Research Article

Electrochemical determination of the levels of lead and cadmium in soil samples from Niger and Ogun States, Nigeria: remediation potential with chitosan phosphate and implications for human health and disease

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Abstract
Lead and cadmium poisoning is common in some parts of Nigeria as a result of artisanal mining of gold. The poisoning has led to the deaths of hundreds of women and children below the age of five years. In this study, the concentrations of lead and cadmium in eight soil samples collected from selected artisanal gold mining locations in Niger State and battery dismantling site in Ogun State were electrochemically determined. Linear sweep stripping voltammetry technique was used with glassy carbon as working electrode, Ag/AgCl as reference and platinum as auxiliary electrode. The cathodic peak current for the reduction of lead was observed at – 490 mV while that of cadmium was observed at – 675 mV. The concentrations of lead in the soil samples ranged between 19 and 417 mg/kg while that of cadmium was in the range 20–182 mg/kg. The ability of chitosan phosphate to adsorb lead and cadmium in the polluted soil samples was investigated as a step towards carrying out remediation of the polluted environment. Chitosan phosphate was derived from chitosan which was prepared by the deacetylation of chitin obtained from crab. The chitosan phosphate was found to remove the lead and cadmium from all the soil samples studied.

Keywords Heavy metal pollution · Contaminated soil · Linear sweep stripping voltammetry · Chitosan phosphate · Water

1 Introduction

Several heavy metals exist in the environment among which mercury, lead, cadmium, arsenic, and aluminium are known to be of public health concern [1]. Some heavy metals such as cobalt, chromium, copper, manganese, iron, molybdenum, selenium, nickel and zinc are essential nutrients that are required for various physiological and biochemical functions in the body when in very low concentrations. However, they become toxic when they exceed certain threshold concentrations. Unlike organic pollutants, heavy metals once introduced into the environment cannot be biodegraded.

Humans are exposed to heavy metals through various pathways that include the ingestion of plant materials grown in contaminated soil, inhalation of dust, direct ingestion of contaminated soil or water, absorption through the skin [2]. High concentrations of heavy metals in the soil would increase potential uptake of these metals by plants [2] and their entering into the food chain. Contamination of food chain becomes increasingly important in view of its role in human health and nutrition [3]. The main threats to human health from heavy metals are associated with exposure to lead, copper, cadmium, mercury and arsenic.

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For several years, artisanal miners of gold have operated in the mineral-rich parts of Zamfara State of Nigeria without any consideration for the impact on the environment. Several inhabitants in the rural areas live below the average per capita income and hence illegal mining in the state became a lucrative business in 2007 when gold ores were discovered in Bukkuyum and Anka Local Government Areas (LGAs) of Zamfara State. The government failed to develop a technical capacity and carry out community awareness on the dangers of artisanal mining.

In June 2010, Médecins Sans Frontières (MSF) alerted Nigeria's Zamfara State Ministry of Health of the growing number of deaths and illnesses among women and children under the age of five in Abare and Dareta villages in Bukkuyum and Anka Local Government Areas (LGA) [4]. It was thought by the villagers that all the children had contracted malaria but subsequent reports by the Centres for Disease Control (CDC) in Zamfara State under the auspices of the World Health Organization (WHO), found that hundreds of children under the age of five were exposed to lead poisoning. Soil lead levels of 1323.68 and 26,087.70 mg/kg were reported in Abare and Dareta communities respectively [5]. Cadmium was also detected in the soil samples from Dareta (1354 mg/kg) and Abare (1216 mg/kg) [5]. The high levels of lead and cadmium in the soil samples were attributed to artisanal gold mining operations in these communities.

Unsafe gold mining operations is also prevalent in Madaka District in Rafi LGA of Niger State, Nigeria where the deaths of children under five years has been reported [6]. Artisanal gold mining operations have continued unabated in several parts of Northern Nigeria. These unsafe mining operations usually lead to heavy metal pollution of water and soil in the affected environment, destruction of the vegetation, land degradation [7]. The reported death of 28 children below the age of five in Shikira and Madaka attributed to lead poisoning arising from artisanal gold mining operations in Madaka community was disturbing [8]. Unlike the Zamfara episode, livestock such as cows, goat and sheep were affected.

Several workers have carried out studies on the levels of heavy metals in soil samples from different communities in Zamfara State [9–15] but few studies have been carried out on soil contamination in mining communities in Niger State [16–18]. These studies employed the use of atomic absorption spectrometry (AAS) which involve pretreatment procedures such as wet digestion, dry ashing and microwave oven dissolution or extraction. This method is prone to error due to the multi-step processes.

Thus a sensitive, convenient, and cost-effective analytical method for the determination of lead and cadmium in the soil is highly desirable. Electrochemical methods have found important applications in sample analysis and organic and inorganic synthesis. The determination of lead and cadmium in soil and plant samples collected from various locations in Zamfara State by electrochemical method was recently reported [5]. Linear sweep stripping voltammetry (LSSV) is a useful electrochemical technique which can be employed for the accurate measurement of low concentrations of metals at the ppb levels with rapid analysis time and low-cost instrumentation. For this reason, it was chosen for the analysis of metals in this study. The study was extended to a battery dismantling site in Ita-Oshin, Abeokuta North LGA in Ogun State, Nigeria in order to evaluate the soil pollution status.

2 Experimental

2.1 Collection of soil samples

Soil samples were collected from mining sites, processing sites as well as residential areas. These sites were chosen because the processing of gold ore involves crushing, grinding and washing. Soil samples were taken at 5 cm depth. The sampling sites designated MG 02, MD 01 and KA 01 were residential areas in Ungwar Maigiro and Kawo communities in Rafi LGA where grinding of the ore was carried out.

Sampling sites MG 01, MG 03 and KA 02 are washing sites around boreholes located in Ungwar Maigiro and Kawo communities in Rafi LGA. Sample AB 01 and was collected from a metal processing site at Lafenwa while sample AB 02 was collected from a battery dismantling site at Ita Oshin in Abeokuta North LGA.

The coordinates of the sampling sites were recorded using a Garmin 38 global positioning system (GPS) device. About 500 g of each soil sample was collected in polythene bags and labelled. Each sample was then air-dried, sieved (through a 0.5 mm sieve) to maintain uniform particle size, and stored in an airtight glass jar.

Soil samples were collected from grinding sites and washing sites. These sites were chosen because the processing of gold ore involves mining, grinding and washing.

2.2 Digestion of soil samples

1.0 g of each soil sample was added to 20 cm^3 of a 3:1 ratio mixture of concentrated HNO_3 and H_2O_2 (30%) (Sigma-Aldrich, St. Louis, USA). The mixture was heated gradually to 120 °C and kept at this temperature for 2 h till a clear solution was obtained. The solution was allowed to cool and filtered into a 50 cm^3 standard flask and made up to the mark with deionized water before transferring to a pre-cleaned plastic bottle.

2.3 Voltammetric measurement

A Basi-Epsilon potentiostat/galvanostat from Bioanalytical Systems Inc., 2701 Kent Avenue, West Lafayette, USA was used in the study. The concentrations of lead were determined by linear sweep stripping voltammetry technique. The working electrode (3 mm diameter) was glassy carbon, while platinum electrode (1.6 mm diameter) served as the auxiliary electrode and Ag/AgCl as the reference electrode. These electrodes were also purchased from Bioanalytical Systems Inc. The working electrode was polished with alumina powder to obtain a mirror-like image, washed with de-ionized water, sonicated in ethanol for 2 min, washed with de-ionized water and dried.

2.4 Calibration curve

Standard solution of Pb (1000 mg/L) (Merck, Darmstadt, Germany) was used in the study. 0.2745 g of Cd $(NO_3)_2 \times 4H_2O$ (Sigma-Aldrich St. Louis, USA) was weighed and dissolved in 100 cm^3 of deionized water to give 1000 mg/L of cadmium. Serial dilutions were made with supporting electrolyte (0.05 M potassium nitrate and 0.16 M nitric acid) (BDH Chemicals Ltd., Poole England) to give working concentrations 250, 500, 100 and 4000 ppb of Pb or Cd. These solutions were used to obtain the calibration curves. For this purpose, 10 cm^3 each of the standard solution of the metal was transferred into the electrochemical cell and purged with nitrogen for 10 min. The pre-concentration step of the metal was carried out at − 900 mV for 120 s with stirring and after a quiet time of 30 s, the stripping process was carried out by scanning the potential from − 900 to 200 mV using a scan rate of 20 mV/s. The peak currents were observed at − 490 mV (Pb) and − 675 mV (Cd). The values were used to construct the calibration curve for the metal.

2.5 Analysis of real samples

5.0 mL of each digested soil sample and 5 mL of the supporting electrolyte were added and mixed thoroughly. The solution was purged with nitrogen for 10 min and the potential scanned as described for the standard solutions. The values of the cathodic peak current obtained at − 490 and − 675 mV were used to determine the concentrations of Pb or Cd in the samples.

2.6 Preparation of chitosan phosphate

Chitin was obtained from crab shells and deacetylated to give chitosan [19]. The chitosan obtained was washed severally with 0.05 M EDTA (BDH Chemicals Ltd., Poole England) solution and methanol (BDH Chemicals Ltd., Poole England) and air-dried. 10 g of chitosan was added to 500 mL of 2% acetic acid (BDH Chemicals Ltd., Poole England) solution containing 16 mL of ortho-phosphoric acid (BDH Chemicals Ltd., Poole England) and refluxed at 80 °C under nitrogen for two hours. The resultant solution was cooled, precipitated in excess methanol [20]. The product was then dried under vacuum oven at 80 °C.

2.7 Adsorption of lead and cadmium with chitosan phosphate

2.0 g the synthesized chitosan phosphate was placed in a beaker and 10 mL of water was added. The slurry was transferred to a 50 mL glass burette to pack a column. 10 mL of the digested soil sample was neutralized with NaOH (Sigma-Aldrich, St. Louis, USA) and then passed through the column. The metal content of the eluent was determined using the method described for the analysis of real samples. Spiked water samples (1, 2, 4, and 1000 ppm) of Pb were similarly passed through the column and the metal concentration in the eluents determined by LSSV.

3 Results and discussion

The suitability of linear sweep stripping voltammetry for the accurate determination of lead in soil and water samples are presented in the form of voltammograms in Fig. 1. No cathodic peak current was observed in the voltammogram of the supporting electrolyte, but was observed at − 490 mV for the solution of Pb.

The voltammograms for the reduction of Pb (250, 500, 1000 and 2000 ppb) ions are shown in Fig. 2. The variation in peak currents with concentration shows that Pb can be

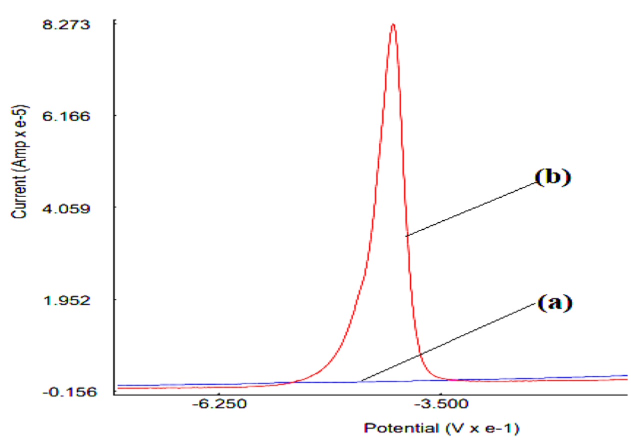
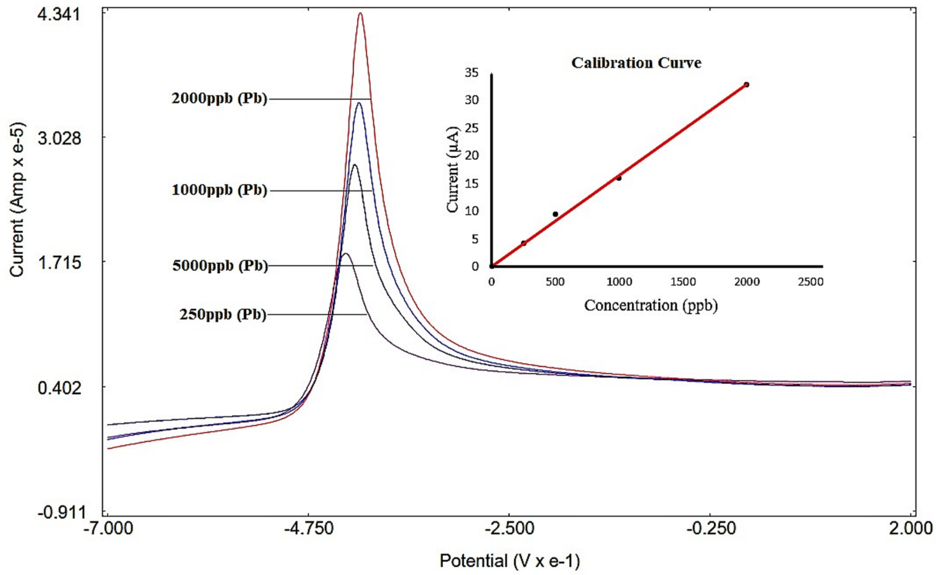


Fig. 1 Overlay of voltammograms of **a** supporting electrolyte (0.05 M potassium nitrate and 0.16 M nitric acid) and **b** Pb solution (4000 ppb)

Fig. 2 Voltammograms of 250, 500, 1000 and 2000 ppb of Pb solutions in supporting electrolyte (0.05 M potassium nitrate and 0.16 M nitric acid)



measured quantitatively by linear sweep stripping voltammetry as shown in Fig. 2 (inset).

The concentration of lead in the various soil samples were obtained from the calibration curve.

The calibration plots for cadmium earlier described were used in this study [5]. The voltammogram for the determination of Pb and Cd in soil sample MG 01 is shown in Fig. 3.

The results of the determination of Pb and Cd levels in the soil samples are shown in Table 1.

Maigiro and Kawo are two remote villages in Niger State, Nigeria where lead poisoning lead to the deaths of 28 children days after suffering from symptoms of convulsions, insomnia and hallucinations. The processing of gold ore involves mining, grinding and washing. In order to ascertain the full picture of the epidemic in Niger State, soil samples were collected from grinding sites and washing sites in Maigeiro and Kawo communities where artisanal gold mining is prevalent. Samples MG 01–MG 03 were collected from Maigiro community. MG 01 and MG 03 are washing sites located in the premises of Head of District and community center respectively while MG 02 is an abandoned grinding site. Sample KA 01 and KA 02 were from Kawo community in Niger State. KA 01 was obtained from a grinding site while sample KA 02 was obtained from a washing site. The authors could not obtain samples from the mining sites which

Fig. 3 Voltammograms for the determination of Pb and Cd in digested soil sample MG 01 in 0.05 M potassium nitrate and 0.16 M nitric acid

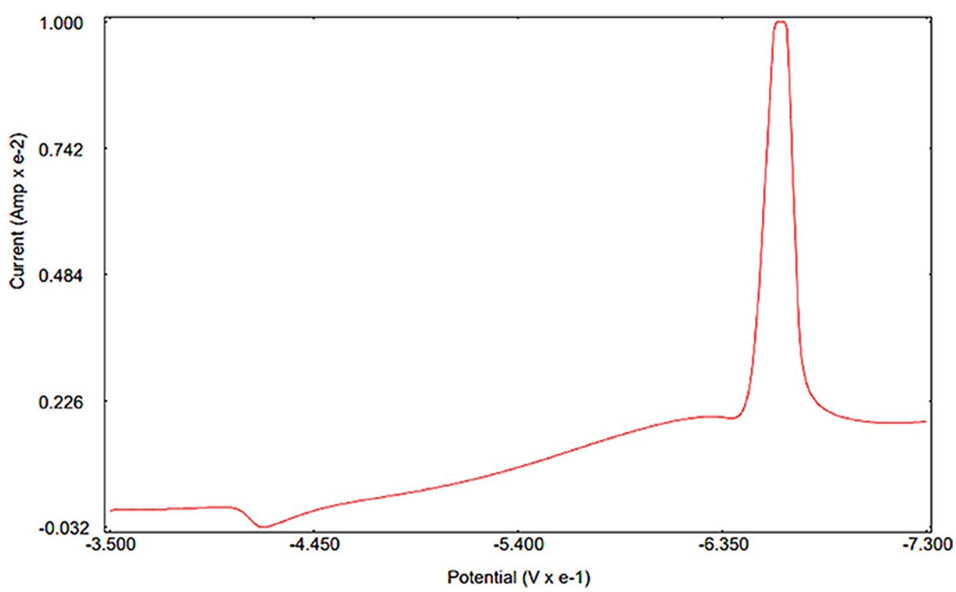


Table 1 Metal concentrations in soil samples from selected locations in Niger and Ogun States

Sample code	GPS location	Metal concentration (mg/Kg)	
		Pb	Cd
MG 01 washing site	N 10° 01.309′ E 6° 30.826′	31.41	24.34
MG 02 abandoned grinding site	N 10° 00.166′ E 6° 32.017′	77.93	21.95
MG 03 washing site	N 10° 00.191′ E 6° 32.081′	416.54	152.43
KA 01 grinding site	N 10° 00.677′ E 6° 30.248′	117.76	182.33
KA 02 washing site	N 10° 00.604′ E 6° 30.294′	356.73	174.22
MD 01 washing site	N 10° 00.561′ E 6° 27.407′	18.98	166.16
AB 01 metal processing site	N 7° 9.20′, E 3° 19.43′	ND	50.30
AB 02 battery dismantling site	N 7° 8.15′, E 3°18.53′	19.41	20.12
Wedepohl guide, 1995		17 m	0.102 m

ND Not detected

were located in Angwan Kawo where radionuclides on the surface soil have been reported [21].

Sample AB 01 was collected from a metal processing site in Lafenwa in Ogun State while AB 02 was obtained from a battery dismantling site in Ita-Oshin in Ogun State.

The concentration of Pb in the soil samples from Maigiro are in the range 3.41–416.54 mg/kg while cadmium is in the range 24.34–152.43 mg/kg. In Kawo Pb levels in the soil was in the range 117.76–356.73 mg/kg while Cd was in the range 174.22–182.33 mg/kg. In Madaka, Pb level in the soil sample taken from the premises of the district head is 18.98 mg/kg while the cadmium level is 166.16 mg/kg. The guideline value for Pb level in our continental crust is 17 ppm while the value for cadmium is 0.102 ppm [22]. The results in Table 1 show that levels of lead and cadmium in the soil samples are well above the recommended limits.

The highest level of Pb was found in sample MG 03 which is a washing site close to a borehole located in the community center in Maigiro. It is expected that members of this community including the artisanal miners will have unrestricted access to this borehole which explains the very high value of Pb detected in the soil sample from this site. Cd level was also high in sample MG 03 which is not unexpected. The lowest level of Pb was found in the soil sample close to the borehole in the premises of the Emir's palace where there is restricted access. However, the Cd level in this sample exceeded the recommended limit. High levels of Pb and Cad were also found in the abandoned grinding site in Maigeiro. Although abandoned, this site remains a health risk for members of the community.

The lowest level of Pb in the soil samples from Rafi LGA was found in Madaka community in site MD 01- premises of the Head of Madaka district. However, the Cd level in this sample is notably high (166.16 mg/kg).

In Kawo community, sample KA 02 was found to have very high levels of Pb and Cd. This sample was obtained from a washing site around the community borehole where large numbers of artisanal miners are expected to converge for the washing of the gold ores. The Pb level in sample KA 01 (grinding site in Kawo community) is lower than that found in KA 02 but Cd level in KA 01 was found to be higher than KA 02.

In an earlier study, we observed that high levels of Pb were found in ponds and streams where artisanal miners regularly carry out washing of gold ores in Dareta, Zamfara State [23]. This observation supports the results obtained for the Pb and Cd levels in washing sites MG 03 and KA 02 in this study. The results obtained for the Pb and Cd levels in sample KA 01 are also high.

In a study on the utility of pollution indices in the assessment of soil quality around Madaga gold mining site, Niger State, North-Central Nigeria, it was reported that the soil around the gold mining sites is seriously polluted by mercury, cadmium and lead, moderately polluted with arsenic, lightly polluted with iron and copper and very lightly polluted with manganese, zinc, nickel and cobalt in the order of Hg > Cd > Pb > As > Fe > Cu > Mn > Zn > Ni > Co [16]. The highest levels of Pb and Cd in the study where 808.16 and 116.91 mg/kg respectively. A study on the environmental impact of artisanal gold mining in Luku, Minna, Niger State, Nigeria has also been reported [17]. The results of the study show that soil samples from Luku, Minna had Pb (85.73 m), As (9.27 m, Cu (56.46 m), Zn (31.0 m), Ni (85.55 m), Mn (283.77 m), Cd (1.68 m), Co (10.91 m), Mo (0.91 m), Hg (0.27 m), Ag (0.73 m) and Zr (143.27 m). It is noted that the reported levels of metals in the soil samples from Luku, Minna are considerably lower than the values we obtained in our study in Rafi LGA of Niger State. No death was reported in Luku, Minna.

The results shown in the present study as well as those reported in the literature [16] show that the soil samples from Maigiro, Kawo in Rafi LGA are heavily contaminated by Pb and Cd. Contamination in Madaka was found to be lower. The high concentrations of Pb and Cd in the soil samples are linked to the artisanal gold mining activities in these locations in Rafi LGA of Niger State, Nigeria. Galena (PbS) has been reported as the compound in the gold ore present in this community [16]. After excavation, the galena is discarded by the miners as gangue on the soil in the environment where it is subsequently leached into the subsurface. High values of Pb and Cd in the soil samples from Abare and Dareta in Zamfara in the ranges of 18.99–26,087.70 and 0.00–1354.25 mg/kg respectively were earlier reported [5]. Nwanosike et al. [6] reported the concentration of Pb in the water samples from Madaka district of Rafi Local government of Niger State in the range 0.00–11.05 mg/L with an average value of 0.85 mg/L. The Pb pollution in Madaka appears to be less severe than Magiro and Kawo communities in Niger State as shown in our study. Umar-Tsafe et al. [18] reported elevated soil lead levels of 150,000 and 550,000 ppm, in Zamfara and Niger States, respectively.

Pb was not detected in the metal processing site in Lafenwa in Ogun State but Cd was detected at a level of 50.30 mg/kg. At the battery dismantling site in Ita-Oshin in Ogun State, Pb and Cd levels in the soil samples were 19.41 and 20.12 mg/kg.

The health implications of the findings presented in this study are the potential incidence of Pb and Cd poisoning in all persons exposed to the gold ores in Rafi LGA in Niger State. Lead toxicity in human adults can lead to poor muscle coordination, nerve damage to body-controlled sensory organs and nerves, increased blood pressure, impairment of hearing and vision and decreased sperm count. In children, it can lead to damage to the brain, nervous system, liver, kidney and death [24]. Cadmium poisoning affects several organs in the body that can lead to death. Long-term exposure to cadmium through the air, water, soil, and food leads to cancer and organ system toxicity such as skeletal, urinary, reproductive, cardiovascular, central and peripheral nervous, and respiratory systems [25].

As a way of carrying out the remediation of the polluted gold mining environments in Maigiro, Kawo and Madaka, chitosan phosphate was investigated as an adsorbent for the metals in the soil samples. Conversion of chitosan to chitosan phosphate results in an increased binding ability for Pb [20]. This is proposed to be a consequence of the increase in the amount of –OH group by the addition of the phosphate group. Metal-binding ability or binding specificity depends on the balance of different functional groups on chitosan phosphate, where the binding is performed by cooperative reactions of the plural functional groups. In this study, 2 g of chitosan phosphate was used in the column packing. It was found to adsorb all Pb in the water samples spiked as shown in Fig. 4. The chitosan phosphate also removed the Pb and Cd in the contaminated soil samples studied as shown in Fig. 5 (Table 2).

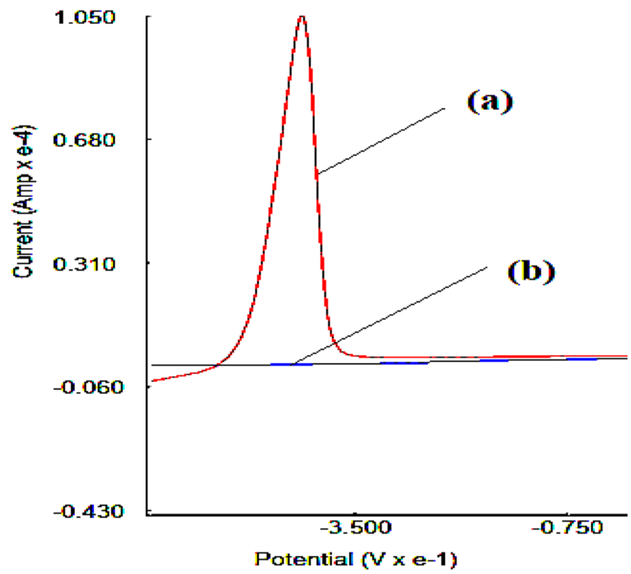


Fig. 4 Overlay of voltammograms of LSSV determination of **a** Pb in spiked water sample and **b** Pb in water after passing through the column packed with chitosan phosphate

4 Conclusion

The study has shown that Pb and Cd levels in contaminated soils in Maigiro, Kawo and Madaka communities in Rafi LGA can be accurately determined by linear sweep stripping voltammetry. It has shown that the elevated level of these metals in the soil samples is due to artisanal gold mining operations. Pb was highest in sites where community members including the artisanal miners converge to wash the gold ore. Cd level in the soil samples was highest in the washing sites in Maigiro and Kawo communities. The study also shows that soil samples from metal processing site in Lafenwa and battery processing site in Ita-Oshin in Ogun State are also contaminated with Pb and Cd.

Chitosan phosphate was shown to be effective in the removal of Pb and Cd from the soil samples studied at neutral pH. The strong affinity of metal ions for this sorbent is explained by the relatively high proportion of hydroxyl groups. This result is an indication that chitosan phosphate could be used for the remediation of the polluted soil environment in Rafi LGA of Niger State. It also shows that chitosan phosphate can be useful in the removal of Pb from water samples on a macro scale.

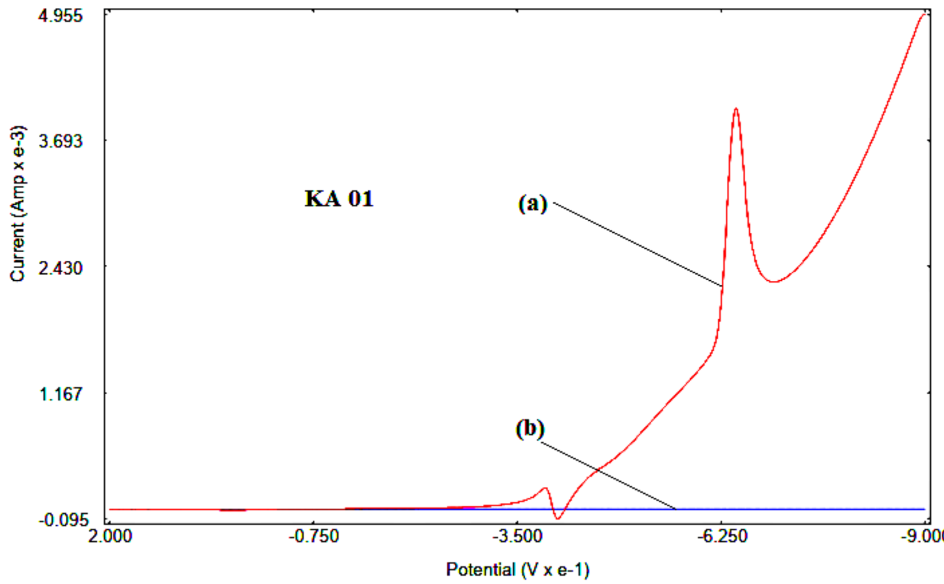


Fig. 5 Overlay of voltammograms for LSSV determination of Pb and Cd in sample KA 01 **a** before passing though column of chitosan phosphate and **b** after passing through column packed with chitosan phosphate

Table 2 Adsorption of Pb^{2+}, Cd^{2+} by chitosan phosphate in contaminated soil samples

Samples	Chemical composition	Volume (mL)	Conc. of metal in soil before sorption (ppm)		Conc. of metal in soil after sorption (ppm)	
			Pb	Cd	Pb	Cd
MG 01	Pb^{2+}, Cd^{2+}	10	31.41	24.34	0	0
MG 02	Pb^{2+}, Cd^{2+}	10	77.93	121.95	0	0
MG 03	Pb^{2+}, Cd^{2+}	10	416.54	152.43	0	0
KA 01	Pb^{2+}, Cd^{2+}	10	117.76	182.33	0	0
KA 02	Pb^{2+}, Cd^{2+}	10	356.73	174.22	0	0
MD01	Pb^{2+}, Cd^{2+}		18.98	166.16	0	0
AB 01	Pb^{2+}, Cd^{2+}	10	0	50.30	0	0
AB 02	Pb^{2+}, Cd^{2+}	10	19.41	20.12	0	0
Spiked water	Pb^{2+}	40	1	0	0	0
Spiked water	Pb^{2+}	40	2	0	0	0
Spiked water	Pb^{2+}	40	4	0	0	0
Spiked water	Pb^{2+}	40	1000	0	0	0

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Availability of data and materials The data and materials for this research are available on request.

Compliance with ethical standards

Conflict of interest The author declare that they have no conflict of interest.

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