



COMPARATIVE EXTRACTION OF Mn AND Pb USING EDTA AND CITRATE TO ASSESS THEIR MOBILITY FROM TWO DUMP SITES IN ZARIA METROPOLIS

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ABSTRACT

An estimate of the labile fractions of different trace metals (Mn and Pb) in soil from two dumpsites with complexing agents (EDTA and Citrate) was carried out. The dump sites used for this study receives both commercial and domestic wastes. Physiochemical parameters and the total metal concentrations of the soil was determined, extraction with EDTA and Citrate were used to study the potential metal extraction capacity at different time intervals and the extraction rates of metal released as a function of time (between 0 to 24 hr). The relatively low levels of silt, clay, organic matter and CEC indicates high permeability, hence leachability of heavy metals in the soil and suggest that it might be amenable to remediation by soil washing. The removal efficiency showed that complete solubilization of metals did not occur, as not all the complexing agents added to the soil, was bound to the target metal. This might be due to the presence of other ions such as Ca and Fe which form relatively high stable complexes. EDTA yielded much more than citrate for both metals under consideration. Lead was extracted more than Manganese, which suggest Lead has been more labile in solution than Manganese and EDTA as a stronger complexing agent than citrate. The level of extraction was constant for the period of 60 min to 720 min after which it increased considerably.

Keywords: Extraction, Complexing agent, Mobility, Soil, Metals

INTRODUCTION

Industrial development and urbanization have led to serious increase in the amount of solid wastes frequently discharged into the natural environment. This has increased the amount of many chemical substances in the environment. The chemical substances which are of great environmental interest are the heavy metals. Heavy metals are of special interest because of the major risks they contribute to the environment, they enter human body through the food chain, causing serious hazards to lives (Liu *et al.*, 2020).

Heavy metals are toxic to humans as well as other organisms; they are released by metal-bearing soil constituents and migrate through the soil solution downward to the water table (Van Oort *et al.*, 2006; Shina and Alok, 2010). The contamination by these metals is a threat to the quality of groundwater, if these metals are not properly treated. Unlike organic compounds that can be biodegraded with time or can be incinerated, metals are robust and remain a potential threat to the environment and human health for a long time (Hong *et al.*, 2002). The concentrations of these heavy metals have been found to increase along time. Soil and sediments are rich in these heavy metals since they are not subject to degradation phenomena (Di Palma and Mecozzi, 2007).

The environmental impact of soil contamination depends not only on the total amount of metals in the soil but mainly on their mobility and availability. This is influenced by leaching and interactions with other components of the ecosystem such as air and water. Soil washing remediation technology is used to remove undesirable contaminants in soil and sediments by dissolving or suspending them in a washing solution (Freeman and Harris, 1995; Moutsatsou *et al.*, 2006; Weihua *et al.*, 2010), and also by concentrating contaminants in small volume of soil through particle size separation (Detzner *et al.*, 1998; McCready *et al.*, 2003). This is based on findings that contaminants tend to bind either physically or chemically to clay, silt or organic soil particles.

Chelating agents are most effective extractants, which can be introduced in the soil washing to enhance heavy metal extraction from contaminated soils. The advantages of chelating agent include high efficiency of metal extraction, high thermodynamic stabilities of the metal complexes, and low absorption of the chelating agents to a catalyst (Jerome *et al.*, 2007). In addition, the chelating agents cause only minor impact on the physical and chemical properties of the solid matrix as compared to acids (Lee and Marshall, 2002 ; Chen *et al.*, 2019).

Several types of extractants can be used to extract heavy metals and metalloids from contaminated soil for soil washing technology. The extractants can be acids, chelating agents, electrolytes, oxidizing agents and surfactants (Reddy and Chinthamreddy, 2000; Schramel *et al.*, 2000 and Sun *et al.*, 2001), out of which acids and chelating agents are the most used extractive reagents for heavy metal decontamination. Acids washing leads to decreased soil productivity and adverse changes in the chemical and physical structures of soil due to mineral dissolution (Reed *et al.*, 1996). Chelating agents are regarded as more attractive alternatives to acids because they can form strong metal-ligand complexes and are thus highly effective in remediating heavy metal contaminated soil (Kim and Ong, 1998; Wei *et al.*, 2011 and Cheng *et al.*, 2020). Hence this study is aimed at estimating the labile fractions of Mn and Pb from dump sites by comparing EDTA and Citrate extractions.

MATERIALS AND METHODS

Two dump sites were selected for this study. The first is located adjacent the new Jos road in Zaria Local Government Area (11°4'31.8''N, 7°43'31.08E) and the second is located behind the Total Filling station opposite Union bank headquarters in PZ area (11°6'1.44''N, 7°43'14.16''E) of Sabon – Gari Local Government Area, both in Zaria, Kaduna State, Nigeria. The sites are dump sites which receive both commercial and domestic wastes which are incinerated and composite from the sites are collected and often used as manure on agricultural farmlands.

For understanding of overall soil development, behaviour and metal distribution, the GPS was used to mark different points of about 50 cm intervals where soil was collected at 0 to 10cm deep. 1kg of soil sample was collected at five different points using a stainless steel hoe on each of the sites. The soil samples collected at different points were dried at room temperature and a composite was made by pounding and sieving to < 2 mm to remove large particles. The composites form was then stored at room temperature in polythene bag for further experiments.

Characteristic physico-chemical parameters of the soil were determined using standard methods (ASTM, 1985). The properties determined include; particle size, pH, CaCO₃ content, Cation Exchange Capacity (CEC) and organic matter content. Total metal concentrations in the soil sample were determined using the flame atomic absorption spectrophotometer after HF/HClO₄ acid digestion.

Extraction with EDTA and Citrate was conducted to assess the effects of chelating agent and reaction time. The extractions were conducted in a 60 cm³ plastic bottle. The bottle containing 1 g of soil sample and 10 cm³ of complexing agent were agitated using an end-over-end shaker at a speed of 120 rpm at room temperature for 30 min. this was repeated at 1 hr, 3 hr, 12 hr, and 24 hr. The solutions was centrifuged at a rotating speed of 400 rpm for 15 min and then filtered.

The extractions were carried out in triplicates. 0.05 mol dm⁻³EDTA and 0.1 mol dm⁻³Citrate solutions was used for the extractions, as it has been found optimal for assessing the maximum extractability of metals (Jerome *et al.*, 2007 and Figueiro *et al.*, 2002). All extracting solutions had their pH adjusted to 6.5, as a pH of 6 guarantee minimal variations of pH during extraction and hence, prevent competitive extraction by H⁺.

The concentration of metals (Mn and Pb) in the filtrate was determined using the flame atomic absorption spectrophotometer.

The experimental results from the extractions were express in terms of metal removal rates per time unit. The amount of metal M extracted per weight unit of soil between time 0 i.e.t_i and another time t_f is defined as;

$$M_{(t_f < t_i)} = \frac{[C_M(t_i) - C_M(t_f)]V}{m}$$

where C_M (t) represents the metal concentration at time t
V represents the volume of extracting solution
m represents the sample mass.



Figure 1: Administrative Map of Kaduna State, (Aliyu *et al*; 2016)

RESULTS AND DISCUSSION

Physicochemical parameters and Total Metal Concentration of site A and site B.

Table 1 shows the results of physicochemical parameters of the soil from the two sites of study, the soil from the two sites have higher percentages of sand than clay and silt which are 78 and 58 for sites A and B respectively, pH values of the sample sites were 6.50 and 8.80. Organic matter (OM) is higher in site B at 15.31 than site A at 3.40. The values for carbonate were 1.00 mg/kg and 0.00 mg/kg for sites A and B respectively. Bicarbonate was 9.60 mg/kg and 2.40 mg/kg for sites A and B.

Table 2 shows the total concentration of metals under study in the two sites. All the two metals under study (Mn and Pb) were found in the two sites though at low concentrations. Site B has higher concentration of the metals compared to site A. Mn has a lower concentration of 0.19 and 5.62 for sites A and B, compare to Pb which has 3.89 and 5.20 for sites A and B.

Table 1: Physicochemical Parameters of the Soil Samples from the Studied Areas.

Sites	Clay	Silt	Sand	Colour	Textural Class	pH (H ₂ O)	OM (%)	CEC (cmol/kg)	CO ₃ (mg/kg)	HCO ₃ (mg/kg)
A(Jos Road)	16	6	78	Dark-grey	Sandy loam	6.50	3.40	7.80	1.00	9.60
B(PZ)	10	32	58	Dark-grey	Sandy loam	8.80	15.31	7.70	0.00	2.40

Table 2: Total metal concentration present in the soil samples analyzed (mg/kg).

Sites	Pb	Mn
A	3.89 ± 0.12	0.19 ± 0.12
B	5.20 ± 0.17	5.62 ± 0.25

Extracted Amount of Heavy Metal after Washing with Complexing Agents.

The extracted amount of the metal is an average result obtained from triplicates of each of the heavy metal under study.

Extracted Mn Concentration after washing with EDTA and Citrate

Open circles represent average result obtained from triplicates.

Figures 2 and3 showed results of extraction with EDTA and Citrate for site A respectively. Extraction started slow at 30 min, after which the concentration of extracted metal increases significantly to 60 min thereafter a slow increase was observed between 180 min to 720 min. a significant increase was again observed at 1440 min showing that a slow reaction took place between 60 min and 720 min. result for EDTA; 0.0182, 0.0372, 0.0453, 0.0469, 0.0619 and result for Citrate; 0.0154, 0.0526, 0.0562, 0.0570, 0.0829 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively.

Results obtained for extraction with EDTA and Citrate for site B is presented in Figures4 and 5 respectively. The extraction was slow in the first 180 min and thereafter an increase was observed. EDTA; 0.0073, 0.0126, 0.0255, 2.0044 and 5.2836. Citrate; 0.0049, 0.0388, 0.0763, 0.1367 and 0.3174, for 30 min, 60 min, 180 min, 720 min and 1440 min respectively.

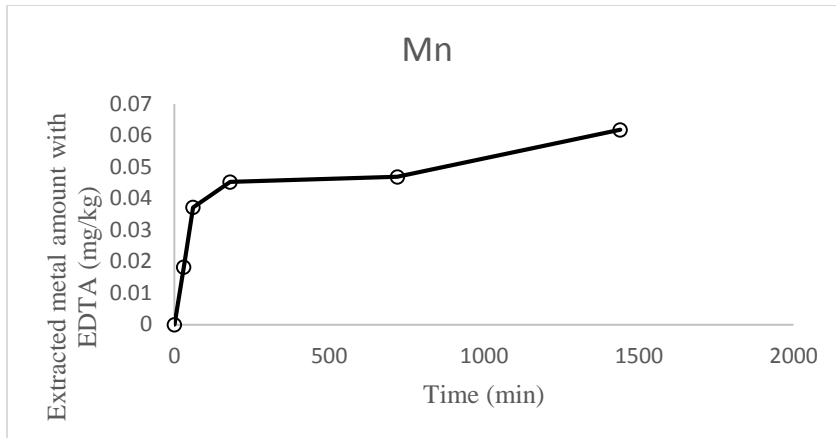


Figure2: Extraction of Mn with EDTA in site A

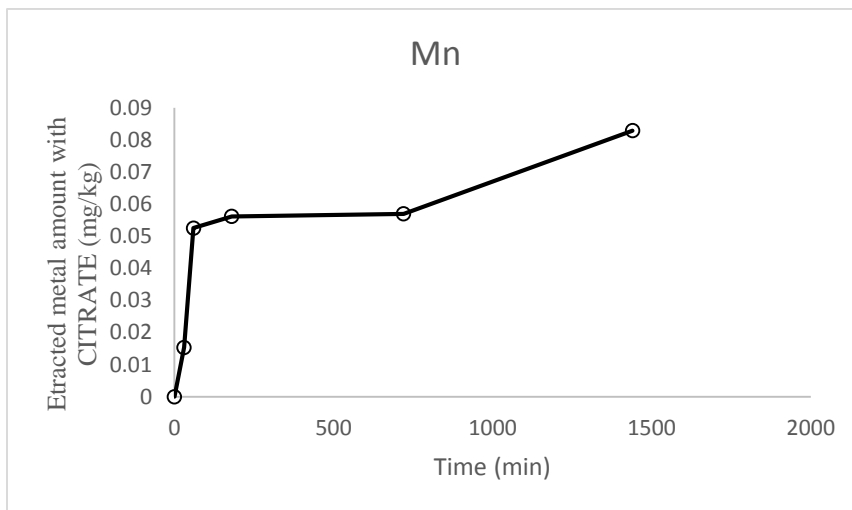


Figure 3: Extraction of Mn with Citrate in site A

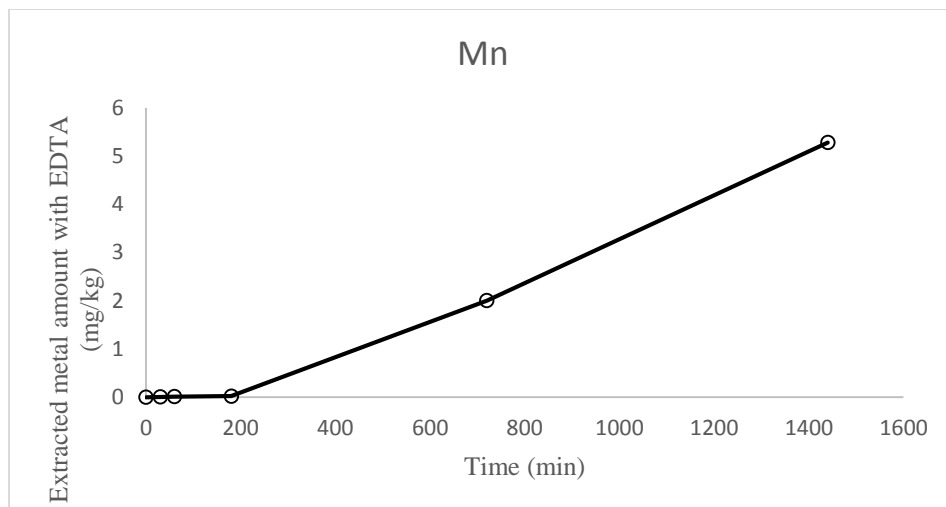


Figure 4: Extraction of Mn with EDTA in site B

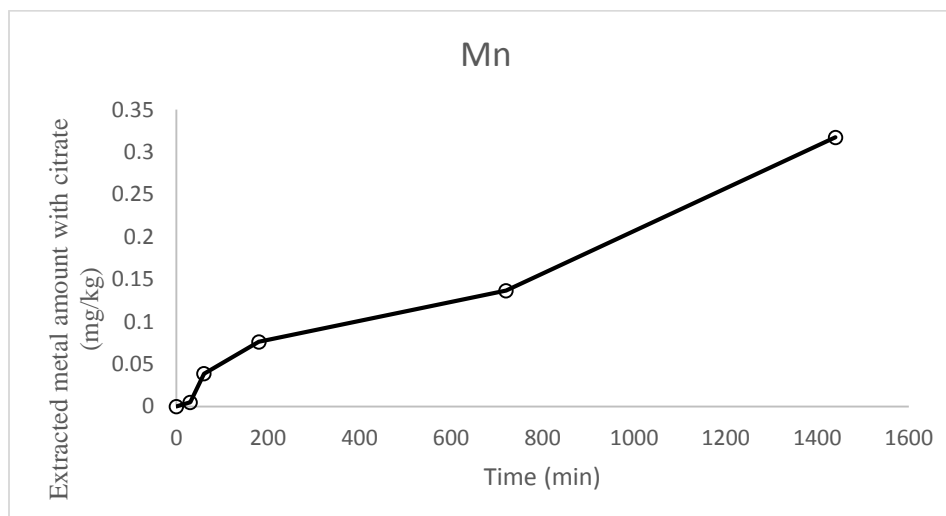


Figure 5: Extraction of Mn with Citrate in site B

Extracted Pb Concentration after washing with EDTA and Citrate

Figures 6, 7, 8 and 9 represent the results obtained from extraction with EDTA for site A, Citrate for site A, EDTA for site B and Citrate for site B respectively. Progressive and consistent increase was observed for the amount extracted showing that amount of lead removed from contaminated soil increased significantly with increase in time. Open circles represents average result obtained from triplicates.

EDTA extraction for site A was 2.5380, 2.5739, 2.6044, 2.6207 and 2.6485 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively.

Citrate extraction for site A was 2.2753, 2.3058, 2.3186, 2.3369 and 2.3404 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively.

EDTA extraction for site B was 3.5405, 3.5852, 3.5852, 3.6354 and 3.6462 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively.

Citrate extraction for site B was 2.1209, 2.3071, 2.3186, 2.3234 and 2.3633 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively.

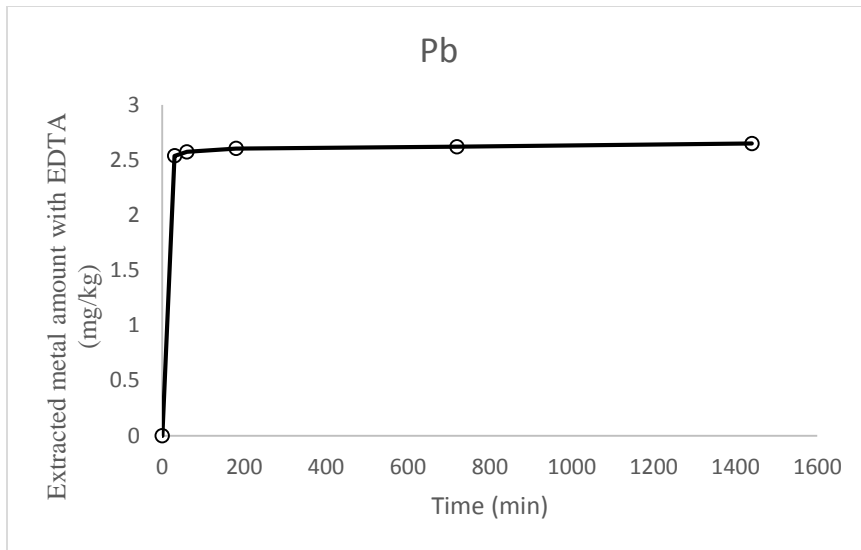


Figure 6: Extraction of Pb with EDTA in site A

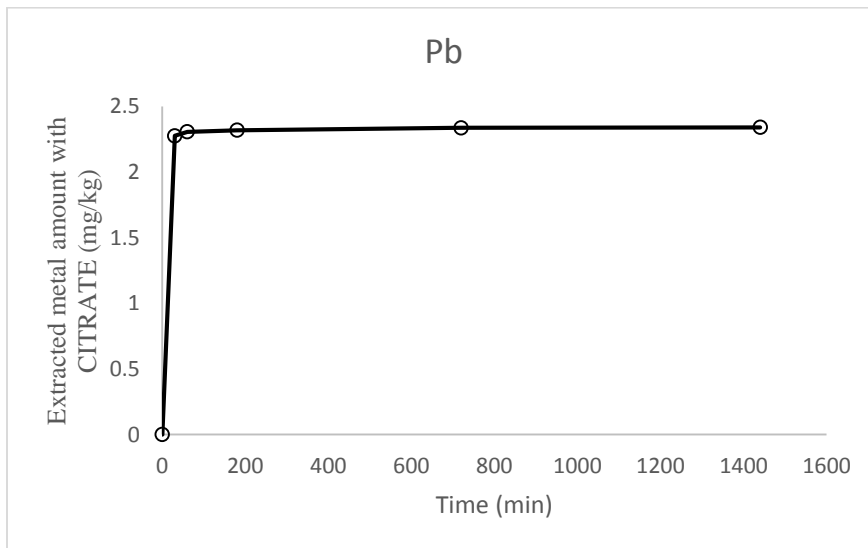


Figure 7: Extraction of Pb with Citrate in site A

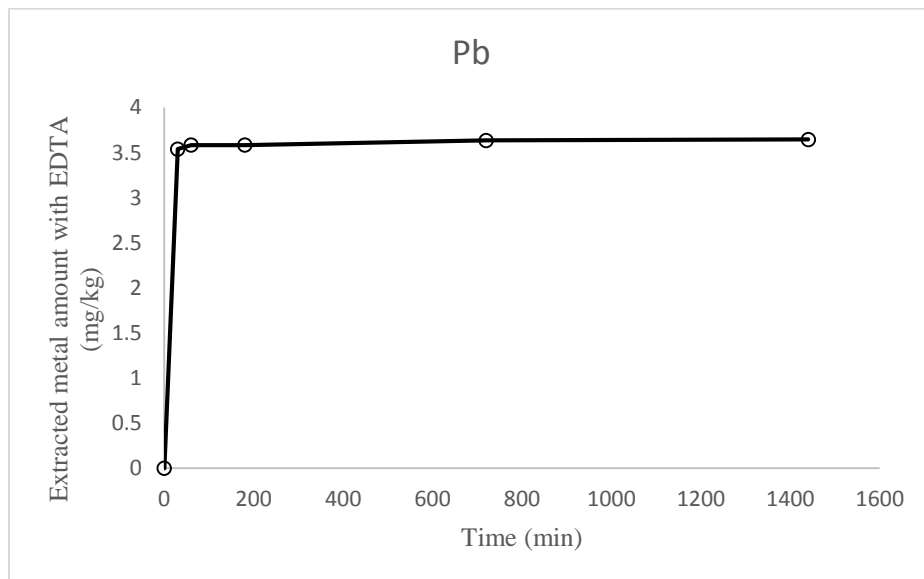


Figure 8: Extraction of Pb with EDTA in site B

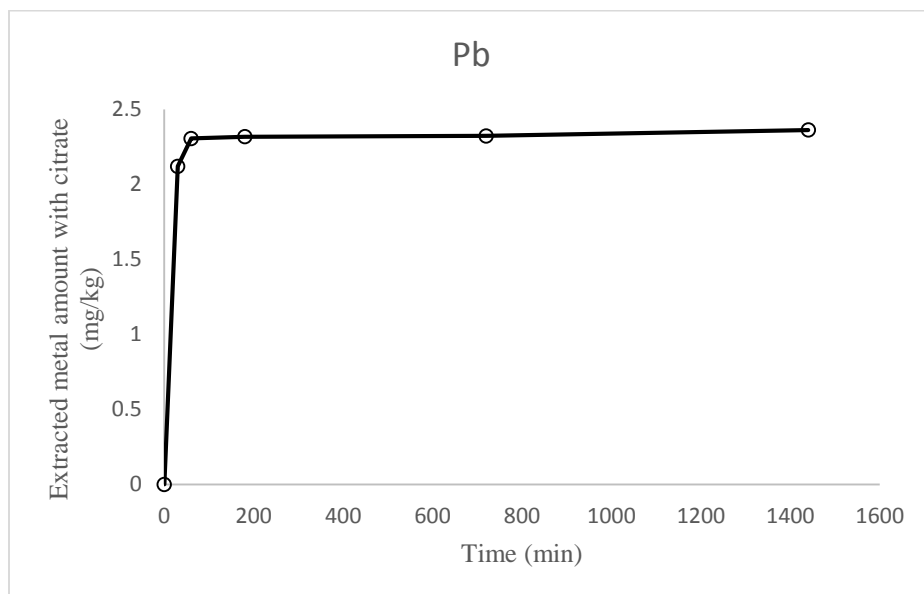


Figure 9: Extraction of Pb with Citrate in site B

DISCUSSION

Preliminary visual inspection showed that the soil was dark-grey in colour indicating a low amount of humus. Colour is one of the characteristics of soil which tells much about the origin of the soil and its composition (Wuana, *et al.*, 2010). Textual analysis showed the preponderance of sand fraction, followed by clay while silt has the lowest composition, thus classifying

the soils as sandy loam. Sandy soils are known to have a poor retention capacity for both water and metals (Masakazu *et al.*, 2008; Wei *et al.*, 2011). The high level of sand indicates high permeability, therefore increased leaching of heavy metals.

The soil pH measured for site A and B is within the range for agricultural soil (Wasay *et al.*, 1998; Ann and Clain, 2005; Weihua *et al.*, 2010). Based on this, it means that the soil from

these dump sites will not have adverse effect on pH of agricultural soil if used. Soil pH plays a major function in the absorption of heavy metals as it directly controls the solubility and hydrolysis of metal hydroxides, carbonates and phosphates. It also influences ion-pair formation, solubility of organic matter as well as surface charge of some ions, organic matter and clay edges (Tokalioglu *et al.*, 2006).

Cation Exchange Capacity (CEC) measures the ability of soils to allow for easy exchange of cations between its surface and solution. Estimated CEC was found to be low for the studied sites, this is because of the low amount of organic matter on the sites. The relatively low levels of silt, clay, organic matter and CEC indicates high permeability, hence increased leachability of heavy metals in the soil and suggest that it might be amenable to remediation by soil washing as also reported by Ehsan *et al.* (2006) and Atafar *et al.* (2010).

Total metal concentration was however low and did not point to a marked industrial pollution. Generally site B tend to show higher concentrations for the studied heavy metals than site A.

The concentrations of extractable heavy metals and extraction yield varied considerably with the nature of complexing agent (Liu *et al.* 2020). The removal efficiency was enhanced by the addition of a masking agent to stop the reaction of other ions such as Ca and Fe as their presence in the soil also interact with the complexing agent due to high concentrations and relatively high stability of their complexes. The discrepancies observed in the percentage extractions for the heavy metals of interest and the two complexing agents may be due to the soil properties such as, metal distribution and physicochemical forms in the soil. Kirpichtchikova *et al.* (2006) gave two reasons for lack of correlation between metal extractability and the affinity of the organic ligand for the metal in pure solutions; the first is the competitive binding of other cations such as Fe and Ca to the chelant and the second reason is that the heavy metals are bound unevenly to several constituents in soil having different solubilities.

Extraction yield for the complexing agents used shows EDTA having a higher yield than Citrate for all the metals under study, this is in agreement with other works that reports EDTA as a more stronger complexing agent than Citrate (Jerome *et al.*, 2007; Masakazu *et al.*, 2008; Wuana *et al.*, 2010; Wei *et al.*, 2011; Chen *et al.*, 2019; Cheng *et al.*; 2020). This observation is explicable by the fact that chelate effect is more in EDTA; this effect is found to confer extra stability on chelates and largely originates from an increase in entropy resulting from an increase in the number of free molecules liberated as the chelate is formed. The size, number of rings, substituents on the rings, nature of the metal and donor atoms is among factors that can affect the thermodynamic stability of the chelate systems (Chao *et al.*, 1998). EDTA's superlative extraction yields can also be attributed to its ability to; (i) complex any metal in soil solution; (ii) its ability to absorb and complex loosely held metal ions; and (iii) its ability to dissolve some minerals containing trace metals

and complex the freed metals (Di palma and Mecozzi, 2007; Wuana *et al.*, 2010; Wei *et al.*, 2011, Cheng *et al.*, 2020).

Desorption of metals and metalloid from soil is an equilibrium process. Therefore extraction time plays a very important role in soil washing process and determines the optimum contact time for contaminants removal. For the metals under consideration, the results showed that an equal time was observed between 60 min to 720 min before a rise is observe again which might be due re-dissolution of the metals in the washing solution.

CONCLUSION

Extraction with EDTA yielded greater amount of metals from the soil than citrate implying that EDTA is a stronger complexing agent than Citrate. Mn is more bonded to soil than Pb implying that it is a less labile metal hence difficult to be completely removed from the soil.

REFERENCES

- Aliyu, A.M., Olonitola, O.S., Aminu, M., Umar, M. and Tahir, M.I.(2016). Seroprevalence and molecular detention of human cytomegalovirus in HIV positive patients attending some selected hospitals in Kaduna state , Nigeria. *Journal of Advances in Biology and Biotechnology*, 9(3): 1-22.
- American Society for Testing and Materials. (1985) Standard test method for particle-size analysis of soils D 422-63.
- Ann, M., and Clain, J. (2005). Basic Soil Properties. Soil and Water Management Module1. pp. 1-3
- Atafar, Z., Mesdaghinia, A.R., Nouri, J., Homae, M., Yunesian, M., Ahmadimoghaddam, and Mahvi, A.H. (2010). Effect of fertilizer application on soil heavy metal concentration. *Environmental Monitoring Assessment*, 160(1-4) 83-89.
- Chao, J.C., Hong, A., Okay, R.W., and Peters, R.W. (1998). Selection of chelating agents for remediation of radionuclide-contaminated soil. *Proceedings of the 1998 Conference on Hazardous Waste Research*, 142-155.
- Chen, L., Wang, D., Long, C. and Cui, Z. (2019). Effect of biodegradable chelators on induced phytoextraction of uranium and cadmium contaminated soil by zebrina pendula schizl. *Scientific Reports*. <https://doi.org/10.1039/s41598-019-56262-9>.
- Cheng, S., Lin, Q., Wang, Y., Luo, H., Huang, Z., Fu, H., Chen, H. and Xiao, R. (2020). The removal of Cu, Ni and Zn in industrial soil by washing with EDTA-organic acids. *Arabic Journal of Chemistry*, 13: 5160-5170.
- Detzner, H.D., Schramm, W., Doring, U., and Bode, W. (1998). New technology of mechanical treatment of dredged material from hamburgharbour. *Water Science Technology*, 37: 337-343
- Di Palma, L. and Mecozzi, R. (2007). Heavy Metals Mobilization from Harbor Sediments using EDTA and Citric

- Acid as Chelating Agents. *Journal of Hazardous Material*, 147: 768–775.
- Ehsan , S., Prashner, S.O. and Marshall, W. D. (2006). A washing procedure to mobilize mixed contaminants from soil: Heavy metals. *Journal of Environmental Quality*, 35 (6): 2084 - 2091.
- Freeman, H.M., and Harris, E.F. (1995). Harzadous waste materials: innovative treatment. *Technomic publishing company inc., Lancaster Basel*. 2nded, pp 5-11.
- Hong, A.P.K., Chelsea, L., Banerji, S.K., and Wang, Y. (2002). Feasibility of metal recovery from soil using DTPA and its biostability. *Journal of Hazardous Materials*, B94: 253–272
- Jerome, L., Fabrice, M., Alain, B., Philippe, C., Christelle, F., Isabelle, L. and Folkert, V., (2007). Kinetic Extraction to assess mobilization of Zn, Pb, Cu and Cd in a metal-contaminated soil: EDTA vs citrate. *Environmental Pollution*, 152: 693–701.
- Kim, C. and Ong, S.K. (1998). The selective reaction of lead and amorphous iron with EDTA in lead sulfate-contaminated soil system. *Environmental Engineering Research*, 3(3): 167-174.
- Kirpichtchikova, T.A., Manceall, A., Spandini, L., Panfili, F., Marcus, M.A. and Jacquet, T. (2006). Speciation and solubility of heavy metals in contaminated soil using fluorescence, EXAFS spectroscopy chemical extraction and thermodynamic modeling. *Geochimicaetcosmochimicaacta*, 70: 2163-2190.
- Lee, C.C. and Marshall, W.D. (2002). Recycling of complexometricextractants to remediate a soil contaminated with heavy metals. *Journal of Environmental Monitoring*, 4:325-329.
- Liu, L., Luo, D., Yao, G., Huang, X., Wei, L., Liu, Y., Wu, Q., Mai, X., Liu, G and Xiao, T. (2020). Comparative activation process of Pb, Cd and Ti using chelating agents from contaminated red soils. *International Journal of Environmental Research and Public Health*, Doi :10.3390/ijerph17020497.
- Masakazu, N., Koudai, N., and Kenji, A. (2008). Removal of lead from contaminated soils with chelating agents. *Materials Transactions*, 49(10): 2377-2382.
- McCready, S.; Birch, G.F.; and Taylor, S.E. (2003). Extraction of Heavy Metals from Harbor Sediments using 1M HCl and 0.05M EDTA and Implications for Sediments. *Australian Journal of Earth Sciences*, 50: 249–255
- Moutsatsou, A., Gregou, M., Matsas, D., and Protonotaris, V. (2006). Washing as a remediation technology applicable in soils heavily polluted by mining metallurgical activities. *Chemosphere*, 63: 1632–1640.
- Reddy, K. R. and Chinthamreddy, S. (2000). Comparison of Extractants for Removing Heavy Metals from Contaminated Clayey Soil. *Soil and Sediment Contamination*, 9(5): 449-462.
- Reed, B.E., Carriere, P.C., and Moore, R. (1996). Flushing of a Pb(II) contaminated soil using HCl, EDTA and CaCl₂. *Journal of Environmental Engineering*, 122(1): 48 – 50.
- Schramel, O., Michalke, B. and Keltrup, A. (2000). Study of Copper Distribution in Contaminated Soil of Hop Field by Single and Sequential Extraction Procedure. *The Science of the Total Environment*, 263(1-3): 11-22.
- Shina, G. and Alok, G. (2010). Effect of Chelating Agents on Mobilization of Metal from Waste Catalyst. *Hydrometallurgy*, 101(3-4): 120 - 125
- Sun, B., Zhao, F. J., Lombi, E. and McGrath, S. P. (2001). Leaching of Heavy Metals from Contaminated Soil Using EDTA. *Environmental Pollution*, 113(2): 111-120.
- Tokalioglu, S., Kartal, S. and Gultekin, A. (2006) Investigation of heavy metal uptake by vegetables growing in contaminated soils using the modified BCR sequential extraction method. *International Journal of Environmental Analytical Chemistry*, 86 (6): 417-430.
- Van Oort, F., Jongmans, A.G., Citeau, L., Lamy, I., and Chevallier, P. (2006). Micro Scale Zn and Pb Distribution Patterns in Subsurface Soil Horizons: An Indication for Metal Transport Dynamics. *European Journal of Soil Science*, 57: 154-166.
- Wasay, S.A., Barrington, S.F., and Tokunaga, S. (1998). Remediation of soils polluted by heavy metals using salts of organic acids and chelating agents. *Environmental Science Technology*, 19:369-379.
- Wei, J., Tao, T., and Zhiming, L. (2011). Removal of heavy metals from contaminated soil with chelating agents. *Open Journal of Soil Science*, 1: 70-76.
- Weihua, Z.; Hao, H.; Fenfang, F.; Hong, W. and Rongliang, O. (2010). Influence of EDTA Washing on the Species and Mobility of Heavy Metals Residual in Soils. *Analytical ChimicaActa*, 173(1-3): 369-376
- Wuana, R.A., Okeieimen, F.E., and Imberungu, J.A. (2010). Removal of heavy metals from a contaminated soil using organic chelating acids. *International Journal of Environmental Science and Technology*, 7(3): 485-496.

