Extraction of Cobalt and Cadmium in Municipal Dump Sites around Zaria, Kaduna State Using EDTA and Citrate as Complexing Agents

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Abstract
Heavy metals contamination of the soil is detrimental to the environment with implications for human health. This result from several anthropological activities, urbanization and industrialization. Cobalt and cadmium are among the heavy metals of interest in Nigeria.The labile fractions of cobalt and cadmium in the soil from two dumpsites using EDTA and Citrate as complexing agents was evaluated. The 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 was released as a function of time . 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. Thus result shows that EDTA yielded much more than citrate for both metals under consideration. Therefore extraction time plays a very important role in soil washing process and determines the optimum contact time for contaminants removal. Hence the removal of metals from the soil is a function of time and concentration. Cadmium was extracted more than cobalt, which suggests cadmium has been more labile in solution than cobalt and EDTA as a stronger complexing agent than citrate.

Keywords: Extraction, Complexing agent, Mobility, Soil, Cobalt, Cadmium, Heavy metals.
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1. Introduction

Heavy metals contamination of the soil poses a serious environmental challenge with implications for human health. This result from anthropological activities, urbanization and industrialization (Madiha *et al.,* 2022).

These trace metals are of special interest because of their chronic toxicity, non-biodegradability and environmental bioaccumulation. They enter human body through the food chain, and are being released by metal-bearing soil constituents thus migrating through the soil solution downward to the water bed (Ugonna *et al.,* 2020). Several of these trace metals such cadmium, chromium, lead, cobalt have being known to have carcinogenic and teratogenic effect on both aquatic and terrestrial organism (Ugonna *et al.,* 2020, Kano *et al*., 2021).

The presence of trace metals in soil depends not only on the total amount of metals in the soil but mainly on their mobility and bio-availability. This bioavailability of heavy metals in soil is affected by soil properties, environmental conditions, soil PH and organic content being the most important parameter upon which heavy metal speciation and partition depends and also by concentrating contaminants in small volume of soil through particle size separation. This is based on findings that contaminants tend to bind either physically or chemically to clay, silt or organic soil particles. (McCready *et al*., 2003).

Chelating agents are most effective extractants, which can be introduced in the soil remediation to enhance heavy metal extraction from contaminated soils. The merits of chelating agent include their ability to complex metal ions, removing target metal ions from the environment, decrease/stoppage of metal precipitation and favouring ion crossing through biological machine (Nurchi *et al*., 2020). 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).

Different types of extractants such as EDTA, NTA, DTPA, Succinic, oxalic, glycine, and cysteine can be used to extract heavy metals and metalloids from contaminated soil (Jewari *et al*., 2018). Hence as a remediation agent, 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). Hence Chelating agents are regarded as more effective 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 cobalt and cadmium from two municipal dump sites around Zaria using EDTA and Citrate extractions.

2. Materials and Methods

Two Municipal 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 receive both commercial and domestic wastes which are incinerated, as composite from the sites are collected and often used as manure on agricultural farmlands.

Pursuant to determination of overall soil development, behaviour and metal distribution, 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, $CaCO_3$ 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 $HF/HClO_4$ 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 cm^3 plastic bottle. The bottle containing 1 g of soil sample and 10 cm^3 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^{-3} EDTA and 0.1 mol dm^{-3}Citrate solutions was used for the extractions, as it has been found optimal for assessing the maximum extractability of metals (Fangueiro *et al.*, 2002 and Jerome *et al.*, 2007). 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 Cadmium and cobalt 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.

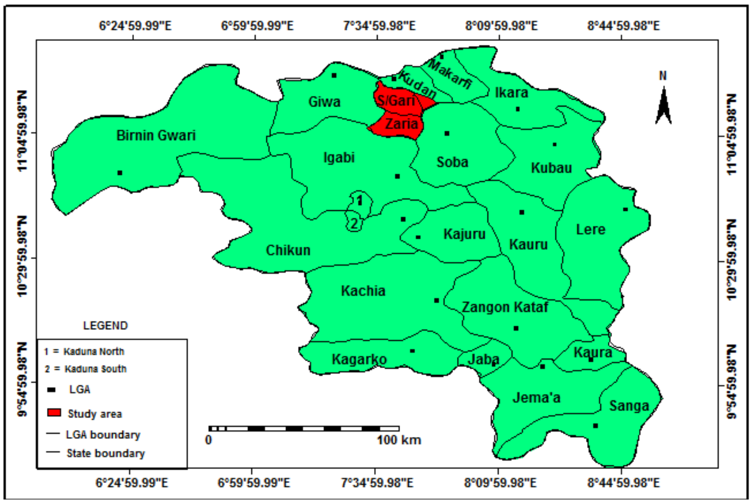

Figure 1: Administrative Map of Kaduna State, (Samuel–Okey and Ajibola, 2021)

3. Results

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

Table 1 shows the results of physiochemical 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. Both Cadmium and cobalt were found in the two sites though at low concentrations. Site B has higher concentration of the metals compared to site A. Cadmium has a lower concentration of 0.16 and 0.52 for sites A and B respectively , compare to cobalt which has 0.26 and 0.35 for sites A and B
(Samuel–Okey and Ajibola, 2021).

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

Sites	Clay	Silt	Sand	Colour	Textural Class	pH (H_2O)	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	Cadmium	Cobalt
A	0.16 ± 0.01	0.26 ± 0.23
B	0.52 ± 0.03	0.35 ± 0.30

3.2 Extracted Cadmium (Cd) Concentration after washing with EDTA and Citrate

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

Figures 2, 3, 4 and 5 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 cadmium removed from contaminated soil increased significantly with increase in time. Open circles represents average result obtained from triplicates. EDTA extraction for site A was 0.0158, 0.0197, 0.0413, 0.0443 and 0.0501 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively.

Citrate extraction for site A was 0.0138, 0.0177, 0.0305, 0.0344 and 0.0403 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively. EDTA extraction for site B was 0.3961, 0.4001, 0.4364, 0.4610 and 0.4933 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively.

Citrate extraction for site B was 0.0275, 0.0364, 0.0403, 0.0531 and 0.0915 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively.

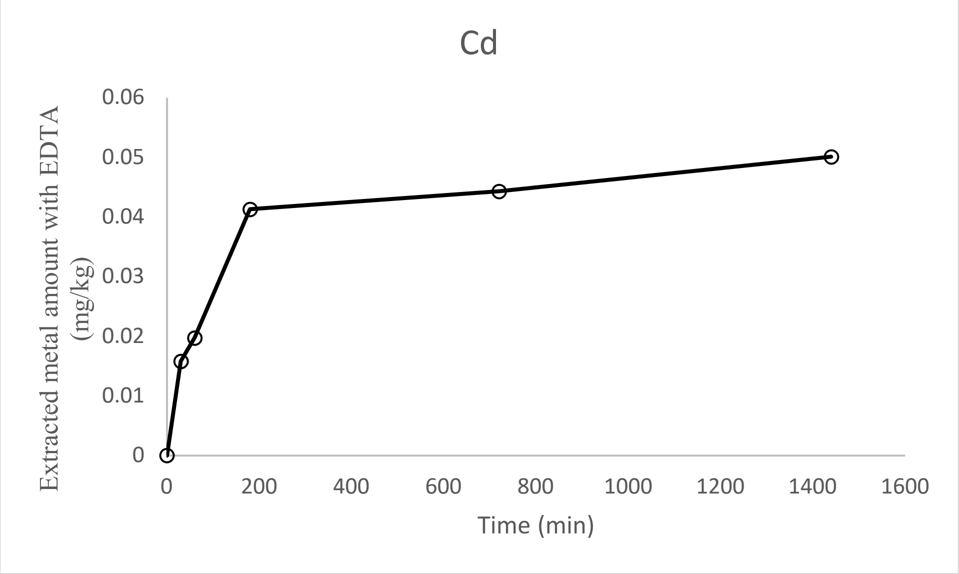

Figure 2: Extraction of cadmium (Cd) with EDTA in site A

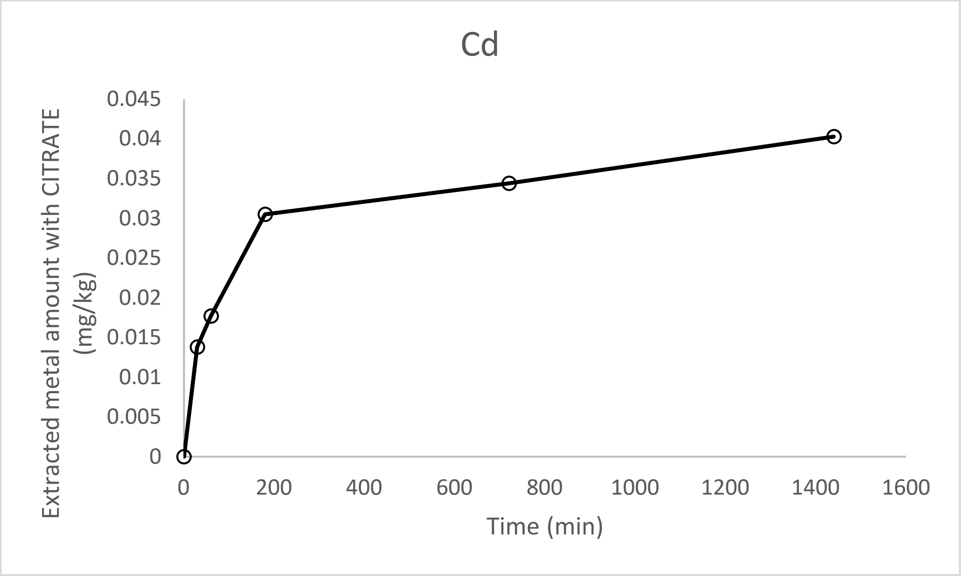

Figure 3: Extraction of cadmium (Cd) with Citrate in site A

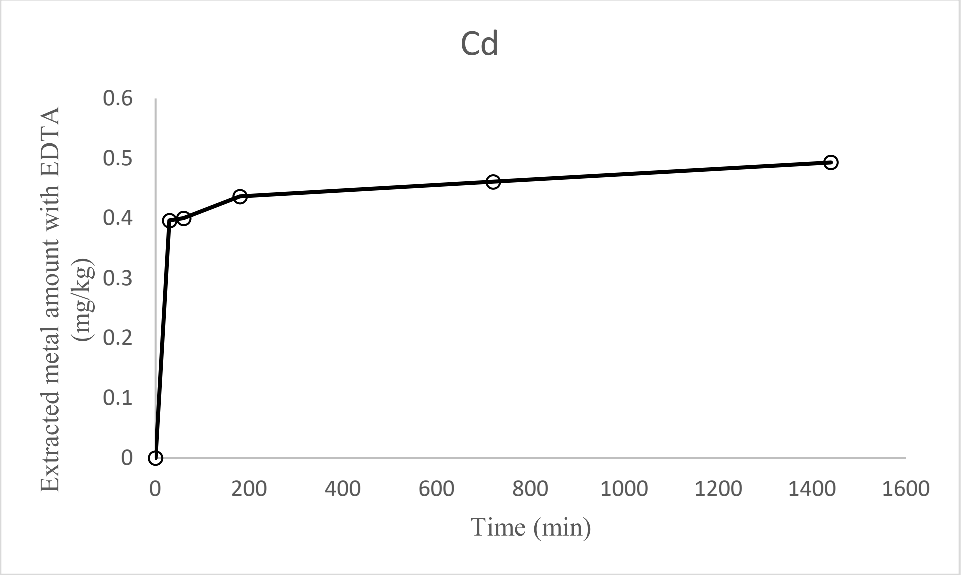

Fig 4: Extraction of cadmium Cd with EDTA in site B

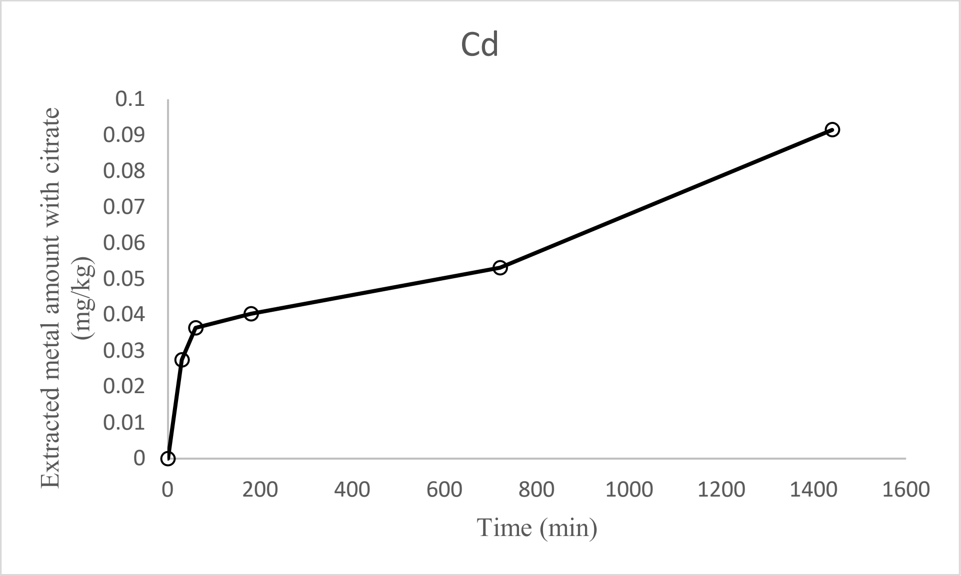

Fig 5: Extraction of cadmium (Cd) with Citrate in site B

3.3 Extracted Cobalt (Co) Concentration after washing with EDTA and Citrate

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

EDTA extraction for site A was 0.0453, 0.0526, 0.0701, 0.0864 and 0.1057 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively. Citrate extraction for site A was 0.0248, 0.0574, 0.0701, 0.0773 and 0.1226 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively.

EDTA extraction for site B was 0.0320, 0.0399, 0.0423, 0.0436 and 0.0495 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively. Citrate extraction for site B was 0.0224, 0.0707, 0.0713, 0.0815 and 0.1316 for 30 min, 60 min, 180 min, 720 min and 1440 min respectively.

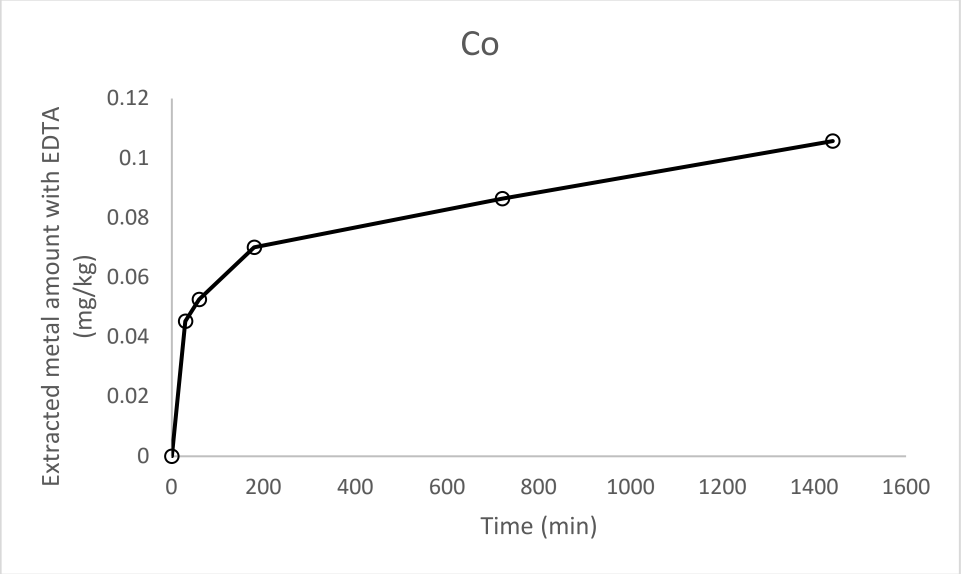

Figure 6: Extraction of cobalt (Co) with EDTA in site A

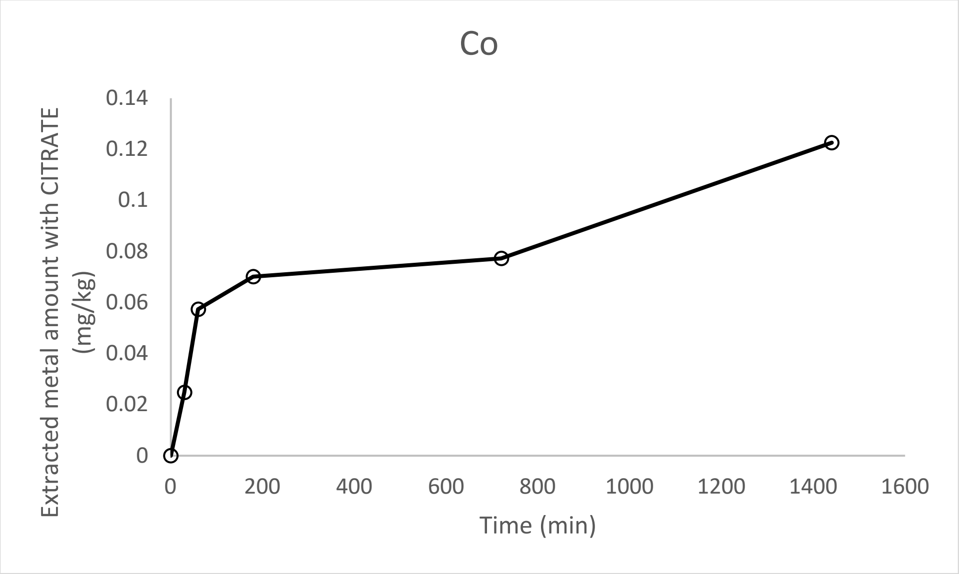

Figure 7: Extraction of cobalt (Co) with Citrate in site A

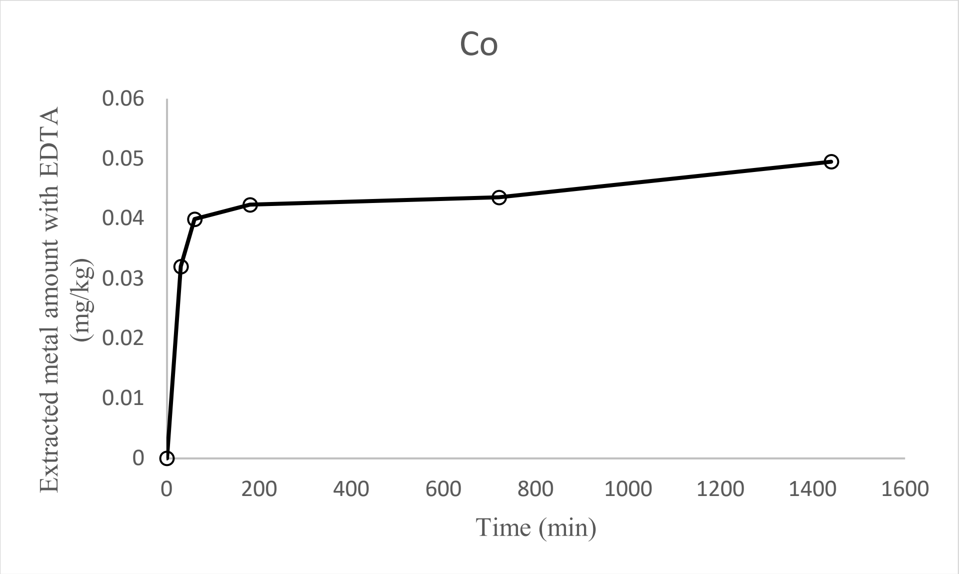

Fig 8: Extraction of cobalt (Co) with EDTA in site B

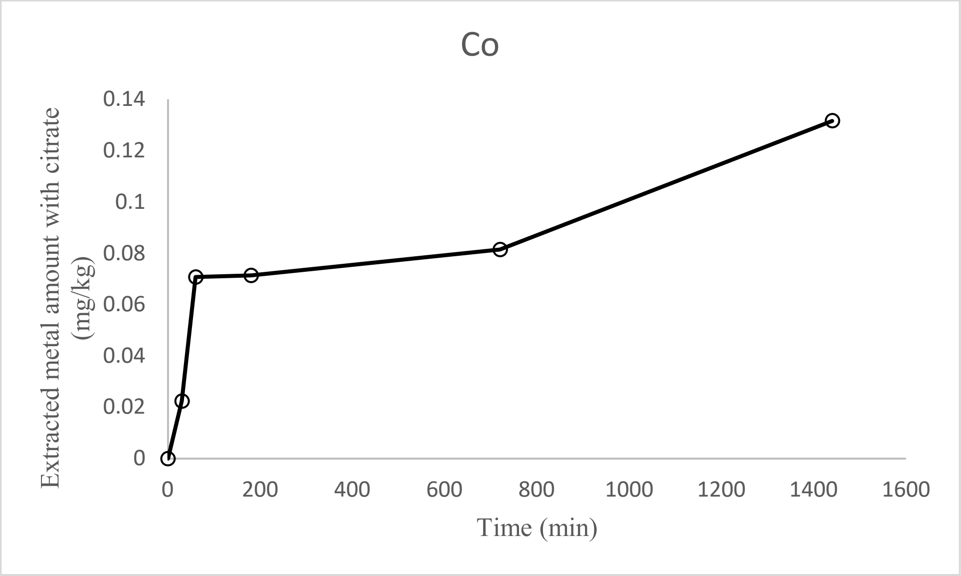

Fig 9: Extraction of cobalt (Co) with Citrate in site B

4. Discussion

Coloration of the soil is a pointer to its formation and composition. Visual inspection of the experimental soil shows experimental soil shows dark-gray colour indicative of low organic matter content (Samuel-Okey and Ajibola, 2021). 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 (Gzar *et al*., 2014). 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 soil washing as reported by Gazar *et al*.(2014) and Senila *et al*.(2022).

Total metal concentration for cadmium and cobalt was however low and did not point to a marked industrial pollution, hence making it safe for agricultural activites since these metals in low concentration are essential for functioning of soil micro-organisms, providing cofactor for enzymatic activities in biological organisms (Parveen *et al*.,2021). Generally site B tend to show higher concentrations for the studied heavy metals than site A, this consistent with increased anthropogenic sources in site B than site A, hence The application of agrochemicals, disposal of urban wastes or atmospheric contaminants tend to increase their concentrations (Wuana *et al*., 2011; Subasic *et al*., 2022).

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.

The results showed that the process of complexing agents extracting metals from the soil included two adsorptions, in which a rapid desorption within the first 180 minutes occurred followed by a gradual release that occur over the following minutes, from 180 min it remained almost constant. The fast step corresponds to the solubilization of accessible metals (exchangeable and slightly adsorbed) and the slower step corresponds to solubilization of less mobile and accessible metals that also bound to oxides. 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. Hence the removal of metals from the soil is a function of time and concentration (Jean *et al.* 2007; Gzar *et al*., 2014).

Chelating agents; EDTA shows a higher extraction yield than Citrate for both cobalt and cadmium in this present study, this is in agreement with other works that reports EDTA as a more attractive complexing agent than Citrate (Chao *et al*., 1998; Jerome *et al*., 2007; Masakazu *et al*., 2008; Wuana *et al*., 2010; Chen *et al*., 2019; Cheng *et al*; 2020). This is due to its ability to form strong metal-ligand complexes which increases its chelating effect. 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 (Wei *et al.,* 2011). Both EDTA and Citrate have being proven to prevent precipitation and absorption of heavy metals in the soil,

Facilitate desorption of heavy metal from soil particles, hence increasing heavy metal bioavailability and its uptake by plants (Yan *et al*., 2020).

5. Conclusion

Heavy metal contamination has a serious implication for agriculture and human health, hence remediation technique such as the use of chelating agents like EDTA (inorganic agent); and citrate (organic agent) has being found useful in forming water–soluble metallic complexes that will increase its bioavailability in the soil. Cadmium was extracted more than cobalt, which suggests cadmium has been more labile in solution than cobalt while EDTA is a stronger complexing agent than citrate as seen in this study.

6. Recommendation

It is therefore recommended that further studies should be carried out with:

(i) Other complexing agents alongside EDTA and citrate to elucidate synergetic roles of complexing agents.
(ii) The variation of concentration and the pH of the EDTA and Citrate on heavy metals extraction.

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