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Effect of Acid Digestion Methods on Total Metals Recovery from Sludge from Water Treatment Plants (WTPS) in Nigeria

Emmanuel U. Dan, Edu J. Inam

Department of Chemistry, University of Uyo, Uyo, PMB 1017, Akwa Ibom State, Nigeria

Abstract Effect of acid digestion methods on total metal recovery from sludge from water treatment plants in Nigeria was conducted. Sludge samples from four (4) different water treatment plants namely Lower Usuma Dam Water Treatment Plant, Bwari (LUDWTP), Le-Meridien Ibom Hotel and Golf Resort Water Treatment Plant, Uyo (LMWTP), Akwa Ibom State Water Company Water Treatment Plant (AKWTP) and Champion Brewery Water Treatment Plant (CBWTP) were collected and analysed for total metal recovery using Atomic Absorption Spectrophotometer after digestion using two different acid combinations (aqua regia and HNO_3/ $HClO_4$ 2:1). The results reveal that $HNO_3/HClO_4$ extract recorded the highest mean total 16.58 $mgkg^{-1}$ Zn, 0.40 $mgkg^{-1}$ Cu and 0.47 $mgkg^{-1}$ Cd than aqua regia extract in all the fifteen metals analysed. Aqua regia extracts had the highest mean total 61.99 $mgkg^{-1}$ Ca, 3.60 $mgkg^{-1}$ K, 29.57 $mgkg^{-1}$ Mg, 52.19 $mgkg^{-1}$ Fe, while Co, Cr, Pb, Mn and Na were 0.07, 0.27, 1.47, 19.37 and 12.69 respectively. Aluminium and arsenic levels were not detected in all the four samples extracted with aqua regia and $HNO_3/HClO_4$. From the results of this work, aqua regia digestion method is very effective for use in routine monitoring of metals in sludge from water treatment plants in Nigeria.

Keywords Acid digestion, Sludge, Water Treatment Plant, Nigeria

Introduction

Sludge is defined as residue or waste generated from the treatment of waste water [1]. This substance has been reported to be rich in nutrient (nitrogen and phosphorus), organic matter and trace elements that are beneficial to plant growth and better yield [2]. Also, there are many literatures available that has reported other applications of this waste ranging from production of biogas, bio-ethanol and bio-diesel, adsorbent, application in making ceramics product for construction [3] to agricultural uses such as sources of some trace and essential metals into the soil where they are poured, a suitable substitute for commercial fertilizer [4].

Heavy metals are of particular interest to environmental scientists because of their major effect on environmental quality. However, they are considered to be problematic in the contamination of the environment and this has raised concerns to scientists' worldwide. The main sources of trace metal pollution in the environment are industrial effluents, anthropogenic activities and sewage discharges, among others [5]. The utilization of sewage sludge is strictly limited by the presence of toxic compounds in its chemical composition, including trace metals. As the effect of the negative impact of these elements on the environment are commonly known and thoroughly described, sewage sludge undergoes a strict process of verification in terms of total heavy metal content. It is a common practice that sludge generated after treatment of wastewater are discharge into the environment (soil and water) and this has posed a serious environmental pollution challenge to the environment in which they are being discharged.

The technique for determination of trace metal levels in sludge generated from water treatment plants is not different from other environmental samples analyses, as it involves sample pre-concentration technique, hot plate or microwave digestion among others [6]. Sample digestion techniques received more attention in the field of analytical chemistry; because they are able to liberate metal ions into solution and detectable form [7]. On the basis of this, improvements are needed on the existing digestion systems to accurately monitor the concentration of the metals being released into the environment. Therefore, this work seeks to compare the strength of different acid digestion combinations (aqua regia and $HNO_3/HClO_4$) on the extraction of metals (Cd, Cr, Cu, Mn, Pb, Zn, Co, K, Pb, Fe, Na, Al, Si, As, and Mg) in sludge from four different wastewater treatment plants in Nigeria. The choice of the plants was based on different treatment methods employed and the tonnes of sludge generated.

Materials and Methods

Sources of Sludge Samples

Under strict safety precautions, Grab sludge samples were obtained from

(i) Lower Usuma Dam Water Treatment Plant (LUDWTP) located between latitude 9º 01' 12" N and longitude 7º 25' 16" E, 26 kilometers from Abuja City center and 10 kilometers away from Bwari. It has a capacity to process 120 million liters of water and provide Abuja and its neighboring areas with the same amount of clean drinking water per day

(ii) Le-Meridien Ibom Hotels and Golf Resort Water Treatment Plants (LMWTP) located between latitude 5^o 03'26.8" N and longitude 8^{o}02'20.7" E at Nwaniba, Uyo, Akwa Ibom State.

(iii) Akwa Ibom Water Company (AKWTP) located between 5^{o}02'1.1" N and longitude 7^{o}56'19.6" E at Dominic Utuk Ave, Uyo, Akwa Ibom state. It has a capacity to provide 196 liters of potable water to urban and semi-urban and rural communities of Akwa Ibom state.

(iv) Champion Brewery PLC (CBWTP) located between latitude 5^o 04'55.7" N and longitude 9^{o}20'08.3" E at Aka Road Uyo, Akwa Ibom State.

Sampling / Sample Pre-Treatment

Sludge used in the study came from four (4) sewage treatment plants located in Nigeria. Sludge samples from Lower Usuma Dam water treatment plant, Gwari, Abuja (LUDWTP), Champion Brewery PLC (CBWTP) and Le Meridien water treatment plant (LMWTP) were collected using polyethylene sample bottle already washed and pre-treated with dilute nitric acid and rinsed with deionised water. Samples from Akwa Ibom Water Company (AKWTP) which was in a solid form since the samples were already stored over a period of time were collected in a polyethylene bag. The samples were labelled, put in an ice chest thermocool, and immediately transported to the laboratory. The samples were then acidified by adding 2ml HNO_3 to pH 2 or less to prevent the precipitation of metals and also convert the metal to same oxidation state before being stored in a refrigerator at 4^{o}C for metal analysis [8].

Prior to digestion, the sludge sample were dried in an oven to eliminate water and other liquids and then passed through a 2mm sieve to eliminate roots, stones, plastics, grass and other impurities. The samples were then desegregated to fine sizes using mortar and pestle and thoroughly mixed to achieve homogeneity. The powdered sludge were then sieved mechanically to obtain fractions that were far less in particle size than the one obtain early approximately 60µm. The dried sample were stored in a polyethylene bag and put in an air tight container to avoid moisture and oxidation.

Sample Digestion

One gram each of the dry sludge samples was placed in pre-weighed crucibles for digestion. Ten millilitres of aqua regia (HCl/HNO_3 3:1) which was already mixed and allow to stand for 10 minutes for it to saturate was then added to one of the crucible, while 10ml of $HNO_3/HClO_4$ (2 :1) was added to the other crucible simultaneously. The resulting solution was then heated in a hot plate under a fume-hood [6] until the volume reduced to half. To each of the crucible, 5ml of deionised water was added and heated again to boiling. After cooling, the solutions were filtered using filter paper (whatman 125mm Dia Cat No 1001125) into measuring cylinders and deionised water added to make up to 10ml before transferring them quantitatively into the sample bottles for atomization using Atomic Absorption Spectroscopy (UNICAM 939). Blank samples were also prepared using the two acid mixtures. The determination was done in triplicate and the mean concentration evaluated.

For metal recovery analysis, each of the two extracts was spike with corresponding standards solutions before atomisation for each of the metal analysed. The percentage recoveries of the metals were calculated using the relationship given below:

$$Percentage\ recovery = \frac{Spike\ value - Unspike\ value\ \ x\,100}{Spike\ value}$$

Results and Discussion

A mixture of mineral acids is usually preferred for certain inorganic matrices and is generally more advantageous for the decomposition of organic compounds. The capabilities of these acid mixtures to digest the sewage sludge, taking into account the amount of the metal recovered were evaluated. The results of the trace metal levels obtained from extract with aqua regia and $HNO_3/HClO_4$ combinations are presented in table 1 and 2 respectively.

Metal Levels of Sludge Extracted with Aqua Regia and $HNO_3/HClO_4$

Table 1: Level of metals (mean ±SD) (mg/kg) of wastewater sludge extracted with aqua regia

Elements	LUDWTP	AKWTP	LMWTP	CBWTP
Zinc	40.46±1.10	8.35±0.31	30.96±4.32	16.23±1.24
Calcium	72.64±2.02	68.27±3.34	48.14±2.00	58.89±4.11
Potassium	4.12±0.42	4.65±0.41	2.40±0.06	3.24±0.18
Magnesium	31.42±1.31	34.10±2.11	24.05±2.56	28.73±2.98
Iron	58.15±0.12	49.18±4.08	60.59±7.52	40.87±1.54
Cobalt	0.12±0.00	0.08±0.01	0.02±0.00	0.06±0.00
Chromium	0.38±0.01	0.24±0.01	0.26±0.01	0.18±0.01
Copper	0.45±0.00	0.24±0.03	0.48±0.11	0.13±0.00
Cadmium	0.13±0.02	1.28±0.06	ND	0.48±0.04
Lead	ND	1.43±0.08	0.16±0.02	ND
Manganese	18.23±1.45	28.44±2.07	12.15±0.50	18.65±1.16
Sodium	20.66±1.33	10.24±1.06	11.18±0.34	8.67±1.90
Silicon	ND	ND	ND	ND
Aluminium	ND	ND	ND	ND
Arsenic	ND	ND	ND	ND

LUDWTP= Lower Usuma Dam Water Treatment Plant; LMWTP = Le-Meridian Water Treatment Plants; AKWTP = Akwa Ibom Water Company sludge; CBWTP= Champion Brewery Water Treatment Plant; ND= Not Detected

Table 2: Levels of trace metals (mg/kg) in wastewater sludge extracted with $HNO_3/HClO_4$

Elements	LUDWTP	AKWTP	LMWTP	CBWTP
Zinc	26.05 ±1.11	15.00 ±0.12	49.02 ±3.35	16.23±1.04
Calcium	46.48 ±3.82	58.89 ±3.04	54.35±1.08	41.53 ±0.91
Potassium	1.03±0.03	3.24±0.16	3.56 ±0.16	2.87±0.10
Magnesium	34.10±2.31	28.73±1.15	22.87±1.61	25.51±0.89
Iron	30.54±0.12	40.87±2.00	57.75±5.05	59.97±3.13
Cobalt	0.06±0.00	0.05±0.01	0.04±0.00	0.04±0.00
Chromium	0.02±0.01	0.22±0.01	0.42±0.01	0.14±0.01
Copper	0.68 ±0.10	0.17±0.08	0.52 ±0.11	0.23±0.00
Cadmium	5.24±0.71	0.34 ±0.00	0.34 ±0.00	2.32 ±0.02

Lead	1.62 ±0.00	1.24±0.03	1.24 ±0.01	0.05 ±0.00
Manganese	13.29±0.41	25.64±1.07	11.21±0.54	20.96±1.23
Sodium	3.21±0.03	8.67±1.18	12.06±0.31	8.43±0.92
Silicon	ND	0.03 ±0.00	ND	0.01 ±0.00
Aluminium	ND	ND	ND	ND
Arsenic	ND	ND	ND	ND

LUDWTP= Lower Usuma Dam Water Treatment Plant; LMWTP = Le-Meridian Water Treatment Plants; AKWTP = Akwa Ibom Water Company sludge; CBWTP= Champion Brewery Water Treatment Plant; ND= Not Detected

The levels of metal in sludge extracted with aqua regia and $HNO_3/HClO_4$ all varied as a result of different composition of the sludge based on treatment process or storage. The sludge samples were rich in elements such as calcium, potassium, magnesium, iron, copper, manganese, sodium and zinc. The levels of calcium ranged from 48.14 – 72.64 mg/kg; potassium 2.40 – 4.12 mg/kg, magnesium 24.05 – 31.42mg/kg, iron 40.87 – 60.59mg/kg, copper 0.13 – 0.45 mg/kg, manganese 12.14 – 28.44 mg/kg, sodium 8.67- 20.66 mg/kg and zinc 8.35 – 40.46 mg/kg. The results for zinc, calcium, magnesium, and copper obtained are lower than those reported for sludge [9-10] for these elements using the same extractant, but lower than those reported in literature [11-12]. For $HNO_3/HClO_4$, the levels of calcium, potassium, magnesium, iron, zinc and sodium ranged between (41.53 - 58.89) mg/kg, (1.03 - 3.56) mg/kg, (22.87 - 34.10) mg/kg, (30.54-59.97) mg/kg, (15.00 - 49.02) mg/kg and (3.21 - 12.06) mg/kg respectively (Table 2). The concentration of all the essential elements analysed for in this study fell within the accepted limit for sludge stipulated by USEPA and EU guidelines. Among the numerous groups of elements present in the sludge, trace metals (heavy metals) are undoubtedly the most crucial and at the same time the most controversial ones as those for pollution cadmium, chromium, cobalt, and lead are of primary concern. From the results in Table 1 and 2, all the samples recorded levels of silicon, aluminium and arsenic ranged from very low to not detectable levels for both aqua regia and $HNO_3/HClO_4$ extractant. Also, mean concentration ranging from 0.02- 0.12 mg/kg Co, 0.18 - 0.38 mg/kg Cr, 0.13 – 0.48 mg/kg Cd, and 0.16 – 1.43 mg/kg Pb were obtained for sludge extracted with aqua regia. The mean value obtained for the sludge is lower than reported by researchers [13-15]. Cadmium, lead, cobalt, copper, chromium and manganese levels in sludge extracted with $HNO_3/HClO_4$ ranged from 0.34-5.24mg/kg Cd, 0.05-1.62mg/kg Pb, 0.04 - 0.06 mg/kg Co, 0.23 - 0.68 mg/kg Cu, 0.14 - 0.42 mg/kg Cr and 11.21 - 25.64 mg/kg Mn although they were within the normal range of the allowed established guidelines by USEPA. Trace metals are very hazardous at a certain concentration and it's toxic to humans and other living organism especially in the aqueous medium [16]. Sources of these elements in sludge may be attributed to paint pigment used in the coating of the sludge tank as well as oils used in lubricating of the machine before and after production, from the plating and metal processing in the plant. High concentration of lead in waste water sludge has been attributed to emission from exhaust pipe of generating plants used to power machines during production according to report of [14].

Acid Strength and Extraction of Total Metal in Sludge

Determination of metal in sludge from wastewater treatment plant requires sample pre-treatment prior to analysis because of certain challenges such as the complexity of the physical state of the sample which may lead to wrong readings in the measurement. This is particularly the case with low analyte concentration to be detected by the instrument. The purpose of this work is to assess the effect of acid strength (aqua regia and $HNO_3/HClO_4$) on the extraction of metals in wastewater sludge prior to atomization.

From the results, it is observed that the levels of each metal varied in all the samples with respect to the acids used. The levels of silicon, aluminium and arsenic in all the samples were not detected in both aqua regia and $HNO_3/HClO_4$ digestion. Table 3 shows the mean total of each metal from the four sampling stations. The result shows that $HNO_3/HClO_4$ extract recorded the highest mean total for zinc (26.58 mg/kg), copper (0.40 mg/kg) and cadmium (0.47 mg/kg) than aqua regia extract in all the fifteen metal analysed. Aqua regia showed a significant strength in the extraction of calcium, potassium, magnesium, iron, cobalt, chromium, lead, manganese and sodium than $HNO_3/HClO_4$ pairs. These result confirmed the validity of using aqua regia digestion method for extraction of metal ions from sludge from wastewater treatment plant sample matrices based on the percentage recoveries of the metals. In addition, these results confirmed the use of aqua regia as a suitable sample preparation method that can be applied for routine analysis in sludge to check the amount of metals.

Table 3: Total means average ($mgkg^{-1}$) of metal recovered in sludge

Metals	Aqua regia	$HNO_3/HClO_4$ (2:1)
Zinc	24.03	26.57
Calcium	61.99	50.31
Potassium	3.60	2.67
Magnessium	29.57	27.80
Iron	52.19	47.28
Cobalt	0.07	0.05
Copper	0.33	0.40
Chromium	0.27	0.20
Cadmium	0.47	2.06
Lead	1.47	1.04
Manganese	19.37	17.78
Sodium	12.69	8.09

Table 4: Mean percentage recoveries of metals

Metals	Aqua Regia	$HNO_3/HClO_4$ (2:1)
Zinc	82.15	94.23
Calcium	78.97	68.65
Potassium	90.05	74.32
Magnesium	86.44	71.90
Iron	97.24	71.76
Cobalt	93.27	73.11
Copper	77.32	81.45
Chromium	75.34	71.16
Cadmium	71.05	74.17
Lead	94.12	76.11
Manganese	80.09	72.94
Sodium	91.45	81.53

Conclusion

Investigated sludge samples from four different water treatment plants in Nigeria exhibited different chemical composition which was especially evident in the total amount of metals. Aqua regia and $HNO_3/HClO_4$ (2:1) digestion methods were successfully assessed and validated for the digestion of metals using Atomic Absorption Spectroscopy as the instrument for detection. Based on the result obtained, aqua regia demonstrated very good efficiency in strength for the extraction of metal based on the highest mean total of metal extracted and percentage recovery for determination of Ca, K, Mg, Fe, Co, Cr, Pb, Mg, and Na. Nitric acid and perchloric acid combination was very effective for the detection of Zn, Cu and Cd in sludge from wastewater treatment plants in Nigeria. The results reveal that aqua regia digestion can be used for routine monitoring of metals in sludge from water treatment plants in Nigeria.

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