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Evaluation of Digestion Procedures on Heavy Metals in Soil of a Dumpsite in Ibadan, South-western Nigeria

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Abstract

Acid digestion is important in solubilizing metal ions in heavy metals determination. A number of procedures exist and the one used is dependent on different factors. This work is aimed at investigating the performance of three different acid digestion procedures (Aqua Regia, 2 M HNO_3 and $HNO_3/HClO_4$) for the extraction of Pb, Cd and Zn in soil sample from an abandoned dumpsite of a lead-acid producing industry in Lalupon, Oyo State. Heavy metals in soil extracts were determined using atomic absorption spectrophotometer. Results revealed that Aqua Regia gave the highest content level of Pb and Cd, $HNO_3/HClO_4$ showed best performance for Zn while 2 M HNO_3 had the least performance for the metals considered. Result of 2 M HNO_3 was less than the other two and could not represent total metal content of the soil. Without losing focus of the objectives of research, variation in the effectiveness of acid digestion procedures should be borne in mind when making a choice.

Keywords: Digestion procedure, Extractants, Heavy metals, Dumpsite, Soil

1. Introduction

Metals are found naturally on earth in rocks, soils and sediment trapped in different forms. Anthropogenic input of heavy metals in soil results in contamination. Chemicals are a major source of contamination introduced during washing of agricultural wastes like fertilizer and pesticide from farmland or effluent generated from industrial activities (Abegunde, 2017). The chemical behaviours of these contaminants are controlled by soil composition, properties such as pH and a number of processes such as metal cation release from contaminated source, cation exchange and specific adsorption onto surface of minerals (Guveni & Akinci, 2011; Hlavay, Prohaska, Weisz, Wenzel, & Stingeder 2004). Their impacts depend on the total metal concentrations in soil, mobility and bioavailability (Kaasalainen & Yli-Halla, 2003; Roundhill, Slangi, Memon, Bhanger & Yilmaz, 2009; Szakova, Miholova, Tlustos, Sestakova, & Frkova, 2010).

Several methods have been used by researchers in the digestion of soil samples for the determination of metallic levels. Such methods have been through the use of fluxes or inorganic acids such as HCl, H_3PO_4, HNO_3, $HClO_4$, HF, H_2SO_4 or their combination. These acids (extractants) exhibit various properties which enable them to perform specific functions during extraction (Tam & Yao, 1999; Alam & Tokunaga, 2006; Kislik, 2002). The choice of extractants depend on the aim of the study, type of contaminants, properties of the extractant, experimental conditions and need for minimum interference by contaminants (Kaasalainen & Yli-Halla, 2003; Roundhill, Slangi, Memon, , Bhanger & Yilmaz, 2009; Guveni & Akinci, 2011; Wilson et al., 2005; Twyman, 2005). Improper selection of extractant could cause effects such as partial dissolution of soil sample resulting in decreased metal content levels in soil samples (Hlavay et al., 2004; Twyman, 2005). Extractants may be acidic or basic depending on the mode of action. This depends on interacting mechanisms such as the metal-ion extractant affinity, metal ion concentration, extraction temperature and acidity of the medium (Tam & Yao, 1999; Nogoles et al., 1995; Szakova et al., 2010). Successful extraction, determination and isolation of biologically active components from a material are largely dependent on the type of solvent used in the extraction procedure (Abegunde & Ayodele-Oduola, 2015*)*. The extent to which ions of extractant show affinity for metals also depends on concentration of the metal in soil and inter metal interference in heterogeneous contaminated soil during extraction (Tam & Yao, 1999; Nogales et al., 1995). Extractants are specific in action; for example, H_2SO_4 is not used to digest samples containing Barium (Ba) and neither is HCl used for samples containing Silver (Ag) and Lead (Pb). Besides, Arsenic compounds form volatile compounds with HCl and H_2SO_4 is not suitable as extractant to analyze some metals (especially alkaline earth metals) simultaneously because of the possibility of forming insoluble sulphate salts (Twyman, 2005; Nogales, 1995). Their specificity can be improved by combining a series of acids during extraction (Guveni & Akinci, 2011; Kislik, 2002; Wilson et al., 2005; Tam & Yao, 1999; Szakova et al., 2010). Mixtures of HCl, HNO_3, $HClO_4$ and HF dissolve most metals in soils and this is reported to have great accuracy in analysis (Twyman, 2005). Report is given on the use of Aqua regia in the dissolution of sulfides, phosphates, many metals and alloys including Gold (Au), Platinum (Pt) and Palladium (Pd) (Tam & Yao, 1999). The use of acids in sequence has been reported to give good results (Argon Lab Systems, 2007). Use of HNO_3 and $HClO_4$ premixed in 3:1 ratio followed by the addition of HF has been used with high extraction yield (Twyman, 2005). Consequently, the aim of this research was to identify the most reliable and best digestion procedure among those used for the heavy metals under consideration. Specific objective was to compare the efficiency of the three procedures being major wet digestion methods for evaluating heavy metals in soil. The three heavy metals were selected because they are major metal pollutants from lead acid battery. The results of the research were analyzed for statistical significance by analysis of variance.

2. Experimental

2.1. Sample Collection and Preparation

Soil from a dumpsite in Lalupon, Lagelu Local Government Area of Oyo State, south-western Nigeria, was used for this work. The soil samples were randomly and extensively collected using a soil auger, transferred into black polythene bags and transported to the laboratory. The samples were air-dried, gently crushed with pestle in agate mortar, sieved through 2 mm fraction, homogenized and stored in polythene bags. The homogenized samples were digested using different acid digestion procedures, filtered and kept in plastic bottles for heavy metals analysis using AAS.

2.2. Digestion with Aqua Regia (concentrated HCl and HNO_3 in the 3:1)

Soil sample (1.0 g) was weighed and transferred into digestion flask. Aqua regia (20 mL) was added to it and digestion carried out on a heating mantle in a fume cupboard. The temperature was gradually increased, and agitation occasionally done until volume of content was reduced to about 5 mL. Excessive evaporation of extractant was prevented by covering each flask with watch glass. The resulting solution was filtered, washed with de-ionized and double-distilled water and transferred quantitatively into a 50 mL volumetric flask and made up to the mark with distilled water.

2.3. Digestion with Nitric–Perchloric Acid ($HNO_3/HClO_4$)

1.0 g of the soil sample was weighed and transferred into a 250 mL digestion tube and 10 mL of concentrated HNO_3 was added. The mixture was boiled gently for 30–45 minutes to oxidize all easily oxidizable matter. After cooling, 5 mL of 70% $HClO_4$ was added and the mixture boiled gently until dense white fumes appeared. After cooling, 20 mL of distilled water was added, and the mixture was boiled further to release any fumes. The solution was cooled, filtered through Whatman No. 42 filter paper and <0.45lm Millipore filter paper and transferred quantitatively to a 50 mL volumetric flask and made up to the mark with distilled water.

2.4. Digestion with concentrated Nitric Acid

A separate 1.0 g soil sample was weighed and transferred into a digestion tube. A 20 mL solution of 2M HNO_3 was added. The tube containing the mixture was placed in a beaker of water and heated for 2 hours with gradual increase in temperature to 100ºC. At intervals, the tube was opened, the suspension shaken and the tube covered again. The suspension was thereafter cooled, filtered into 50mL volumetric flask and made up to the mark with distilled water. The digested samples were analyzed for heavy metals using atomic absorption spectrometer (AAS) Buck Scientific model 210VGP.

3. Results and Discussion Result

Table 1. Heavy metal contents (mg/kg) of soil samples by three digestion

Sample	Digestion Procedure	Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)
AB_1	$HNO_3/HClO_3$	2233.33±57.74a	1.50±0.00a	270.33±0.58a
	Agua Regia	43200.00±173.21b	2.33±0.29b	260.50±0.00b
	2M HNO_3	834.67±404.15c	0.05±0.00b	5.17±0.00c
AB_2	$HNO_3/HClO_3$	3500.00±173.21a	1.50±0.00a	245.33±0.29a
	Agua Regia	44433.33±208.17b	3.00±0.00b	267.83±0.29b
	2M HNO_3	899.33±208.17c	0.04±0.00c	5.22±0.50c
AB_3	$HNO_3/HClO_3$	866.67±57.74a	< DL a	85.67±0.29a
	Agua Regia	900.00v173.21a	0.83±0.29b	112.67±0.58a
	2M HNO_3	26.67±57.74b	0.01±0.00b	2.22±0.29a
AB_4	$HNO_3/HClO_3$	2466.67±115.47a	1.33±0.29a	249.83±0.29a
	Agua Regia	48566.67±472.58b	3.00±0.00b	275.50±0.50a
	2M HNO_3	1097.33±17c	0.05±0.00c	5.28±0.87a
AB_5	$HNO_3/HClO_3$	1900.00±100.00a	0.50±0.00a	103.67±0.29a
	Agua Regia	1.533.33±152.75a	0.50±0.00a	67.17±0.29b
	2M HNO_3	74.67±208.17b	0.01±0.00a	1.41±1.00c
AB_6	$HNO_3/HClO_3$	1066.67±115.47a	1.00±0.00a	327.67±0.76a
	Agua Regia	433.33±57.74b	0.83±0.29ab	95.67±1.04b
	2M HNO_3	46.00±173.21c	0.01±0.00b	2.14±0.76c
AB_7	$HNO_3/HClO_3$	1033.33±152.75a	< DL a	236.33±1.26a
	Agua Regia	1466.67±57.74b	0.50±0.00a	75.17±0.29b
	2M HNO_3	74.00±173.21c	< DL a	1.07±0.00c

Values are means ± standard deviation for three determinations. DL = Detection limit. (DL are 0.08, 0.01 and 0.005 ppm for Pb, Cd and Zn respectively).

Within each column for each sample, means that do not share a letter are significantly different.

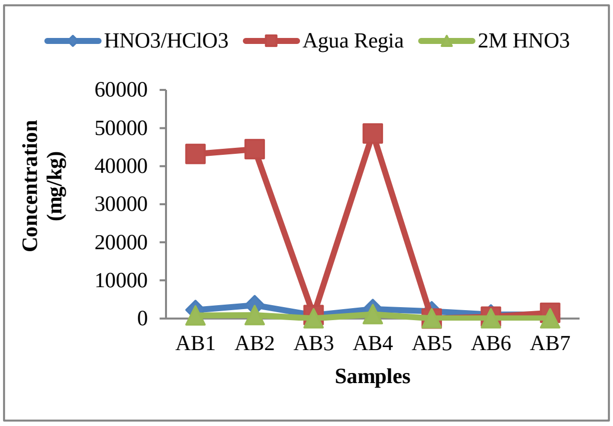

Figure 1. Performance of solvents for the extraction of Pb

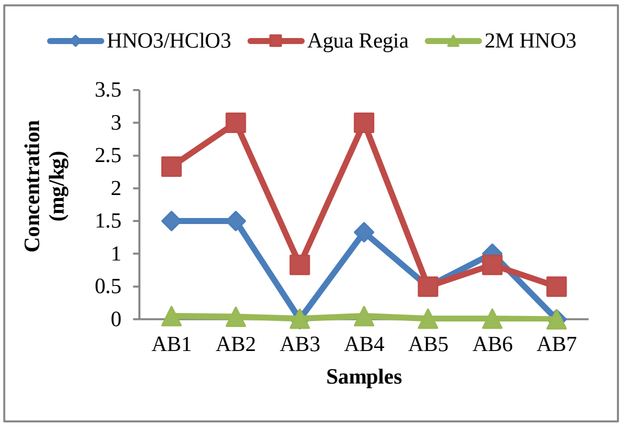

Figure 2. Performance of solvents for the extraction of Cd

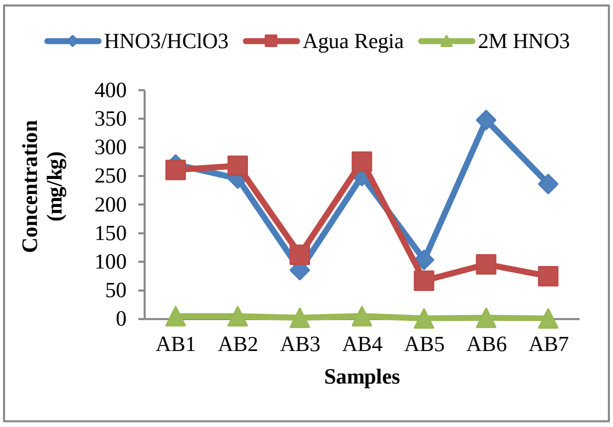

Figure 3. Performance of solvents for the extraction of Zn

4. Discussion

Results of concentrations of the three selected heavy metals in seven soil samples using three different digestion procedures are tabulated in Table 1. Performance of the three procedures for the extraction of each metal was also evaluated and presented in Figures 1, 2 and 3. Aqua regia performed best among the three procedures for the extraction of Pb in all the samples except for sample AB5 and AB6 where the performance of HNO3/HClO4 was the highest. Also, extraction with aqua regia proved most effective among the three procedures for the extraction of Cd. Aqua regia was able to extract at least 0.5 mg from every 1 kg of the soil samples. However, the level of Cd concentration in sample AB3 in the extract by HNO3/HClO4 and in the extracts by $HNO_3/HClO_4$ and 2M HNO3 for sample AB7 were found below the detection limit of the machine used. $HNO_3/HClO_4$ showed better performance than aqua regia in the extraction of Zn for soil samples AB1, AB5 and AB7.

Aqua regia showed to be most effective for extraction of Pb, Cd and Zn while 2 M HNO_3 was the least. The latter also performed extremely poor in extracting Zn when compared with aqua regia and $HNO_3/HClO_4$. Effectiveness of aqua regia and $HNO_3/HClO_4$ could be attributed to the fact that both are mixtures of different acids. The variations in extractability showed in this research work further confirmed the reports that some extractants have more affinity for some contaminant metals than others due to the soft nature of such metal ions, the type, size and the geometry of the extractant ions and also probably due to inter-metal interference in heterogeneous contaminated soils during extraction (Kislik, 2002; Guveni & Akinci, 2011). The relatively high Pb levels of some of the soil samples were expected as the samples were taken from an abandoned dump site of a defunct lead-acid battery producing plant.

On the other hand, the results of the analysis of variance and Tukey pairwise comparisons of the experimental results as presented in table 1 shows significant difference in the performance of the three digestion procedures for the three metals considered in all the samples except for the extraction of Zn in samples AB3 and for the extraction of Cd in sample AB5.

5. Conclusion

The variation in the level of metals extracted by each digestion procedure shows that the acids or the digestion procedures have different extractive ability. Understanding the behaviour of each metal in relation to the acids will help to choose the best extractant or digestion procedure at any instance of metal extraction from soils.

6. References

Abegunde, S. M., Adejuwon, O. M., & Olorunfemi, T. O. (2017). Safety Assessment of Hand-Dug Well Water Samples from Selected Towns in Ekiti State, Nigeria. *Journal of Advanced Research in Applied Chemistry & Chemical Engineering, 4*(1&2). Retrieved from http://science.adrpublications.in/index.php/JoARACCE/article/view/351

Abegunde, S. M. & Ayodele-Oduola, R.O. (2015). Comparison of efficiency of different solvents used for the extraction of phytochemicals from the leaf, seed and stem bark of *Calotropis Procera*. *International Journal of Science and Research (IJSR), 4*(7), 835 - 838.

Alam, M. G. M. & Tokunaga, S., (2006). Chemical extraction of arsenic from contaminated soil. *Journal of environmental science and health, Part A: toxic/hazardous substances and environmental engineering, 41*(4), 631 - 643.

Argon Lab Systems, Argon Technology. (2007). Retrieved from https://pdfs.semanticscholar.org/de9e/2eee9cd723970ca6275bfe5b629d4157d5e6.pdf

Guveni, D. E. & Akinci, G. (2011). Comparison of acid digestion techniques to determine heavy metals in sediment and soil samples. *Gazi University Journal of Science, 24*(1), 29 – 34.

Hlavay, J., Prohaska, T. M., Weisz, M., Wenzel, W. W., & Stingeder G. J. (2004). Determination of trace elements bound to soils and sediment fraction. *Pure and Applied Chemistry (IUPAC Technical Report), 76*(2), 415 - 442.

Kaasalainen, M. & Yli-Halla M., (2003). Use of sequential extraction to assess metal partitioning in soils. *Environmental pollution, 126*(2), 225 - 233.

Kislik, V. (2002). "Competitive complexation/ solvation" Theory of solvent extraction: II, solvent extraction of metals by acidic extractions. *Separation Science and Technology, 37*(11), 2623 - 2657.

Nogales, R., Gallardo-Lara, F., Benitez, E., Soto, J., Hervas, D., & Polo, A. (1997). Metal extractability and availability in soil after heavy application of either nickel or lead in different forms. *Water, Air, and Soil Pollution, 94*(1-2), 33 – 44.

Roundhill, D. M., Slangi, I. B., Memon, S., Bhanger, M. I. & Yilmaz, M. (2009). The liquid-liquid extraction of toxic metals. *Pakistan Journal of Analytical & Environmental Chemistry, 10*(1&2), 1-13.

Szakova, J., Miholova, D., Tlustos, P., Sestakova, I., & Frkova, Z. S. (2010). Effect of soil properties and sample preparation on extractable and soluble Pb and Cd fractions in soils. *Agricultural Sciences, 1*(3), 119-130.

Tam, N. F. Y. & Yao, M. M. (1999). Three digestion methods to determine concentrations of Cu, Zn, Cd, Ni, Pb, Cr, Mn, and Fe in mangrove sediments from SaiKeng, ChekKeng and Sha Tau Kok, Hong Kong. *Environmental Contamination and Toxicology*, *62*(6), 708-716.

Twyman, R. M. (2005). *Sample Dissolution for Elemental Analysis: Wet Digestion*. In: P. Worsfold, A. Townshend, & C. Poole (Eds.), Encyclopedia of analytical science: the 2nd (pp. 146-153), London: Elsevier Science

Wilson, B., Braithwaite, A., & Pyatt, F. B. (2005). An evaluation of procedures for the digestion of soils and vegetation from areas with metalliferous pollution. *Toxicological & Environmental Chemistry*, *87*(3), 335 – 344.