COMPARATIVE ASSESSMENT OF THE LEVELS OF SOME HEAVY METALS IN VIRGIN AND USED WATER PLASTIC BOTTLES AND SACHETS IN NIGERIA

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ABSTRACT

Plastic bottles and sachets for water packaging manufactured from 3 different factories in Minna, Niger State of Nigeria were collected and analyzed to determine the concentration of heavy metals (Mn, Fe, Cu, Zn, Co, Cd, Pb and Ni) in them. The plastics are categorized as virgin and used plastics. The plastics were first processed by dry ashing and then digested with analar grade HNO_3 in accordance with CPSC-CH-E 1002-08 method. Thereafter, the samples were quantitatively analyzed using AAS. The total mean and the standard deviation of the concentration of Mn, Fe, Cu, Zn, Co, and Ni in all the virgin plastic bottles are given as: 18.3±0.86 µg/g, 333.3±1.47µg/g, 8.3±0.68 µg/g, 889.2±1.98µg/g, 72.0±0.10µg/g and 2.5±0.10 µg/g, respectively. The total mean and the standard deviation of the levels of Mn, Fe, Cu, Zn, and Pb in the virgin plastic sachets are: 53.3±1.19µg/g, 1150.8±3.08µg/g, 206.7±2.80µg/g, 1048.3±1.91µg/g and 630.0±0.83µg/g, respectively. Cd and Pb were not detected in the virgin bottles while Cd and Co were not detected in the virgin sachets. Generally, the concentrations of these metals in the virgin plastics were found to be very low when compared with their concentration in used plastics. It was also noted that the detected heavy metals have lower concentration in virgin plastic bottles than in virgin sachets. It is concluded that environmental pollution with heavy metals arising from various human activities accounted for the relatively high concentration of these heavy metals in used plastics. On the other hand, the high concentration of these metals in plastic sachets was attributed to the colorants used to provide manufacturers' information directly on the sachets unlike plastics bottles, which bears such information on stick label. *[African Journal of Chemical Education—AJCE 7(2), July 2017]*

INTRODUCTION

Plastics are synthetic materials that are made up of long chain monomer linked up together to form a polymer by polymerization process [1]. The term "Plastic" connotes the property of the materials to be moulded into almost any shape, may be soft or hard, coloured or colourless as crystal [2]. Plastics products are one of the most important materials used globally today and the amount needed is still growing. The products are very attractive, durable, easy to use and long lasting; used every day in our homes to make our lives more comfortable and our work lighter. The most common uses include food and water storage and packaging, household items, toys and furniture [3].

Plastic packaging accounted for 30% of the packaging in the market today [4]. Around 70% of overall consumer packaging consumption is used for food and beverage packaging [5]. Many different types of plastics are being used as packaging materials like plastic water bottles and sachets.

Most plastic water bottles are manufactured from polyethylene terephthalate (PET), a polymer derived from oil that adds flexibility, colour, and strength to plastic [6]. It is resistant to heat, mineral oils, solvents, acids and it is impermeable to carbonation. It is strong, light, impact resistant, naturally transparent, and completely recyclable. It does not impart a taste to its contents. This is making PET the most common plastic used for packaging food and water [7]. Roughly, 80% of the PET manufactured in the United States of America ends up in Nestlé, Coke, or Pepsi containers [7].

Polyethylene (PE) is the most common plastic used for household packaging. Polyethylene resins are milky white, translucent substances derived from ethylene, which is permeable to gases, soft waxy surface, chemical resistance, stronger, and translucent. It is used to

produce grocery bags, car fuel tanks, packaging, and piping, jerry cans, toys, bottle caps, crates [1, 8, 4, 2].

Most polymers are petrochemical compounds with additive materials to give them properties of flexibility, elasticity and resistance to fracture and transparency to light [9, 4]. Hence, the final plastic material produced contains other substances like additives, manufacturing aids, and by-products from the complex polymerization reaction that were not intentionally added to the polymers [10].

The polymers used in plastics are generally nontoxic. However, they are not used in pure form. Some inorganic compounds of heavy metals are added to the polymer. Almost all commercial plastics are compounded with monomeric ingredients to improve their processing and end-use performance [11].

The additives used in plastics processing are generally not chemically bound to the polymer; as such, they can leach out of the plastics during normal use or in response to light, chewing and other environmental factors [12]. The migration of additives or contaminants from plastic food packaging to foodstuff may be categorized into three different, but inter-related, stages: diffusion within the polymer, solvation at the polymer food interface, and dispersion into bulk food [9].

This study was carried out to asses and compare the levels of some heavy metals in virgin and used water plastic bottles and sachets in Nigeria.

MATERIALS AND METHODS

As a first step, the plastics were cut to smaller pieces and then heated. The essence of heating the plastic is to soften and deform it so that they become brittle and breakable after cooling.

The plastic were ground/pulverized to a grain size with a Mechanical grinder (Model: THOMAS WILEY MILL) which is equipped with the offset hard-metal cutters and powerful drive to make it ideally suited for the preliminary size reduction and homogenizing of the plastic sample. The plastics were ground to ensure efficient extraction of the stabilizer and other additives in the plastic sample and to increase the rate of dissolution of the sample. Appropriate amount of the ground sample was taken for further analysis.

The pulverized plastic samples were ashed to break down the organic molecules in the plastic and then digested in accordance with CPSP-CH-E1002-08 Test Method [13]. Some grams of the grounded samples were transferred into pieces in a large silica crucible where it was charred on a hot plate till all the fume escaped, as reported by [14]. This is then followed by complete ashing in muffle furnace at 500 ^{o}C for 6 hours. The crucible was then taken out of the furnace and kept in desiccators for cooling. After cooling, the samples were powdered and homogenized in the silica crucible. Then 0.2g of the sample was taken in separate silica crucible for acid digestion. 5 ml of Analar grade Nitric acid was used for digestion in an open vessel. After the initial reaction of the acid and the sample were completed, the digest was filtered using a Whatman 41 filter paper to remove the insoluble particles and the solution was brought to a final volume of 50 ml with distilled deionized water. Blank sample was also prepared similarly. Glass wares, crucibles and plastic containers were washed with liquid soaps, rinsed with distilled water and soaked in 10% HNO_3 for 24 hours; cleaned with distilled deionized water and in such a manner that no contamination occurred [15].

The processed samples were quantitatively analyzed using Buck Scientific VGP 210 Flame Atomic Absorption Spectrophotometer. After every three samples analyzed using AAS, the first sample was repeated for quality check. The result from AAS was subjected to statistical analysis.

The total mean, standard deviation and range of each heavy metals was determined using Microsoft excel.

RESULTS AND DISCUSSIONS

The concentration of Mn, Fe, Cu, Zn, Co, Cd, Pb and Ni in plastic water bottles and sachets were determined in this study. The results of the level of these heavy metals in virgin and used plastic bottles are presented in Table 1 below.

Table1: Mean and standard deviation of heavy metals concentration in virgin and used plastic bottles

Sample	Heavy Metals Concentrations in µg/g							
	Mn	Fe	Cu	Zn	Co	Cd	Pb	Ni
SBVB	25.0±1.14	460.0±1.80	5.0±0.70	1567.5±4.11	BDL	BDL	BDL	BDL
SBUB	27.5±2.26	465.0±5.00	15.0±0.50	1947.5±0.44	BDL	BDL	2.5±0.44	2.5±0.10
GAVB	27.5±0.89	207.5±1.14	5.0±1.08	1052.5±0.46	72.0±0.10	BDL	BDL	2.5±0.17
GAUB	55.0±0.98	410.0±1.66	20.0±0.36	1152.5±0.50	275.04.04	BDL	BDL	BDL
SPVB	2.5±0.56	BDL	15.0±0.26	47.5±1.37	BDL	BDL	BDL	BDL
SPUB	27.5±0.50	130.0±1.32	17.5±0.70	2075.0±1.00	BDL	BDL	BDL	BDL

From Table 1, Mn, Cu, Zn and Fe (with the exception of SPVB sample), are detected in all the analyzed plastic bottles at varying concentrations. Cd and Pb are not detected in any of the virgin bottles. This is because Cd and Pb are banned from being used in commodity plastics [16]. This indicates that manufacturers of these plastic products have complied to this regulations and that Cd and Pb have been completely replaced by other nontoxic substances in plastic pellet used to manufacture water bottles [17]. Cobalt (Co) and Ni were both detected in GAVB. Co is used as pigment to impact blue or green color to materials) [18]. Thus, GAVB contains Mn, Cu, Fe, Zn,

Co and Ni at varying concentration. It is also seen from Table 1 that GAVB contains more heavy metals than the other virgin plastics (SBVB and SPVB). SPVB contains the least amount of heavy metals, with only Mn, Cu and Zn present at a very low concentration in comparison to either SBVB or GAVB. On the other hand, SBVB have the highest concentrations of Fe and Zn compared to other virgin plastics.

From the results (Table1), it is also observed that the concentrations of the detected heavy metals are generally lower in virgin bottles than in their used counterparts. The high concentration of these heavy metals in used plastic is attributed to environmental contamination of the plastics by the respective heavy metals. Several studies have shown that heavy metals are present in the environment at different concentration and that these metals can migrate and contaminate food, water and other materials [19, 20, 21].

For the same reason, it was observed that some heavy metals which are detected in used plastic bottles are not detected in their virgin counterparts produced by the same manufacturer. Metals like Pb and Ni were not detected in any virgin bottles but are detected in used plastic at very low concentration. This implies that these metals were not intentionally added to the plastic during production but got into them as a result of contamination. This is in agreement with the study conducted by [22] on polyethylene litters. They observed that after 10 times duplicate measurement of virgin PE pellets, the quantification limit for Pb and Cr are 11mg/kg and 12mg/kg, respectively. On the contrary, the level of Pb and Cr ranged from below the quantification limit to 10,000mg/kg in PE litters. They further observed that Pb and Cr contained in PE plastic litter exceeded 100mg/kg, which is far above the level of the metals in the virgin PE.

The results of heavy metal concentration in virgin and used plastic sachets analyzed are presented in Table 2 below. From the results, it is seen that Mn, Fe, Cu and Zn are detected in all

the plastic sachets at varying concentrations while Co, Cd and Ni are not detected in any sachets because their salts are not used in the plastics. Quite unexpected is the detection of Pb in SBVS and SPVS at 2.5μg/g and 1257.5 μg/g, respectively. Pb due to its toxicity is one of the regulated heavy metals in plastics.

Table 2: Mean and standard deviation of heavy metals concentration in virgin and used plastic sachets

Sample	Heavy Metals Concentrations in μg/g						
	Mn	Fe	Cu	Zn	Co	Cd	Pb
SBVS	85.0±0.79	1772.5±4.77	190.0±3.00	740.0±1.80	BDL	BDL	2.5±0.44
SBUS	237.5±056	6102.5±1.80	1252.5±1.04	842.5±1.40	BDL	BDL	137.5±2.06
GAVS	25.01±1.12	657.5±3.61	25.0±1.15	1247.5±2.57	BDL	BDL	BDL
GAUS	280.0±3.60	10522±4.73	60.0±2.95	1455.0±117.07	BDL	BDL	BDL
SPVS	50.0±1.67	1022.5±0.87	405.0±4.26	1157.5±1.37	BDL	BDL	1257.5±1.21
SPUS	607.5±3.60	13875.0±2.19	2605.0±2.00	3475.0±7.81	BDL	BDL	8612.5±0.87

Virgin plastic sachets are most often made from polyethylene (PE), a polymer which does not require additives to soften it. PE can be made from hard to soft by modifying the hydrocarbon chain length or cross-linking [23]. Therefore, the main sources of heavy metals to virgin sachets are colorants used to print manufacturers' useful information.

Also evident from Table 2 is that the concentrations of the detected heavy metals are relatively high in the virgin plastics. This could be as a result of the application of high amount of compound of heavy metals as pigment during the manufacture of such plastics. All plastic sachets analyzed in this work are surface painted with ink base colorant. The manufacturers of this plastic sachet do this to make the plastic more attractive to consumers and also to indicate the

manufactures' names and addresses. The pigments used to infer colors to plastics are compounds of heavy metals [24].

It was remarked that colorful plastics contain higher concentration of heavy metals in them than non-colored plastics [25]. It was also observed that plastic toys with outer coating paints contain high amount of tested heavy metals compared to non-painted toys [12]. As reported [26], the highest concentration of Pb is found in yellow plastic, Ni in pink and purple plastic, Zn in green and purple plastics. It was stated that heavy metals in plastic are loosely bound to the surface and can easily leach out [12]. It was further observed that heavy metals could migrate from candy packages into the candy because the ink on the packages are poorly designed that they did not maintain their structural integrity [25].

The above results (Table 2) show that the concentrations of the detected heavy metals are higher in used sachet than in the virgin sachets. The used sachet contains higher concentration of heavy metals because of environmental contamination of the used plastics sachets. It is reported that heavy metals are present in the environment, in water, food, air and our daily tools and they can be absorbed or adsorbed by materials [24, 27].

The results of the total mean value and standard deviation of the detected heavy metals in both virgin bottles and virgin sachets are as shown in Table 3 below. The range of each heavy metal in the entire virgin bottles and virgin sachet is also presented in Table 3.

Table 3: Total Mean value with standard deviation of heavy metals concentration and range of Heavy metals in virgin plastic bottles and virgin plastic sachets

Sample	Heavy Metals Concentrations in µg/g							
	Mn	Fe	Cu	Zn	Co	Cd	Pb	Ni
V.S	53.3±1.19	1150.8±3.08	206.7±2.80	1048.3±1.91	BDL	BDL	630.0±0.83	BDL
Range	25.0-85.0	657.5-1772.5	25.0-405.0	740.0-1157.5	–	–	2.5-1257.5	–
V.B	18.3±0.86	336.2±1.47	16.7±0.68	889.2±1.98	72.0±0.10	BDL	BDL	2.5±0.1
Range	2.5-27.5	207.5-465.0	15.0-20.0	47.5-1567.5	–	–	–	–

It is observed from the Table 3 that virgin sachet contains higher concentration of detected metals than virgin bottles. Both PET and PE are polymers that do not require the addition of stabilizer and plasticizers, which are contributors of heavy metals, to soften them or make them flexible. The high amount of heavy metals in virgin sachets is, therefore, attributed to the higher amount of colorants applied to sachets' surfaces to make them more attractive. Since the entire analyzed sachets are painted on the surfaces with ink based paint, it is assumed that the pigments used to color the plastic sachets are compounds of heavy metals [24, 14, 26, 25].

Mn, Fe, Cu and Zn are detected in the entire plastic sachets at high concentration when compared to their concentration in plastic bottles. Among these, Fe and Zn control predominant concentration in the virgin plastics. This could be attributed to the fact that these heavy metals are the most common metals used in plastics. Seth [28] stated that FeO is the second most common pigment used in the plastic industry and that ZnS is one of the most common white pigment used in plastics. Zn is also used as catalyst during plastic production [29]. Co and Cd were not detected in any of the sachet plastic, but Pb and Ni were detected in some of the sachet plastic.

CONCLUSIONS

In this study, the following conclusions are deduced:

1. Virgin bottles contain fewer heavy metals than used bottles.
2. Virgin bottles have lower concentration of detected heavy metals compared to used plastic bottles.
3. Virgin bottles have lower concentration of detected heavy metals compared to virgin sachets.
4. Virgin sachets have lower concentration of heavy metals compared to used sachets.
5. Compounds of Pb and Cd are no longer used in production of plastic virgin bottles.
6. Compounds of Cd and Co are no longer used to produce virgin sachets.
7. Fe and Zn are detected in all the samples at concentrations above 200ug/g.
8. Compounds of Pb are still used to color some plastic sachets.
9. Plastic products manufactured from recycled plastics will have higher concentration of heavy metals than virgin plastic products.
10. Compounds of Fe and Zn are the most popular colorant used to color plastic water bottles and sachets.

REFERENCES

1. Richardson, T. L., (2008). Plastics. Microsoft Encarta 2009 [DVD]. Redmond, WA: Microsoft Corporation.
2. Sophie Van Den Berg, (January 2009). Recycling plastics. A technical briefing for Practical Action. Retrieved from www.practicalaction.org on 21-02-2012.
3. U.S. EPA, (2007). Municipal Solid Waste (MSW): Plastics. Accessed June 18, 2012.
4. Al-Dayel O., O. Al-Horayess, J. Hefni, and A. Al-Durahim, (2009). Trace Elements in Packaging Polymers. Research Journal of Chemistry and Environment, 13; 1, 92.
5. WPO, (2008). Market Statistics and Future Trends in Global Packaging.
6. Royte, E., (2008). Bottlemania: Big Businesses, Local Springs, and the Battle over America's Drinking Water. New York: Bloomsbury USA.

7. Gleick, P. H., (2010). Bottled and Sold: The Story Behind Our Obsession with Bottled Water. Washington DC: Island Press.
8. PACIA (Plastic and Chemical Industries Association), (1992). Manufacturing plastic: the process and environmental impact. Melbourne. Accessed through www.pacia.org.au on 20-12-2012.
9. Oi-Wah, L., and W. Siu-Kay, (2000). Contamination in food from packaging material, Journal of Chromatography A, 882; 255.
10. Bradley, E. and L. Coulier, (2007). An investigation into the reaction and breakdown products from starting substances used to produce food contact plastics. London: Central Science Laboratory.
11. Deanin, R. D., (1975). Additives in plastics. Environmental Health Perspective, 11; 35-39.
12. Omolaoye, J.A., A. Uzairu, and C.E. Gimba, (2010). Heavy metal assessment of some soft plastic toys imported into Nigeria from China. J. Environ. Chem. and Ecotox, 2;126-130. ISSN-2141-226x.
13. U.S. CPSC (Consumer Products Safety Commission), (1997). Staff Report on Lead and Cadmium in Children's Polyvinylchloride (PVC) Products.
14. Abhay, K., and P. Prashant, (2007). Lead and Cadmium in Soft Plastic Toys. Current Science, 45; 2055-2056.
15. Adnan, M. M., (2003). Determination of Cadmium and Lead in different cigarette brands in Jordan. Environmental Monitor and Assessment, 104; 163-170.
16. Taco, Van Der M., (2006). Setting new standard for the analysis of additives in polyethylene. Plastic additive and compounding, Pp40-43. ISSN 1464-391x106. Elsevier ltd. Retrieve from www.panalytical.com on 23-03-0122.
17. Heavy metals in plastic pallets and plastic crates (11th April, 2008) retrieved on 31-10-2012.
18. Henderson, J. (2000). Glass. The Science and Archaeology of Materials: An Investigation of Inorganic Materials. Routledge, (p. 60). ISBN 978-0-415-19933-9.
19. Emsley, J., (2001). Manganese. Nature's Building Blocks: An A-Z Guide to the Elements. UK: Oxford University Press, (pp. 249–253).
20. McDonald, I., G. C. Sloan, A. A. Zijlstra, N. Matsunaga, M. Matsuura, K. E. Kraemer, J. Bernard-Salas, and A. J. Markwick, (2010). "Rusty Old Stars: A Source of the Missing Interstellar Iron?" The Astrophysical Journal Letters, 717; L92–L97.
21. CSEM (Case Studies in Environmental Medicine), Cadmium . Agency for Toxic Substances and Disease Registry. Archived from the original on 2011-06-06. Retrieved 2011-05-30.
22. Nakashima, E., A. Isobe, S. Kako, S. Magome, N. Deki, T. Itai, and S. Takahashi, (2011). Toxic metals in polyethylene plastic litter. Interdisciplinary Studies on Environmental Chemistry-marine environmental modelling and analysis, Pp 271-277.

23. AHT (The alliance for a Healthy Tomorrow). Hazards of polyvinylchloride (PVC) children product. Toxic additives in PVC children product. Retrieved from www.healthytomorrow.org on 28-08-2012.
24. Sindiku, O.K., and O. Osibanjo, (2011). Some priority heavy metals in children toy's imported to Nigeria. J. Toxcol.Environ.Health Sci, 3;109-115.
25. Ki-Cheol, K., P. Yong- Bae, L. Myung-Jin, K. Jung-Beom, H. Jeong-Weon, K. Dae-HwanL. Jung-Bok, and K. Jong-Chan, (2008). Level of heavy metals in candy packages and candies likely to be consumed by small children. Food Research Int., 41; 411-418 doi:1016/j.foodres.2008.01.004.
26. Naseem, A., N. Malik, H. Firoj, A.K. Singh, D.K. Patel, A.R. Khan, and R. Masihur, (2012). Heavy metal assessment of leachates of some plastic toys purchased from different district of UP, India. International Research Journal of Environmental Science, 1; 32-36.
27. WHO (World Health Organization), (1995). Inorganic lead Environmental Health Criteria Number 165 (Geneva: World Health Organization), pp. 188.
28. Seth, B., (2003). Polymer, additives and Environment: problems and solutions. Polymer and the Environment. San Jose State University.
29. ATP (Analysis of traces in polymers). ARL ADVANT' XP + sequential x-ray fluorescence spectrometer. Applied Research Laboratories, S.A. retrieved from www.arl.ch on 31-10-2012.