

Physicochemical and Heavy Metal Analysis of Effluent from Pharmaceutical Industry for Sustainable Development and Its Risk Assessment

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To cite this article:

Nnaeme Esther Uchechukwu, Okoye Nkechi Helen. Physicochemical and Heavy Metal Analysis of Effluent from Pharmaceutical Industry for Sustainable Development and Its Risk Assessment. *American Journal of Applied and Industrial Chemistry*. Vol. 5, No. 2, 2021, pp. 27-32. doi: 10.11648/j.ajaic.20210502.11

Received: June 11, 2021; Accepted: July 5, 2021; Published: August 18, 2021

Abstract: Pollution is an act of contaminating the environment by harmful or toxic substances that could be of solid, liquid or gaseous materials. Effluents containing heavy metals that are indiscriminately discharged into the environment pollute the ecosystem and pose great risks to the organisms in it. Here, we review effluent discharged from a pharmaceutical industry in Awka, Anambra state, Nigeria and analyzed for heavy metal pollution. The twenty heavy metals analyzed were: magnesium, calcium, zinc, copper, Nickel, Cobalt, Iron, chromium, sodium, aluminum, vanadium, potassium, silver, manganese, mercury, cadmium, lead, molybdenum, selenium and arsenic. The heavy metals were analyzed using Atomic Absorption Spectrophotometer (model 240FS AA). The study presented the several risks and environmental effects associated with heavy metal toxicity. The environmental risk assessment was performed in which the chronic daily intake through ingestion for adults was calculated. The hazard quotient (HQ) for non-carcinogenic risk assessment and cancer risk assessment were also calculated. The obtained HQ values for Pb (7.857), Hg (4.333×10^1), As (1.867×10^2), Ni (4.521×10^2), Cr (3.333), Al (5.753), Mo (11), Ag (1.13) and Se (19) were greater than 1 and they were in the order: Se > Mo > Pb > Al > Ni > Hg > Cr > As > Ag. This means that the population is exposed to health risks with non-carcinogenic effects from this study. Metals with HQ values less than 1 were Cd (0.425), Fe (0.346), Zn (0.199), Cu (0.123), Mn (0.023) and Co (0.011). Cancer risk assessment was also carried out based on Pb, As, Ni, Cr and Cd with values 3.887×10^{-5} , 3.6×10^{-2} , 3.526 , 2.184×10^{-3} and 2.73×10^{-3} respectively and nickel (Ni) proved to be the highest contributor to cancer risk in this study. Long term exposure to heavy metals possesses both potential non-carcinogenic and carcinogenic health risks to the local residents.

Keywords: Pollution, Heavy Metals, Pharmaceutical Effluents

1. Introduction

Industrialization, no doubt, is key in development and attempt to better human living condition through creation of wealth and employment opportunities. Ironically, human lives are being hunted by the huge volume of wastes emanating from these industries, especially when they are discharged into the environment without proper treatment [10, 16].

Industrial effluents contain toxic and hazardous substances from the wastes that settle in river water as bottom sediments and constitute health hazards to the urban population that depend on the water as source of supply for domestic uses [1].

Untreated waste water from processing factories in urban

areas or cities are discharged into inland water bodies resulting to stench, discoloration and a greasy oily nature of such water bodies [2]. The indiscriminate handling and release of industrial effluents or waste water into surrounding terrestrial or aquatic habitat has been implicated as one of the major sources of environmental pollution.

Pharmaceutical and personal care products industries suffer from inadequate effluent treatment due to the presence of recalcitrant substances which include antibiotics, and cosmetic ingredients containing oil and grease [9]. The industry is characterized by a diversity of products, processes, plant sizes as well as wastewater quantity and quality.

Pharmaceutical effluents are wastes generated by pharmaceutical industries during the process of drugs manufacturing. Pharmaceutical compounds may enter the environment by different routes such as discharge of treated wastewater, seepage from landfill sites, sewer lines, run off from animal wastes [5]. Effluents from these industries have been found to contain solids, biodegradable and non-degradable organic compounds and they are also categorized by their unusual turbidity, conductivity, chemical oxygen demand (COD), total suspended solids, total hardness [17].

Pharmaceutical effluents usually contain toxic metals which are toxic at elevated concentrations and these effluents percolate into the ground water, cultivated crops and pose a significant threat to human health and ecological systems [15].

Heavy metals tend to be non-biodegradable, toxic at certain levels and bioaccumulate in the environment, leading to several health effects when in contact with living organisms which includes plants, animals and microorganisms [7]. Heavy metals present in the soil tend to be potential threats to the environment and can destroy human health through direct ingestion, dermal contact, diet through the soil–food chain, inhalation, and oral intake which are the various absorption pathways [12].

In recent times, water pollution that arises from pharmaceuticals and drug residues has been increasing rapidly and are referred to as emerging pollutants. These “emerging pollutants” are undesirable due to their genetic, hormonal and endocrine nature of disturbance [3].

Risk assessment is the scientific process in which the risks posed by inherent hazards involved in the process or situations are estimated either quantitatively or qualitatively [4].

Human health risk assessment is a process used to estimate the health effect that might result from exposure to carcinogenic and non-carcinogenic chemicals [21]. The purpose of exposure assessment is to measure or estimate the intensity, frequency and duration of human exposures to an environmental contaminant [24]. The aim of hazard identification is to investigate chemicals that are present at any given location, their concentrations and spatial distribution. These chemicals can be classified as carcinogenic or non-carcinogenic chemicals or substances.

2. Materials and Method

2.1. Study Design

The study involved sampling of effluents from a pharmaceutical industry. The samples were collected from the effluent pit prior to discharge in order to avoid external contaminants from the gutters outside the industry.

2.2. Sampling

A pharmaceutical company in Awka, Anambra state was selected because it has the largest production capacity in the state and offers the opportunity to cover all the sample needed for the analysis. Sample of effluents were taken at different times represented by Sample A and Sample B

between July 2019 and September 2019. On the days of sample collection, Dextrose Normal Saline (DNS) was manufactured. The effluent was collected in tightly closed polyethylene bottles at the point before the effluent was discharged to the waste channel and then it was taken to the laboratory for analysis.

2.3. Digestion

Sample A and B were collected in separate beakers (200 cm³). 2 cm³ of nitric acid was added to sample A and B and slowly heated in a hot water bath for about 180 minutes.

2.4. Sample Preparation

After digesting and heating, sample A and sample B were hot filtered using filter paper and clean beakers rinsed with distilled water. 50cm³ each of the filtered samples were collected in plastic bottles with lids and were labeled and then taken for analysis using the Flame Atomic Absorption Spectrophotometer (AAS model: 240 FS AA). The metals in the digested sample were determined using flame atomic absorption spectrophotometer with a hollow cathode lamp and a fuel rich flame (air acetylene). The samples A and B were aspirated and the mean signal response was recorded.

2.5. Environmental Risk Assessment

In order to estimate the risk caused by long time exposure to the metals, chronic daily intake (CDI) was calculated.

$$CDI_{Ingestion} = \frac{C_{water} \times IRS \times EF \times ED \times CF}{BW \times AT}$$

CS=Exposure point concentration [23]

C_{water}=concentration in water sample: mg/L

IRS=Ingestion rate: 100mg/day for adults and 200mg/day for children [23]

EF=Exposure frequency: 350 days/year [23]

ED=Exposure duration: 30 years [23]

BW=Body weight: 70kg for adults [20]

aAt=Average time for carcinogens=365 days × 70 years [22]

bAT=Average time for non-carcinogens=365 × 30 years [22]

CF=Unit conversion factor: 10⁻⁶ kg mg⁻¹ [22]

$$\text{Cancer risk} = CDI \times SF$$

Where cancer risk represents the probability of an individual lifetime health risks from carcinogens; CDI is the chronic daily intake of carcinogens (mg kg⁻¹ d⁻¹)

SF=Slope factor of hazardous substances (mg kg⁻¹ d⁻¹).

For non-carcinogenic substances, the risk is determined as the hazard quotient, HQ.

$$HQ = \frac{CDI(non-carcinogenic)}{RfD}$$

Where the non-cancer hazard quotient (HQ) is the ratio of exposure to hazardous substances, and RfD is the chronic reference dose of the toxicant (mg kg⁻¹ d⁻¹).

$$RfD = \frac{NOAEL}{UF}$$

RfD=reference dose factor

The RfD is the ratio of the No-observable Adverse Effect Level (NOAEL) over the uncertainty factor (UF)

HQ is a dimensionless quantity and the RfD value that go in

its denominator are such that the critical value for HQ is unity.

If HQ is less than 1=safe

If HQ is greater than 1=unsafe. [24, 11].

Table 1. Exposure parameters used for health risk assessment (US EPA, 2012).

Parameter/ Factor	Definition	Unit	Adult	Children	References
CS	Exposure point concentration	Mg/L	—	—	
IR	Ingestion rate	Mg/day	100	200	USEPA (1989, 2002)
EF	Exposure frequency	Days/years	350 (residents) 365	250 (residents) 365	USEPA (2002)
ED	Exposure duration	Years	30	6	USEPA (2002)
BW	Body weight of exposed individual	Kg	70	20	
AT	Average time	Years	8760	2190	USEPA (2002)
CF	Conversion factor	Kg/mg	1×10 ⁻⁶	1×10 ⁻⁶	USEPA (2002)

For non- carcinogenic substances, AT=ED

For carcinogenic substances, AT=365 days/year × 70 years

The ratio of CR/BW is called the dose.

3. Results and Discussion

3.1. Results

The obtained concentrations in mg/L of the samples and the WHO permissible limit in drinking water is presented in the below.

Table 2. Heavy metal concentrations of samples of effluents discharged and their permissible limits according to WHO.

Parameters	Concentrations of sample 1 (S1) (mg/L)	Concentrations of sample 2 (S2) (mg/L)	WHO standard (mg/L)
Magnesium	12.015	4.208	NGD
Calcium	7.138	13.441	NGD
Zinc	3.979	0.378	NGD
Copper	0.198	0.135	2
Nickel	0.066	0.00	0.07
Cobalt	0.016	0.00	0.02
Iron	17.057	0.594	NGD
Chromium	0.472	0.272	0.05
Sodium	64.00	54.058	NGD
Aluminum	0.00	0.168	0.2
Vanadium	0.00	0.00	NGD
Potassium	0.064	0.863	NGD
Silver	0.00	0.414	NGD
Manganese	0.205	0.035	0.4
Mercury	0.643	0.297	0.006
Cadmium	0.00	0.031	0.003
Lead	0.217	0.562	0.01
Molybdenum	2.448	1.566	0.07
Selenium	6.237	0.733	0.01
Arsenic	0.396	1.640	0.01

NGD-No Guideline.

3.2. Discussion

According to the World Health Organization (WHO), the main heavy metals include beryllium, aluminium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, selenium, molybdenum, silver, cadmium, tin, antimony,

barium, mercury, thallium and lead (WHO, 2011).

The concentrations of mercury in S1 and S2 being 0.643mg/L and 0.297mg/L respectively are greater than the recommended value of mercury which is 0.006mg/L according to the WHO standard for drinking water (WHO, 2017). The discharge of effluent containing mercury exposes the environment and the

human body to great risks because the brain remains the target for mercury and it can impair any organ and lead to malfunctioning of nerves, kidneys and muscles, interrupt with intracellular calcium homeostasis and can also cause bronchitis, temporary respiratory problems and asthma when mercury is in its vapour state [8].

The concentrations of arsenic in S1 and S2 being 0.396 mg/L and 1.640 mg/L, respectively are also higher than the recommended value which is 0.01 for arsenic (WHO, 2017). Arsenic pollutes the environment and contaminates the air, food and water of which humans are exposed to [8]. Mild exposure to Arsenic causes nausea and vomiting, abnormal heartbeat, damage to blood vessels [8] while chronic exposure to arsenic causes pigmentation and keratosis [14].

In S1 and S2, the concentrations of lead are 0.217 mg/L and 0.562 mg/L which is greater than the WHO standard for lead in drinking water which is 0.01 mg/L (WHO, 2017). Lead contaminated water can be very toxic to the human body and because of its integral toxicity, it can cause renal, neurological, gastro intestinal and reproductive effects [13]. Chronic exposure to lead can result in mental retardation, birth defects, paralysis, and weakness of the muscle, dyslexia, loss of weight, brain and kidney damage and may cause death [14]. According to the WHO, exposure to lead is associated with a wide range of effects which include various neurodevelopmental effects, mortality due to cardiovascular diseases, hypertension, impaired renal function, impaired fertility and adverse pregnancy outcomes (WHO, 2017).

The concentrations of selenium in S1 and S2 being 6.237 mg/L and 0.733 mg/L are greater than the WHO standard which is 0.01 mg/L (WHO, 2011). The concentration of S1 is far greater than the permissible limit by WHO standard and this is capable of contaminating surface and ground water. High intakes of selenium are also associated with a number of specific diseases and the potential for adverse effects. Symptoms in people with high urinary selenium levels include gastro-intestinal disturbances, discoloration of the skin, decayed teeth, hair or nail loss, nail abnormalities and changes in peripheral nerves (WHO, 2011).

The concentrations of molybdenum in S1 and S2 are 2.448 mg/L and 1.566 mg/L respectively and are also higher than the recommended WHO standard for drinking water which is 0.07 mg/L for molybdenum (WHO, 2011). Although molybdenum is an essential trace element for human, animal and plant health, exposure to it can be harmful and although the evidence for symptoms in humans is sparse, it has been linked with a number of health conditions in animal models [18]. Animals, most especially ruminants are vulnerable to the exposure of molybdenum and can suffer from both high and low intakes of molybdenum, while in plants, the most notable manifestation is yellow-orange chlorosis with brown tints on young leaves [18, 6].

The high concentration of sodium in S1 and S2 is as a result of the active pharmaceutical ingredients (API) used in

the production of the dextrose normal saline (DNS). The ingredients include D-glucose and sodium chloride. WHO has no permissible limit for sodium because it is not of health concern at levels found in drinking water and it is needed by the body where it functions as an essential electrolyte that helps to maintain the balance of water in and around the cells. It is also important for proper muscle and nerve function (WHO, 2017).

The slightly high concentrations of magnesium and calcium with no specific guidelines by the WHO is because calcium and magnesium are vital to the human body system. Calcium is a necessary component of all living things and is also abundant in many non-living things. Teeth, sea shells, bones and cave stalactites are all products of calcium. Magnesium helps to maintain normal nerve and muscle function, supports a healthy immune system.

The concentrations of manganese and copper in S1 and S2 are less than the values of the WHO standard and as a result, manganese and copper concentrations in the effluent samples cannot be termed as hazardous.

Through the aid of the analyses carried out in this research work, it can be said that mercury, arsenic, lead, selenium and molybdenum present in high concentrations in the effluent discharged from this pharmaceutical industry pose a great risk to that environment or surrounding.

Non-carcinogenic risk (hazard quotient) for adults was calculated based on reference dose (RfD) values and CDI values in table 3.

When hazard quotient values are above 1, they pose a great risk to the population and there may be some concern for potential non-carcinogenic effects. When HQ values are less than 1, there is no risk to the environment. From this study, in table 3, the calculated HQ values for lead (7.857), mercury (4.333×10^1), arsenic (1.867×10^2), nickel (4.521×10^2), chromium (3.333), aluminum (5.753), molybdenum (11), silver (1.13) and selenium (19) are greater than 1 and exist in the following order: Se > Mo > Pb > Al > Ni > Hg > Cr > As > Ag. With these metals having values greater than 1, the population is at risk of any non-carcinogenic effects caused by the metals.

The calculated HQ values for Co (0.011), Mn (0.023), Zn (0.199), Fe (0.346), Cu (0.123) and Cd (0.425) are less than 1 and exist in the following order: Cd > Fe > Zn > Cu > Mn > Co. For these heavy metals, the population is not at risk of any non-carcinogenic effect.

The US Environmental Protection Agency considers cancer risk in the range of 1×10^{-6} to 1×10^{-4} as acceptable (US EPA, 2004). The cancer risk values for Pb, As, Ni, Cr and Cd being 3.887×10^{-5} , 3.6×10^{-2} , 3.526, 2.184×10^{-3} and 2.73×10^{-3} respectively are all found to be higher than the acceptable values. The cancer risk value of nickel (Ni) from this study being 3.526 is discovered as the highest contributor to cancer risk among the metals studied.

Table 3. Calculated values of the environmental risk assessment.

Element/metal	Chronic daily intake (mg/Kg.d) Carcinogenic	Chronic daily intake (mg/Kg.d) Non-carcinogenic	Hazard quotient, HQ Non-carcinogenic	Risk factor Carcinogenic
Lead	4.573×10^{-3}	0.011	7.857	3.887×10^{-5}
Mercury	5.519	0.013	4.333×10	—
Arsenic	0.024	0.056	1.867×10^2	0.036
Nickel	3.875	9.041	4.521×10^2	3.526
Chromium	4.368×10^{-3}	0.010	3.333	2.184×10^{-3}
Cadmium	1.820×10^{-4}	4.247×10^{-4}	0.425	2.73×10^{-3}
Aluminum	9.863×10^{-4}	2.301×10^{-3}	5.753	—
Copper	1.955×10^{-3}	4.562×10^{-3}	0.123	—
Iron	0.1036	0.02418	0.346	—
Zinc	0.0256	0.0597	0.199	—
Molybdenum	0.024	0.055	11	—
Manganese	1.409×10^{-3}	3.288×10^{-3}	0.023	—
Vanadium	—	—	—	—
Silver	2.431×10^{-3}	5.671×10^{-3}	1.13	—
Selenium	0.041	0.095	19	—
Cobalt	9.393×10^{-5}	2.192×10^{-4}	0.011	—

4. Conclusions

The study has shown that there were considerable amount of heavy metals present in the discharged effluent of this pharmaceutical industry. The concentration levels of some of the metals such as manganese, copper, aluminum, nickel, cobalt, vanadium and potassium were below the WHO maximum permissible levels for drinking water while mercury, arsenic, lead, molybdenum and selenium have concentration levels that exceeded the WHO permissible limits.

Based on the environmental risk assessment carried out in this study, it can be concluded that the effluent discharged from this pharmaceutical industry is unsafe and poses great risks (carcinogenic and non-carcinogenic) to the population which includes all living things in the ecosystem especially man.

From this research, we recommend that;

- The levels of arsenic, mercury, lead, molybdenum and selenium should be monitored or checked continuously because they can be poisonous even in their smallest quantities.
- Treatment of the effluent prior to discharge should be made mandatory by waste management bodies. The treatment procedures should target the toxic or poisonous heavy metals.
- Workshops should be organised by health bodies in order to enlighten producers or manufacturers, workers and the general public in the dangers of a polluted environment and how it affects the ecosystem.
- New guidelines and standard operating procedures (SOP) should be put in place as regards the treatment and discharge of wastewater by industries.
- Routine check or inspection should be done by concerned bodies to ensure that proper treatments are carried out prior to discharge.
- Further studies similar to this should be carried out in other industries to ascertain the heavy metals and their concentrations in the effluents discharged.

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