



Evaluation of Heavy Metals in Soil Using Modified BCR Sequential Extraction

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Abstract: Recent studies have shown that strong acid digestions for the determination of heavy metals in soils and sediments can be misleading when assessing environmental effects. Therefore, this study adopted the use of modified community bureau of reference (BCR) sequential extraction scheme in order to overcome the limitation. The physicochemical properties of the soil such as pH, cation exchange capacity (CEC) and soil organic matter (SOM) were determined. The pH, CEC and SOM were found to be 5.90, 0.0023 cmol/kg and 99.8% respectively. The concentrations of the heavy metals in the solution were also measured using atomic absorption spectrophotometry. Pseudo total metal content in the soil (aqua-regia digestions) for cadmium, lead, chromium, nickel, zinc and copper were 0.12, 0.74, 0.48, 0.26, 15.9 and 11.0 mg/kg respectively. These concentrations are within the World Health Organization (WHO) permissible limit in agricultural soils. The heavy metals were partitioned into four fractions (exchangeable, reducible, oxidizable and residual fractions) in the soil using modified BCR sequential extraction. Cd, Zn and Cu were predominantly in the first two fractions, thus, mobile and bioavailable for plant uptake, while Pb, Cr and Ni were found in the last two fractions (less mobile and immobile residual fractions). Thus, Cd, Zn and Cu may pose high environmental risk. The results indicate the reliability of the Modified BCR scheme in risk assessment of heavy metals in soils.

Keywords: Heavy Metal, Modified BCR Sequential Extraction, Soil Pollution, Bioavailability, Metal Partitioning

1. Introduction

Soil contamination is any addition of compounds in the soil that results in detectable adverse effect on soil functioning. Soil pollution however, is the soil contamination that has become severe and the adverse effects have become unacceptable resulting in malfunctioning of the soil and consequent soil degradation [1]. Soil becomes polluted mainly due to the presence of man-made waste. Waste produced naturally from plants and animals adds to the fertility of the soil [2]. These also leave elevated levels of heavy metals, hydrocarbons, nutrients and other compounds on land and possibly in the ground water. Heavy metals can also occur naturally in the soil environment from the pedogenetic processes of weathering of parent materials at levels that are regarded as trace ($<1000 \text{ mg kg}^{-1}$) and rarely toxic [3]. Heavy metals constitute an ill-defined group of inorganic chemical hazard. Those most commonly found at

contaminated sites are Cd, Pb, Cr, Ni, Zn, Hg and Cu. Rapid industrialization and urbanization are majorly responsible for the soil pollution commonly observed in recent time [6].

Remediation of contaminated soil is necessary to reduce the associated risks, make the land resource available for agricultural production, enhance food security and scale down land tenure problems arising from changes in the land use pattern [4]. Thus, soil pollution has become a serious concern and heavy metal removal from the soil is crucial for healthy living and sustainable growth. However, it is widely accepted that the total metal concentration in the soil is not a relevant indicator for assessing the risk posed by the presence of heavy metals for environment and food chain. The ecological effects of heavy metals are related to the mobile fraction rather than the total concentration; though not all pollutants are mobile, most hazardous pollutants tend to be mobile [5]. Heavy metals exist in different forms due to their binding to different soil constituents. The determination of these different forms

usually called speciation or fractionation gives more information on mobility, bioavailability, potential toxicity and consequently the related risks [5].

Sequential extraction procedures are operationally defined methodologies that are widely applied for assessing heavy metals mobility in sediments, soils and waste materials [6]. To determine the different binding pools and to provide information on the potential mobility and availability of heavy metals. Modified community bureau of references (BCR) protocol has been developed, modified and generalized as an attempt to harmonize different methodologies of the sequential extraction processes [5]. This work is aimed at assessing the efficiency of modified BCR sequential extraction technique in partitioning of heavy metals in the soil.

2. Materials and Methods

2.1. Sample Collection

Surface soil (0-15 cm depth) was collected in Kaduna North Local Government Area, Kaduna State, Nigeria using a soil auger. At the sampling site, 10 samples of the soil (20 g each) were collected and put in labeled plastic bags. The samples were air dried for 24 hours by spreading into thin layer on a clean piece of paper. Visible roots and debris were removed by hand and the samples thoroughly mixed to give about 200 g composite sample which was ground using pestle and mortar, sieved using a 0.5 mm sieve and stored in labeled plastic containers until needed.

2.2. Physicochemical Analysis

2.2.1. Determination of Soil pH

10g of the soil sample was placed in 100 cm³ of distilled water in a clean bottle which was then stoppered and shaken occasionally for about 5 minutes. The solid was allowed to settle and a pH meter was gently immersed in the solution to determine the pH of the solution.

2.2.2. Determination of CEC of the Soil Using Ammonium Acetate Method

125 cm³ of 1 M ammonium acetate was added to 25.0 g of the soil sample in a 500 cm³ Erlenmeyer flask, shaken thoroughly and allowed to stand overnight. A 5.5 cm Buchner funnel was fitted with retentive filter paper. The paper was moistened with a minimum amount of the ammonium acetate and inserted into a 500 cm³ suction flask. The vacuum pump was turned on to seat the moistened filter. The soil-ammonium acetate mixture was stirred and filtered. The filtrate was refiltered to obtain a very clear solution. The soil was gently washed four times with 25 cm³ of the ammonium acetate and then with eight separate additions of 95% ethanol to remove excess ammonia. The leachate was discarded and the receiving flask cleaned. The adsorbed ammonia was extracted by leaching the soil with eight separate 25 cm³ additions of 1 M KCl. The soil was discarded and the leachate transferred to a 250 cm³ volumetric flask and

subsequently diluted to the mark with additional KCl. The concentration of NH₄-N in the KCl extract was determined using UV-Visible spectrophotometer (Spectrumlab 752s) [6].

2.2.3. Determination of Total Organic Carbon in the Soil

The total organic carbon was determined using modified Walkley and Black method. A small portion of the soil sample (1.00 g) was weighed into a 1000 cm³ beaker and 10 cm³ of 1.0 M K₂Cr₂O₇ solution was added followed by rapid addition of 20 cm³ of concentrated H₂SO₄. This was done in a fume hood since strong acid fume was evolved. The mixture was immediately swirled vigorously by hand for 1 minute and then allowed to stand for 30 minutes. A volume (500 cm³) of distilled water, 10 cm³ of H₃PO₄ and 1.0 cm³ of ferroin indicator were added to the solution and stirred with a magnetic stirrer. FeSO₄.7H₂O solution was rapidly added from a burette until the liquid in the beaker became purple or blue, then more slowly until the color flashed to green. The ferrous sulphate solution was standardized by titrating it against 10 cm³ of the 1 M K₂Cr₂O₇ solution to obtain the true molarity of the ferrous sulphate solution [6].

2.3. Pseudo-Total Determination of Heavy Metals in the Soil

Pseudo-total metal concentrations in the soil were determined by weighing 1 g of the soil sample into 250 cm³ beaker and digesting with 10 cm³ of aqua-regia. The beaker was heated at moderate temperature of 110°C on a hot plate for 1 hour in a fume hood until the content is about 2 cm³. The digest was allowed to cool, 20 cm³ of deionized water was added to the mixture then filtered into a 100 cm³ volumetric flask using Whatman No. 42 filter paper and made up to the mark with the deionized water. The mixture was transferred into a plastic sample bottle and kept for analysis. The metals in this solution were determined by Buck scientific atomic absorption spectrophotometer (506).

2.4. Extraction

A three step modified BCR sequential extraction procedure was used to obtain exchangeable, reducible-iron/manganese oxides, oxidizable-organic matter and sulfides and residual fractions [7].

2.4.1. Step 1 (Exchangeable Fractions)

40 cm³ of acetic acid (0.11 M) was added to 1 g of soil and shaken for 16 hours using mechanical agitator. The extract was separated from the solid residue by centrifugation, filtered with a filter paper (0.45 μm) and stored in a polyethylene container at 4°C until needed. The residue was washed with 20 cm³ of deionized water, shaken for 20 minutes, centrifuged and the supernatant discarded ensuring that no solid residue was lost.

2.4.2. Step 2 (Reducible-Iron/Manganese Oxides)

40 cm³ of hydroxyl ammonium chloride solution (0.5 M, pH = 2) was added to the residue obtained in step 1 and extracted using the procedure in step 1.

2.4.3. Step 3 (Oxidizable-Organic Matter and Sulfides)

10 cm³ of hydrogen peroxide solution (30%) was added to the residue obtained in step 2 and digested at room temperature for 1 hr. The digestion was continued by heating at 85°C in the digestion block for 1 hr to reduce the volume to less than 3 cm³. A second aliquot of hydrogen peroxide solution (30%, 10 cm³) was added and the digestion procedure repeated. 50 cm³ of ammonium acetate (1 M, pH = 2) was added to the cool moist residue. The sample was shaken, centrifuged and the extract separated as described in step 1.

2.4.4. Residual Fraction

12 cm³ of aqua regia was added to the solid residue obtained in step 3, the sample digested and was analyzed using buck scientific Atomic Absorption Spectrophotometer (506).

2.5. Metal Analysis

The metal (Cd²⁺, Cr³⁺, Cu²⁺, Ni²⁺, Pb²⁺ and Zn²⁺) concentrations were analyzed using atomic absorption spectrophotometer with an air-acetylene flame. This was done by aspirating the working standards to calibrate the AAS machine and obtaining a calibration curve; the sample solution was also aspirated under the same condition. A calibration curve was plotted to determine metal

concentration of the sample by extrapolation. Working standards were prepared using dilution formula as follows:

$C_1V_1=C_2V_2$, Where C_1 is the concentration of the stock solution (mg/L), V_1 is the volume of the stock solution (cm³), C_2 is the concentration of the required dilute solution (mg/L) and V_2 is the volume of dilute solution required (cm³)

3. Results and Discussion

Preliminary visual inspection of the soil reveals that the soil is dark brown in color, it is gritty when wet and rubbed with finger. These characteristics classified the soil as sandy soil. The soil color (dark brown) also indicates that the soil is very rich in organic matter which was further confirmed using a modified Walkley and Black method (99.8% OM). The soil pH was found to be moderately acidic (5.90). CEC of the soil was determined using ammonium acetate method and was found to be 0.0023 cmol/kg which is within the normal range in agricultural soils.

Statistical analysis obtained from correlation analysis of physicochemical properties of the soil indicated a high positive correlation of 0.99 since p-value (<0.001) $\alpha= 0.05$. Therefore, it can be concluded that there is a significant relationship between the physicochemical properties.

Table 1. Physicochemical properties of the soils.

| Sample | pH | Soil Organic Carbon (%) | Soil Organic Matter (%) | Cation Exchange Capacity (cmol/kg) |
|--------|------|-------------------------|-------------------------|------------------------------------|
| Soil | 5.90 | 58.0 | 99.8 | 0.0023 |

The total metal concentrations recorded in the soil indicate that Zn (70.0 mg/kg) has the highest concentration while Cd (1.34 mg/kg) has the lowest concentration. The availability as well as the mobility of the metals decreased in the order: exchangeable fractions > reducible fractions > oxidizable form > residual form. This is consistent with the findings made by Sungure *et al.*, [8]. Therefore, the first two fractions constitute the mobile form while the last two fractions constitute the least

mobile and immobile oxidisable and residual fractions respectively. Fraction 1, the exchangeable fraction is the metals associated with carbonates and are weakly bound at cation-exchange sites in the matrix; fraction 2, the reducible fraction is the metals associated with Fe and Mn oxides; fraction 3, the oxidizable fraction is the metals associated with organic matter and sulfides; fraction 4, the residual fraction is the metals found in mineral lattice of the soil.

Table 2. Total metal contents using BCR sequential extraction technique.

| Heavy metal | Concentrations (mg/kg) |
|-------------|------------------------|
| Cadmium | 1.34 |
| Lead | 2.46 |
| Chromium | 3.14 |
| Nickel | 1.18 |
| Zinc | 70.0 |
| Copper | 3.15 |

The results obtained from speciation of the heavy metals in the soil indicate that cadmium was primarily in the non-residual fractions, of which 69% was mainly associated with reducible Fe/Mn oxides fraction. This indicates that cadmium in the sampling site is highly mobile and available for plant

uptake. In similar studies using BCR and modified Tessier sequential extraction methods, Cd was mainly present in the mobile fractions [9, 10]. This shows that Cd in the sediments poses a high risk to the local environment.

Table 3. Percentage of Heavy metals in each fraction.

| Step | Fraction | Cd | Pb | Cr | Ni | Zn | Cu |
|------|--|-------|-------|-------|-------|-------|-------|
| 1 | Exchangeable | 7.50 | 13.00 | 10.00 | 12.0 | 77.0 | 37.5 |
| 2 | Reducible Fe/Mn oxides | 69.0 | 18.00 | 23.00 | 26.00 | 20.00 | 24.00 |
| 3 | Oxidizable organic matter and sulfides | 15.50 | 9.00 | 12.00 | 39.00 | 3.00 | 6.50 |
| 4 | Residual | 8.00 | 60.00 | 55.00 | 23.00 | ND | 32.00 |

The results show that lead was mainly associated with the residual fractions as shown in Table 3. Only 31% was found in the first two fractions. This indicates that lead is relatively immobile as observed by Li [7]. Thus, it does not pose any significant risk in the environment. However, Dalmacija *et al.* reported that pseudo-total lead showed a severe contamination with the metal, contrary to BCR sequential extraction in which Pb was present in immobile fractions despite its high pseudo total content [11]. The percentage of chromium in the mobile fractions is 33%. Therefore, it is relatively immobile and less bioavailable for plant uptake. This is in agreement with the observations made by other literatures [7, 12, 13].

Approximately 38% of nickel was observed in the first two mobile fractions. It was mainly associated with the oxidizable-organic matter and sulfides fraction (39%). However, Jena *et al.* reported that the amount of nickel in bioavailable form (fractions 1 and 2) is very low (below 1%). They attributed this to physicochemical characteristics of the soil which can strongly influence the metal partitioning in the soil [14]. Zinc was primarily in the mobile fractions (fraction 1 and 2) of which about 77% was found in exchangeable fractions. This metal was not detected in the residual fraction which indicates that zinc is highly mobile and plants can take up a significant concentration of the metal from the soil. About 61.5% of copper was present in fraction 1 and 2. The highest percentage was observed in exchangeable fraction (37.5%). This conforms to the observations made by Li indicating that copper is mobile and readily available for plant uptake [7]. Generally, the availability as well as the mobility of these heavy metals decrease in order of Zn>Cd>Cu>Ni>Cr>Pb. Zn and Pb have the highest and lowest mobility and availability to plants.

4. Conclusions

The mobility, hence, bioavailability of metals decreases in the order: exchangeable, reducible, oxidizable and residual forms. Cadmium, zinc and copper were found to be mainly in mobile forms, as such pose high environmental risk. However, lead, chromium and nickel were mainly in immobile forms and do not pose any risk in the environment. These results indicate that Modified BCR sequential extraction provides reliable results for risk assessment of metals since the amount of mobile metals (bioavailable species) can be estimated. It is a low cost technique that should be used in remediation of contaminated soils.

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