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Chemical Analysis of Essential Trace Elements in Wastewater Samples Collected from Four Different Mines

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Abstract

Mine water contains trace heavy metals which are some essential trace elements in high concentrations causing the pollution of nearby water bodies, related ground waters and soils degradation. The aim of the study is to identify and quantify the essential trace elements present in the different mine water samples and their level of toxicity. Digestion technique was employed to pretreat the mine wastewater before analysis. Physicochemical analysis was conducted for pH, electrical conductivity (EC), total dissolved solids (TDS), and salinity. The samples collected from four different locations are Sample A (Gold mine), Sample B (Copper mine), Sample C (Iron mine), Sample D (Tin mine). The raw or untreated mine water samples were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES). The results showed the essential trace elements present in all the mine water samples are Mn, Cu, Fe and Zn. Cu is highly concentrated in copper (73.87 mg/L) and tin (2.09 mg/L) mine water while Fe is dominant in water samples collected from gold (7.19 mg/L) and iron (13.12 mg/L) mine. In conclusion, the essential trace elements Mn, Cu, and Fe present in all the mines are very high and can be harmful to human life in the environment but the concentrations of Zn in the entire mine water samples are within the permissible level of standard drinking water and hence it can pose no threat to human life.

Keywords: Mines; Wastewater; Essential trace elements; Physicochemical parameters; Inductively coupling plasma.

1. Introduction

Mining activities in most parts of the world have been found to contribute immensely to their environmental pollution and degradation as we experience today globally. Metal mining industries have been found to generate significant quantities of mining wastes, which are usually discharged into the river systems [1-5]. Water is very important natural resource in every part of the world which can be used for the following purposes: industrial, domestic, commercial or agricultural purposes and entering into the environment in various sources [6-8]. However, mining and mineral processing industries usually creates more problem of water quality because water pollution is more severe in those areas where they carry out their mining activities [7]. Heavy metals are metallic elements that have a high density that have progressively accumulated in the food chain with negative effects for human health. Essential trace elements required in the human body include Fe, I, Co, Zn, Cu, Mn, Mo, Se, etc to maintain various physiological functions and are usually added as nutritional additives in animal feed [9-11]. Heavy metals are described as metals that have high atomic weight and density, and in the field of biology heavy metals are referred to the metals that are toxic for organisms even in a small amount [12, 13]. Due to the properties of heavy metals, they are non-biodegradable and remain in the environment for a very long time [14, 15]. Essential trace elements occurs naturally in aquatic environments but most of these elements can be toxic, depending on their concentrations in which they are present [16]. Pollution of magnetic materials that is related to heavy metal pollution emanated from anthropogenic and transportation activities [17]. The essential micronutrient metals are also called as trace elements (Ni, Mn, Cu, Mo, Fe, Zn, and Co etc.) and this is due to their concentration in trace amount (10 mg L^{-1}) in the environmental matrices. Essential trace elements are heavy metals such as iron, magnesium, zinc, selenium, chromium, copper, and cobalt; although, these elements occur at very low concentrations in the environment. Living things need very small amounts of some trace metals, but high levels of these same metals can be toxic. For example, iron is an essential element for many living things. In human blood, iron transports oxygen around the body. If too much iron is consumed, however, there can be negative effects on human health. Studies have shown that mining is considered to be the prime source of heavy metal contamination in the surrounding environment. Some of the heavy metals that are of serious concern include Nickel, Zinc, Copper, Lead, Arsenic, Selenium, Cadmium, Chromium, Manganese, Cobalt and Mercury. However, most environmentalists are focusing majorly on heavy metal contaminated soil and water bodies.

The presence of essential trace elements (Fe, Zn, Cu, Cr, etc.) are micronutrient for living system in small amounts in the body may preserve cells and the presence of more of these metals may cause damage to plant and animal organisms or illnesses in human body [18-22]. The excess uptake of trace heavy metals than it is required in the plants and animals is called toxic effects and some of the essential heavy metals like Cu, Fe, Zn, Mn, and Mo play biochemical and physiological functions in plants and animals [23-25]. The aim this study is to analyze some essential trace elements present in wastewater samples collected from four different mines. Some important essential trace elements are:

1.2. Zinc

Zinc (Zn) is naturally present in the environment and it is an essential trace element required by organisms for their essential biological functions. Zinc is a natural component of the earth's crust and an inherent part of our environment. Zinc is present not only in rock and soil, but also in air, water and the biosphere. They are normally associated with the lead and other metals including copper, gold and silver. Deposits containing zinc from hot or hydrothermal fluids generated within the earth, some fluids may reach the ocean floor in areas of underwater volcanic activity to form volcanogenic deposits. The deficiency of zinc causes birth defects. Zinc can be utilized by plants, bacteria and humans as a micronutrient for many biological metabolic functions but if it exceeds normal physiological value then it is toxic for the organisms as it reacts with the sulfhydryl groups of amino acids and replaces other vital metals that are used in a wide range of proteins. Zinc (Zn) plays an important role in many biological processes and is an essential trace element for proper growth and reproduction of plants and the health of animals and humans beings and can cause contamination of water, soil, and food chains [26, 27]. Human activities such as mining and metallurgic operations are potential sources of zinc pollution in the environment. Zinc is an essential nutrient for metabolism, bone development, and wound healing and high concentration of zinc level in blood may cause a mental illness called metal fume fever [28-30].

1.3. Copper (Cu)

Copper is a chemical element with the symbol Cu and atomic number 29, which is widely deposited in many parts of the world mainly as mineral combine with iron, carbon, sulfur, and oxygen. Copper occurs both in combined and free state, also it contains many ores, such as copper pyrites (Cu FeS2), Cuprite and copper glance. Copper is essential to all living organism as trace dietary minerals because it is a key constituent of the respiratory enzyme complex cytochrome C oxidase. In molluscs and crustacean, copper is a constituent of the blood pigment hemocyanin, which is replaced by the iron-complexes hemoglobin in fish and other vertebrate. Mining operations, weathering and erosion of rocks, and geological deposits are the natural major sources of copper in water. Serious exposure to copper leads minerals can cause alteration of brain functioning and gastrointestinal disorders [28-30].

1.4. Iron (Fe)

Iron is an abundant element in the universe, it is found dissolved in ground waters and the ocean to a limited extent. It is made up of 5 percent of the earth's crust and second in abundance to aluminum among the metals and fourth in abundance behind oxygen, silicon and aluminum, iron which is the chief constituent of the earth's core is the most abundant element in the earth as a whole, contributing to the creation of the earth's magnetic field. In the earth crust the free metal is rare, occurring as terrestrial iron (alloyed with 2-3% nickel) in basaltic rocks. Iron in groundwater is in the soluble form of ferrous ion Fe^{2+} and can be oxidized to the ferric state Fe^{3+} which is soluble and precipitates out as ferric hydroxide, causing a brown discoloration of the water and give a characteristic brown [31]. Iron is essential for biological systems.

1.5. Manganese

Manganese (Mn) is essential for the formation of bone and amino acid, lipid, protein, and carbohydrate metabolism. It is also needed for normal immunity system, regulation of blood sugar and cellular energy, reproduction, digestion, and for the defence mechanisms against free radicals. This trace element is required for the proper function of several metalloenzymes such glutamine synthetase, phosphoenolpyruvate decarboxylase, arginase, and manganese superoxide dismutase [32]. The major route of intake for Mn is via food consumption, but inhalation exposure may also occur. Some of the richest food sources of manganese are bread, nuts, and cereal product. Adequate intake of Mn for adult men and women are 2.3 and 1.8 mg/day, respectively, as it is the Tolerable Upper Intake Level for adults of 11 mg/day. Humans maintain stable tissue levels of Mn. Manganese is excreted very rapidly into the gut via bile, however, the potential risk of manganese toxicity is very high when bile excretion is low such as in the liver disease. Excessive Mn tends to accumulate in the liver, pancreas, bone, kidney and brain. Hepatic cirrhosis, polycythemia, hypermanganesemia, dystonia and Parkinsonism-like symptoms have been reported in patients with manganese poisoning [33]. It has been reported that high concentration of manganese that is slightly above the WHO and NSDWQ maximum permissible limit causes neurological and gastrointestinal disorder [28, 30].

2. Materials and Methods

2.1. Sampling and Sample Collection

Wastewater samples of gold, copper, iron, and tin mines were collected from four different mining locations using high density polyethylene or plastic bottle containers. The samples were collected in triplicate, in which one sample from each mine was spiked with concentrated acid labeled as spiked and the other containers were labeled un-spiked that is without spiking with acid and water samples were transported in ice cooler or ice to the laboratory and preserved in a refrigerator regulated at 4 ^{0}C prior to analyses. Hand trowel was used to collect the sample (sand) into a plastic bottle and the plastic bottle was dipped into mine wastewater in the site for sample collection. 5 mL of concentrated nitric acid was added to the each waste mine water to prevent it from undergoing metal oxidation. Then the samples were taken to the laboratory for physicochemical analysis. The sample was subjected to filtration and the filtrate was collected and sent for analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES).

2.2. Description of Sample Location

Samples of mine wastewater were collected from four different mines which are gold mine, copper mine, tin mine and iron mine. The gold mine is located in Sabo town, Ilesha in South West Local Government Area (LGA), Osun State, South West Nigeria. Gold mining has GPS coordinates of latitude 7.623914^{o} N and longitude 4.715163^{o} E. Copper mine is located at Dawa Town, located in Toro LGA of Bauchi State, Northern Nigeria with GPS coordinates of latitude 10.431790^{o} N and longitude 8.986784^{o}E. Tin mine is located at in Bisichi Town, Sabon Gida Danyaya, Barikin Ladi LGA of Plateau State, Northern Nigeria with GPS coordinates of latitude 9.71445^{o} N and longitude 8.91072^{o} E. Iron mine wastewater sample is located at in Ijero Town, Ekiti State, South West, Nigeria with GPS coordinates of latitude 7 ^{o} 48'54.50" N and longtitude 504'1.78 E"4^{o}.

2.3. Chemicals/Glass wares

The chemicals used are nitric acid and hydrochloric acid purchased from Merck chemicals. All the chemicals were used without any other further treatment. All the glass wares and plastic containers used were washed thoroughly with liquid soap and de-ionized water and later soaked in 10% v/v HNO_3 for 24 hours and cleaned thoroughly with de-ionized water and dried in a regulated oven at a temperature of 80 ^{0}C to ensure that no contamination occur. All the chemicals used in this research are of analytical grade reagents.

2.4. Sample Digestion

50 mL wastewater sample was digested at 85 °C in 12 mL of aqua regia (HCl/HNO_3 v/v) in ratio 3:1 placed on hot plate in a fume cupboard until white fumes was observed. The sample was allowed to cool until room temperature then diluted with 20 mL of Nitric Acid 2% (v/v). The mixture was then transferred into sample bottle after using Whatman No.42 filter paper and made to the mark with distilled water. The sample was analyzed using Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP – OES).

2.5. Analytical Techniques

Physicochemical parameters such as pH, EC, TDS and salinity of the mine water as received were determined using Hach water quality multifunction pH meter, model EZ- 9909.

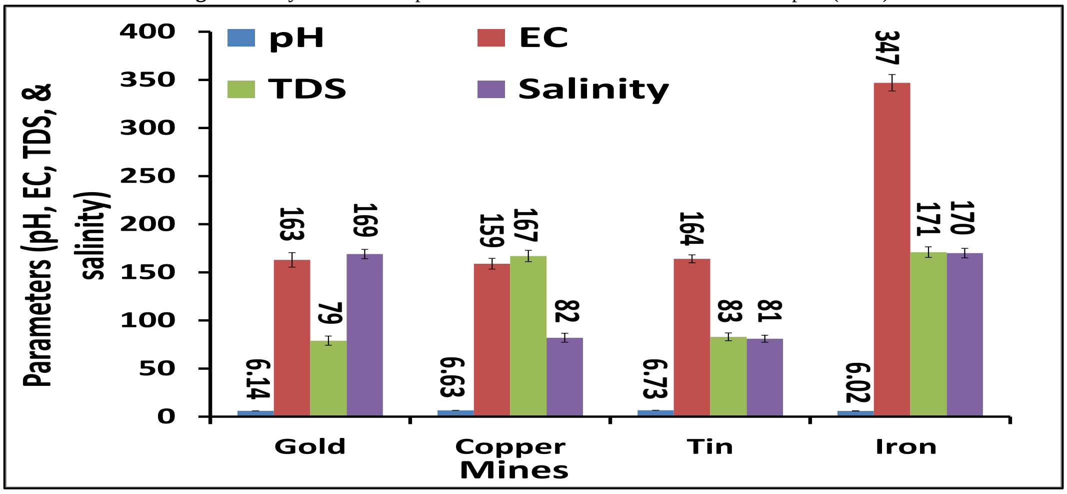
The multifunction pH meter was calibrated with buffers pH 4.0, 7.0, 12 and the electrical conductivity meter was calibrated using 10 μScm^{-1}, 500 μScm^{-1} and 1288 μScm^{-1} standard KCl solutions before testing the wastewater solution. The essential trace elements were determined using Variance Liberty II inductively coupled plasma optical emission spectroscopy (ICP-OES) analytical technique.

3. Results

3.1. Physicochemical Analysis

Physicochemical analysis was conducted for the four different mine water samples and the results is presented in Figure 1. The pH of all the mine water was slightly acidic as they are less than 7 and but the copper (6.63) and tin (6.73) mine water falls within the WHO standard drinking water permissible limit in the range of 6.5 - 8.5 while gold (6.14) and iron (6.02) mine water [28, 30]. The electrical conductivity (EC), and total dissolved solids (TDS) falls within the WHO/NSDWQ allowable range for standard drinking water permissible limits range of 500-1000 mS/cm and 500-1000 mg/L respectively. The salinity of the all the water samples are less than 600 mg/L which falls within the WHO/NSDWQ standard drinking water permissible limit.

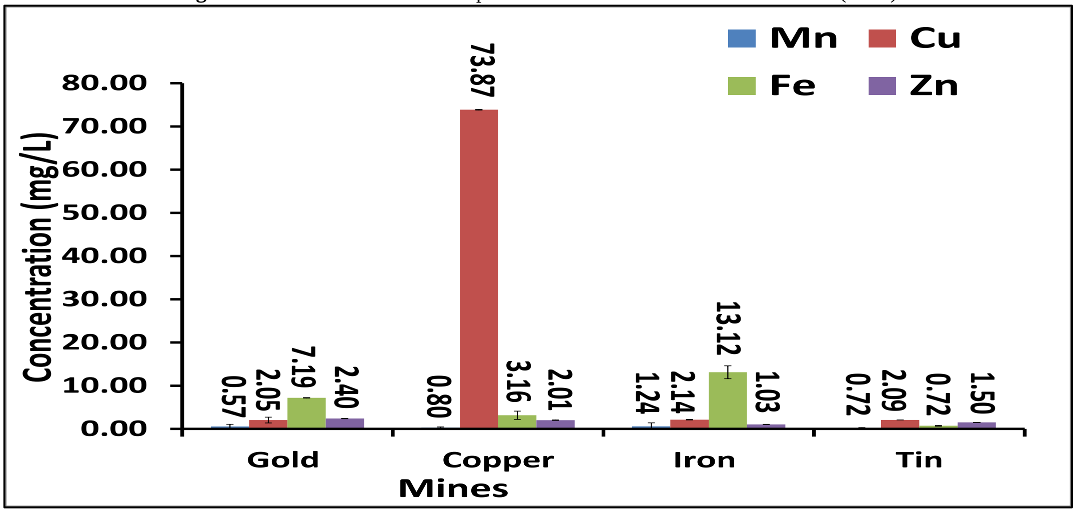
Figure-1. Physicochemical parameters of four different mine water samples (n = 3)



3.2. Essential Trace Elements

Figure 2 presents the results of all the essential trace elements present in all the mine water samples for easy comparative study of all the four mines. The essential trace elements present in each mine showed the presence of Mn, Cu, Fe and Zn. The concentrations of essential trace elements present in the gold mine are Fe > Zn > Cu > Mn. The essential trace element concentrations present in the copper mine are Cu > Fe > Zn > Mn. The essential trace element concentrations present in the iron mine are Fe > Cu > Zn > Mn. The essential trace element concentrations present in the tin mine are Cu > Zn > Fe > Mn. Comparative analysis of the concentration of essential elements in each mine is reported for Mn as iron > copper > tin > gold, for Cu as copper > iron > tin > gold, for Fe as iron > gold > copper > tin, and for Zn as gold > copper > tin > iron. The concentrations of Mn and Fe in the entire mines are within the WHO permissible level of standard drinking water [28, 30]. The concentrations of Cu in the entire mines are within the WHO/NSDWQ standard permissible drinking water level except for copper mine. The concentrations of Zn in the entire mines are within the permissible level of standard drinking water. The result of this study agrees with previous result that the high concentrations of iron, copper and manganese can give drinking water undesirable taste [28, 29].

Figure-2. Essential trace elements present in four different mine wastewater: (n = 3)



4. Conclusion

- The physicochemical parameters of the different mine water samples were within the WHO/NSDWQ permissible limits
- This study has shown that the various water samples collected from the four mines contained essential trace elements such as Mn, Cu, Fe and Zn.
- The people living around these mines are not exposed to serious health danger, since most of essential trace elements have benefits on human health.
- The concentrations of some of the essential trace elements in some of the mines are above the WHO standard permissible limits.
- Some of these mine wastewater samples could be of a high risk to humans if it runs into the natural water bodies being used by the inhabitants of the community for domestic cooking and drinking purposes.

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