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ORIGINAL ARTICLE

Concentration of Heavy Metals in Five Pharmaceutical Effluents in Ogun State, Nigeria

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ABSTRACT
The concentrations of some heavy metals in the effluents of five pharmaceutical companies operating in Ogun State of Nigeria were determined using atomic absorption spectrophotometer. The heavy metals analyzed in this study included Cobalt, Nickel, Cadmium, Lead, Chromium, and Copper. Eighty (80) % of the samples were found to contain the metals in varying concentrations. The results indicate the order of abundance of these heavy metals in the effluent samples as follows: Nickel > Copper > Chromium > Cobalt > Cadmium > Lead. Largely, the concentrations were above the WHO maximum acceptable concentration for each metal. Nickel which has the highest concentration, has a value of 0.935 mg/L. Highest concentrations for other heavy metals were found to be 0.028mg/L for Lead, 0.083mg/L for chromium, 0.021 mg/L for Cadmium, 0.043 mg/L for Cobalt and 0.227 mg/L for copper. This research reveals the need to implement measures that will allow treatment of industrial effluents before their final discharge to surface water to reduce their potential negative effects on the ecosystem.
Key words: *Heavy metals, Pharmaceutical effluents, Ecotoxicity, Surface water.*

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INTRODUCTION

Pharmaceutical effluents are waste generated by pharmaceutical industry during the process of drugs manufacturing. Some pharmaceutical effluents are known to contain high concentration of organic compounds and total solids, mercury, cadmium, isomers of hexa-chlorocylohexane, 1,2-dichloroethane and other solvents. The biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids as well as phenol and pH of pharmaceutical effluent is however not consistent, depending on the product manufactured, materials used and the processing details [1].
Generally, industrialization in the last few decades has given rise to the discharge of liquid, solid, and gaseous emissions into natural systems and consequent degradation of the environment [2]. This in turn has led to an increase in various kinds of diseases, which has necessitated the production of a wide array of pharmaceuticals in many countries. Wastewater treatment and disposal problems have also increased as a result of this increase in production [3].
Recent decades have brought increasing concerns for potential adverse human and ecological health effects resulting from the production, use and disposal of numerous chemicals that offer improvements in industry, agriculture, medical treatment, and common household conveniences [4].
One of such contaminants in the environment are heavy metals. Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water which is 1 at 4°C (39°F). They are a member of a loosely-defined subset of elements that exhibit metallic properties. It also includes the transition metals, some metalloids, lanthanides, and actinides and they have been associated with contamination and potential toxicity or ecotoxicity. Heavy metals occur naturally in the ecosystem with large variations in concentration [5].
Industrial or municipal wastewater is mostly used for the irrigation of crops due to its easy availability, disposal problems and scarcity of fresh water. Irrigation with wastewater is known to contribute significantly to the heavy metals content of soil. Heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives and their potential to accumulate in different body parts. Wastewater contains substantial amounts of toxic heavy metals, which create problems which may not only result in soil contamination but also affect food quality and safety [6-8].

Heavy metals such as Lead, Mercury, Cadmium, Nickel, Chromium and other toxic organic chemicals or phenolic compounds discharged from pharmaceutical industries are known to affect the surface and ground waters [9]. And due to mutagenic and carcinogenic properties of heavy metals, much attention has been paid to them since they have direct exposures to humans and other organisms [10].
A number of overwhelming ecological effects and human disasters in the last 40 years have arisen majorly from industrial wastes causing environmental degradation (Abdel-Shafy 1995; Sridhar 2000). The discharges from these industries constitute biohazard to man and other living organisms in the environment because they contain toxic substances detrimental to health [13-15].
Thus regular monitoring of these toxic heavy metals from effluents and sewage, in vegetables and in other food materials is essential, to prevent their excessive build-up in the food chain [16].
A recent research in Lagos State-Nigeria by Chimezie *et al* [17] showed the concentrations of some heavy metals in the effluents of some pharmaceutical companies operating in Lagos. Most of the samples were found to contain the metals in varying concentrations. The highest concentration of heavy metal detected was Zinc with concentration of 1.437 mg/L. Mostly, the concentrations were above the WHO recommended maximum contaminant concentration level. This may pose adverse consequences on health and environment.
This study was aimed at determining the presence of six heavy metals, namely Lead, Chromium, Cadmium, Cobalt, Copper and Nickel in the effluents of five selected pharmaceutical companies in Ogun State of Nigeria. The results obtained may form the basis for intervention by encouraging the pharmaceutical companies to effectively treat their effluent before being discharged into the environment.

METHODOLOGY

Chemicals and reagents

All chemicals and reagents were of analytical grade and were obtained from BDH Chemicals Ltd, UK. Concentrated Aqua Regia (mixture of conc. HNO_3 And conc. HCL in ratio 1:3) was used for the digestion of the samples while corresponding metal salts (namely: $CdCl_2.H_20$, $Cu(SO_4)_2$, $Co(NO_3)_2$, $Pb(NO_3)_2$, $NiCl_{2.6}H_2O$ and $Cr(NO_3)_{3,}$) were used as standards.

Instrumentation

AAS instrument (PERKIN ELMER A. Analyst 200; Germany) consisting of a hollow cathode lamp, slit width of 0.7 nm and an air-acetylene flame was used for this work. The samples were analyzed for six heavy metals namely, Chromium which was analyzed at wavelength of 357.87 nm, Nickel at 232.00 nm, Cadmium at 228.80 nm, Cobalt at 240.70nm, Lead at 283.31 nm and Copper at 324.75 nm.

Sampling

Five Pharmaceutical companies in Ogun-State Metropolis were selected due to their strategic location and high production capacity. These companies are represented here with the letters A to E. Samples were taken at three different times represented by 1st Batch, 2nd Batch and 3rd (between June 2011 and January 2012). The pharmaceutical effluent samples were collected into a sterile 250 ml Pyrex^{R} bottles at the point where the effluents leave the companies to the environment and then stored in a refrigerator at 2 - 8°C before analysis. A total of 10 samples were collected at various peak production periods.

Sample Preparation

This was carried out according to Anyakora *et al* (2011) whereby, 50 ml each of the sample was digested using 10 ml concentrated Aqua regia in a 250-ml conical flask placed in a fume cupboard to ensure removal of organic impurities and prevent interference during analysis. The samples were properly covered with aluminum foil to avoid spillage and heated on a hot plate until the solution reduced to half of its original volume that is 30 ml. This was allowed to cool and made up to mark with distilled water before filtering into a 50-ml volumetric flask, labelled and ready for analysis. The blank was also prepared without the sample.

Standard Preparation

This served as the stock solution equivalent to 1000 ppm. Subsequently lower concentrations of 2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm were prepared from the stock by serial dilution. The same method was adopted for Cr, Ni, Pb, Cu and Co.

RESULTS AND DISCUSSION

Standard calibration curves were obtained using a series of varying concentrations of the standards for all six metals. Calibration curve for all the metals were linear with a correlation coefficient of approximately one. The effluents analyzed contain some heavy metals in varying concentrations. Tables 1, 2 and 3 give the summary of the results obtained in this study while Table 4 summarizes guidelines by different international agencies.

Table 1: The Average Concentration Of Heavy Metals Present In 1st Batch Of The Effluent

Company	Cr^{3+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Pb^{2+}	Co^{2+}
A	0.083	0.008	0.206	0.934	ND	0.004
B	0.039	0.008	0.211	0.652	0.002	0.006
C	0.045	0.012	0.115	0.351	ND	0.020
D	0.053	0.011	0.227	0.539	0.010	0.031
E	0.152	0.016	0.210	0.351	0.021	0.043

TABLE 2: The Average Concentration Of Heavy Metals Present In 2nd Batch Of The Effluent

Company	Cr^{3+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Pb^{2+}	Co^{2+}
A	0.075	0.010	0.196	0.935	ND	ND
B	0.031	0.011	0.208	0.615	0.006	0.009
C	0.035	0.014	0.115	0.329	ND	0.029
D	0.050	0.021	0.194	0.470	0.028	0.040
E	0.022	0.009	0.218	0.489	0.013	0.011

Table 3: The Average Concentration Of Heavy Metals Present In 3rd Batch Of The Effluent

Company	Cr^{3+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Pb^{2+}	Co^{2+}
A	0.079	0.085	0.211	0.867	ND	ND
B	0.029	0.009	0.200	0.595	0.003	0.005
C	0.025	0.014	0.100	0.300	ND	ND
D	0.069	0.018	0.191	0.400	ND	0.026
E	0.019	0.081	0.200	0.495	0.002	ND

Table 4: Comparison Between International Drinking Water And Fda Bottled Water Guidelines For The Parameters Analyzed In The Study

Parameter	USEPA MAC (mg/L)	Canada MAC (mg/L)	EU MAC (mg/L)	Japan MAC (mg/L)	WHO guideline (mg/L)	Bottled water US Federal Drug Administration level (mg/L)	NSDQW(Nigeria Standard for Drinking Water Quality) (mg/L)
Chromium	0.1	0.05	0.05	0.05	0.05	0.1	0.05
Cadmium	0.005	0.005	0.005	0.1	0.003	0.005	0.003
Copper	1.3	1.0	2.0	1.0	1.2	1.0	1.0
Nickel	0.1	-	0.02	0.01	0.02	-	0.02
Lead	0.015	0.01	0.01	0.05	0.01	0.01	0.01
Cobalt	-	-	-	-	-	-	0.1*

USEPA- United State Environmental Protection Agency; MAC- Maximum Allowable Concentration; EU- European Union; WHO- World Health Organization; *-Radioactive material.

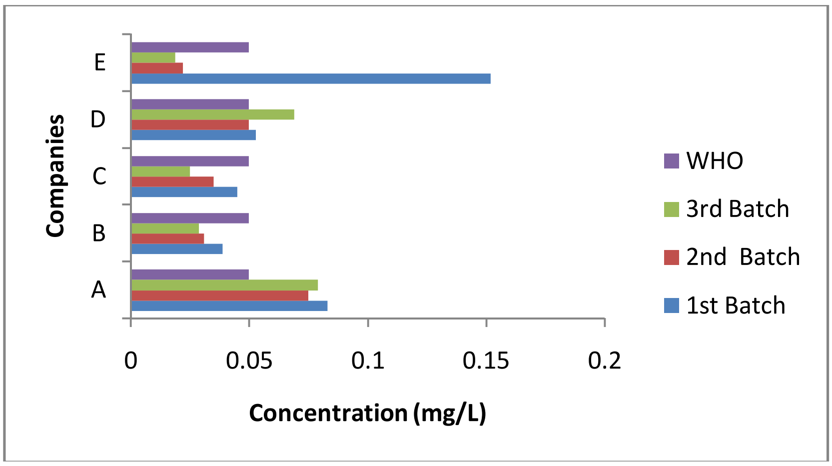

Figure 1- Chromium concentration in the samples.

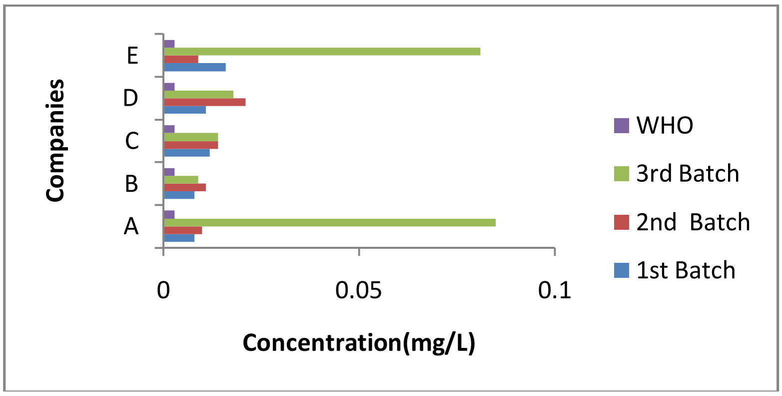

Figure 2- Cadmium concentration in the samples.

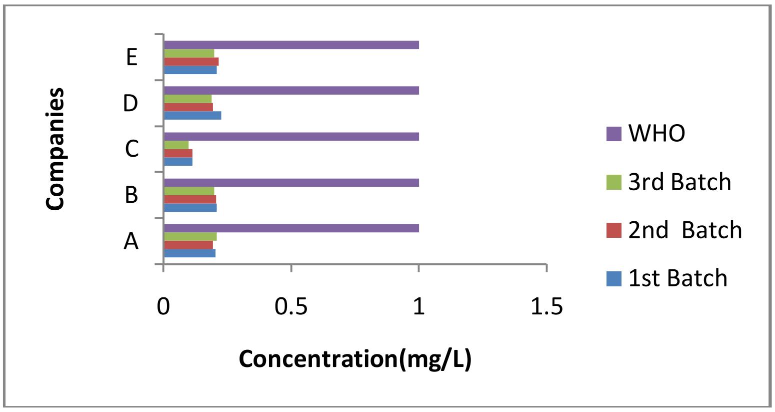

Figure 3- Copper concentration in the samples.

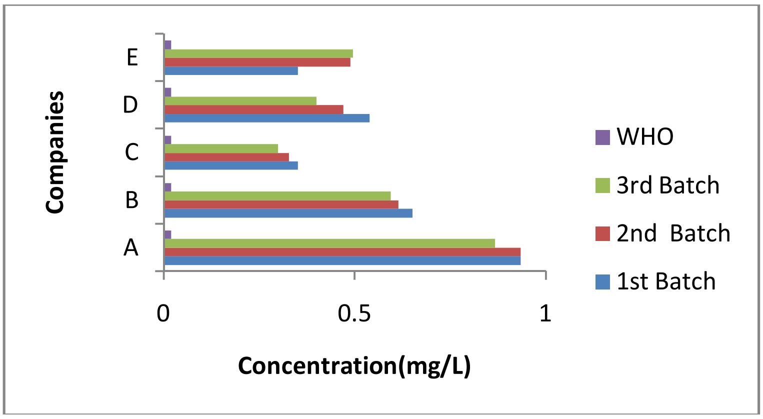

Figure 4- Nickel concentration in the samples.

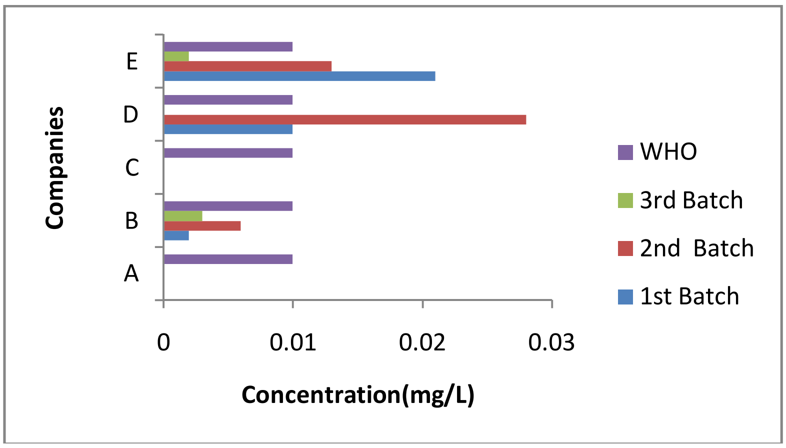

Figure 5- Lead concentration in the samples.

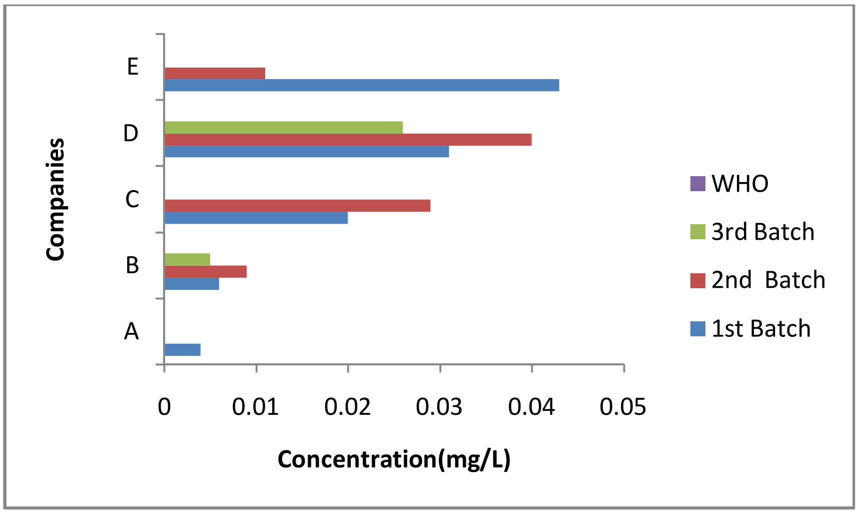

Figure 6- Cobalt concentration in the samples.

Effluents from companies A, B, C, D and E has the highest concentration of Nickel, as it present the highest value of 0.935mg/L, 0.934mg/L and 0.867mg/L in 1st, 2nd and 3rd batch respectively. The other concentrations (mg/L) in descending order are 0.652, 0.615, 0.595, 0.495, 0.539, 0.489, 0.470, 0.400, 0.351, 0.329 and 0.300. The concentrations are higher than the normal acceptable contaminant level according to WHO standard of 0.02 mg/L. Increase concentration and long-term exposure of human to Nickel can lead to decreased body weight, heart and liver damage and skin irritation. Nickel toxicity can cause a devastating histological change on plants and animal tissues [18].

There are no detectable values of lead in effluents from companies A and C of 1st, 2nd and 3rd batch. So also company D (3rd batch). But was present in very minute quantities in the effluents from other companies. Only company E (1st batch) and companies D and E (2nd batch) had values (0.021, 0.028 and 0.013 respectively) a little higher than the WHO standard of 0.01mg/L. Overall, company C and E in the 3rd batch has the lowest concentrations of lead (0.003 and 0.002 mg/L). However, even at a very low concentration, lead is very toxic. Organic lead compounds are dangerous to all forms as they are a cumulative poison. Lead can cause both acute and chronic symptoms of poisoning depending on the level and duration of exposure. They cause injuries to mental development such as reduction of intelligence, growth disturbances, spasticity, severe kidney damage and their ability to possibly substitute for calcium in bone causing skeletal anomalies especially in children [10,19,20]. Pb is known to be a very toxic metal and it tends to interfere with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestine, kidneys, reproductive and nervous systems[21]. Hrsak *et al* also reports the toxicity of lead in some plant parts which are either used as food or as medicine [22].

Concentrations higher than the WHO maximum acceptable concentration of 0.05mg/L for Chromium was seen in companies A, D and E in the 1st batch, company A in the 2nd batch and company A and D 3rd batch . These values (mg/L) are 0.083, 0.053, 0.152, 0.075, 0.079 and 0.069 respectively. The curious contraption about Chromium is that it cannot be destroyed once it has entered the environment. It may react with other particles or adsorb on soil particles or water sediments. Chromium will only mobilize under acidic conditions, but ultimately most cobalt will end up in soils and sediments [23].

All the values obtained for Cadmiun in the 1st, 2nd and 3rd batch were higher than 0.003mg/L WHO maximum allowable concentration. Overall, the lowest concentration was 0.008mg/L (1st batch) and the highest concentrations was 0.021mg/L (2nd batches). Cadmium has being shown to be associated with renal dysfunction, obstructive lung disease which has been linked to lung cancer. It may also produce defects (osteomalacia), or can cause skin irritation and cause ulceration. In Japan, the ltai-itai sickness (associated with bone damage) is a result of the regular consumption of rice highly contaminated with Cadmium [19].

Of all the heavy metals analysed, in both batches, only Copper had concentrations that were within the WHO maximum acceptable concentration of 1.2 mg/L. the highest concentration was 0.227mg/L evident in company D (1st batch). When in the environment, Copper can seriously influence the proceedings of certain farmlands, depending upon the acidity of the soil and the presence of organic matter. Mainly sheep suffer a great deal from copper poisoning, because the effects of copper are manifesting at fairly low concentrations [23].

For most international agencies there is yet no adequate standard for Cobalt, except for its radioactive forms. This may be due to absence of Cobalt in most of the heavy metals analysis carried out on water and/or pharmaceutical effluents. Since the above values showed that Cobalt are present in pharmaceutical effluents, therefore the need for quick establishment of standard for Cobalt is in great need in order to curb possible bioaccumulation in the nearest future since International Agency for Research on Cancer (IARC), has listed cobalt and its compounds as agents which are possibly carcinogenic to humans.

The concentration of heavy metals observed in the effluent samples showed that about 80% of the samples had heavy metal concentrations that are beyond the permissible limit as stated by WHO and Nigeria standard for drinking water quality. The discharge of these effluents into the environment may have also contributed to the bioaccumulation of heavy metals in the bionetwork. Researches in Ogun state have indicated the bioaccumulation of heavy metals in gills, heart, kidney, muscle and vertebrae of some fishes, consumable plants (Amaranthus grown along major highways), soil and underground water [24-27].

Figures 1 to 5 show the distribution of the metals in different samples, and they illustrate these variations well.

CONCLUSION

The results obtained indicate the order of abundance of heavy metals in the collected effluent samples as follows: Nickel > Copper > Chromium > Cobalt > Cadmium > Lead. These, if not checked, may possibly pose harmful consequences on our environment and man may not be spared from the consequences, hence, there is a need to implement effluent treatment to reduce health and environmental risk that could result from direct discharge of effluent into the ecosystem.

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