



CHELATE EXTRACTION OF HEAVY METALS FROM CONTAMINATED SOIL – CASE STUDY- BONNY LIGHT CRUDE OIL CONTAMINATED SOIL

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Abstract

Human and its anthropogenic activities are increasingly resulting in serious environmental health and ecotoxicological issues in the world. Contamination of the soil by relatively high concentrations of inorganic (heavy metals) and organic (petroleum/crude oil) hydrocarbons is becoming a course for concern all over the world and Nigeria is not left out as a major producer of crude oil. Since most heavy metals and aromatic compounds are recalcitrant and persist in the environment for long periods, remediation (cleaning up) is important to remove them. In this article, chelate extraction of heavy metals from contaminated soil was studied using bonny light crude oil contaminated soil as a case study. Aqueous solution (0.05M) of five chelating agents; oxalic acid, malonic acid, citric, succinic acid and ethylene diamine tetra acetic acid (EDTA) at 1:10 soil/liquid ratio and 6 hours contact time was used to wash the soil (soil washing method). The results shows that the chelating agents are efficient in the release of heavy metals from the crude oil spill soil, efficiency being in the order EDTA > Citric acid > Oxalic acid > Malonic acid > Succinic acid. The results indicates that a single-step extraction of the crude oil contaminated soil with aqueous solution of EDTA was sufficient to reduce the levels of heavy metals in the soil.

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Keywords

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1. Introduction

Soil contamination has increased over the last decades. Heavy metal contamination together with crude oil spill is increasingly posing serious eco-toxicological threats due to increasing industrialization (Ahmad-Dasuki et al, 2015). Heavy metals may be deposited in soils by atmospheric input, the use of mineral fertilizers or compost, waste disposal, spill of petrochemical and so on while polycyclic aromatic hydrocarbons (PAHs) and BTEX (benzene, ethylbenzene, toluene and xylene) are

frequently found, at relatively large concentrations, around oil refineries, agrochemical, petrochemical and pharmaceutical industries (Mrozik and Piotrowska-Seget, 2010). The presence of these contaminants in the environment has posed a danger to public health due to their toxicity, mutagenic and carcinogenic properties and their ability to accumulate in the food chain (Mrozik and Piotrowska-Seget, 2010; Rohrbacher and St-Arnaud, 2016; Nwankwoala et al, 2020).

Heavy metals, basically reported to be detected in crude oil spill site include Cadmium (Cd), Lead (Pb), Nickel (Ni), Vanadium (V) and Zinc (Zn) [Ahmad-Dasuki et al, 2015]. So, crude oil contamination is a significant contributor for the higher levels of heavy metals in different types of environment such as soil, seawater and freshwater (Olubodun and Eriyamremu, 2015).

Heavy metal contaminated soil is one of the most common problems constraining remediation (cleaning up) at hazardous waste sites. Groundwater, surface water, seawater and fresh water may easily be contaminated by heavy metals from leachate and run-off from soil contaminated sites. Also, wind erosion tends to spread contamination over large areas (Groeningen et al., 2020). Soils that may be contaminated with heavy metal such as cadmium, copper, lead, zinc, etc, as a result of improper waste disposal practices, industrial activities and spill of chemicals such as pesticides, crude oil (petroleum) or petroleum products, often require remediation practices. Soils contaminated by heavy metals are relatively immobile in subsurface systems due to precipitation or adsorption reactions. So, remediation activities at contaminated sites are mainly done on the solid-phase sources of metals, such as, contaminated soils, sludges, wastes, or debris (Usman et al, 2017). Generally, the two main conventional remediation technologies and strategies for decontamination of soils from heavy metals are: techniques that leave the metals in the soil and technique that remove the metals from the soils (Wuana and Okieimen, 2011). Solidification or stabilization which are in-situ chemical fixation and vitrification or separation i.e. soil washing (Zhang et al, 2010), which immobilize the metals thereby reducing their migration.

Soil washing is a relatively simple and useful ex-situ remediation technology, in which washing water added and heavy metal can be transferred from the dredged soil to the wash solution (Peng, 2009; Zhang et al, 2013). Soil washing and in-situ soil flushing transfers the metals to a liquid phase by desorption and solubilization (Wuana and Okieimen, 2011; Kim et al, 2019). The soil washing technique can be a physical and/or chemical process that results in the separation, segregation and

volume reduction of hazardous materials and/or the chemical transformation of metals to non-hazardous materials (Zhang et al, 2013). The performance of soil washing can be increased by adding various additives, such as acid washing (e.g. H₂SO₄ and HNO₃), chelating agents (e.g. EDTA, EDDS, NTA and DTPA) or surfactants (e.g. rhamnolipid) (Griffiths, 1995).

A chelant is a ligand that contains two or more electron-donor group such that more than one bond is formed between the metal ion and the ligand (Wuana and Okieimen, 2011). Acids and chelating agents are generally used to remove heavy metals from soils (Wuana and Okieimen, 2011) but the particular reagent added can depend on the metals involved and the specific metal compound or species involved. The changes in the acidity, changes in solution ionic strength, changes in the redox potential and the formation of complexes are the four ways Pickering (1986) identified for mobilizing metals in soils. Acid washing leads to decreased soil productivity and affect the physical and chemical structures of soils due to mineral dissolution.

Chelating agents have been shown to form strong metal-ligand complexes and are highly effective in remediating lead, copper, zinc and cadmium contaminated soil (Zou et al, 2009; Zhang et al, 2013), although extraction efficiency depends on many factors such as how labile the metals are in the soil, the strength of EDTA, electrolysis, pH and soil matrix. (Kim et al, 2005). Soil washing is useful for treating soils contaminated with heavy metals, hydrocarbons but it is not effective for pesticides and volatile organic compounds (Peters, 1999; Mohanty and Mahindrakar, 2011).

The study investigated the efficiency of citric acid, EDTA, malonic acid, oxalic acid, and succinic acid in the remediation of heavy metals in soil using Bonny Light Crude oil (BLCO) contaminated soil as a case study.

2. Materials and Method

Study Location

The ex-situ study was carried out at the University of Benin, Benin City, Edo State, Nigeria. The soil from an uncultivated land with no history of crude oil contamination as well as soil where there was crude oil spill was collected from Ubeji, Delta State, Nigeria (same geographic region as the study site).

Soil Sampling and Pre-Treatment

Top soil (0 – 10cm depth) sample was collected from an uncultivated land with no history of crude oil contamination in a Community in Delta State. Holes were dug at ten different points within the land to a 10cm depth each using plastic spade. Also, soil from the same community where there was crude oil spill from a Bonny light crude oil pipe line (referred to as BLCOSS) was also collected, put into polythene bags and taken to the laboratory. A composite of all the samples was made by mixing thoroughly equal amounts of soil from each point. The composite soil was crushed in a porcelain mortar and sieved through a 2mm sieve. The experimental tests were performed on an aggregate sample prepared by mixing thoroughly equal amount of soil samples collected from the crude oil spill site and the un-contaminated site.

The soils were air-dried at ambient temperature (28-31oC), crushed in a porcelain mortar and sieved through a 2mm sieve. The air-dried < 2mm samples were stored in polythene bags and labelled.

The physicochemical properties of the composite sample were characterized according to standard procedures. Characterization analysis included total metal concentration, cation exchange capacity, soil pH, metal speciation, through sequential extraction, total organic carbon, organic matter and particle size analysis. The results are shown in Table 1.

Particle size was carried out using the methods described by Day (1965). The soil pH was determined by a Suntlet digital pH meter using soil/water mixture volume of ratio 1:2 (Folson et al., 1981). Total organic carbon was determined by the Walkley and Black rapid oxidation method (Nelson and Sommers, 1982) and converted ($1.72 \times C$) to percent organic matter (25). Cation exchange capacity was estimated by summing the

exchangeable acidity determined by flame photometry and titration method. Total concentrations of Fe, Cd, Pb, Cu and Zn in the samples were determined in the crude oil contaminated soils and the control soil by digesting 1g of soil in a mixture of concentrated HNO₃/HClO₄ (v:v 5:1). The digesting tube was cooled and the sides rinsed with distilled water, and filtered with Whatman No.1 filter paper. The solution was diluted to 100ml with distilled water, the concentration of Fe, Cd, Pb, Cu and Zn was measured in the supernatant with Bulk Scientific VGP 210 Atomic Absorption Spectrophotometer.

Soil Fractionation

The method described by Salbu and Oughton, (1998), a modified version of Tessier et al, (1979), was used to identify the chemical form (speciation) of the soil before and after soil wash treatment. The extraction procedure was performed by extracting 2g of Bonny Light crude oil contaminated soil sample in 50ml polypropylene bottle. The sequential scheme is given in Table 2.

After each extraction the mixture was filtered (Whatman No. 1 filter paper) and kept for analysis. To compare the total concentrations of heavy metals measured in the samples, a sixth extraction (residual fraction, step 6) was added to the scheme. Before carrying out the 6th step, the residue was dried and 1g was digested as above using the acid method. All extractions were carried out in triplicate and blanks of the different extractions were analysed.

Soil washing

The Bonny Light crude oil spill soil was subjected to a single-shaker experiment to evaluate the amount of Pb, Cu and Zn removed and mobilized by citric acid, malonic acid, oxalic acid, succinic acid (natural aliphatic acids) and ethylene diamine tetra acetic acid (EDTA – synthetic acid). The washing experiments were performed by placing 5g portion of the Bonny Light crude oil contaminated soil in 100ml polypropylene bottle and adding 50ml of chelating solution (0.05M) and agitated in an end-over-end Heidolph shaker, at 3500rpm. Contact time was 6 hours. Following the agitation, the sample was filtered through a Whatman No. 1 filter paper.

Quality Control

For accuracy and reliability of results, all reagents used were analytical grades (BDH or Sigma). All glasses and plastics used were acid-washed. Buck Scientific standard solutions (Buck scientific Inc.) were used to calibrate the Spectrophotometer. Procedural blank samples were subjected to similar extraction method using the same amounts of reagents and all experiments were done in triplicate.

Statistical Analysis

The result of the study was expressed as mean ± standard error of mean (SEM). Analysis of variance was used to test for differences in the groups, while Duncan’s multiple comparisons test was used to determine significant differences between means. The Instat-Graphpad software, San Diego, California, USA, was used for this analysis. A P<0.05 was considered statistically significant

3. Results and Discussion

3.1 Soil characteristics and levels of contamination

The soil characteristics shown in Table 1 was already reported in an earlier publication (Olubodun and Eriyamremu, 2015; Olubodun and Eriyamremu, 2017). Results obtained showed that cation exchange capacity, and total organic carbon were significantly higher (P < 0.05) in the Bonny Light Crude Oil Contaminated Soil (BLCOCS) and the Bonny Light Crude Oil Spill Soil (BLCOSS) when compared with the control soil. The soil was characterized by moderately acidic pH which was significantly lower (P < 0.05) in the BLCOCS (5.84± 0.03) but higher in the BLCOSS (6.74± 0.01) when compared with the control soil (6.44± 0.03). Cation exchange capacity (CEC) of the control soil was found to be lower than that of BLCOCS and BLCOSS. The highest percent organic carbon was observed in BLCOSS. The metals, Zn, Cu and Pb recorded higher concentrations in the BLCOCS and BLCOSS when compared with the control soil.

The concentration of heavy metals in the crude oil spill soil and estimated intervention values are presented in Table 3. The values of Pb, Cu and Zn for the spill soil were above the value of control soil.

Table 1: Physicochemical characteristics and levels of some metals in control and Bonny

Light Crude Oil (BLCO) contaminated soils (dry weight).

Parameter/Sample	Control	BLCOCS	BLCOSS
pH(H ₂ O)	6.44±0.03 ^a	5.84±0.14 ^b	6.74±0.01 ^c
Soil Texture	Sandy clay loam	Sandy clay loam	Sandy loam
Cation Exchange Capacity (Cmol/kg)	7.08±0.01 ^a	9.05±0.07 ^b	9.98±0.02 ^c
Total Organic Carbon (%)	1.26±0.01 ^a	3.31±0.02 ^b	3.89±0.01 ^c
Clay (%)	26.68	28.0	16.28
Silt (%)	10.30	12.0	10.70
Sand (%)	63.02	60.0	73.02
Lead (Pb)	0.08±0.01 ^a	0.84±0.23 ^b	5.00±0.12 ^c
Zinc(Zn)	10.00±0.03 ^a	46.12 ±0.03 ^b	50.00±0.04 ^c
Cadmium (Cd)	0.01±0.01 ^a	0.05±0.03 ^a	0.01±0.01 ^a
Copper (Cu)	1.05±0.02 ^a	4.60 ±0.02 ^b	6.00±0.02 ^c

Values are mean of three (n=3) replicates ± standard error of mean, BLCOCS= Bonny Light Crude Oil Contaminated Soil, BLCOSS= Bonny Light Crude Oil Spill Soil, THC = Total Hydrocarbon Content. Means of the same row carrying different notations are statistically different at P<0.05 using Instat graphpad.
Source: Olubodun and Eriyamremu, 2017.

Table 2: Schematic representation of sequential extraction scheme

	Reagents	L/S	Duration
Step 1	Distilled water	10	1 hour
Step 2	1M NH ₄ OAc (pH 7)	10	2 hours
Step 3	1M NH ₄ OAc (pH 5)	10	3 hours
Step 4	0.04M NH ₂ OH.HCl	10	6 hours at 60°C
Step 5	30% H ₂ O ₂ (pH 2)	7.5	5.5 hours at 80°C
	3.2M NH ₄ OAc	2.5	30 minutes
Step 6	Concentrated HNO ₃	100	6 hours

Source: Salbu and Oughton, 1998

Concentration of some metals in the BLCOCS and BLCOSS and estimated intervention values.

The intervention values for soil contamination, in Nigeria, is calculated for organic carbon content and clay content of the soil based on the following equation:

$$I_c = I_{st} \times \frac{X_A + B \times X \%Clay \times X \%Org \text{ carbon}}{A + B \times X25 + CX10} \quad (\text{DPR guidelines, 2002}).$$

Where

I_c = Intervention value applying for the soil being evaluated (mg/kg)

I_{st} = Intervention value for the standard soil (Lead

530mg/kg, Copper 190mg/kg and Zinc 720mg/kg)
 %Clay = measured percent clay in the soil being evaluated

%Organic matter = measured percent organic matter in the soil being evaluated

AB and C = constant depending on the substances

Cu, A = 15, B = 0.6, C = 0.6

The intervention values of Pb, Cu, and Zn obtained using the equation above is shown in Table 3. were above the concentrations obtained from the crude oil spill soil but below the standard intervention values recorded for the metals (Lead 530mg/kg, Copper 190mg/kg and Zinc 720mg/kg) [DPR, 2002].

Table 3: Concentration of heavy metals and estimated intervention values for some metals in BLCOSS (mg/kg soil dry weight)

Metals	Control	BLCOSS	Std. Intervention values	Estimated values	Intervention values
Lead (Pb)	0.08±0.01 ^a	5.00±0.12 ^b	530	221.34	
Zinc(Zn)	10.00±0.03 ^a	50.00±0.04 ^b	720	300.51	
Copper (Cu)	1.05±0.02 ^a	6.00±0.02 ^b	190	79.80	

Values are mean of three (n=3) replicates ± standard error of mean. Std. = Standard, BLCOSS = Bonny Light Crude Oil Spill Soil. Means of the same row carrying different notations are statistically different at P<0.05 using Instat graphpad.

Sequential extractions of metals (Pb, Cu and Zn) in BLCOSS before washing

The results of the sequential extraction of Pb, Cu and Zn distribution in BLCOSS before washing is presented in Table 4. The metals were categorized into five fractions namely: exchangeable fraction, oxidizable fraction (bound to organic matter), Acid soluble fraction (bound to carbonate), reducible fraction (bound to Fe-Mn oxides) and residual fraction (bound to silicates and detrital materials).

The total extractable Pb in the crude oil spill soil was 4.16 mg kg⁻¹. Lead was found to be more concentrated in the residual fraction of the soil even though it was below detection limit in some fractions. Total extractable Zn recorded was 51.07 mg kg⁻¹ while total extractable Cu was 6.00 mg kg⁻¹ (Table 4). Copper and Zn were also found to be more concentrated in the residual fraction (4.11 and 30.35 mg kg⁻¹ respectively).

Table 4: Sequential extraction tests in each fraction of soil (mg/kg soil dry weight) before soil washing

Fraction/Sample	Lead (Pb)	Zinc (Zn)	Copper (Cu)
Exchangeable	1.34±0.03	8.85±0.03	1.89±0.03
Oxidizable	ND	10.11±0.03	ND
Acid soluble fraction	1.00±0.05	7.75±0.03	ND
Reducible	0.24±0.02	9.08±0.05	ND
Residual	1.58±0.03	30.35±0.03	4.11±0.03
Total extractable metals	4.16±0.11	51.07±0.06	6.00±0.05
Mobile phase (%)	56	33	32

Values are mean of three (n=3) replicates ± standard error of mean, ND = Not Detectable.

Soil washing with different chelating agents

Soil washing was carried out to determine the concentrations of Pb, Cu and Zn removed from BLCOSS by the different chelating agents after 6 hours wash test. The results of the percentage removal of the metals from crude oil spill soil is presented in Table 5. At the end of the wash test.

Table 5: Percentage Removal of some metals by chelate agents after washing (%)

Chelates/Sample	Pb	Cu	Zn
EDTA	89	78	72
Citric acid	45	53	65
Oxalic acid	43	45	47
Malonic acid	38	40	42
Succinic acid	32	39	39

Values are mean of three (n=3) replicates ± standard error of mean.

4. Discussion

Physicochemical characteristics of Bonny Light crude oil spill soils

Earlier record of the physicochemical characteristics of the BLCOSS agrees with the results reported by other researchers for soils in Nigeria (Oviasogie and Ofomaja, 2007; Noma *et al*, 2008). The degree of acidity and/or alkalinity has been considered a master variable that affects nearly all soil properties. For example, the amount of acid (or alkali) in soils determines the availability of many nutrients for plant growth and maintenance (Arias *et. al.*, 2005). Thus, the measured pH values may well have implications on the availability and uptake of metals by plants.

The high cation exchange capacity may act as a buffer which may slow down leaching of nutrient cations and positively charged contaminants because they affect both soluble and exchangeable metal levels (Ng *et al.*, 2022).

The total organic carbon (TOC) values obtained in the results are comparable to those reported by Uba *et al.*, (2008), however, the values are high than others reported (Enwezor *et al.*, 1988). The high organic carbon is suggestive of the presence of degradable and compostable wastes in the spill soil and this may influence the chemical and physical processes of the soil as a conducive environment for plants (Obasi *et al.*, 2012).

Concentration of selected metals in the soil with Bonny Light crude oil spill.

The occurrence of heavy metals in various aspects of the environment has been attributed to anthropogenic activities (Rohrbacher and St-Arnaud, 2016). Over the years, these activities have neither been regularized nor monitored (Sarkodie *et al.*, 1997). The situation has led to serious impacts on both the terrestrial and aquatic environment due to their high toxicity, recalcitrance and persistence in the environment (Rohrbacher and St-Arnaud, 2016)

The low concentrations of lead obtained in this study indicates that the crude oil spill soils is slightly contaminated with lead. However, because of their recalcitrant and persistent characteristics in the environment, they may become a major environmental and health issue if and when there is continuous spill and industrial activities in the area that may accumulate to toxic concentrations.

The concentrations of zinc shown in the study were lower than concentration of zinc reported for some contaminated sites in Nigeria (Iwegbue *et al.*, 2013) and other parts of the world (Kashem *et al.*, 2007). The solubility of Cu and Zn are governed by pH and redox conditions of the soil. In acidic pH, Cu and Zn are distinctly more soluble under oxidizing conditions than reducing conditions (Iwegbue *et al.*, 2013).

The normal range for copper in soil falls within (7- 8.0 mg/kg). The values of the spill soils are high compared with control but below selected average (13-24 mg/kg) reported by other researchers (David *et al.*, 2009). The metal concentrations of the crude oil spill soil are below the permissible/toxic limits for agricultural lands set by

USEPA (1986). This result does not agree with those of other researchers who had higher values (Obasi *et al.*, 2012). Generally, the results indicates that the estimated intervention values are lower than the standard intervention values for Nigerian soils (DPR 2002) as such, the soil may be classified as slightly contaminated.

Sequential extractions of metals (Pb, Cu and Zn) in Bonny Light crude oil spill soil before soil washing

The sequential extraction of the metal concentration in BLCOSS is categorized into five fractions (Table 4). The metals in the exchangeable fractions determines mobility of the metals to the aqueous phase (Sparks, 2003). Carbonates on the other hand, are stable at acidic pH and provides adsorbing surfaces as well as buffering soil pH (Olubodun and Eriyamremu, 2017).

The highest concentrations of metals in BLCOSS were observed in the exchangeable, acid soluble and residual fractions. This results is at variance with those reported for soils in mining environment (Kakulu and Matthews-Amune, 2012).

The high concentration of the metals in the residual fraction may be due to the presence of acid resistant minerals. Also, it may be due to the sandy nature of the soil (Olubodun and Eriyamremu, 2017). The metal may have co-precipitated with various silicate species consequent to their absorption into the minerals lattice (Groeningen *et al.*, 2020).

Soil washing of Bonny Light Crude Oil Spill Soil with different chelating agents

The role of organic acids in decontamination of soil has been tied to the type of organic acid, pH, and soil organic matter content among others (Vranova *et al.*, 2013). The results after the 6-hour wash test indicates that EDTA had the highest efficiency for removing the metals. This may be due to the strength of the bond between a metal and a synthetic chelate agent, which is generally stronger for synthetic chelates when compared with natural organic chelates. This study is at variance with the report that natural organic acids solubilized the highest amount of metals that are plant nutrients (Zn and Cu), while the synthetic chelates EDTA desorbs toxic metals (Pb) from soil in highest amounts (Vranova *et al.*, 2013). EDTA were noticeably effective in desorbing Pb, Cu and Zn whereas the natural organic acids solubilized lesser

percentage of this metals from the crude oil contaminated soil.

The major drawback for using synthetic chelate (EDTA) in field conditions is their high persistence to biodegradation, with consequent high risks of metal leaching through soil profile. The levels of heavy metals in soil solution after EDTA application can be much higher than plant's ability to absorb them (Nascimento, 2006; Yan *et al*, 2020). However, only high metal solubilization from soil is not enough to guarantee efficient phyto-extraction because the chelate must be capable, also of increasing the transfer of metals from roots to shoots (Nascimento, 2006).

The least effective of malonic and succinic acids in desorbing the metals from BLCOSS may be due to the low water solubility of the acids in comparison to the other chelates. This fact leads to a lesser extent of reaction with metals bound to soil colloids or precipitated. The low ability of malonic and succinic acids to complex Pb, Zn and Cu, the least soluble among the studied metals, agrees with such assumption. If increase in their concentration could however, remove as much metals from contaminated soil as EDTA without increasing the leaching risk is possible (Nascimento, 2006; Yan *et al*, 2020), more studies is required on concentrations and application time of natural organic acids to make their use in phyto-extraction a viable alternative to synthetic chelates application.

5. Conclusion

Aliphatic organic acids and synthetic acids play an important role in soil, in decontamination of metals from crude oil contaminated sites. The study reveals that soil washing using chelate agents may be applied as a primary removal agent in remediation of heavy metals from crude oil contaminated soil. The efficiency being in the order EDTA > Oxalic acid > malonic acid > Succinic acids. Remediation of crude oil contaminated soil is necessity in order to have a safe and healthy environment that will in turn results in healthy lifestyle across the globe.

6. Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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