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Effectiveness of Calcined Calcium Carbide Waste (CCCW) in Mitigating the Leachability of Lead and Cadmium from Contaminated Soil from Evbareke Spare Parts Market Benin City Edo State Nigeria

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Abstract

Heavy metal contamination of soil can present dangers besides threats to humans as well as the ecosystem via uninterrupted intake or interaction with contaminated soil and the food chain. The purpose of this research is to examine the effectiveness of calcined calcium carbide waste (CCCW) in mitigating the leachability of lead and cadmium ions in contaminated soil from Evbareke spare parts market Benin City, Edo State Nigeria. Contaminated soil samples were collected using quadrant sampling method at the depth of 0-15cm with soil auger. The calcium carbide waste was obtained from a panel beating workshop dumpsite. The calcium carbide waste was dried to constant weight in an oven at 105^{o}C. 50g of the dried calcium carbide waste (CCW) was crushed in a mortar to obtain a powdered form. The X-ray diffraction analysis for the CCCW revealed that it was made up of predominantly portlandite (47%), calcite fraction (23.0%), dolomite (12.7%), coesite (8.6%), muscovite (4.5%) and lime (4.0%), this was corroborated by FTIR analysis. SEM analysis revealed that CCCW possess a rough surface with pore of varied size and irregular shape. The contaminated soil from the Evbareke spare parts market was contaminated with petroleum hydrocarbons, the soil was saline with low C.E.C. The soil texture was loamy-sand. As the amount of CCCW amended increase in the soil, the amount of cadmium and lead ions that was releasable in the soil reduced. The cadmium and lead ions in contaminated soil was stabilized hence reducing the cadmium and lead availability in the soil. The optimum amender amount in the contaminated soil to immobilize lead ion was 4% w/w and ≥2% w/w for cadmium ion. The CCCW effectively mitigated the leachability of lead and cadmium

Keywords: Remediation, Immobilization, Contamination, Automobile, Heavy metal

INTRODUCTION

Soil is a key reservoir for heavy metals discharged into them by anthropogenic actions (Selvi *et al.,* 2019; Briffa, *et al.,* 2020; Xu *et al.,* 2021). Toxic metals existence in soil can sternly impede organic contaminants biodegradation (Hananingtyas *et al.,* 2022). Heavy metal contamination of soil can present dangers besides threats to humans as well as the ecosystem via uninterrupted intake or interaction with contaminated soil and the food chain (Hange and Awofolu 2017; Briffa, *et al.,* 2020). Lead is acknowledged to be responsible for haemoglobin and anaemia biosynthesis illness, upsurge in blood pressure, waned fertility of men via sperm destruction and behavioural disturbances of children, such as aggression, impulsive behavior and hyperactivity. It is also acknowledged to trigger protein precipitation, via lead ions

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contact with the sulphydryl homeostasis (-SH) groups of proteins (Ojo, 2017; Asmoay *et al.*, 2019; Briffa, *et al.,* 2020).. Cadmium is acknowledged to affect several enzymes in the body. The renal destruction that ensues in proteinuria is the effect of cadmium negatively having an effect on enzymes in charge of proteins reabsorption in kidney tubules. Cadmium is responsible for *itai itai* disease, which results in hurting bone disease (osteomalacia) linked with kidney malfunction (Ojo, 2017; Asmoay *et al.*, 2019; Briffa, *et al.,* 2020).

Heavy metal bioavailability in soil is by and large articulated as a correlation connecting the heavy metals quantities take up by plant tissues and it's concentrations in soil (Agrelli *et al.,* 2020; Petruzzelli *et al.,* 2020; Ndzana *et al.,* 2021). Heavy metals bioavailability in soils to a great degree depends on their spread between the solid and solution phases (Wang^b *et al* 2021; Xu et al., 2022). This spreading is sequentially reliant on the soil processes such as; specific adsorption, cation exchange, precipitation as well as complexation (Liu *et al.*, 2018; Ojebah and Uwague, 2018; Petruzzelli *et al.,* 2020). pH is commonly known to be the very significant factor affecting metal bioavailability in soils, with solubility and pH more often than not displaying an inverse correlation with metal bioavailability (Petruzzelli *et al.,* 2020). The existence of clays besides hydrous Fe and Mn oxides in soil tends to build up metal adsorption and consequently decrease soluble metal contents, whereas the consequences of organic matter content and redox potential are unclear (Petruzzelli *et al.,* 2020).

Remediation plans focal-pointing on decreasing metal bioavailability are most appropriate, because decreased bioavailability is equitable with decreased risk (Petruzzelli *et al.,* 2020). There are three principal risk management tactics by which the 'source–pathway–receptor' pollutant nexuses can be smashed - through source elimination or source control by remedy, controlling their pathway and modifying exposure of the receptor. By and large, contaminated locations are remedied by linking these three approaches. For instance, Source control consist of *in-situ* and *ex-situ* remedy technologies for sources of contamination, pathway control consist of containment technologies which can encapsulate the contaminants and put off or significantly reduce their migration or distribution while altering the exposure of the receptor (Hu *et al.,*2019; Cao *et al.,* 2021).

Immobilization technology time and again utilizes organic and inorganic amendment to fast-track weakening or eradication of metal mobility and toxicity in soils (Khalid *et al.,* 2017). The principal task of immobilizing amendments is to modify the initial soil metals to more geochemically stable phases through sorption, precipitation, and complexation means (Petruzzelli *et al.,* 2020; Wang^a *et al.,* 2021). The frequently used amendments consist of clay, cement, zeolites, minerals, phosphates, organic composts as well as microbes (Khalid *et al.,* 2017; Liu *et al.*, 2018).

In order to reduce disposal issue or accumulation of this kind of waste as well as its cheapness or its availability, this study proposed the use of calcined calcium carbide waste in remediation of heavy metal contaminated soil. The calcination of calcium carbide waste aids removal of harmful waste as well as decompose some components of the waste to increase its calcium oxide component. Oxides (comprising hydroxides, hydrous oxides and oxyhydroxides) have been widely examined as immobilizing agents for heavy metals owing to their exceptional sorption affinities (Petruzzelli *et al.,* 2020; Wang *et al.*, 2021). The regular liming materials employed to amend acidity are calcium oxide (CaO) and calcium carbonate ($CaCO_3$) in powdery formulations (Kebede *et al.,* 2021). Calcitic ($CaCO_3$) and dolomitic [$CaMg(CO_3)_2$] lime are regularly utilized to raise pH. At pH 6.4 the carbonate component in lime acts as a buffer and the cations in lime are nutritionally important (Ca and Mg) (Schreiber and Nunez, 2021).

This research work is designed to study the consequences of calcined calcium carbide waste (CCCW) in mitigating the leachability of lead and cadmium from contaminated soil.

MATERIALS AND METHOD

Study Area, Soil Sample Collection and Pre-treatment

A set of fifty-eight (58) samples out of a probable sixty-four (64) sampling points of contaminated soil samples were collected from Evbareke spare parts market in Evbareke (latitude 6^0 22′ N and longitude 5^0 36′ 00″E) and the control soil was taken from Evbareke Secondary School (latitude 6^0 21′ 33″N and longitude 5^0 37′ 00′E) in Egor Local Government Area, Edo State, Nigeria at a depths of 0-20cm using soil auger, on a land area of roughly $450m^2$. The system grid sampling method was utilized for gathering the soil sample. The debris in the collected soils was removed, followed by air-drying the soil samples at ambient temperature which was ground and sieved to give ≤ 2mm particle size and composited as the parent soil. The left over moisture was eliminated by heating at 105 ± 5^oC for 3 hours in an oven.

Physicochemical Characterization of Soil Sample

The soil sample was physicochemically characterized for pH, Particle size analysis – Hydrometer method, electrical conductivity, cation exchange capacity, total phosphorus, total petroleum hydrocarbon, total organic carbon and moisture content using standard method (North Central Region-13, 1998).

Heavy Metal Determination in Soil Sample

The heavy metal in the soil was verified using sequential extraction procedures-Fractionation, adopted from Tessier *et al.*, (1979). The heavy metal content in each fraction was determined using atomic absorption spectrophotometric (AAS) with the aid of VGP 210 model-Buck Scientific Equipment Inc.

Preparation of Calcined Calcium Carbide waste (CCCW)

The calcium carbide waste (CCW) was collected from a panel beating workshop located at Isiohor near Nigeria Army School of Supply and Transport (NASST) in Isiohor, Benin city, Edo state. CCW was dried at 105^oC for 24 hours in an electrical oven. The dried CCW was crushed and ground into powdery form, after wards, the CCW was calcined in a muffle furnace at 600^oC for 5 hours and it was observed that the calcined calcium carbide became whitish in colour. It was further puverised to obtain a powdery and very smooth form and then placed in the desiccator till it was needed for application.

Characterisation of Calcined Calcium Carbide Waste

The calcined calcium carbide waste prepared was characterized using Fourier Transform-Infra Red (FT-IR System, spectrum BX, PerkinElmer, England), Scanning electron microscopy (SEM; phenom pro suite desktop scanning electron microscope) and x-ray diffraction (with X-Ray diffractometer, Schimadzu 6000 model).

Leaching of Heavy Metals from Soil Sample Amended with Calcined Calcium Carbide Waste (CCCW) Using Column Test Leaching Method (CTLM).

Column test leaching method adopted from Chezom *et al.* (2013) with slight alterations was applied to verify the level of insitu-immobilization of lead and cadmium. The leaching technique was done in a column filled with different mass proportions of the calcined calcium carbide waste and the soil sample at L/S ratio of 2:1. The column containing the amended soil sample of 50g was supported on a retort stand. The end of the column was covered with a semi permeable membrane and 100ml of distilled water loaded with 1% HCl (v/v) was poured into the column and allowed to stand for 1hour after which it was perforated so that the leacheate passes through the vertical column of the amended soil in a down-flow manner and the leachate obtained was analyzed for lead and cadmium using AAS. Table 1 show the different mixture ratio of contaminated soil sample and calcined calcium carbide waste placed in each column.

Table 1: Ratios of Soil Sample and Calcined Calcium Carbide Waste (CCCW) Composite Mixture.

Percentage	Weight of CCW (g)	Weight of Soil (g)
2%	1	49
4%	2	48
6%	3	47
8%	4	46
10%	5	45

RESULTS AND DISCUSSION

Results

Physicochemical Characterization of Soil Samples

The Results of the physicochemical characterization of the contaminated soil sample as well as that of the control site soil where automobile disassembly was not taking place are presented in Table 2.

Table 2: Results of the Physicochemical Characterization of the Soil Sample

Parameters	Units	Contanminated soil	Control Soil
pH	-	6.24	5.43
Electrical conductivity	µS/cm	1037.50	235.00
Total phosphorus	mg/kg	372.58	202.20
Total petroleum hydrocarbon	mg/kg	107,304.59	4.04
Cation exchange capacity	Cmol/kg	9.89	4.34
Total organic carbon	%	3.63	1.11
Moisture content	%	1.05	0.84
Particle size analysis	Clay (%)	4.38	5.88
	Silt (%)	3.60	7.60
	Sand (%)	92.02	86.52

Geochemical Characterization of Lead and Cadmium in Soil Samples.

Geochemical characterization results for Lead and Cadmium in the contaminated soil as well as the control site soil where automobile disassembly was not taking place is presented in Table 3.

Table 3: Results of the Geochemical (Soil Fractionation) Characterization of the Soil Sample for Lead and Cadmium.

Fraction	Contaminated soil (mg/kg)		Control soil (mg/kg)	
	Lead	Cadmium	Lead	Cadmium
Soluble	0.21	0.03	BDL	BDL
Exchangeable	1.07	0.20	BDL	BDL
Carbonate-bound	7.50	0.20	0.71	BDL
Fe-Mn oxide bound	21.07	0.47	0.71	BDL
Organically bound	3.21	0.20	BDL	0.07
Residual	19.64	BDL	BDL	BDL
Total	52.70	1.10	1.42	0.70

BDL=below detectable level

Bioavailability of Lead and Cadmium in the Soil Samples vis-à-vis Highest Acceptable Concentration (HAC) by NESREA.

The results of evaluation of the most reactive, most labile and most possibly available or bioavailable fractions of lead and cadmium ions in the contaminated soil as well as the control site soil where dismantling activities was not taking place is presented in Table 4, which also revealed a comparison of the total quantity of bioavailable fractions of lead and cadmium ions in the contaminated soil vis-à-vis highest allowable concentration (HAC) by NESREA.

Table 4: Bioavailable Lead and Cadmium of the Geochemical Fraction in the Soil Samples vis-à-vis Highest acceptable Concentration (HAC) by NESREA.

Fraction	Contaminated soil (mg/kg)		Control soil (mg/kg)	
	Lead	Cadmium	Lead	Cadmium
Soluble	0.21	0.03	BDL	BDL
Exchangeable	1.07	0.20	BDL	BDL
Carbonate-bound	7.50	0.20	0.71	BDL
Total	8.78	0.46	0.71	BDL
HAC (NESREA, 2009)	10	3.0		

BDL=below detectable level

Mobility Factor Determination

An estimation of risk of contamination of lead and cadmium ions to receptor organism such as plant in the contaminated soil as well as the control site soil site where dismantling activities was not taking place is presented in Table 5. The relative index mobility of these metals was determined as mobility factor (MF) (Osakwe, And Okolie, 2015) applying the following equation:

$$\mathrm{MF} = \frac{F_1 + F_2 + F_3}{F_1 + F_2 + F_3 + F_4 + F_5 + F_6} \mathrm{X}\ 100 \qquad (1)$$

Where F_1, F_2, F_3, F_4, F_5 and F_6 are water soluble, exchangeable, carbonate, Fe-Mn oxide bound, Organically bound and Residual fractions respectively.

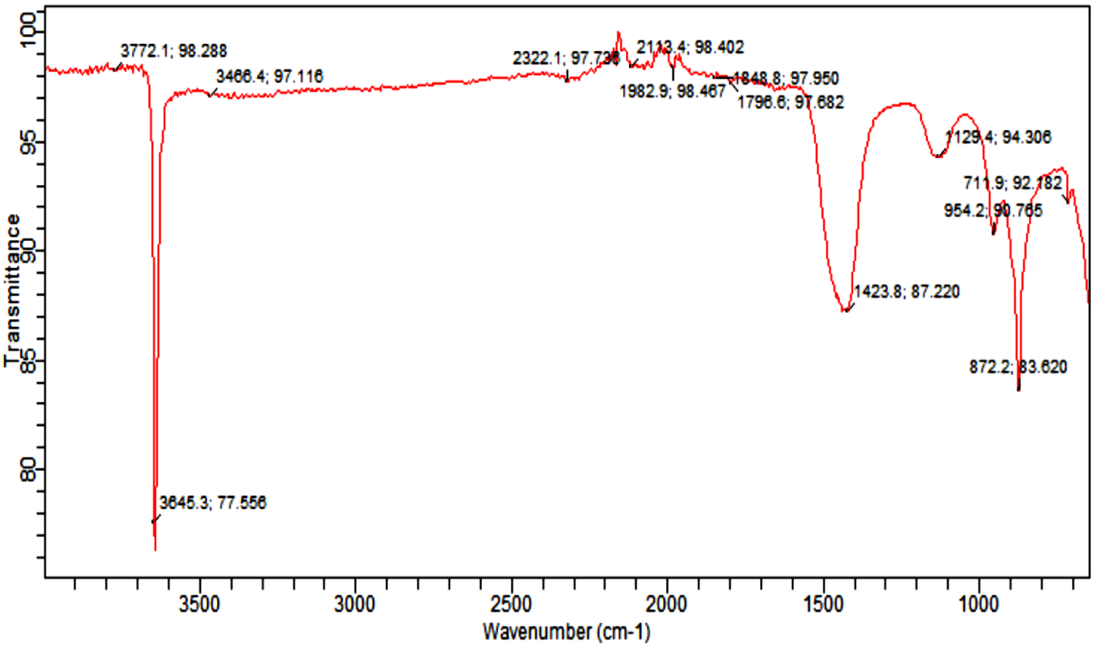
Table 5: Mobility Factor Determination for Lead and cadmium in Soil Samples.

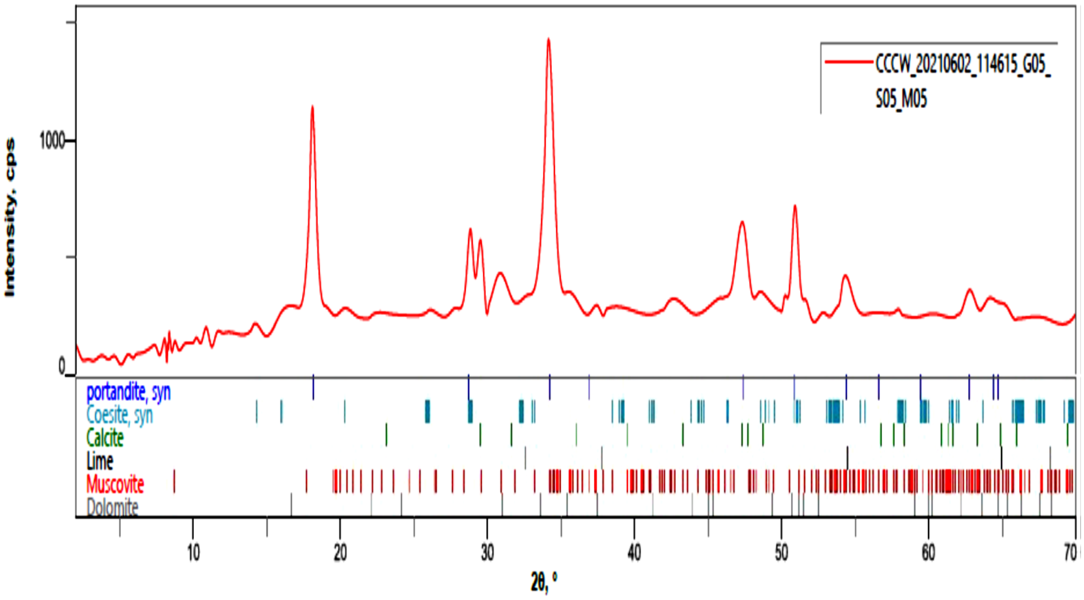
Fraction	Contaminated soil (%)		Control soil (%)	
	Lead	Cadmium	Lead	Cadmium
Soluble	0.40	2.73	BDL	BDL
Exchangeable	2.03	18.18	BDL	BDL
Carbonate-bound	14.23	18.18	50.00	BDL
Fe-Mn oxide bound	39.98	42.73	50.00	BDL
Organically bound	6.09	18.18	BDL	100.00
Residual	37.27	BDL	BDL	BDL
Mobility Factor	16.66	39.09	50.00	BDL

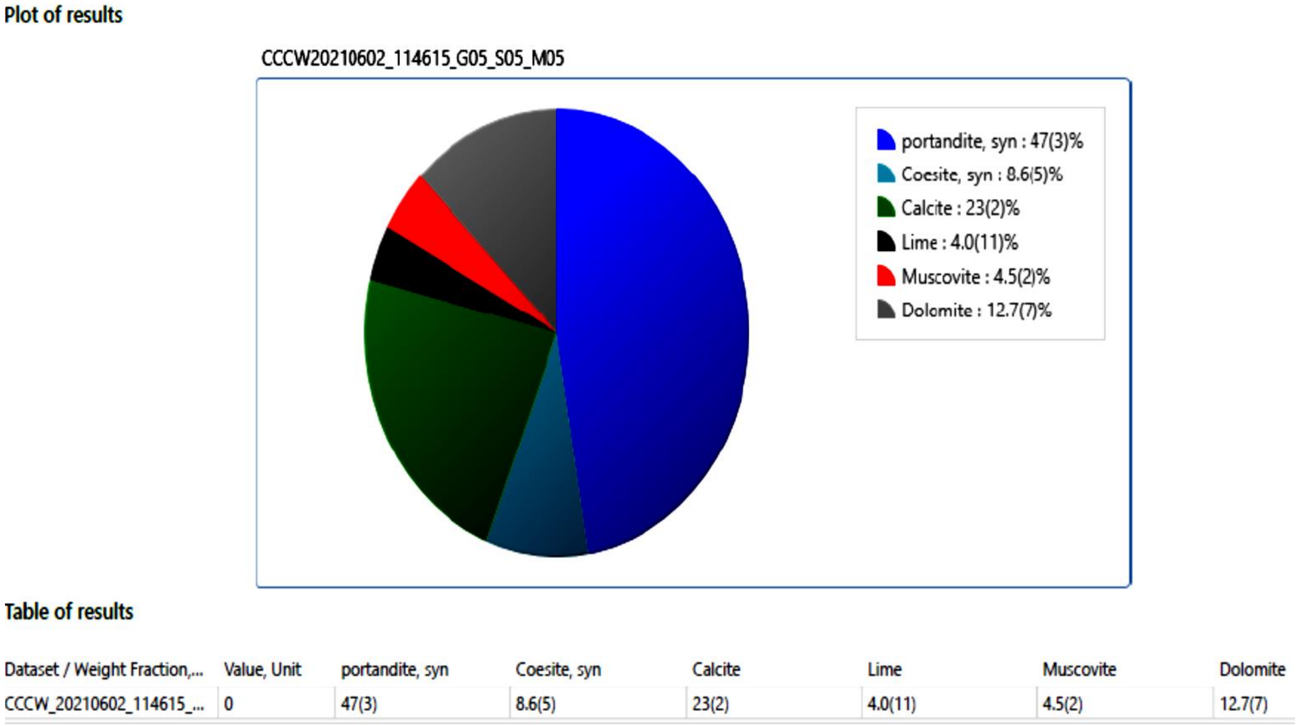
BDL=below detectable level

Characterisation of Calcined Calcium Carbide Waste

The results of the characterization of calcined calcium carbide waste (CCCW) using Fourier Transform-Infra Red (FT-IR), Scanning electron spectroscopy (SEM) and x-ray diffraction (XRD) are shown in the Figures 1, 2, 3 and plate 4:





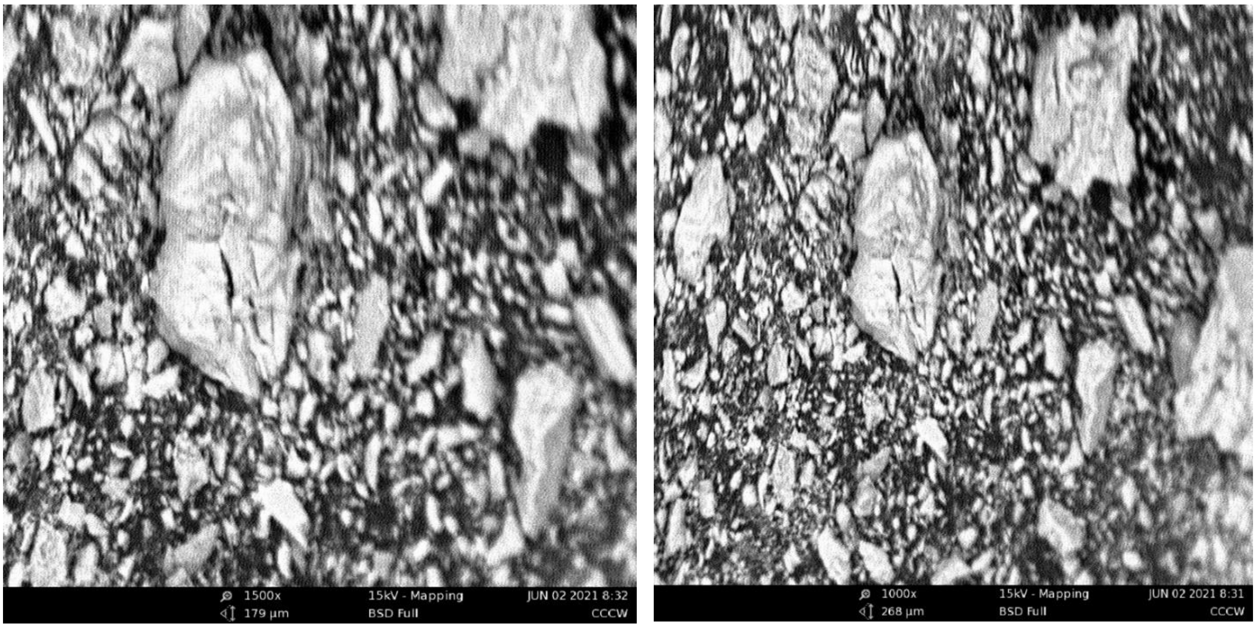


Plot of results

CCCW20210602_114615_G05_S05_M05

Table of results

Dataset / Weight Fraction,...	Value, Unit	portandite, syn	Coesite, syn	Calcite	Lime	Muscovite	Dolomite
CCCW_20210602_114615_...	0	47(3)	8.6(5)	23(2)	4.0(11)	4.5(2)	12.7(7)



a b

Figure 4: SEM pictures of CCW-CLAS composite (a) at 1500x magnification and (b) at 1000x magnification

Effect of calcined calcium carbide waste (CCCW) on leaching of cadmium and lead from contaminated soil

Results of effect of calcined calcium carbide waste (CCCW) on leaching of cadmium and lead from contaminated soil is shown in Table 6 and Figure 5.

Table 6: Effect of calcined calcium carbide waste (CCCW) on leaching of cadmium and lead from contaminated soil.

Percentage	Weight of CCCW (g)	Weight of Soil (g)	Amount of Leached lead from contaminated soil (mg/g)	
			Lead	Cadmium
2%	1.00	49.00	0.03	BDL
4%	2.00	48.00	0.02	BDL
6%	3.00	47.00	0.01	BDL
8%	4.00	46.00	0.01	BDL
10%	5.00	46.00	0.01	BDL

BDL=0.00

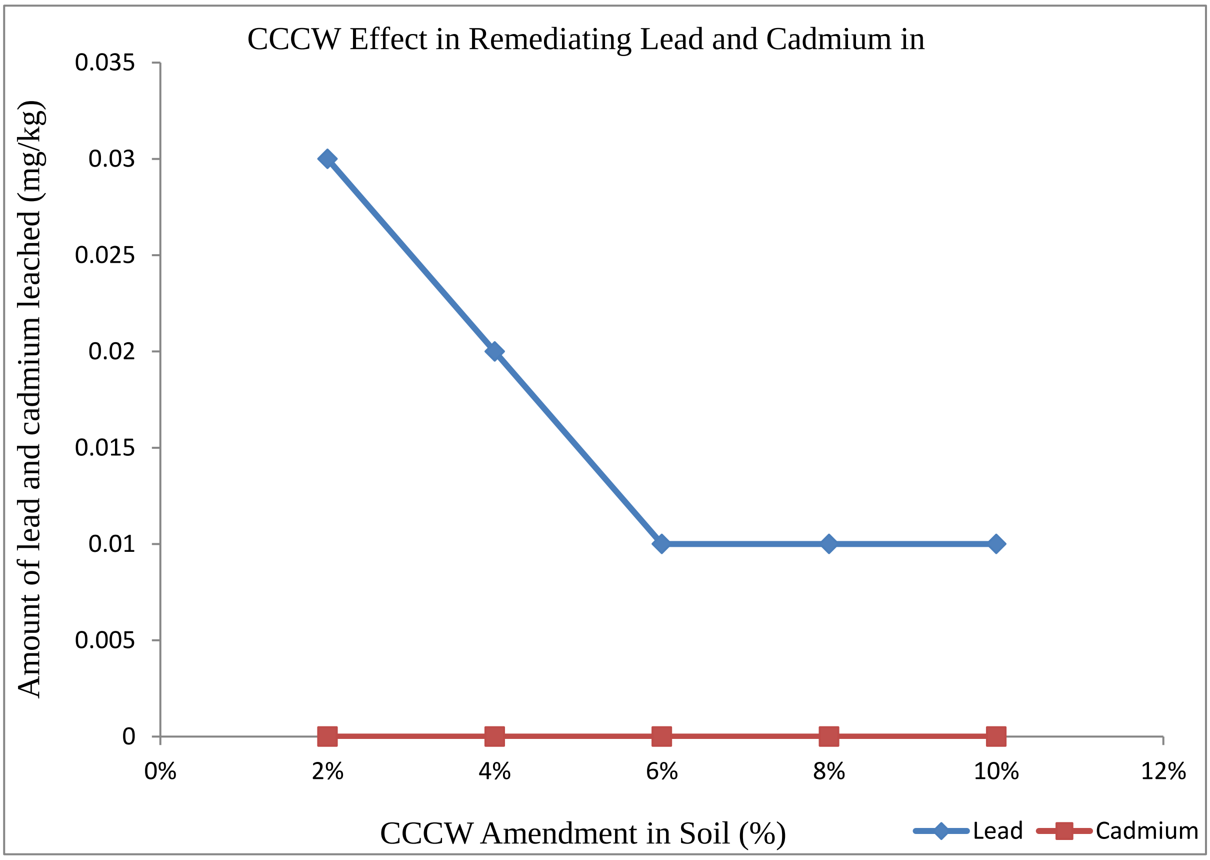


Figure 5: Effect of CCCW Effect in Remediating Lead in Contaminated Soil

DISCUSSION

Physicochemical Characterization of Soil Samples

The physicochemical characterization of the contaminated soil from Evbareke spare parts market revealed that the soil was heavily polluted with total petroleum hydrocarbon (Table 2). Judging from the electrical conductivity, the contaminated soil contains high level of electrolyte or soluble salt content (salinity) compared to the soil from control site, this in agreement with lead and cadmium availability vis-a-vis control soil as asserted by Du Laing *et al.* (2007) that metal availability increases with increase in salinity. The cation exchange capacity is rated low, because its value falls between 6-12 Cmol/kg (Hazelton and Murphy, 2007) an indication that the soil has a low resistance to change in soil chemistry caused by land use (Table 2). The chemical activity of the H^+ and OH^- is lowest when the pH is close to neutral and goes a long way to affecting the availability of lead and cadmium in the contaminated soil, the value of pH obtained for the contaminated soil is 6.24 (Table 2), it is slightly acidic, and could have contributed to the bioavailability of cadmium and lead ion in the contaminated soil. The particle size analysis for the contaminated soil revealed that the soil textural class was loamy sand and the clay quantity is very low (< 5%) hence having a little or no withholding effect on the cadmium and lead ions.

Geochemical Characterization, Bioavailability and Mobility Factor Determination of Lead and Cadmium in Soil Samples.

The amount of lead and cadmium ions in the soluble, exchangeable and carbonate bound fraction combined were less than its amount in the Fe-Mn oxide bound fraction (Table 3). Chengo *et al.,* (2013), asserted that heavy metals in soil are possibly available for plant absorption, if the Mobility Factor is above 10%, This indicated that the cadmium and lead ions were possibly bioavailable since they had a mobility factor of 16.66 and 39.09% respectively (Table 5). On comparing the cadmium and lead ions in the contaminated soil with highest allowable concentration (HAC) from NESREA, it revealed that the amount of lead and cadmium ions in the contaminated soil from Evbareke spare parts market were lesser (Table 4) an indication that the contaminated soil was below pollution level however, they are bioavailable and the total lead content in the contaminated soil exceeded that of HAC while the total cadmium content was less than NESREA standard (Table3).

Despite the mobility factor of cadmium and lead ions were low, CCCW was able to further reduce their bioavailability in the soil by insitu immobilization remediation pattern thereby making it to be further less available for uptake by plants hence reducing its transmission to man and animals, an indication that the CCCW amendment has transform majority of the cadmium and lead ions into insoluble or unavailable form. Ogundiran and Osibanjo, (2009) asserted that If heavy metals are found primarily in the soluble form, they may be leached down the soil profile getting to the groundwater or absorbed and stored by plants, invertebrates, animals and man.

Characterisation of Calcined Calcium Carbide Waste

The FT-IR spectra (Figure 1) revealed the characteristics bands at 3772.1 cm^{-1}; 3466.4 cm^{-1} and a sharp peak at 3845.3 cm^{-1} due to OH-stretching of hydroxyl group attributed to calcium hydroxide (hydrated lime), calcium oxide (quick lime) and silicon hydroxide, SiOH. The weak band at 1882.9 cm^{-1} is attributed to $Ca(OH)_2$ while the weak band at 1796.8 cm^{-1} and strong broad and sharp band is a pointer to the presence of CO_3^- ions attributed to calcium carbonate. The appearance of weak broad peak at 1129.4 cm^{-1} indicated the presence of a silicate and a phosphate ion. The characteristic weak band at 954 cm^{-1} reveal the presence of silicate ion and magnesium oxide (MgO) and a very strong sharp band at 872.2 cm^{-1} and a weak band at 711.9 cm^{-1} further indicated the presence of CO_3^- ion attributed to calcium carbonate ($CaCO_3$).

The defractogram, plot and table of result of the x-ray for CCCW (Figure 2 and 3) revealed that it was made up of predominantly portlandite fraction (47.0%) which is a calcium hydroxide mineral component of limestone (Figure 3). This closely followed by calcite (23.0%) which is the naturally occurring form of calcium hydroxide. The other constituents of the composite include, coesite (8.6%) – a form of silicon oxide (SiO_2), muscovite (4.5%) – a form of hydrated phyllosilicate mineral of aluminium and potassium, dolomite (12.7%) - a type of limestone rich in magnesium and calcium carbonate ($CaMg(CO_3)_2$) and lime (4.0%) – this is a calcium containing inorganic mineral composed primarily of oxides and hydroxides. The CCCW is made up of 86.7% of carbonates, oxides and hydroxides of calcium put together, which can raise the soil pH in the environment thus decreasing availability of the lead and cadmium ions for uptake by plants to large extent. The SEM photograph, revealed that CCCW posesses a rough surface with pores of varied size and irregular shapes. The fragmention of the particles and the difference in pore size reveals its ability adsorb cadmium and lead ions, thus preventing its leaching.

Effect of calcined calcium carbide waste (CCCW) on leaching of cadmium and lead from contaminated soil

As the amount of CCCW amendment increased in the soil, the amount of cadmium and lead ion that was releasable or made available in the soil reduced. However, no soluble or available form of cadmium ions was leached. When the proportion of CCCW amendment reached 4% w/w level, the amount of lead ions leached remained constant at 0.01mg/kg and the cadmium ions was below detectable level, even when the amendment dosage increased to 10% w/w CCCW. This study revealed that the optimum amount for the remediation of the contaminated soil was at 4% w/w (2.00g-CCCW/48.00g-contaminated soil) for the lead contaminant and <2% w/w (<1.00g-CCW/49.00g-contaminated soil) for cadmium contaminant. The carbonates, oxides and hydroxides of calcium may have acted as the strong absorbent for lead and cadmium ions and since it can complex as double salts like $CaCO_3.MCO_3$ (Rostami and Ahangar, 2013) this implies that the combined effect of the complexation and adsorbent, is most likely responsible for the insitu immobilization of the lead cadmium ions in the contaminated soil.

CONCLUSION

CCCW was able to further reduce the lead and cadmium ions availability in the soil by insitu adsorption and complexation remediation pattern, thereby making it to be further less available for uptake by plants hence reducing its transmission to man and animals. The CCCW was effective in mitigating the leaching of lead and cadmium. However, the amender was more effective for the immobilization of cadmium ion in the contaminated soil.

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