Fractional Distribution of Heavy Metals from the Tailings of Itagunmodi Goldmine Site Osun State, Nigeria

Abiodun O. FATOYE[1,2*] and Albert. O ADEBAYO[1]
[1*]Department of Chemistry, Federal University of Technology, Akure, Ondo State, Nigeria.
[2]Department of Science Technology, Federal Polytechnic Ado Ekiti, Ekiti State, Nigeria.

Geliş Tarihi: 2015-11-19   Kabul Tarihi: 22.03.2016

Abstract

The distribution of heavy metals (Cu, Ni, Cd, Cr, Zn and Fe) in goldmine tailing was determined using multi- step sequential extraction. Chemical properties such as pH, conductivity, cation exchange capacity, organic matter, residual humidity and particle size were also analyzed. Similar characteristics distribution patterns were observed for Cd, Cr, Fe and Zn except Cu. The percentage recovery of Ni ranged from 95.25-99.24%. The high Mobility factor and bioaccumulation factor values of soil Ni may be interpreted as symptoms of relatively high liability and biological availability of the metals in soil.

Keywords: Tailings, Heavy Metals, Goldmine, Sequential Extraction, Distribution

1. Introduction

Mining gives rise to soil erosion and environmental contamination by generating waste during the extraction, beneficiation, and processing of minerals. After closure, mines can still impact the environment by contaminating air, water, soil, and wetland sediments from the scattered tailings, as well as pollution of groundwater by discharged leachate, unless the proper remediation is conducted [1].

Mining activities contribute to heavy metal pollution of the environment [2,3]. Progressive accumulation of heavy metals in soils surrounded by mines, result in increased heavy metal uptake by plants. This is worrisome because of potential health risk to the people leaving in the surrounding areas [4].

Elements like Cd, Cr and Ni, are said to be non biodegradable thus, persist everywhere in the environment and have the ability to be deposited in various body organs which poses a great threat to the human health. Several studies have shown that plants, growing in heavy metal contaminated soils have higher concentrations of heavy metals than those grown in uncontaminated soil [5]. It has been reported that serious health problems may develop as a result of excessive accumulation of heavy metals such as Cd, and Pb in the human body [6]. Despite Zn and Cu being essential elements in the diet, high concentration in plants is of great concern because they are toxic to humans and animals [7]. Pb and Cd metals are believed to be potential carcinogens and are implicated in the ontology of many diseases, especially cardiovascular diseases, kidney, nervous system, blood as well as bone ailments [8].

Heavy metal contamination of agricultural soils and crops surrounding the mining areas is a serious environmental problem in many countries, Nigeria inclusive [9].

It is well known that metals in soil are presented in different chemical forms, which influence their reactivity and hence their mobility and bioavailability. Evaluating metal pollution of soils on the basis of total metal content provides little information on the mobility and bioavailability of heavy metals and thus gives poor guidance for the selection of appropriate remediation strategies for contaminated soil.

Recently, pollution of general environment has increasingly gathered a global interest. In this respect, contamination of agricultural soils with heavy metals has always been considered a critical challenge in scientific community [10].

*Corresponding author: Department of Chemistry, Federal University of Technology, Akure, Ondo State, Nigeria, E- mail: abiodun.fatoye@yahoo.com, Phone: +2348036605518

Doi:10.21541/apjes.61578

A sequential chemical extraction technique fractionates heavy metals into forms of different solubilities and mobilities, and can therefore furnish potential valuable information for predicting metal availability and metal movement in the soil.

Speciation of metals in soils, sediments and solid wastes is often studied using sequential extraction techniques whereby the target metals are fractionated into several fractions using extractant solutions of increasing strength [11] Several such sequential extraction schemes have been described [11,12]. The technique has been used to study the speciation of heavy metals in soils, street sweepings and urban aquatic sediments, lake sediments, pelagic sediments, semiarid soils, dredged sediment derived surface soils, and solid waste materials [12]. The technique has also been used to study the speciation, mobility and bioavailability of radionuclides [13,14,15]. It is very important to evaluate the mine tailing to actually ascertain the distribution of the heavy metals which is the focus of the research.

2. Material and Method

Itagunmodi is a small community lies between latitudes 7°30’ and 7°33’ N and between longitudes 4°36’ and 4°39’ E in Atakumosa West Local Government Council southwestern Nigeria (Figure 1). The study area as shown in the map below is a rural community of about 2,400 to 2,600 people that engage predominantly in subsistence farming and cocoa plantation. Itagunmodi is a community with many dilapidated buildings.

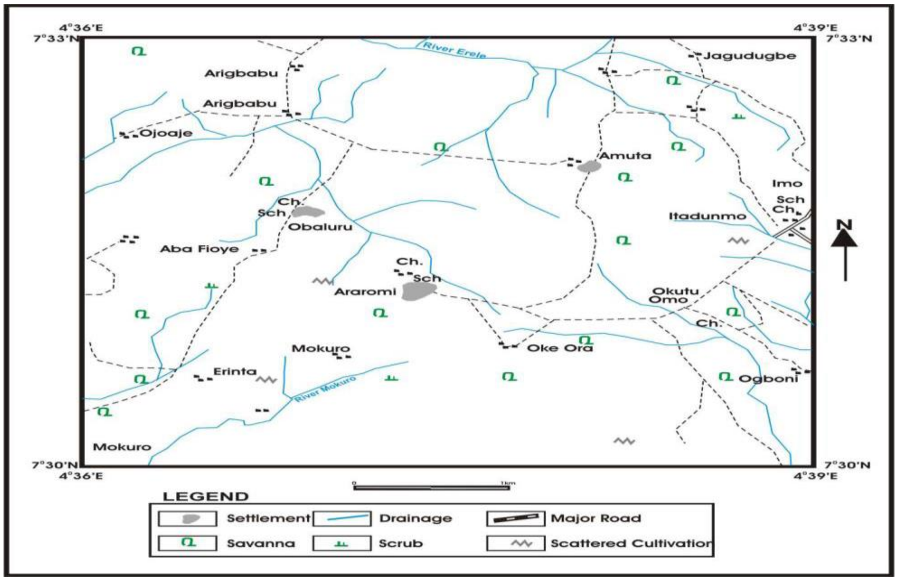

Figure 1. A map is belonging to Itagunmodi

Tailings samples were oven dried at 40^0C for two weeks. Samples were sieved through a 0.8mm mesh and stored in clean polythene bags for further analysis.

The pH was determined by the method [16], particle size analysis by (hydrometer meter), conductivity by (conductivity meter), CEC by ammonium acetate method [17], Organic matter content [18], Residual humidity [19].

Dried and powdered soil sample of 1.2 g was digested with aqua regia (3:1 HCl: HNO_3) in 100 ml conical flask on a hotplate and diluted to volume with distilled water. Fe, Cr, Cu, Zn, Cd, and Ni in the digest were determined using 210 VGP (Buck Scientific) atomic absorption spectrophotometer. The detection limit of the atomic absorption spectrophotometer used is 0.01.

The sequential extraction of metals was done by the method of Tessier *et al*,1979 which partitions metals into exchangeable, bound to carbonates, bound to Fe – Mn Oxides, bound to organic matter and residual. 1g of air dried tailing sample were used.

Table 1. Testing parameters

Fraction	Extractant	Shaking Time(hr)	Temp(^{o}C)	Designation
F1	1M $MgCl_2$,pH 7	1	RM	Exchangeable
F2	1M NaAC, pH 5	5	RM	Carbonate
F3	0.04M $NH_2(OH)Cl/25\%CH_3COOH$	5	96	Fe-Mn oxide
F4	0.02M $HNO_3/30\%H_2O_2$, pH2	5	85	0rganic/Sulphide
F5	$HClO_4/HF$			Residual

Source : Tessier *et al*, (1979).

Validation of the analytical results was tested by recovery experiments because there was no standard reference material (SRM), which is more preferential or needed to control the accuracy of the method studied, in our laboratory. An important consideration in the reliability of a sequential extraction data is the percentage recovery relative to a single digestion using a mixture of strong mineral acids or generally a mixture of strong acids at the digestion of the residual phase of the sequential extraction protocol employed [20]. Recovery is defined as follows:

$$R=\frac{F1+F2+\cdots Fn}{SDSA}X100$$

F is the different fractions while SDSA is the single digestion for single acid

The distribution of heavy metals in the sample allows us to predict their mobility and bioavailability. The bioavailability factor was expressed as the ratio of the available concentration of a metal in soil to its total concentration. It shows the potentials of a particular metal from the soil matrix to enter the soil solution from which it can be absorbed by plants. Mobility factor was expressed as percentage of the Bioavailability factor

3. Results

Table 2. Showing the result of physicochemical characteristics of tailing samples

	pH	EC (uS/cm)	CEC (Meq/100g)	OC (%)	OM (%)	RH (%)	Sand (%)	Clay (%)	Silt (%)	Texture
1	4.27±0.77	66.0±6.50	3.16±5.35	0.45±1.13	0.78±1.97	0.30±0.02	75.0±4.30	18.0±5.80	7.0±4.20	Sand
2	4.30±0.77	70.0±6.50	2.30±5.35	0.72±1.13	1.25±1.97	0.22±0.02	78.0±4.30	5.0±5.80	17.0±7.40	Loamy Sand
3	4.84±0.77	75.0±6.5	3.06±5.35	0.35±1.13	0.60±1.97	0.20±0.02	74.0±4.30	3.0±5.80	23.0±7.40	Loamy Sand
4	5.61±0.77	79.0±6.50	13.48±5.35	2.49±1.13	4.28±1.97	0.26±0.02	85.0±4.30	10.0±5.80	5.0±7.40	Sand
5	5.98±0.77	82.0±6.50	11.70±5.35	2.62±1.13	4.59±1.97	0.25±0.02	78.0±4.30	8.0±5.80	14.0±7.40	Loamy Sand
Av.	5.0	78.4	6.74	1.33	2.30	0.246	-	-	-	-
Ran	4.27-5.98	66-95	2.30-13.48	0.35-2.62	0.60-4.59	0.20-0.30	-	-	-	-

Av: Average, Ran: Range

P value=0.834, then P>0.05, there is no significant difference (ANOVA & DUNCAN)

EC= Electrical conductivity, CEC= Cation exchange capacity, OC= Organic carbon, OM= Organic matter, RH= Residual humidity

Table 3. Concentration of Tailing Cu in individual Fractions (mg/kg)

Loc	F1	F2	F3	F4	F5	Total	Cu in original Sample	%Recovery	%BF	%MF
1	$0.00^{a,b}$	$1.00^{a}\pm0.35$	0.00^{a}	$6.00^{a}\pm0.20$	$36.0^{b}\pm0.20$	43.0	48.13	99.69	0.023	2.3
2	$0.00^{a,b}$	$2.00^{a}\pm0.20$	0.00^{a}	0.00^{a}	$28.0^{b}\pm0.20$	30.0	30.71	97.68	0.07	7.0
3	$0.00^{a,b}$	0.00^{a}	0.00^{a}	0.00^{a}	$30.0^{b}\pm0.10$	30.0	31.80	94.38	0.00	0
4	$0.00^{a,b}$	$1.00^{a}\pm0.35$	0.00^{a}	$0.50^{a}\pm0.10$	$15.5^{b}\pm0.20$	17.0	18.05	94.18	0.06	6.0
5	$0.50^{a,b}\pm0.3$	0.00^{a}	0.00^{a}	$17.5^{a}\pm0.20$	$45.0^{b}\pm0.25$	63.0	65.0	96.77	0.08	0.8

Value with different superscript on the same row are significant ($p<0.05$)

Table 4. Concentration of Tailing Ni in individual Fractions (mg/kg)

Loc	F1	F2	F3	F4	F5	Total	Ni in original Sample	% Recovery	%BF	%MF
1	$9.00^{a}\pm0.95$	$6.00^{a}\pm0.25$	$5.00^{a}\pm0.10$	$1.00^{a}\pm1.20$	$57.5^{b}\pm0.1$	78.0	79.91	98.25	0.19	19
2	$8.50^{a}\pm2.05$	$7.50^{a}\pm1.40$	$5.00^{a}\pm0.35$	0.00^{a}	$56.0^{b}\pm2.0$	77.0	77.84	98.92	0.21	21
3	$8.00^{a}\pm0.95$	$6.50^{a}\pm0.45$	$0.35^{a}\pm0.12$	$1.00^{a}1.0$	$68.15^{b}\pm1.5$	84.0	84.16	95.25	0.17	17
4	$8.00^{a}\pm0.40$	$8.00^{a}\pm1.40$	$3.00^{a}\pm0.65$	$1.00^{a}\pm1.0$	$35.0^{b}\pm0.5$	55.0	56.15	97.95	0.29	29
5	$7.00^{a}\pm0.30$	0.00^{a}	0.00^{a}	$17.50^{a}\pm0.20$	$45.0^{b}\pm3.2$	55.50	91.69	60.53	0.13	13

Value with different superscript on the same row are significant ($p<0.05$)

Table 5. Concentration of Tailing Zn in individual Fractions (mg/kg)

Loc	F1	F2	F3	F4	F5	Total	Zn in original Sample	%Recovery	%BF	%MF
1	$7.50^{a}\pm0.65$	$11.50^{a}\pm3.70$	$12.30^{a}\pm4.15$	$9.00^{a}\pm2.25$	$28.0^{a}\pm2.30$	68.5	69.19	99.00	0.28	28
2	$2.80^{a}\pm1.25$	$8.00^{a}\pm2.25$	$9.50^{a}\pm1.45$	$8.00^{a}\pm0.05$	$26.0^{a}\pm2.00$	54.5	55.87	97.55	0.19	19
3	$2.00^{a}\pm1.65$	$7.00^{a}\pm1.65$	$8.50^{a}\pm1.50$	$9.50^{a}\pm2.00$	$27.0^{a}\pm1.00$	54.0	55.30	97.65	0.17	17
4	$6.00^{a}\pm0.55$	$7.50^{a}\pm1.25$	$12.0^{a}\pm2.35$	$11.5^{a}\pm1.30$	$6.00^{a}\pm0.50$	43.0	44.18	97.33	0.31	31
5	$1.00^{a}\pm0.30$	$38.0^{a}\pm0.80$	$39.5^{a}\pm0.20$	$32.5^{a}\pm1.10$	$31.0^{a}\pm4.45$	141.5	142.91	99.00	0.28	28

Value with different superscript on the same row are significant ($p<0.05$)

Table 6. Concentration of Tailing Cr in individual Fractions (mg/kg)

Loc	F1	F2	F3	F4	F5	Total	Cr in \ original Sample	%Recovery	%BF	%MF
1	0.00^{a}	$25^{b}\pm0.25$	0.00^{a}	$2.45^{b}\pm0.45$	$0.40^{a}\pm0.04$	5.10	5.58	91.40	0.44	44
2	0.00^{a}	$4.75^{b}\pm0.25$	0.00^{a}	$4.20^{b}\pm0.40$	$0.85^{a}\pm0.45$	9.80	10.40	94.23	0.48	48
3	0.00^{a}	$6.40^{b}\pm0.15$	0.00^{a}	$6.20^{b}\pm0.60$	$0.20^{a}\pm0.05$	12.8	13.48	94.96	0.50	50
4	0.00^{a}	$8.05^{b}\pm0.25$	$1.00^{a}\pm0.20$	$8.45^{b}\pm0.65$	0.00^{a}	17.5	18.55	94.34	0.46	46
5	$6.15^{a}\pm0.65$	0.00^{b}	$1.85^{a}\pm0.20$	$8.20^{b}\pm0.05$	$0.15^{a}\pm0.50$	16.35	17.46	93.64	0.38	38

Value with different superscript on the same row are significant ($p<0.05$)

Table 7. Concentration of Tailing Cd in individual Fractions (mg/kg)

Loc	F1	F2	F3	F4	F5	Total	Cd in original Sample	%Recovery	%BF	%MF
1	0.00^{a}	$0.25^{a}\pm0.05$	$0.25^{a}\pm0.05$	$0.10^{a}\pm0.00$	$0.10^{a}\pm0.05$	0.85	1.54	55.19	0.29	29
2	$1.10^{a}\pm0.50$	$0.50^{a}\pm0.20$	0.35 ± 0.05	$0.05^{a}\pm0.05$	0.00^{a}	0.20	2.17	92.17	0.80	80
3	$0.50^{a}\pm0.10$	$0.30^{a}\pm0.10$	0.15 ± 0.10	$0.85^{a}\pm0.05$	$0.40^{a}\pm0.15$	2.20	2.43	90.95	0.36	36
4	$0.015^{a}\pm0.00$	$0.25^{a}\pm0.00$	$0.30^{a}\pm0.00$	$0.45^{a}\pm0.05$	$0.35^{a}\pm0.10$	1.37	1.49	91.95	0.19	19
5	$0.25^{a}\pm0.05$	$0.30^{a}\pm0.05$	$0.50^{a}\pm0.15$	$0.60^{a}\pm0.05$	$0.20^{a}\pm0.05$	1.85	2.00	92.50	0.30	30

Value with different superscript on the same row are significant ($p<0.05$)

Table 8. Concentration of Tailing Fe in individual Fractions (mg/kg)

Loc	F1	F2	F3	F4	F5	Total	Fe in original Sample	%Recovery	%BF	%MF
1	$10.40^{a}\pm0.50$	$392.15^{b}\pm0.15$	$446.15^{d}\pm0.35$	$345.95^{b,c}\pm1.75$	$338.25^{c,d}\pm0.20$	1552.90	1554.31	100.09	0.26	26
2	$5.50^{a}\pm0.05$	$164.90^{b}\pm0.15$	$435.50^{d}\pm0.30$	$182.80^{b,c}\pm0.20$	$425.0^{c,d}\pm1.50$	1213.70	1634.98	74.24	0.14	14
3	$6.25^{a}\pm0.10$	$388.95^{b}\pm0.40$	$441.80^{d}\pm1.50$	$182.20^{b,c}\pm1.35$	$472.0^{c,d}\pm0.10$	1491.20	1506.20	99.0	0.27	27
4	$6.80^{a}\pm0.60$	$16.25^{b}\pm0.15$	$477.25^{d}\pm0.35$	$276.05^{b,c}\pm1.55$	$476.0^{c,d}\pm1.00$	1052.35	1057.55	99.51	0.022	2.2
5	$4.95^{a}\pm0.10$	$51.15^{b}\pm0.05$	$484.75^{d}\pm0.15$	$474.60^{b,c}\pm1.60$	$486.5^{c,d}\pm0.10$	1401.15	1412.15	99.28	0.040	4.0

Value with different superscript on the same row are significant ($p<0.05$)

4. Discussion

Physicochemical properties of the tailings was conducted and the result is presented on Table 2. The pH values of the tailing samples range from 4.27 to 5.98 with a mean value of 5.0 which shows that the tailings are slightly acidic. Residual humidity range from 0.20-0.30% with an average of 0.246. Since residual humidity is proportional to the content of clay and organic matter, tailing has low residual humidity, it indicated less clay but range from loamy sand to sand.. EC range from 66-95 μS/cm with a mean value of 78.4 μS /cm. Furthermore, CEC ranged from 2.30 to 13.48Meq/100g with a mean value of 6.74Meq/100g. The percentage organic carbon (%OC) ranged from 0.35 to 2.62 with a mean value of 6.74. Also, percentage organic matter (%0N) ranged from 0.60-4.59 with a mean value of 2.30. Similar results are reported [1].

The sequential extraction procedures results provided information on the potential mobility and bioavailability of the studied elements in this research. The distribution of heavy metals in the sample allows us to predict their mobility and bioavailability in the tailing. The bioavailability factor was expressed as the ratio of the available concentration of a metal in soil to its total concentration. It shows the potentials of a particular metal from the soil matrix to enter the soil solution from which it can be absorbed by plants. Mobility factor was expressed as percentage of the Bioavailability factor. The speciation of the metals are shown in Table 3-7 for their individual metals.

Cu was mainly presented in the residual fraction and organic matter fraction as shown in Table 3. The content of residual fraction ranged from 68%-91% and varied in the range of 5%-27% in organic matter fraction .the level of copper is exchangeable , carbonate fraction and fraction bond to hydrate oxide of iron and manganese was lower. Copper is bound much more tightly by organic matter than Ni and is much less likely to be displaced by the hydroxylamine hydrochloride reagent. Similar results are reported by [21,22]. Copper in the soil is not present in the ionic forms which reduce its toxicity.
Ni is mainly found in the fraction bound to residual that it varies from 63%-81% as shown on Table 4.

Whereas 0%-27.7% in organic and sulfide fraction. The level of Ni in other fraction is considerably low. Toxicity of nickel is not important because of its low concentration in the mobile and bio available fractions.
Heavy metals in residual fraction are not likely to be discharged under normal environment conditions. Ni was mainly associated with residual fractions, so its status in the soil was considered stable [22].

The analysis from Table 5 shows that Zn has been bound to hydrated oxides of iron and manganese fraction and varied in different sample in the range of 15.7%-27.9%. The amount of zinc found in the carbonated fractions varies from 13%-26.9%.Similar results are reported by [24].

Chromium in the tailings sample is mainly found in the organic and sulfide metal fraction with an average of 48% and little lesser in the range of 44%-46% bound to carbonate. Whereas it is smaller in residual ranges from 0%-8.7% as shown on Table 6.

Thus, the bioavailability of chromium in the tailing sample is considered insignificant. It is low in exchangeable and iron-manganese oxide metal bound fraction.

The analysis of cadmium from Table 7 in different soil samples have been found in organic and sulfide metal fraction range from 2.5%-38.65% and varied in the range of 6.8%-27% in iron manganese oxide metal fraction. The level of cadmium in exchangeable, carbonate bound, and residue fraction was lower absorption by hydrated $CaCO_3$ has been shown to be reversible [23].

The results shows that iron occurred more in residual fraction which is varied between 26% and 34.7% in different sample and also 27.5%-45.4% of iron is bound to oxide fraction as presented in Table 8. It is also found in different ranges- carbonate, organic and sulfide metal fraction but minor amount of iron were detected in the exchangeable fractions . Similar results were reported by [25].

The metal concentrations, percentage recovery, mobility and bioavailability factors of all the sequential extraction steps including the residual phase fractions, determined at each extraction step in Tables 3-8, indicate that each metal has a characteristic distribution pattern.

Table 4, shows the mobility and bioavailability factors and percentage recovery of Ni for all the sequential extractions steps. The MF of Ni gave average value of 20% while average Bf of Ni was 0.20. The percentage recovery of Ni ranged from 95.25 -99.24%. The high MF and BF values of soil Ni may be interpreted as symptoms of relatively high liability and biological availability of the metals in soil [26,27]. Similar characteristics distribution patterns were observed for Cd, Cr, Fe and Zn except Cu with low Mf of 3.2% and Bf of 0.032(Tables 1 - 6). The average mobility of Ni, Cu, Cd, Cr, Fe and Zn levels in all the six fractions were in the order: Cr> Cd > Zu > Ni > Fe> Cu.

Conclusion

The distribution of heavy metals (Cu, Cr, Cd, Ni, Zn, Fe) in the tailings of Itagunmodi Gold mine was assessed. The results obtained in the heavy metal speciation indicated that all metals were mainly associated with the residual and organic& sulfide fraction whereas only small fraction of heavy metals is extracted in exchangeable, carbonate and Fe-Mn oxide fraction.

References

[1] Ekwue Y.A, Gbadebo A.M, Arowolo T.A, and Adeosun J.K. Assessment of metal contamination in sooil and plants from abandoned secondary, and primary goldmines in osun state, Nigeria. Journal of soil science and environmental mgt 2012, vol3 (11), pp 262-274.

[2] Navarro MC, Perez-Sirvent C, Martinez-Sanchez MJ, Vidal J, Tovar PJ, Bech J. Abandoned mine sites as a source of contamination by heavy metals:A case study in a semi-arid zone. J. Geochem. Explor., (2008) 96: 183-193.

[3] Singh AN, Zeng DH, Chen FS. Heavy metal concentrations in redeveloping soil of mine spoil under plantations of certain native woody species in drytropical environment, India. J Environ. Sci., (2005) 1: 168-174.

[4] Pruvot C, Douay F, Herve F, Waterlot C. Heavy metals in soil, crops and grass as a source of human exposure in the former mining areas. J Soils Sediments, (2006) 6: 215-220.

[5] Akan JC, Abdulrahaman FI, Sodipo OA, Lange AG. Physicochemical parameters in soil and vegetable samples from Gongulon Agricultural site, Maiduguri, Borno state, Nigeria. J. Am. Sci., (2010) 6: 12.

[6] Zhuang P, McBride MB, Xia H, Li H, Li Z . Heavy metal contamination in soils and food crops around Dabaoshan mine inGuangdong, China: implication for human health. Environ. Geochem. Health, (2008) 31: 707-715.

[7] Kabata-Pendias A, Mukherjee AB. Trace elements from soil to human. NewYork: Springer-Verlag (2007).

[8] Jarup L . Hazards of heavy metal contamination. Brit. Med. Bull., (2003)68: 167-182.

[9] Aslibekian O, Moles R. Environmental risk assessment of metal contaminated soils at silver mines abandoned mine site, co tipperary, Ireland. Environ. Geochem. Health (2003) 25:247-266. (Pub Med)

[10] Faruk O, Nazim S, Kara SM . Monitoring of cadmium and micronutrients in spices commonly consumed in Turkey. Res. J. Agric. Biol. Sci. (2006) 2:223-226.

[11] Tessier A, Campbell PG, Bisson M . Sequential extraction procedures for the specification of particulate trace metals. Anal. Chem., (1979) 5: 844-855.Ma

[12] Gibson MJ, Farmer JG . Multi-step sequential chemical extraction of heavy metals from urban soils. Environ. Pollut. Ser. B, (1986)11(2): 117-135.

[13] Riise G, Bjornstad HE, Lien HN, Oughton DH, Salbu B. A study on radionuclide association with soil components using a sequential extraction procedure. J. Radioanal. Nuclear Chem., (1990)142(2): 531-538.

[14] Salbu, B, Oughton DH, Ratnikov AV, Zhigareva TL, Kruglov SV, Petrov KV,Grebenshakikova NV, Firsakova SK, Astasheva N P, Loshchilov NA, HoveK, Strand P. The mobility of 137Csand 90Sr in agricultural soils inthe Ukraine, Belarus, and Russia, 1991. Health Phys., (1994) 67(5): 518-528.

[15] Blanco P, Tome VF, Lozano JC. Sequential extraction for radionuclidefractionation in soil samples: A comparative study. Appl. Radiat. Iso., (2004) 61(2-3): 345-350.

[16] Carter Mr, ciregorich E G(19940. Soil sampling and method of analysis. P. 99, accessed on www.amazon.com

[17] Thomas G W (1982). Exchangeable cations in A. L page et al (ed) methods of soil analysis: part 2. Chemical and microbiological properties. ASA monograph 9 :159-165.

[18] Nelson D W sommers L.E(1982). Toltal carbon, organic matter .pp 539-580. In page et al (ed) methods of soil analysis. Part 2 2nd ed . argon monogr.9 ASA and SSSA, Madison, WI.

[19] Yobouet Y. A., Adouby K., Trokourey A. and Yao B.Cadmium, Copper, Lead and Zinc speciation in contaminated soils. International Journal of Engineering Science and Technology ,2010,Vol. 2(5), 802-812.

[20] Boch, K. Schuster, M., Risse, G., Schwarzer, M. Anal Chem. Acta (2002) 257 – 459.

[21] Mclarem R.G and clucas L.M, fractionation of copper, nickel and zinc in metal spiked sewage sludge, journal of environmental quality, vol. 30, no.6.2001 pp 1968-1975.

[22] Huang s, Fractional distribution and risk assessment of heavy metals contaminated soil in vicinity of a lead/zinc mine, trans nonferrous met. Soc. China 24(2014) 3324-3331.

[23] Sager M. Chemical speciation and environmental mobility of heavy metals in sediments. In Hazardous Metals in the Environment, Stoeppler M, Ed., Elsevier Science Publ., Amsterdam,(1992) pp. 133-174.

[24] Kwapulisnski J and Wiechula D., forms of science heavy metals in the bottom sediment of goczalkowice reservoir, chemistry and environmental protection, polythenic university of lubhin, lubhin Poland, 1993.

[25] Cotton F A,Wllkinson G(1972c).nadvanced inorganic chemistry; wiley interscience, new York, p. 513.

[26] Ma, L.Q and Rao, G.N. Chemical Fractionation of Calcium, Copper, Nickel and Zincin contaminated soils. J. Env. Qual. 1997,26: 259 – 264.

[27] Gzyl, J. Lead and Cadmium Contamination of Soil and Vegetables in the Upper Silasia Region of Poland. Sci. Total Env. (1996);119 – 209.

[28] Akintola, A.I, Olorunfemi,A.O, Bankole,S.I, Omotoye,S.J and Ajayi, B.O. Petrography and Geochemical evaluation of major and trace elements concentrations in the stream sediments of Itagunmodi and its environs, Southwestern, Nigeria. Journal of Earth Sci & Geochemical Engineering Vol 3 no. 4, 2013, pg 1-24.