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Use of Surface Modified Calcium Oxide Nanoparticle in Immobilizing of Lead and Cadmium Contaminated Soil

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Abstract

Remediation is vital in advancing the agriculture yield and decreasing the hazard of food poisoning in contaminated soil. The aim of this study was to remediate lead and cadmium contaminated soil from Evbareke spare parts market using surface modified calcium oxide nanoparticle (SMCON). Soil samples were collected from Evbareke spare parts market, Benin City, Edo state Nigeria, using quadrant sampling method at the depth of 0-15cm using soil auger. The soil samples obtained were physicochemically and geochemically characterized. The SMCON was synthesized and characterized using Fourier Transform-Infra Red, Scanning electron spectroscopy and x-ray diffraction. A leaching experiment was carried out to authenticate the immobilization efficiency and capacity of SMCON on the lead and cadmium in the contaminated soil. The SMCON efficiency for lead and cadmium immobilization in the contaminated soil increased with increase in immobilizer up to the optimum 4% of SMCON in contaminated soil for lead and ≤1% of SMCON for cadmium. Likewise, the immobilization capacity of SMCON in the contaminated soil also revealed that more of lead and cadmium were immobilized as SMCON content in the contaminated soil mixture increased, thereby disallowing leaching of lead and cadmium from the contaminated soil. The SMCON effectively decreased the lead and cadmium in the soil by in situ adsorption, ion exchange and complexation mechanism thus reducing its accessibility for uptake by plants and its transmission to man and animals.

Keywords: *Soil; Remediation; Immobilization; Contamination; Nanoparticle*

Introduction

Soil is the natural environment indispensable to agriculture and ultimately favorable to human's health. Numerous anthropogenic activities contaminate the soil with a load of organic and heavy metal contaminants (Chen *et al.,* 2021; Rajput *et al.,* 2022). Heavy metal pollution is one of the key factors limiting crop production by principally altering the normal cell structure, the antioxidant system and hence plant growth thus portending food security (Zhou *et al.,* 2021). Heavy metals mainly affect the plants and lower soil organisms by inducing the generation of reactive oxygen species (ROS), which further results in the damage of macromolecules such as proteins and nucleic acids. One of the key methods for the removal of heavy metals includes site stabilization that immobilizes them at a specific site thus decreasing their mobility and availability in the soil and stops them from leaching across the sites (Rajput *et al.,* 2022).

The possibility and conveyance of heavy metals in soil is expressively centered on its chemical form and speciation. The instant heavy metals are in soil, it is first adsorbed with rapid reactions in minutes or hours, ensued with sluggish adsorption reactions in days or years as well as subsequent rearrangement into diverse chemical types alongside variable bioavailability, mobility as well as toxicity (Galdames *et al.,* 2017). Heavy metals redistribution in soil is assumed to be regulated with reactions within soils such as mineral precipitation and dissolution, biological immobilization and mobilization, adsorption and desorption, ion exchange, aqueous complexation and plant uptake (Galdames *et al.,* 2017).

Among existing remediation technologies, in situ immobilization of heavy metals using a chemical amendment is an economical and environmentally maintainable remediation technique. Immobilization mechanism provide a long-term remediation solution by decreasing heavy metals mobility, availability and leachability through pH and alkalinity control to minimize their solubility, or by amplifying adsorption, ionic exchange and precipitation of pollutants (Hea *et al.,* 2013; Mallampati *et al.,* 2013; Wang *et al.,* 2020). Consequently, the selection of soil amendments requires that the amendments must reduce heavy metals transfers from contaminated soils to the surface water or groundwater and uptake by plants and organisms thus decreasing the harmful consequences of heavy metals on environmental receptors, such as microorganisms, plants, animals, water bodies and humans (Hea *et al.,* 2013; Wang *et al.,* 2020).

Lead (Pb) build up in the body organs can cause poisoning (plumbism) or mortality. Children are at danger for impaired growth, inferior intelligent quotient, reduced responsiveness duration, hyperactivity, and mental depreciation while adults more often than not encounter decreased reaction period, deficiency of memory, nausea, insomnia, anorexia, and fragility of the joints due to Pb exposure (Bakshi *et al.,* 2018; Proshad *et al.,* 2019). Cadmium (Cd) in the body is understood to impinge on a number of enzymes and it is responsible for *itai itai* disease, whose warning sign are excruciating osteomalacia (bone disease) linked with kidney failure (Proshad *et al.,* 2019; Mohamadiun *et al.,* 2018). Elevated concentration of Pb and Cd in the soil poses threats to human and animal health by leaching these metals from the soil into water and consumption of edible plants grown in the contaminated soil. Therefore, appropriate remediation is essential to decrease metal availability in soil for human health protection (Hea *et al.,* 2013; Roy and Bhattacharya, 2015).

Nanomaterials are groundbreaking materials beneficial as efficient adsorbent and catalysis to prevail the environmental problem because they have properties that include nanoscale size, large specific surface area and great reactivity. Nanomaterials possess considerable prospective for remediating heavy metal-contaminated water and soil (Chen *et al.,* 2021; Kristanti *et al.,* 2021; Yu *et al.,* 2021; Maqbool *et al.,* 2019). They have been found to proffers such alternative with the ability not to only lessening the whole fee of cleaning up widespread contaminated soil and water, but also to lessen cleaning time, eliminate the need for managing and discarding of contaminated soil and lessen the concentration of certain contaminants to near nothing level (Okonkwo *et al.,* 2020; Mensah *et al.,* 2021; Awan *et al.,* 2022). Nanoparticles could affect mobility of soil pollutants. When compared with ordinary materials such as lime, organic matter, calcium carbonate, red-mud, bone meal, fly ash and so on, it has many advantages, such as high surface activity, more surface reaction sites, good catalytic efficacy and exceptional optical and magnetic properties (Zhou *et al.,* 2021).

Calcium oxide (CaO) is stable, with exceptional structural and optical properties. It has multifunctional and antimicrobial properties as well as safe to human and other organisms (Balaganesh *et al.,* 2018; Okwunodulu *et al.,* 2020). Calcium oxide (CaO) is a promising metal oxide having many applications such as catalyst, dopant added to modify the electric and dielectric properties, remediation agent for toxic wastes (Cyprinus *et al.,* 2016; Kamboj *et al.,* 2020), CO_2 capture, desulfurization of flue gas and emission control agent in pollution, purification of hot gases etc (Khine *et al.,* 2022). Calcium oxide is abundant in nature, low-priced, easy to produce, useful for offsetting acidic soil nature (Balaganesh *et al.,* 2018; Atchudan *et al.,* 2022; Khine *et al.,* 2022). Calcium carbonate-heavy metal complexes can be fashioned in the soil as a consequence of carbon dioxide capture by calcium oxide ensuing formation of complexes with heavy metals to form double salts like $CaCO_3.MCO_3$ thereby acting as a strong absorbent for heavy metals (Rostami and Ahangar, 2013; Khine *et al.,* 2022). Calcium oxide nanoparticles (CaO NP) are low-cost, easily accessed and biocompatible (El-Aziz and Yousef, 2017). The usefulness of nanoparticles have been explored lately to remove contaminants in a variety of ways, including by adsorption, redox reactions, precipitation, and co-precipitation, all of which are aided by their enormous specific surface area (Rajput *et al.,* 2022). The effect of nanoparticle on the soil depends on their concentration, soil type, and enzymatic activity of soil (Javed *et al.,* 2019).

In order to evade agglomeration and inadequate spreading of nanomaterials, the surfaces of the nanomaterials are modified with some organic functionality. Owing to the outstanding interfacial interaction between the surfaces of the nanomaterials, surface-modified nanomaterials have attracted a great deal of interest likened to unmodified nanomaterials. The surface functionalization of nanomaterials is carried out with a variety of organic functional groups for instance alcohols, thiols, sulfonic, carboxylic acids, and amines (Vengatesan and Mittal, 2015).

The immobilization efficiency (IE) and capacity (IC) of amenders for heavy metals in soil can be evaluated by means of the expressions:

$$IE\ (\%) = \frac{M_i - M_e}{M_i} \times 100 \qquad (1)$$

$$IC = \frac{(M_i - M_e)v}{m} \qquad (2)$$

IE = immobilization efficiency; IC = immobilization capacity; M_e = equilibrium extractable concentration of single metal in the immobilized soil (mg L^{-1}); M_i = initial extractable concentration of single metal in preimmobilized soil (mg L^{-1}); v = volume of distilled water used in leaching process (L); m = immobilization agent weight (g). High evaluates of IE and IC signifies the ideal efficiency and capacity of the amender that was used in the study of heavy metal immobilization (Wuana and Okieimen, 2011).

This research study is designed to evaluate the effect of surface modified calcium oxide nanoparticles (SMCON) in immobilizing lead and cadmium contaminated soil from Evbareke spare parts market.

Materials and Method

Study Area, Soil Sample Collection and Pre-treatment.

A set of fifty-eight (58) samples out of a possible sixty-four (64) sampling points of contaminated soil samples were collected from Evbareke spare parts market in Evbareke at latitude 6^0 22’ N and longitude 5^0 36’ 00”E and the control soil was taken from Evbareke Secondary School at latitude 6^0 21’ 33”N and longitude 5^0 37’ 00’E, in Egor Local Government Area, Edo state, Nigeria at the depths of 0-20cm using soil auger, on a land area of approximately 450m^2. The system grid sampling method was used for the collection of the soil sample. The samples were taken at regularly spaced intervals. After removing the debris, the soil samples were air-dried at ambient temperature, ground and sieved to give ≤ 2mm particle size and composited as the parent soil. The residual moisture was removed by heating at 105±5^{o}C for 3 hours in an oven.

Physicochemical Characterization of Soil Sample

The soil sample was physicochemically characterized for pH, particle size, using hydrometer method-Bouyoucos (Fisherbrand model # 14-331-5c), electrical conductivity (conductivity meter CC-01), 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 determined using sequential extraction procedures-Fractionation, adopted from Tessier *et al.*, (1979). The heavy metal content in each fraction was determined using atomic absorption spectrophotometric (Buck scientific model VGP-210).

Synthesis of Calcium Oxide nanoparticle (CONP)

Calcium oxide nanoparticle was synthesized using the co-precipitation and thermal degradation method adopted from Balaganesh *et al.,* (2019); Moses and Okuo, (2018) and Khine *et al.,* (2020 and 2022) with slight modifications. Solution A was prepared by dissolving 0.55g of calcium chloride ($CaCl_2$) in 50 ml distilled water in 100ml volumetric flask, the solution was made up to the mark with a solution of 2g of PVA in 50ml distilled water and stirred vigorously. In like manner, 0.6g of sodium hydroxide (NaOH) was dissolved in 50 ml distilled water in 100ml volumetric flask, the solution was made up to the mark with a solution of 2g of PVA in 50ml distilled water and stirred vigorously to form solution B. Solution B was added from the burette to solution A drop wisely in a 500 ml flat bottom flask, while stirring. After the last drop, the reaction mixture was stirred continuously for 90 minutes on a magnetic stirrer at a temperature of 90° C. The solution was left to settle down for 5 hours. The precipitate was centrifuged and washed atleast five times with distilled water with repeated centrifugation to remove excess NaOH. The obtained precipitate was then dried in the oven at 100° C and finally, the calcium oxide nanoparticle was obtained by calcining the calcium hydroxide ($Ca(OH)_2$) at 800° C. The chemical reaction can be written as:

$$CaCl_2 + 2NaOH \xrightarrow[\text{PVA}]{\text{2\% W/V}} Ca\,(OH)_2 + 2NaCl \qquad (3)$$

$$Ca\,(OH)_2 \xrightarrow[\Delta]{800\ ^{\circ}C} CaO + H_2O \qquad (4)$$

2.3.1. Preparation of Surface Modified Chromic Oxide Nanoparticle (SMCON)

The surface of calcium oxide nanoparticle was modified using the post-precipitation addition method of capping metal oxide nanoparticle adopted from Moses and Okuo (2019). PVA was used as its capping agent. 1.5% (w/v) solution of PVA was added to the calcium oxide nanoparticle obtained until slurry or paste was formed. The slurry was oven dried at 105°C for 12hr, the dried PVA surface modified calcium oxide nanoparticle was ground using mortar and pestle to separate the agglomerate.

Characterization of Surface Modified Calcium Oxide Nanoparticle (SMCON)

The surface modified calcium oxide nanoparticle 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).

SMCON Heavy metal Immobilization Test Using Column Test Leaching Method (CTLM).

Column test leaching method adopted from Chezom *et* al*.,* (2013) with minor alterations was applied to confirm the level of in-situ immobilization of lead and cadmium. The leaching technique was done in a column filled with different mass proportions of SMCON 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 leachate will flow through the vertical column of the amended soil in a down-flow manner and the leachate obtained was analyzed using AAS. Table 1 show the different mixture ratio of contaminated soil sample and SMCON placed in each column.

Table 1: Ratios of Soil Sample and SMCON Mixture.

Percentage	Weight of SMCON (g)	Weight of Soil (g)
1%	0.50	49.50
2%	1.00	49.00
3%	1.50	48.50
4%	2.00	48.00
5%	2.50	47.50

Result and Discussion

Characterization of Surface Modified Calcium Oxide Nanoparticle (SMCON)

Results of the characterization of surface modified calcium oxide nanoparticle (SMCON) are presented by the Fourier Transform-Infra Red (FT-IR) spectrum, XRD pattern of CaO nanoparticle (Standard), XRD pattern for SMCON, a Table of comparison of ICDD (JPDS) File Data with XRD data obtained from SMCON and Scanning electron microscopy (SEM) picture are presented in Figures 1, Figures 2, Figures 3, Table 2 and Figures 4 respectively.

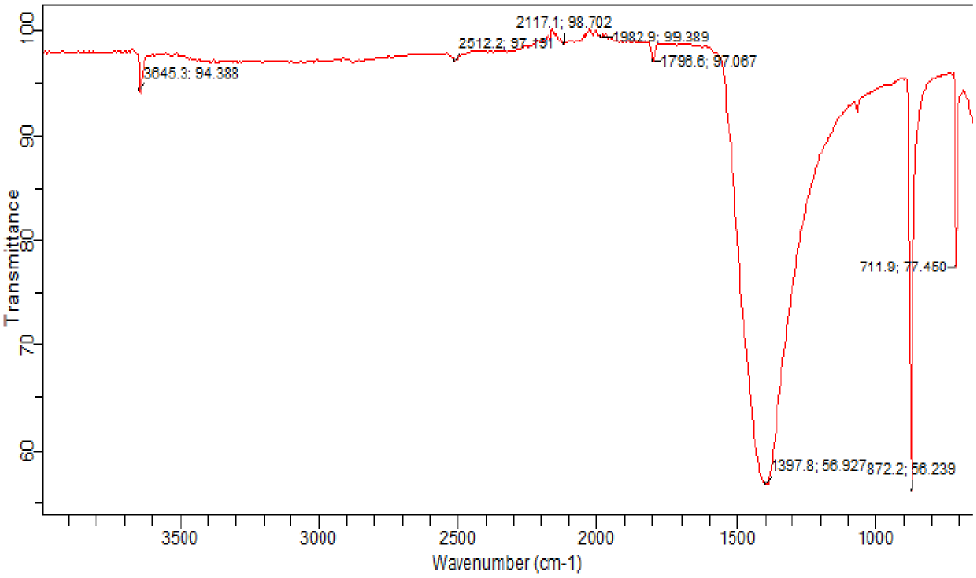

Figure 1: FTIR spectrum for SMCON

The SMCON FT-IR spectra (Figure 1) revealed characteristics bands at 3845.3 cm^{-1} due to -OH bond resulting from moisture absorption by hygroscopic CaO to form some quantity of $Ca(OH)_2$ (Said *et al.,* 2014). The band at 2612 cm^{-1}, 1397.8 cm^{-1} and 1796 cm^{-1} are due to C-O band of CO_3^{2-} ion due to CO_2 capture from the atmosphere by CaO nanoparticle to form calcium carbonate ($CaCO_3$) (Khine *et al.,* 2022). The band at 1397.8 cm^{-1}, is also a sharp appearance for –OH bending due to phenol and alcohol (ArOH) and alcohol (ROH) attributed to the surface modifier – polyvinyl alcohol (PVA). A strong sharp band with medium intensity at 872.2 cm^{-1} is attributed to metal oxide (M=O) stretching attributed to CaO nanoparticle (Said *et al.,* 2014).

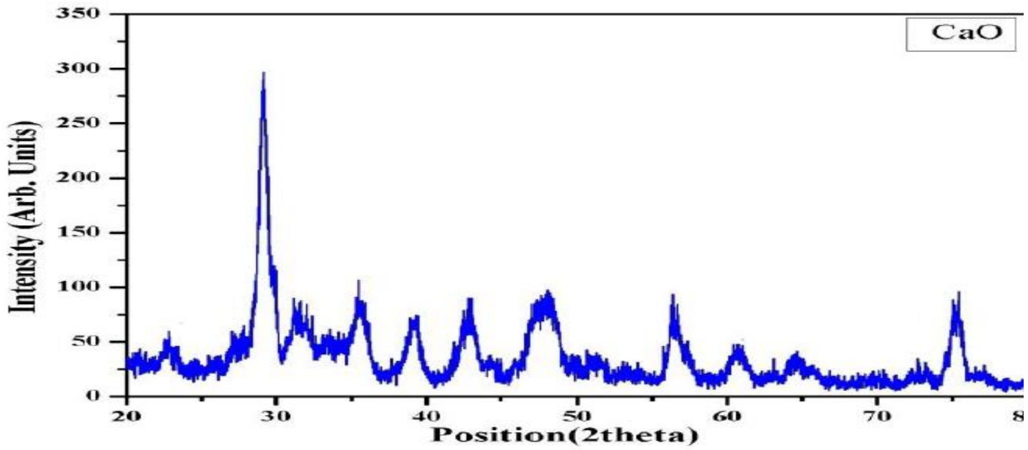

Figure 2: XRD pattern of CaO nanoparticle (Standard)

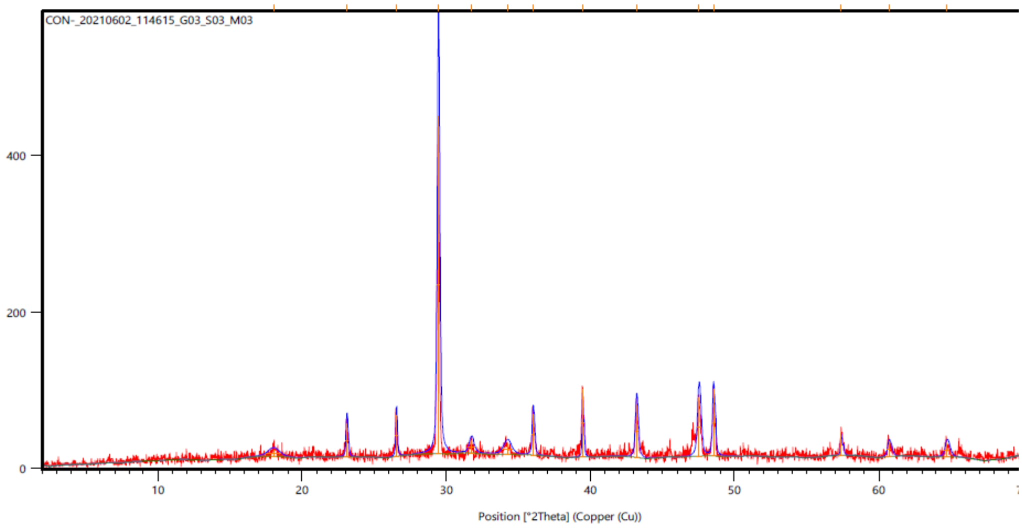

Figure 3: X-ray defractogram for SMCON

Table 2: A Comparison of ICDD (JPDS) File Data with XRD Data obtained for SMCON

Sample	Compound	2ϴ				
JCPDS Data	CaO	32.2^0	37.3^0	58.3^0	64.1^0	67.3^0
SMCON Data	CaO	31.74	36.02	57.41	64.73	-

The XRD analysis was performed to ascertain the purity of the prepared calcium oxide nanoparticle and its structure in SMCON by comparing the obtained XRD pattern of the prepared SMCON shown in Figure 3 with a standard XRD for CaO nanoparticle (Figure 2 and Table 2). The diffraction peaks observed for the prepared SMCON were at 2θ = 31.74°, 36.02°, 57.41° and 64.74° that exhibited a high degree of similarity with values from The International Centre for Diffraction Data (ICDD) file for CaO (JCPDS 37-1497) for standard CaO nanoparticle with an average difference of ±0.50, due to the modified surface of the CaO nanoparticle (Table 2). The sharp peaks in the XRD pattern indicated the crystalline nature and good crystal growth of calcium oxide crystals in SMCON. Thus the presence of CaO nanoparticle with high degree of purity is observed in the prepared SMCON. However, a sharp peak signifying the presence of calcium carbonate ($CaCO_3$) was observed at 2ϴ = 29.45^0, this could be due to CO_2 capture from the atmosphere by CaO nanoparticle. The average particle size (t) of SMCON was estimated from the high intensity peaks using the Debye-Scherer equation (Kurapati and Srivastava, 2018).

$$L = K\lambda/B\cos\theta \quad (5)$$

L= particle size, B (2θ) = FWHM (the broadening of the X-ray peak, in radians), K= Scherer constant (0.94), λ is the x-ray wavelength, and θ is the peak position in degree. The average SMCON particle size was found to be 12.30nm.

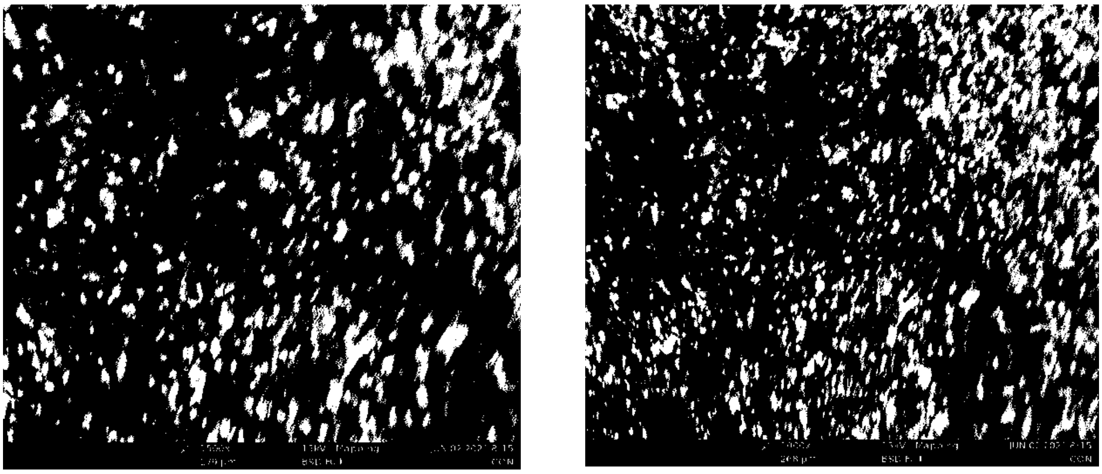

Figure 4: SEM pictures of surface modified calcium oxide nanoparticle

The SEM images (Figure 4), revealed that SMCON posesses a smooth surface with little or no pores. This indicated that one of the mechanism of immobilization of lead and cadmium by SMCON was through adsorption on its surface. The smooth powdery surface avails SMCON a large surface area to adsorb as many as possible lead and cadmium from the soil environment

Physicochemical Characterization of Soil Samples

The results of physicochemical characterization of the soil samples are shown in Table 3. It expressed the quality of the contaminated soil as well as the control site soil.

Table 3: Results of the Physicochemical Characterization of the Soil Sample

Parameters	Units	Contaminated 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

The physicochemical characterization of the contaminated soil from Evbareke spare parts market revealed that the soil was heavily polluted with total petroleum hydrocarbon (Table 3). 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 was 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 little resistance to alteration in soil chemistry brought about via land use (Table 3). 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 3), it is slightly acidic, and could have contributed to the bioavailability of lead ion in the contaminated soil likened with the control. The particle size analysis for the contaminated soil revealed that the soil textural class using a soil textural was loamy sand and the clay quantity is very low (< 5%) hence having a little or no withholding effect on the lead and cadmium ions.

Geochemical Characterization of Lead and Cadmium Soil Sample

The results of the geochemical characterization, mobility factors of lead and cadmium and their bioavailability in the contaminated and control soil sample are shown in Table 4, 5 and 6 respectively. It expressed the quality of the contaminated soil as well as the control site soil so as to determine the level of contamination and their resultant consequences.

Table 4: Results of the Geochemical Fractionation of Lead and Cadmium in Soil Samples

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

Table 5: Mobility Factors of Lead and Cadmium in the Contaminated and control Soil Sample.

Fraction	Contaminated soil (%)		Control soil (%)	
	Lead	Cadmium	Lead	Cadmium
Soluble	0.40	2.73	0.00	0.00
Exchangeable	2.03	18.18	0.00	0.00
Carbonate-bound	14.23	18.18	50.00	0.00
Fe-Mn oxide bound	39.98	42.73	50.00	0.00
Organically bound	6.09	18.18	0.00	100.00
Residual	37.27	0.00	0.00	0.00
Mobility Factor	16.66	39.09	50.00	0.00

Table 6: Bioavailable Lead and Cadmium of the Geochemical Fraction in the Contaminated Soil Sample vis-à-vis Highest permissible Concentration (HPC) 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
HPC (NESREA, 2009)	10.00	3.00		

BDL=below detectable level

The amount of lead and cadmium ions in the soluble, exchangeable and carbonate bound fraction combined was less than its amount in the Fe-Mn oxide bound fraction (Table 4).

The water soluble, exchangeable and carbonate fractions (F_1, F_2 and F_3) are noted as the most possibly accessible or bioavailable fractions because they are feebly or lightly combined to soil components (Table 5). The metals in these fractions are accessible by man via ingestion and are more often than not take into account as being of anthropogenic source. The relative index mobility of these metals was calculated as mobility factor (MF) (Osakwe, and Okolie, 2015) using equation (1).

$$\text{MF} = \frac{F_1 + F_2 + F_3}{F_1 + F_2 + F_3 + F_4 + F_5 + F_6} \text{ X } 100 \qquad (6)$$

The mobility factor of lead and cadmium ions in the contaminated soil was 16.66% and 39.09% respectively (Table 5), this indicated that they are potentially accessible for plant uptake, as asserted by Chengo *et al.,* (2013) that heavy metals in soil are possibly accessible for plant absorption if their mobility factor exceeds 10%.

On comparing the amount of lead and cadmium ions in the bioavailable fraction of the contaminated soil with Highest permissible concentration (HPC) from NESREA (2009), it revealed that the amount of lead and cadmium ions in the contaminated soil from Evbareke spare parts market were lesser (Table 6) however, they are bioavailable based on the fact that their mobility factor was above 10% (16.66 and 39.09% for lead and cadmium respectively) as asserted by Chengo *et al.,* (2013) (Table 5).

Effect of SMCON on Leaching of Cadmium and Lead as well as Immobilization Efficiency and Immobilization Capacity in Contaminated Soil.

The results of the effect of SMCON on leachability of lead and cadmium in the soil samples as well as the immobilization efficiency and immobilization capacity of SMCON in soil samples are presented in Table 7, Figure 5, 6 and 7 respectively.

Table 7: Effect of SMCON on Immobilization Efficiency, Immobilization Capacity and Leaching of Cadmium and Lead from Contaminated Soil.

%	Weight of SMCON (g)	Weight of Soil (g)	Amount of Leached Pb and Cd from Contaminated Soil (mg/g)		Immobilization Efficiency [IE (%)]		Immobilization Capacity [IC (mg/g)]	
			Pb	Cd	Pb	Cd	Pb	Cd
1%	0.50	49.50	0.03	BDL	85.71	100	0.036	6.00 x10^{-3}
2%	1.00	49.00	0.02	BDL	90.48	100	0.019	3.00 x10^{-3}
3%	1.50	48.50	0.01	BDL	95.24	100	0.013	2.00 x10^{-3}
4%	2.00	48.00	0.00	BDL	100	100	0.010	1.50 x10^{-3}
5%	2.50	47.50	0.00	BDL	100	100	0.008	1.20 x10^{-3}

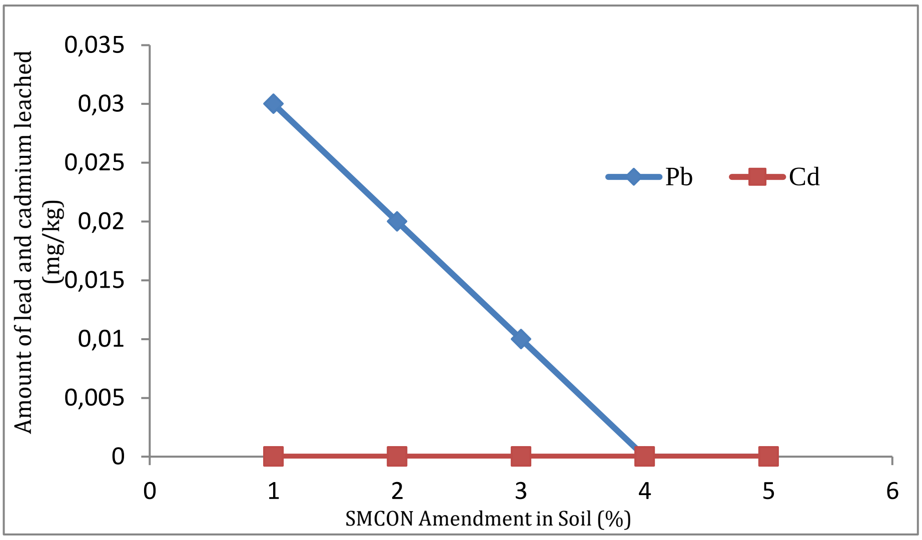

Figure 5: Effect of SMCON in immobilizing lead and cadmium in contaminated soil

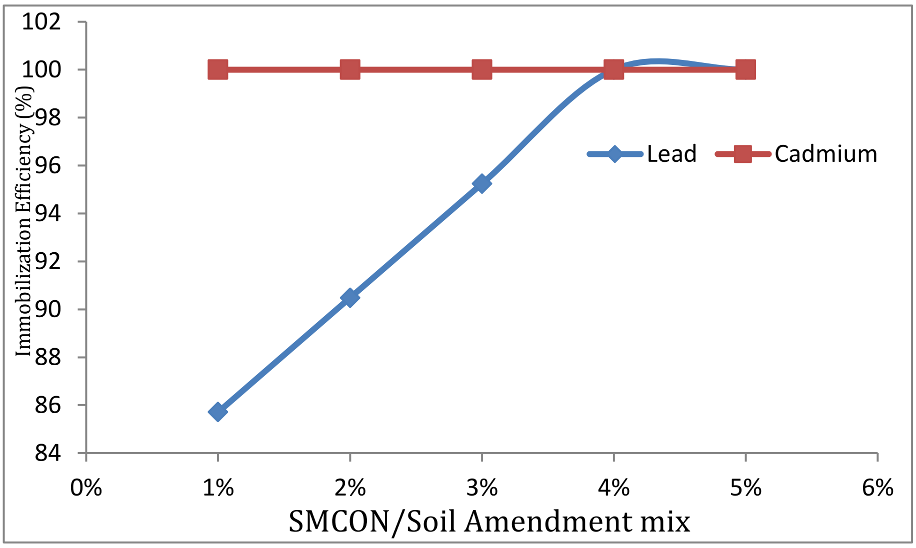

Figure 6: Immobilization efficiency of SMCON on lead and cadmium in contaminated soil

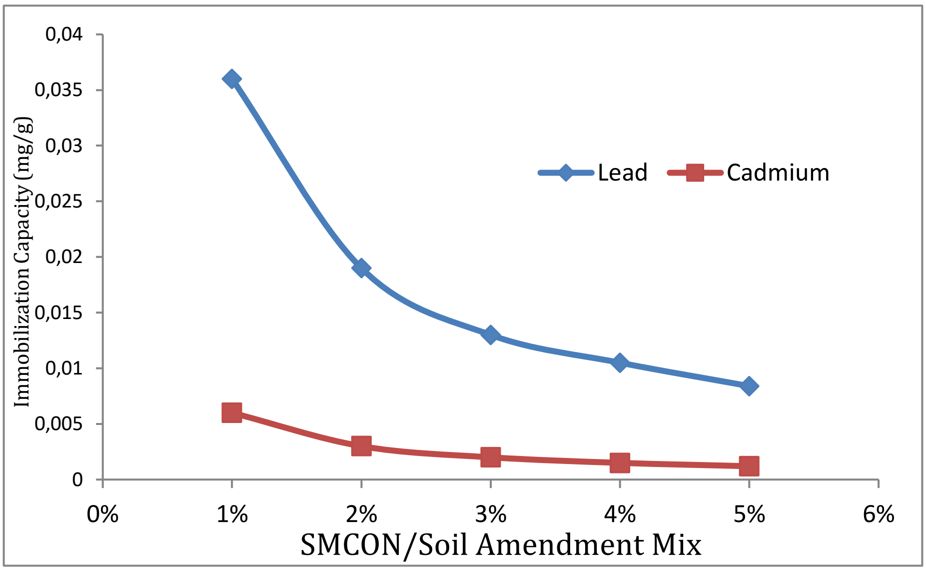

Figure 7: Immobilization capacity of SMCON on lead and cadmium in contaminated soil

It was observed that as the quantity of SMCON amendment increased in the soil, the amount of lead that was available in the soil reduced. However, no available form of cadmium ions was leached (Figure 6). When the proportion of SMCON amendment reached 4% w/w level, lead was below detectable level, even when the amendment dosage increased to 5.0% w/w SMCON/contaminated soil. This revealed that the optimum amount of SMCON for the remediation of the contaminated soil was at 4% w/w (2.00g- SMCON /48.00g- contaminated soil) for the lead contaminant and <1% w/w (<0.50g- SMCON /49.50g- contaminated soil) for cadmium contaminant (Figure 5, Table 7).

The observation from immobilization efficiency study, confirmed that the efficiency of SMCON for lead and cadmium in the contaminated soil increased with increment of the immobilizer up to the optimum 4% SMCON/contaminated soil mixture for lead ions and ≤1% SMCON /contaminated soil mixture for cadmium (Figure 6, Table 7).

Furthermore, a study of the immobilization capacity of SMCON in the contaminated soil, also established that more of lead and cadmium were adsorbed by SMCON as its content in the contaminated soil mixture increased, thereby disallowing leaching of lead and cadmium ions from the contaminated soil (Figure 7, Table 7).

Apart from adsorption, ion exchange and complexation are other mechanism through which SMCON immobilizes heavy metals in the soil. CaO has the ability to form complexes through CO_2 capture resulting in the formation of calcium carbonate which can act as a strong absorbent for lead and cadmium due to complexation to form double salts like $CaCO_3.MCO_3$ (Rostami and Ahangar, 2013; Khine *et al.,* 2022). On the overall, SMCON was able to effectively decreased the bioavailability of lead and cadmium in the contaminated soil by in situ immobilization remediation pattern through adsorption, ion exchange and complexation mechanism, thereby making lead and cadmium to be further less available for uptake by plants thus reducing its transmission to man and animals.

Conclusion

The SMCON effectively decreased the lead and cadmium in the soil by in situ immobilization through adsorption, ion exchange and complexation mechanism to reduce accessibility for uptake by plants thus reducing its transmission to man and animals. As the amount of SMCON amendment increased in the soil, the amount of lead ion available in the soil reduced when the amendment increased from 0 to 4% w/w and remained constant at 0.00mg/kg of lead released, even when the amendment dosage increased to 5%w/w SMCON, However, at the application of the amendment, the amount of cadmium leached was below detectable level (0.00mg/kg). This revealed that the optimum amount of SMCON composite for the remediation of the contaminated soil was at 4% w/w (2.00g- SMCON /48.00g- contaminated soil) for lead contaminant and <1% w/w (<0.50g- SMCON /49.50g- contaminated soil) for cadmium contaminant. The immobilization efficiency and immobilization capacity of the SMCON in soil indicated its effectiveness for decreasing the accessibility of lead and cadmium ions in the contaminated soil to plants.

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