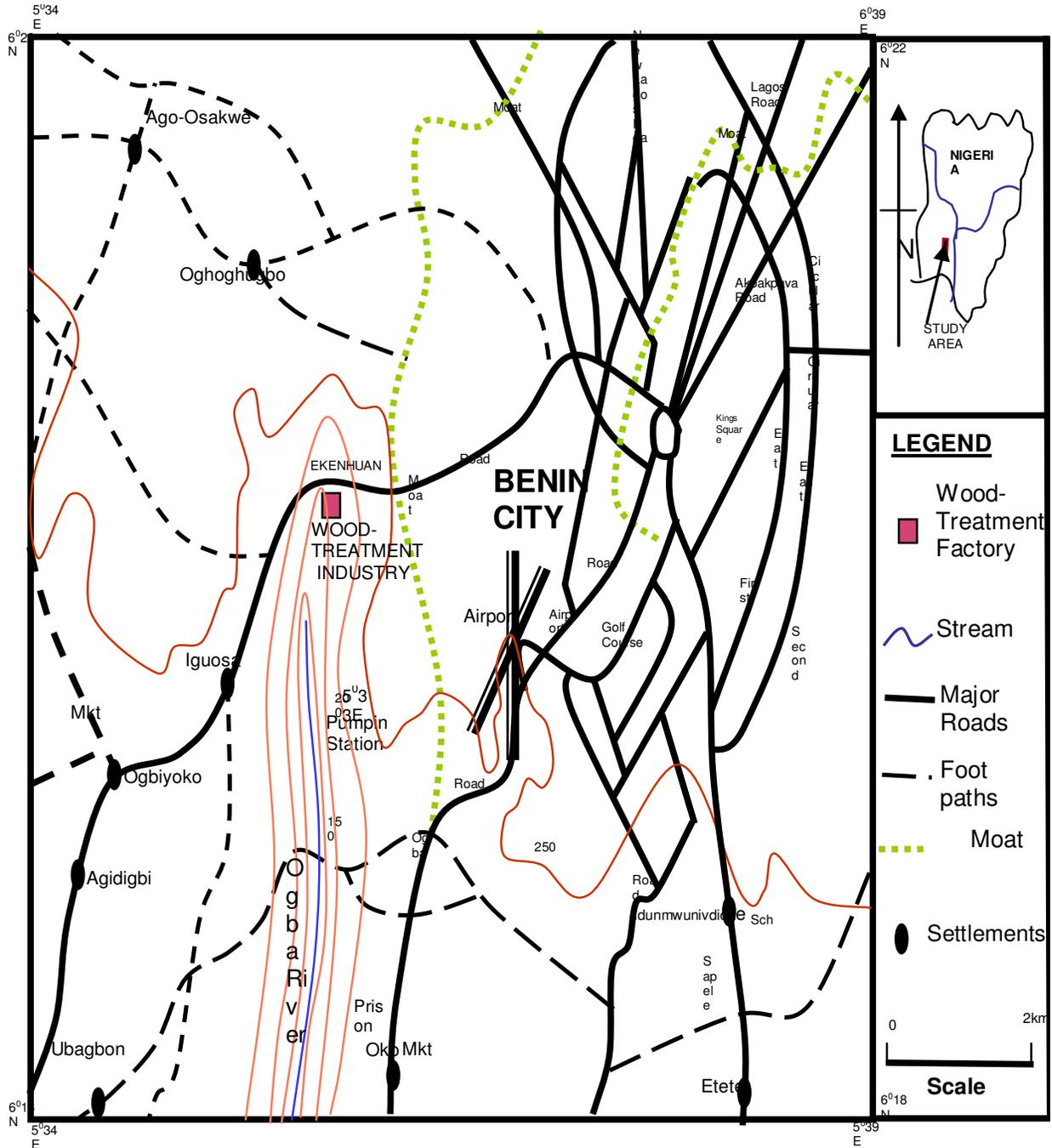


Figure 1. Map of Benin City showing the study site.

absorption spectrophotometer. All reagents were analytical grade and all glass wares were washed, soaked in nitric acid and washed in distilled water. Buck scientific standard solutions were used for the calibration and quality assurance for each analytical test. Procedural blank samples were subjected to similar extraction method using same amounts of reagents.

#### Data analysis

Statistical analysis was performed using SPSS statistical software.

#### Description of the study area

Soil samples (10) were collected from different points in the premises of Bendel Wood Factory located at Ekenwan road, Benin City (Figure 1). The ten locations are shown in the study (Figure 2).

#### Chemical fractionation

The Salbu and Oughton (1998) method, a modified version of Tessier et al. (1979), was used to investigate the geochemical

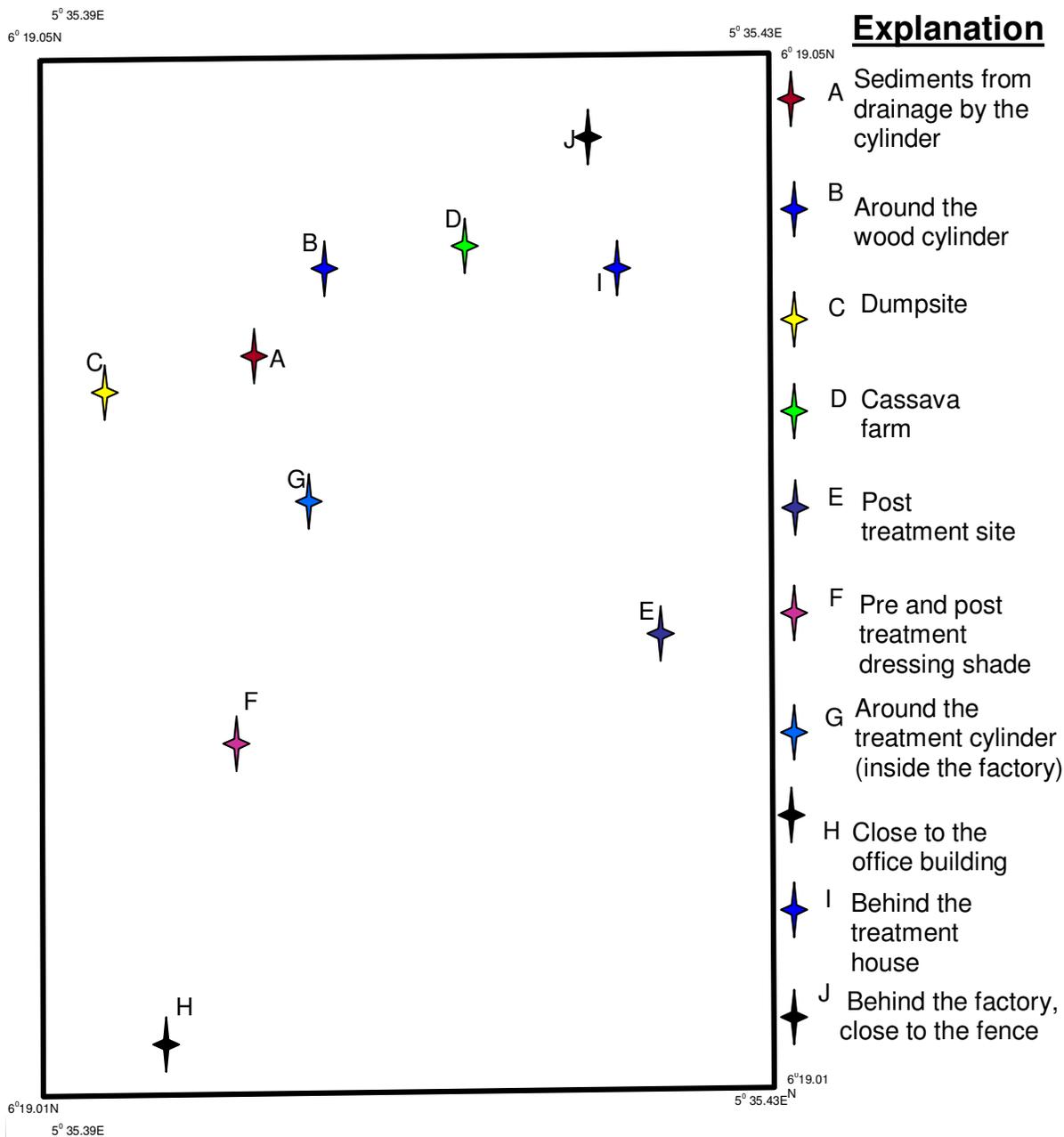


Figure 2. Wood-treatment industry site.

forms (water-soluble, exchangeable, bound to carbonate, bound to Fe-Mn oxides and hydroxides, bound to organic matter and residual) in which the metals are present in the CCA contaminated soil (Table 2). Two grams of soil were used for the extraction (Salbu and Oughton, 1998).

However, the residual fraction was determined after digesting one gram of the residue with 5ml of nitric acid for 6 h.

**Extraction/soil washing tests**

The aim of the extraction tests was to determine the extractive decontamination efficiency of As, Cr and Cu by the extractants, in

which the main operating parameter in the tests was the nature of the extractant used and the time of extraction.

The extractive decontamination tests were performed at room temperature (28 - 31 °C), while four different extractants were tested using 0.05 M aqueous solution of the extractant and 1:10 solid/liquid ratio. The suspension was agitated for a maximum of 6 h at 200 rpm in a mechanical shaker (Heldoph model). Test extractant agents were collected at various times (10 min, 2 h, 4 h and 6 h) during the soil extraction experiment to measure the rate of decontamination of the CCA contaminated soil by the extractants. Residual concentration of metals in the various test soils after 6 h extraction were also measured and fractionated using the Salbu and Oughton (1998) chemical fractionation scheme given

**Table 2.** Chemical fractionation scheme.

	Fractions	Reagents	Duration
Step 1 (F1)	Water-soluble	Distilled water	1 h
Step 2 (F2)	Exchangeable	1 M NH <sub>4</sub> OAc (pH 7)	2 h
Step 3 (F3)	Bound to carbonate	1 M NH <sub>4</sub> OAc (pH 5)	2 h
Step 4 (F4)	Bound to Fe-Mn oxides	0.04 M NH <sub>2</sub> OH.HCl	6 h at 60 °C
Step 5 (F5)	Bound to organic matter	30% H <sub>2</sub> O <sub>2</sub> (pH 2) 3.2 M NH <sub>4</sub> OAc	5.5 h at 80 °C 30 min
Step 6 (F6)	Residual	Concentrated HNO <sub>3</sub>	6 h

**Table 3.** Results of sequential extraction tests performed before the treatment.

Fraction	As (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
Water soluble	5.8 ± 0.2	17.83 ± 0.2	1.6 ± 0.2
Exchangeable	11.0 ± 1.0	23.33 ± 0.0	3.0 ± 0.2
Carbonate	6.4 ± 0.4	19.36 ± 0.4	13.2 ± 0.4
Fe-Mn oxide	4.6 ± 0.2	10.21 ± 0.4	27 ± 0.4
Organic	1.6 ± 0.3	45.61 ± 0.4	37.6 ± 0.2
Residual	9.5 ± 0.0	188.06 ± 0.2	110 ± 0.1
Sum of fraction	38.90	304.40	192.40
Mobility factor (%)	60	20	9

in Table 1.

## RESULTS AND DISCUSSION

### Soil properties

The results of the physico-chemical properties of the CCA-contaminated soil are shown in Table 1, while the results of the triplicate determination were expressed in mean ± standard deviation. It can be seen that the sample is moderately acidic with a pH value of 5.91. The cation exchange capacity (47.84 ± 0.70 meq/100 g) of the soil appears relatively high and was attributed to the high level of calcium in the soil. Particle size shows that the soil is mainly sandy loam, while the clay portion of the soil represents 26.08% of soil component.

The total levels of arsenic, chromium and copper in the CCA contaminated soil were found to be 39.55, 313.97 and 200 mg/kg, respectively. These values were above the stated values of 1.50 mg/kg arsenic, 100.00 mg/kg chromium and 50.00 mg/kg copper for uncontaminated soil by Sparks (2001) and the intervention values of 28.81, 190.52 and 79.61 mg/kg for As, Cr and Cu, respectively [DPR, 1991].

### Fractionation of As, Cr and Cu in the CCA contaminated soil before washing

The results of the fractionation tests performed to assess

geochemical forms of As, Cr and Cu distribution in the CCA contaminated soil are given in Table 3.

The highest amount of As was found in the exchangeable fraction of the soil. The presence of arsenic in these soil fractions shows that arsenic will readily be mobile and available to the environment as metals in the exchangeable fraction and ions, which occur either as free hydrated ions or as various complexes with organic or inorganic ligands as stated by Sparks (2003). Moreover, Cr and Cu were found mostly in the residual fraction. Previous workers, (Manceau et al., 1996, 1999; Asagba et al., 2007) have reported that metals found mostly in the residual fraction, may be due to the sandy nature of the soil which resulted in the co-precipitation of the metals with various silicate species consequent to their adsorption into the mineral lattice.

The results show that arsenic in the soil samples collected from the premises of the wood treatment factory is potentially mobile. Ahumada et al. (1999) and Karczewska (1996) reported in an earlier work that high MF values are symptoms of relatively high lability and biological availability of heavy metals in soils. However, mobility factor describes the potential mobility of metal in soil. The mobility of metals in soil is calculated on the basis of absolute and relative content of fractions weakly bound to soil components. Mobility factor is expressed as the percentage ratio of the sum of the soil's mobile fraction (F1, F2 and F3) to the sum of all fraction of the soil as stated by Cezary and Bal (2001). It is pertinent to note that metals extracted by F3 are relatively less mobile

**Table 4.** Background values for uncontaminated soils and calculated CF before extraction test.

Metals	Target value (mg/kg)	CF	Sparks' uncontaminated value (mg/kg)	CF	Control soil (mg/kg)	CF
Arsenic	29	1.36	1.50	26.37	0.35	113.00
Chromium	100	3.14	100	3.14	0.37	848.57
Copper	36	5.56	50	4.00	9.50	21.05

**Table 5.** Partition coefficients ( $K_d$ ) of As, Cr and Cu in CCA contaminated soil by organic acids.

Extractants	2 h			4 h			6 h		
	As	Cr	Cu	As	Cr	Cu	As	Cr	Cu
Oxalic acid	0.01	0.02	0.06	0.15	0.22	0.31	0.26	0.31	0.32
Malonic acid	0.02	0.02	0.12	0.19	0.32	0.41	0.32	0.41	0.47
Citric acid	0.02	0.03	0.17	0.23	0.37	0.49	0.45	0.45	0.53
Succinic acid	0.03	0.05	0.31	0.26	0.39	0.54	0.47	0.47	0.59

than those extracted by F1 and F2. In this study, the mobility of As was found to be 23.20 mg/kg (60%), 60.52 mg/kg (20%) for Cr and 17.8 mg/kg (9%) for Cu. However, as pointed out by earlier workers, (Rahman et al., 2004, Ahumada et al., 1999; Karczewska, 1996), the high % mobility of As may be attributed to the low organic matter content of the soil.

According to Hakanson (1980) and Agunbiade and Fawale (2009), contamination factor compares the concentration of metals in the surface layer of a contaminated soil to the background values of an uncontaminated soil. In this study, contamination factor (CF) for the CCA contaminated soil was calculated using various background values for uncontaminated soil to ascertain the level of contamination by the CCA use in the wood treatment. The contamination factor was calculated using the expression:

$$CF = \frac{C_s}{C_n}$$

Where CF is the contamination factor (CF),  $C_s$  is the mean of the concentration of individual metal and  $C_n$  is the background concentration of the individual metal.

However, DPR intervention values, DPR target values, Sparks' uncontaminated values and metal value obtained for an uncontaminated (control) soil were used as background concentration of the individual metal (Table 4).

CF was classified into four categories as follows:

- CF < 1 – Low CF
- 1 < CF < 3 – Moderate CF
- 3 < CF < 6 – Considerable CF
- 6 < CF - Very high CF.

### Extraction efficiency of the chelants

The retention of deposited heavy metals by soil particles can minimize their passage into groundwater, but at the same time alters soil conditions, thereby resulting in a release of the accumulated load into the soil solution. This results in pollution of groundwater and/or contamination of plants. Thus, the fate of heavy metals and the toxic risk they pose, depend on their release-retention equilibria and dynamics in the soils on which they are deposited and on how these equilibria change in response to changes in environment conditions.

Empirical investigation of these processes is essential because the nature of the soil tends to have a greater influence on the rate of release-retention of metals in soil than the characteristics of the metals. Also, since it is common for several different heavy metals to be present in the polluted soils, it is pertinent to investigate the release-retention behaviour of metals in soils. These processes can be characterized in part by the ratio of partition coefficients ( $K_d$ ) between the concentration of a given metal retained onto soil particles and the concentration left in solution at equilibrium as indicated by Alloway (1995).

In this study, the competitive retention and release of As, Cr and Cu by oxalic, malonic, citric and succinic acid with time were determined. For each soil after each extraction test, the  $K_d$  values (Table 5) of the metals were calculated as the ratio of amount of metal extracted by the chelants to the amount of metal in the soil.

On comparing the  $K_d$  values obtained for the metals after each time of extraction, it was observed that the values increased with time and the values obtained for Cu were the highest. This was followed by the values obtained for Cr, while the values obtained for As were the least.

**Table 6.** As, Cr and Cu extracted from CCA contaminated soil by organic chelants.

Time of extraction	2 h			4 h			6 h		
	As (mg/kg %)	Cr (mg/kg %)	Cu (mg/kg %)	As (mg/kg %)	Cr (mg/kg %)	Cu (mg/kg %)	As (mg/kg %)	Cr (mg/kg %)	Cu (mg/kg %)
Oxalic acid	0.54 (1)	5.77 (2)	11.95 (6)	5.90 (16)	68.88 (23)	61.30 (32)	10.41 (29)	97.05 (36)	64.00 (36)
Malonic acid	0.73 (2)	6.11 (2)	23.02 (12)	7.58 (19)	101.61 (36)	81.00 (42)	12.50 (33)	123.69 (43)	94.40 (48)
Citric acid	0.98 (2)	10.09 (3)	34.60 (18)	9.10 (24)	115.31 (39)	97.00 (49)	17.71 (45)	140.05 (47)	106.00 (56)
Succinic acid	1.21 (3)	16.04 (5)	61.92 (31)	10.41 (27)	122.92 (41)	108.40 (55)	18.75 (49)	147.28 (49)	118.00 (60)

Also,  $K_d$  values obtained for the different chelating agents varied, of which oxalic acid  $K_d$  for all three metals were the lowest. This was followed by the values obtained for malonic, citric and succinic acid, respectively.

Extraction efficiency of As, Cr and Cu from the CCA contaminated soil by the four chelating agents (oxalic, malonic, citric and succinic acids) were determined. The amount of As, Cr and Cu extracted (%) from the CCA contaminated soil that was determined in the filtrate obtained in the extraction test, with respect to their initial content in the contaminated soil, are given in Table 6.

The mean values of the three replicate tests are reported and the standard deviation calculated for the replicate tests was about 1% of the average value. It was observed that increasing the time of extraction favoured more removal of the heavy metals from the contaminated soil.

The trend of extraction of As, Cr and Cu followed the same general behaviour of increase in metal decontamination with time, while the initial As availability was lower with respect to Cr and Cu. Cu decontamination was generally better than that of As and Cu using all organic acids due to the greater tendency of cuprous ion to complexation.

#### Speciation of metals in the contaminated soil after 6 h extraction test

The speciation of As, Cr and Cu in the CCA contaminated soil after 6 h extraction test is given in Table 7. Arsenic was mostly found in the exchangeable fraction before and after the washing treatment. The result shows that the same amount of As was found in the bio-available form of the CCA contaminated soil before and after the 6 h extraction with oxalic acid, while the amount found in the soil treated with the other three chelating agents (malonic, citric and succinic acid) increased from 60% before washing to 63, 61 and 63% by malonic, citric and succinic acid, respectively.

The speciation of Cr in the treated soils showed that Cr was found mostly in the residual fraction of the soils treated with the four organic acids. Subsequently, the treatment with the organic acids affected the distribution of the metals in the soils. The amounts of Cr in the residual fractions of all treated soils were found to be lower than the amount in the residual fraction of the contaminated soil before treatment. However, the amount of Cr in the bio-available fractions of the treated soil increased. About 38% Cr was

extracted by succinic acid after 6 h extraction, whereas oxalic acid extracted 32% Cr after 6 h.

The results of the speciation of Cu in the different treated soils after the 6 h extraction test showed that Cu was found mostly in the residual fractions of the soils treated with the four organic acids. It was observed that the acids affected the distribution of the metals. The % bio-available Cu increased from 9% before extracting with the organic acids to 38, 43, 44 and 50%, by oxalic, malonic, citric and succinic acid, respectively, after the 6 h washing test. The study also revealed that Cu was mostly affected by the organic acids as its % mobility from the CCA contaminated soil was the highest of the three metals. This may be due to the greater tendency of copper ion to complexation than As and Cr ions as stated by Cotton and Wilkinson (1980).

Organic acid contains carboxyl groups which have the ability to combine or bind with considerable quantities of metal ions by complexation reaction (Alloway, 1995; Selim and Amacher, 1997; Cemik et al., 1994; Yong et al., 1993). Glusker (1980), Francis and Dodge (1994), Bailey et al. (2005), Francis and Dodge (2008) and Weiner (2008) reported that oxalic, malonic and succinic acids are dicarboxylic acids, while

**Table 7.** Results of speciation of metals in the soils after 6 h extraction treatment.

<b>Fractions</b>	<b>Oxalic acid</b>	<b>Malonic acid</b>	<b>Citric acid</b>	<b>Succinic acid</b>
<b>Arsenic (mg/kg)</b>				
Water soluble	2.21 ± 0.10	1.80 ± 0.10	1.80 ± 0.10	0.51 ± 0.10
Exchangeable	11.33 ± 0.10	11.00 ± 0.10	9.45 ± 0.10	9.13 ± 0.10
Carbonate	3.08 ± 0.40	3.04 ± 0.00	1.44 ± 0.60	2.47 ± 0.40
Fe-Mn oxide	2.66 ± 0.60	2.51 ± 0.60	1.55 ± 0.50	2.21 ± 0.50
Organic	1.50 ± 0.60	1.49 ± 0.10	1.18 ± 0.61	1.14 ± 0.10
Residual	6.83 ± 0.10	5.49 ± 0.10	5.33 ± 0.30	3.70 ± 0.10
Sum	27.61 ± 0.40	25.33 ± 0.30	20.70 ± 0.30	19.16 ± 0.10
Total	28.02 ± 0.00	26.60 ± 0.00	21.66 ± 0.60	20.02 ± 0.00
Mobility factor (%)	60	63	61	63
CF (Sparks')	18.68	17.73	14.44	13.35
CF (Control soil)	80.06	76.00	61.89	57.20
<b>Chromium (mg/kg)</b>				
Water soluble	14.54 ± 0.91	14.24 ± 2.54	14.95 ± 4.00	9.88 ± 0.74
Exchangeable	26.06 ± 0.45	27.02 ± 3.76	23.85 ± 3.39	29.95 ± 4.02
Carbonate	21.99 ± 0.91	23.78 ± 2.62	20.55 ± 2.74	19.84 ± 0.47
Fe-Mn oxide	8.37 ± 1.36	8.02 ± 13.04	6.76 ± 3.68	5.81 ± 1.93
Organic	37.26 ± 0.89	31.64 ± 1.19	30.49 ± 0.00	29.00 ± 3.54
Residual	87.12 ± 3.03	69.79 ± 2.75	64.14 ± 0.62	63.83 ± 2.23
Sum	195.33 ± 3.01	174.49 ± 13.46	160.74 ± 7.71	158.31 ± 2.47
Total	201.70 ± 0.00	178.87 ± 0.00	167.55 ± 0.00	159.84 ± 0.00
Mobility factor (%)	32	37	37	38
CF (Sparks')	2.02	1.79	1.68	1.60
CF (Control soil)	545.14	483.43	452.84	432
<b>Copper (mg/kg)</b>				
Water soluble	13.88 ± 0.53	13.00 ± 0.10	9.29 ± 0.20	10.00 ± 0.60
Exchangeable	16.24 ± 0.23	14.07 ± 0.13	11.20 ± 0.60	14.39 ± 0.00
Carbonate	19.41 ± 0.21	16.68 ± 0.10	16.61 ± 0.01	14.35 ± 0.19
Fe-Mn oxide	18.53 ± 0.98	13.31 ± 0.25	14.89 ± 0.02	12.62 ± 0.33
Organic	21.70 ± 0.14	14.99 ± 0.10	13.88 ± 0.88	10.33 ± 0.17
Residual	39.74 ± 0.95	29.82 ± 0.36	18.87 ± 0.31	15.96 ± 0.17
Sum	129.50 ± 4.95	101.87 ± 2.36	84.74 ± 6.31	77.65 ± 3.32
Total	133.00 ± 0.00	104.60 ± 0.00	88.00 ± 0.00	80.00 ± 0.00
Mobility factor (%)	38	43	44	50
CF (Sparks')	2.66	2.09	1.76	1.60
CF (Control soil)	14.00	11.01	9.26	8.42

citric acid is tricarboxylic with a hydroxyl group. Also, they reported that the acids are polydentate ligands and they form stable complexes with metal ions. In this study, succinic acid was found to extract most of the metals from the CCA contaminated soil than the other organic acids.

After the 6 h extraction test, As was still found to be classified as highly contaminated as its CF values that were obtained using Sparks', whereas the control soil were found to be above 6 CF. However, Cr and Cu were classified as moderately contaminated for the test.

The mobility factor of the heavy metals in the CCA contaminated soil before and after the extraction test with the organic acids are shown in Figure 3. The mobility factor of the soil before extraction was found to be lower for all metals except for As where the same mobility factor was obtained for the contaminated soil before and after extraction with oxalic acid. Succinic acid was mostly found to mobilize the metals, while As mobility factor was the highest of the three metals in the soils treated with the organic acid.

The study revealed a decrease in CF after the

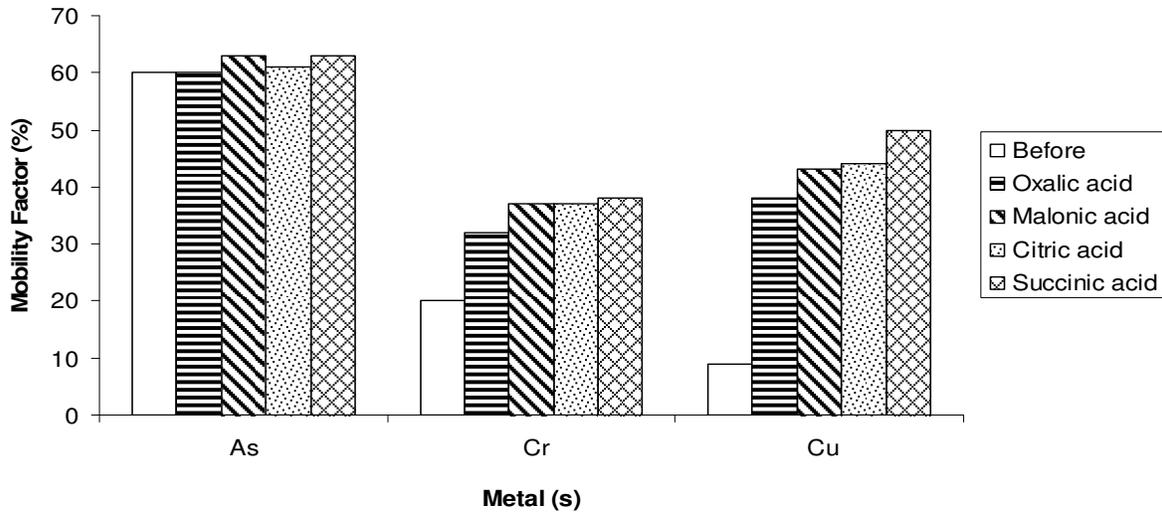


Figure 3. Mobility factor of metals before and after treatment.

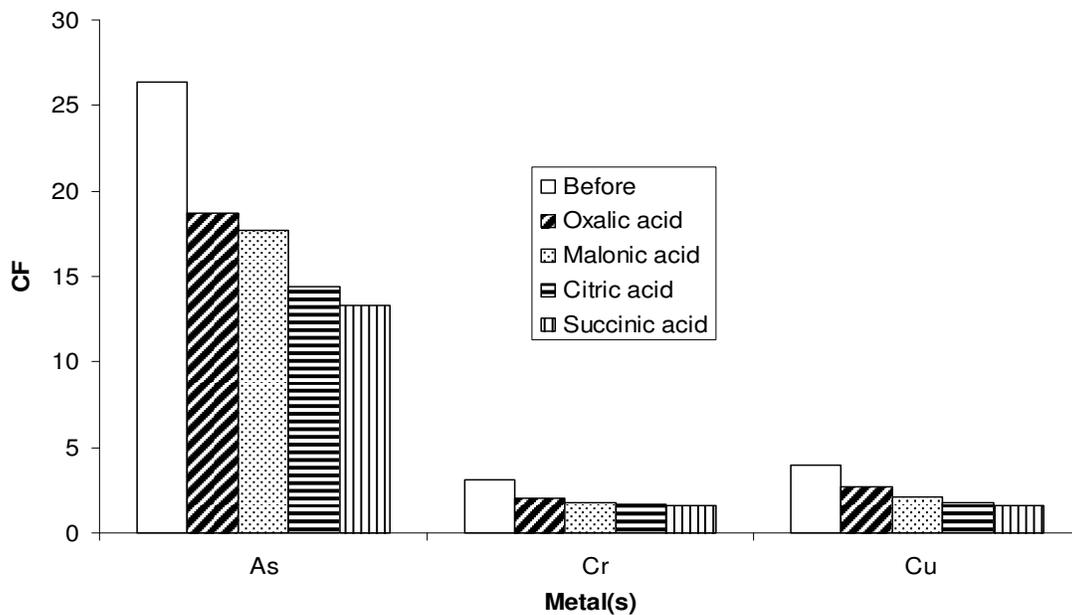


Figure 4. CF of metals before and after extraction test.

extraction test (Figure 4), while the result shows the acids ability in extracting metals from the CCA contaminated soil. The trend of CF in the decontaminated soil is as follows:

succinic acid < citric acid < malonic acid < oxalic acid.

Arsenic in the decontaminated soil was found to have a very high CF value as its CF value was found to be above 6. This may be due to the small amount of As removed by the organic acid from the CCA contaminated soil.

## Conclusion

The study revealed that organic acids such as oxalic, malonic, citric and succinic acids, can extract As, Cr and Cu from CCA contaminated soil. The decontamination efficiencies of the organic extractants were of the order: oxalic acid < malonic acid < citric acid < succinic acid and the explanation, in terms of the variation of the metal ion (that is, chelating agent binding constant), was offered.

At the maximum contact time (6 h) of this study, less than 50% As and Cr and 65% Cu decontamination was achieved using the four organic acids. These results

show a potential for the application of organic chelating agent in the decontamination of metals from CCA contaminated soil.

Excessive accumulation of heavy metals in soils by various human activities poses a high risk of pollution for the environment; hence restoration of such soils relies on metal removal. As a result, the efficiency of organic acid in decontaminating CCA contaminated soil was evaluated in this study. Although the use of the acid was effective, it resulted to an increase in the acidity of the soil. Hence, the effective use of organic acid for decontamination of metals in contaminated soil

Will require liming after treatment to raise the pH of treated soil in order to improve soil properties.

## REFERENCES

- Ahumada I, Mendoza J, Ascar L (1999). Sequential extraction of heavy metals in soils irrigated with wastewater. *Commun. Soil Sci. Plant Anal.*, 30: 1507-1519.
- Alloway BJ (1995). Heavy metals in soils. Blackie Academic and Professional London.
- Asagba EU, Okieimen FE, Osokpor J (2007). Screening and speciation of heavy metal contaminated soil from an automobile spare-part market. *Chemical speciation and Bioavailability*, 19(1): 9-15.
- Bailey EH, Mosselmans JFW, Chofield PFS (2005). Uranyl citrate speciation in acidic aqueous solutions, an XAS study between 25 and 200°C. *Chem. Geol.*, 216: 1-16.
- Benschoten JEV, Matsumoto MR, Young WH (1997). Evaluation and analysis of soil washing for seven lead-contaminated soils. *J. Environ. Eng. ASCE*, 123: 217-224.
- Cemik M, Federer P, Borkovec M, Sticher H (1994). Modeling of heavy metal transport in a contaminated soil. *J. Environ. Qual.*, 23: 1239-1248.
- Cezary K, Bal RS (2001). Fractionation and mobility of copper, lead and zinc in the vicinity of a copper smelter. *J. Environ. Qual.*, 30: 485-492.
- Cotton FA, Wilkinson G (1980). *Advanced Inorganic Chemistry: A comprehensive Text* (33d edn), John Wiley, London, pp. 620-652.
- Cunningham SD, Berti WR (1993). Remediation of contaminated soils with green plants: An overview. *In vitro cell. Dev.*, B29: 207-212.
- D'Amore JJ, Al-Abed SR, Scheckel KG, Ryan JA (2005). Methods for speciation of heavy metals in soils. *J. Environ. Qual.*, 34: 1707-1745.
- Elliott HA, Shastri NL (1999). Extractive decontamination of metal-polluted soils using oxalate. *Water, Air and Soil Pollution*, 110: 335-346.
- Francis AJ, Dodge CJ (1994). Remediation of soils and waste contaminated with uranium and toxic metals. *Environ. Sci. Technol.*, 32: 3993-3998.
- Francis AJ, Dodge CJ (2008). Bio/Photo chemical separation and recovery of uranium DAE-BRNS Biennial Symposium on Emerging Trends in Separation Science and Technology, pp. 1-9.
- Glusker JP (1980). Citrate conformation and chelation, enzymatic implications. *Acc. Chem. Res.*, 13: 345-352.
- <http://www.fwrc.msstate.edu/pubs/phytoremediation.pdf>. 2007, pp. 1-6.
- IITA (1982). Automated and semi-automated methods for soil and plant analysis.
- Irene Lo MC, Yang XY (1999). EDTA extraction of heavy metals from different soil Fractions and synthetic soils. *Water, Air and Soil Pollution*, 109: 219-236.
- Jackson ML (1960). *Soil Chemical Analysis*. Prentice-Hall. New York.
- Karczewska A (1996). Metal species distribution in top- and sub-soil in an area affected by copper smelter emissions. *Appl. Geochem.*, 11: 35-42.
- Kirpichtchikova AT, Manceau A, Spadini L, Panfili F, Marcus MA, Jacquet T (2006). Speciation and solubility of heavy metals in contaminated soil using X-ray micro fluorescence, EXAFS spectroscopy, chemical extraction and thermodynamic modeling. *Geochimica et Cosmochimica Acta*, 70: 2163-2190.
- Manceau A, Boisset M, Sarret G, Hazemann J, Mench M, Cambier P, Prost R (1996). Direct determination of lead speciation in contaminated soils by EXAFS Spectroscopy. *Environ. Sci. Technol.*, 30: 1540-1552.
- Manceau A, Schlegel M, Nagy KL, Charlet L (1999). Evidence for the formation of trioctahedral clay upon sorption of  $\text{Co}^{2+}$  on quartz. *J. Colloid Interf. Sci.*, 220: 11-197.
- Mulligan CN, Yong RN, Gibbs BF (2001). Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Eng. Geol.*, 60: 193-207.
- Ndiokwere CL (1985). The Dispersal of arsenic, chromium and copper from a wood treatment factory, and their effect on soil, vegetation and crops. *Int. J. Environ. Stud.*, 24: 231-234.
- Papassiopi N, Tambouris S, Kontopoulos A (1999). Removal of heavy metals from calcareous contaminated soils by EDTA leaching. *Water, Air and Soil pollution*, 109: 1-15.
- Peters RW (1999). Chelant extraction of heavy metals from contaminated soils. *J. Hazard. Mater.* 66: 151-210.
- Rahman FR, Allan DL, Rosen CJ, Sadowsky MJ (2004). Arsenic Availability from Chromated Copper Arsenate (CCA) - Treated Wood. *J. Environ. Qual.*, 33: 173-180.
- Salbu BTK, Oughton DH (1998). Characterisation of radioactive particles in the environment. *Analyst* 123: 843-849.
- Selim HM, Amacher MC (1997). Reactivity and transport of heavy metals in soils, CRC Press Inc. N.W.
- Sparks DL (2001). Elucidating the fundamental chemistry of soils: past and recent achievements and future frontiers. *Geoderma*, 100: 303-319.
- Sparks DL (2003). *Environmental Soil Chemistry*. 3<sup>rd</sup> edn. Academic Press.
- Tessier A, Campbell PGC, Bisson M (1979). Sequential extraction procedures for the speciation of particulate trace metals. *Anal. Chem.* 51(7): 844-851.
- Tichy R, Rulkens WH, Grotenhuis JTC, Nydl V, Cuypers C, Fajtl J, (1998). Bioremediation of metals from soils or sediments. *Water Sci. Technol.*, 37: 119-127.
- Uwumarongie EG, Okieimen FE, Uwumarongie OH (2008). Spatial distribution and speciation of arsenic, chromium and copper in CCA contaminated soil. *J. Chem. Soc. Niger.*, 33(1): 112-121.
- Weiner N (2008). Malonic acid. *Org. synth.* 2: 376.
- Yong RN, Galvez-Cloutier R, Phadungchewit Y (1993). Selective sequential extraction analysis of heavy metal retention in soil. *Can. Geotech. J.*, 30: 834-847.