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Heavy metal pollutants in wastewater effluents: Sources, effects and remediation

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Abstract: Heavy metals, also known as trace metals, are one of the most persistent pollutants in wastewater. The discharge of high amounts of heavy metals into water bodies leads to several environmental and health impacts. The exposure of humans to heavy metals can occur through a variety of routes, which include inhalation as dust or fume, vapourisation and ingestion through food and drink. Some negative impacts of heavy metals to aquatic ecosystems include death of aquatic life, algal blooms, habitat destruction from sedimentation, debris, increased water flow, other short and long term toxicity from chemical contaminants. Abundant amounts of heavy metals present in soils cause reduction in quality and quantity of food preventing plants' growth, uptake of nutrients, physiological and metabolic processes. Severe effects on animals may include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. To help mitigate the negative impacts of heavy metals on the health of humans, animals and the environment, a variety of remediation processes exists. These remediation processes are broadly classified into chemical and biological, although the latter is advocated in recent years. Biological remediation processes (microbial remediation and phytoremediation) are indicated to be very effective in the treatment of heavy metal pollutants in wastewater. Microbial remediation is the restoration of the environment and its quality using microorganisms, such as bacteria, fungi, protozoan and algae while phytoremediation is the use of plants to degrade or accumulate toxic metals, thereby leading to a reduction in the bioavailability of the contaminant in the soil or water. This paper was therefore aimed at reviewing the sources, impacts and remediation processes for heavy metals in wastewater.

Keywords: Heavy Metals, Remediation, Wastewater

1. Introduction

Heavy metals are elements with an atomic density greater than 6 g/cm^3; they are one of the most persistent pollutants in wastewater. They are also referred to as trace elements and are the metallic elements of the periodic table (Salem *et al*., 2000). The most common toxic heavy metals in wastewater include arsenic, lead, mercury, cadmium, chromium, copper, nickel, silver, and zinc. The release of high amounts of heavy metals into water bodies creates serious health and environmental problems and may lead to an upsurge in wastewater treatment cost. Heavy metals also occur in small amounts naturally and may enter into aquatic system through leaching of rocks, airborne dust, forest fires and vegetation (Fernandez and Olalla, 2000; Ogoyi *et al*., 2011). Their occurrence and accumulation in the environment is a result of direct or indirect human activities, such as rapid industrialization, urbanization and anthropogenic sources.

The persistence of heavy metals in wastewater is due to their non-biodegradable and toxicity nature (Jern, 2006). Some of the negative impacts of heavy metals on plants include decrease of seed germination and lipid content by cadmium, decreased enzyme activity and plant growth by chromium, the inhibition of photosynthesis by copper and mercury, the reduction of seed germination by nickel and the reduction of chlorophyll production and plant growth by lead (Gardea-Torresdey *et al*., 2005). The impacts on animals include reduced growth and development, cancer, organ damage, nervous system damage and in extreme cases, death (Canada Gazette, 2010).To prevent the negative effects of heavy metals toxicity in wastewater, there is need for adequate treatment of effluents before discharge to receiving water bodies. The ultimate goal for treatment is to eliminate any current or potential threat to human/animal health and the environment. Although chemical and biological treatment processes exist, biological processes are advocated in recent years because of the main drawbacks in chemical treatment processes. Biological processes are classified into two broad categories: microbial remediation and phytoremediation (USEPA, 2004).

Microbial remediation is described as the restoration of the environment and its quality using microorganisms (bacterial, fungi, and yeast). The technique uses biological activity to reduce the concentration or toxicity of a pollutant. In some cases, the pollutants may first serve as a source of carbon needed for the growth of the microorganism first before the microorganism can help in the breakdown. In some instances, microbial remediation can occur without the implementation of any engineered step to enhance the process, referred to as natural attenuation or intrinsic microbial remediation. It can also occur by the addition of genetically engineered microorganisms to enhance the naturally occurring process of degradation, referred to as engineered or enhanced microbial remediation. During microbial remediation, the microorganisms can be used at the site of contamination (in-situ) or off site of the contamination site (ex-situ) for remediation. The microbial remediation strategies for heavy metal removal in wastewater include bioaugumentation, biosparging and biosorption (Igwe and Abia, 2006). Phytoremediation is the restoration of the environment and its quality using plants. It is described as an emerging 'green bioengineering technology' for environmental cleanup that use plants for the removal of pollutants (Pilon-Smits, 2005). During phytoremediation in water, plants may degrade and accumulate a toxic metal or cause immobilization in the bioavailability of the contaminant. This review was aimed at reviewing the effects, sources and treatment processes for heavy metal polluted wastewater effluents.

2. Sources of Heavy Metals in Wastewater Effluent

The two main sources of heavy metals in wastewater are natural and human. The natural factors include soil erosion, volcanic activities, urban run offs and aerosols particulate while the human factors include metal finishing and electroplating processes, mining extraction operations, textile industries and nuclear power.

Then main natural sources of heavy metal pollutants in wastewater effluents are volcanic activities, soil erosion, urban run offs and aerosol particles. It is reported that volcanic eruptions produce hazardous impacts to the environment, climate and health of exposed individuals. Apart from the deterioration of social and chemical conditions and the gases (carbon dioxide, sulphur dioxide, carbon monoxide, hydrogen sulphide) released during eruptions, various organic compounds and heavy metals, such as mercury, lead and gold are also released. The presence of these heavy metals in water bodies is known to significantly deteriorate the quality of such waters. Several rocks and volatiles of volcanic origins are indicated to be responsible for the presence of metals in soils and waters. This is because the diffusion of acidic volcanic gases through water permeable rocks contributes to the hydrological material transfer in volcanic strata. The activities from volcanoes are reported to be responsible for the release of metals such as arsenic, mercury, aluminum, rubidium, lead, magnesium, copper, zinc and a host of others (Amaral *et al*., 2006).

Soil erosion is also indicated to be a source of heavy metal pollution in water. The two main agents of soil erosion are wind and water. During rainfall, sediment-bound heavy metals is distributed to the soil. Water containing agrochemicals with toxic metal concentration drop this sediment bound metal in the soil even as it causes erosion (Kaizer and Osakwe, 2010). During run-off due to erosion, heavy metals, may be picked up and distributed to the environment. In some cases, during rainfall, some heavy metal wastes are washed into poor drainage systems and subsequently into nearby rivers (Taiwo *et al*., 2011).

In addition, some aerosol (fine colloidal particles or water droplet in the air, in some cases they can be gas) particles may carry different kinds of contaminant; like smoke cloud and heavy metals. These heavy metal containing aerosols usually accumulate on leaf surfaces in the form of fine particulates and can enter the leaves via stomata (Sardar *et al.*, 2013).

Some of the human sources of heavy metals in wastewater effluents are metal finishing and electroplating, mining and extraction operations, textiles activities and nuclear power. Metal finishing and electroplating involve the deposition of thin protective layers into prepared surfaces of metal using electrochemical processes. When this happens, toxic metals may be released into wastewater effluents. This may be either through rinsing of the product or spillage and dumping of process baths. It is also indicated that the cleaning of process tanks and treatment of wastewater can generate substantial quantities of wet sludge containing high levels of toxic metals (Cushnie, 1985).

Similarly, mining activities can release toxic metals to the environment. Metal mining and smelting activities are regarded as major sources of heavy metals in the environment. In environments where these activities take place, it is indicated that large amount of toxic metals deposits are found in their water, soil, crops and vegetable (Wei *et al*., 2008). Additionally, textile industries are indicated to be major sources of heavy metal pollutants in water. This is said to mostly originate from the dyeing process, which is a major process in such industries. The compounds used for these dyeing processes (coloration) include copper, chromium, nickel and lead which is very toxic and carcinogenic. In some cases, nuclear generating facilities have also been described as source of discharge of heavy metals like copper and zinc to surface water. In the nuclear plants, because large amount of water is consumed for operation, after operation, the nuclear effluent containing heavy metals are discharged into surface water and ground water bodies, which can pollute aquatic systems (Hagberg and Lofgren; Begum *et al*., 2011).

3. Effect of Heavy Metal Polluted Wastewater Effluent

Untreated or inadequately treated heavy metal contaminated wastewater effluents cause a variety of health and environmental impacts, when released into receiving water bodies. In aquatic ecosystems, heavy metals greatly depress the number of living organisms. Heavy metals have negative effect on the growth of aquatic organisms and can cause serious upsets in biological wastewater treatment plants. The presence of heavy metal pollutants serve as great threats to soil and plants growing on such soils, with the consumption of such plants by animals and humans due to their entry into the food chain through biomagnification and bioaccumulation, leading to severe detrimental effects (Saidi, 2010). It is reported that the intake of toxic metals in vegetables and corn products accumulate in the kidney, leading to its dysfunction. Some reports have linked skeletal damage (osteoporosis) in humans to heavy metals, such as high levels of selenium (Abdullahi, 2013).

The nature of heavy metals polluted wastewater effluents on humans may be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic (Duruibe *et al*., 2007). Although it is reported that individual metals exhibit specific signs of their toxicity, the signs associated with cadmium, lead, arsenic, mercury, zinc, copper and aluminium poisoning are gastrointestinal disorders, diarrhea, stomatitis, tremor, hemoglobinuria causing a rust-red colour to stool, ataxia, paralysis, vomiting and convulsion, depression and pneumonia, when volatile vapours are inhaled (McCluggage, 1991; Duruibe *et al*., 2007)

Although heavy metals are natural components of the earth crust that cannot be degradable, they are only toxic when they are not metabolized and synthesized by the body and when accumulated in the soft tissue of the body. As an example, lead is considered the number one health threat to children, whose effects can last a lifetime. Some of such effects include child's growth, damage the nervous system, and cause learning disabilities, but also it is now linked to crime and anti-social behavior in children (Salem *et al*., 2000). It is indicated that the majority of ingested lead is removed from an individual's body through urine, there is still the risk of buildup especially in children. Also, toxicity due to lead accumulation may lead to a decrease in hemoglobin production, kidney, joint, reproductive and cardiovascular systems disorders and long-term injury to the central and peripheral nervous systems (Nolan, 2003; Galadima, *et al*., 2010).

Another highly toxic heavy metal, even when present in humans at low concentrations is cadmium. It is indicated to be carcinogenic and persistently cumulative poison (Lin *et al*., 2005). A long term exposure to cadmium in humans may lead to renal dysfunction; while high exposure levels could cause obstructive lung disease, cadmium pneumonitis, bone defects, osteomalacia, osteoporosis and spontaneous fractures, increased blood pressure and myocardic dysfunctions (Duruibe *et al*., 2007). The level of exposure to cadmium compounds may determine the symptoms, which may include nausea, vomiting, abdominal cramps, dyspnea and muscular weakness. Severe exposure may result in pulmonary odema and death (McCluggage, 1991; INECAR, 2000; European Union, 2002; Young, 2005, Duruibe *et al*., 2007).

With respect to copper, although copper is an essential nutrient to humans, its presence in high concentration in drinking water is indicated to cause liver cirrhosis in patients, anemia, liver and kidney damage. Exposure to water contaminated with copper can lead to the development of anemia, liver and kidney damage and diarrhea, abdominal pain, vomiting, headache and nausea in children (Madsen *et al*., 1990; Bent and Bohm, 1995; Salem *et al*., 2000). In addition, although zinc is a component of several enzymes (alkaline phosphatase, superoxide dismutase, alcohol dehydrogenase, carbonic anhydrase) in humans, when taken at high concentrations can lead to system dysfunctions, which may result in growth and reproduction impairment. The clinical signs of zinc toxicosis include diarrhea, vomiting, icterus (yellow mucus membrane), bloody urine, anemia, kidney failure and liver failure (INECAR, 2000; Nolan, 2003; Duruibe *et al*., 2007).

On the other hand, mercury is known as one of the most dangerous metals for human consumption, for it has no known biochemical function. It is reported that toxicity symptoms of mercury are dependent on the chemical form ingested. The ingestion of its inorganic forms cause spontaneous abortion, congenital malformation and gastrointestinal disorders while ingestion of its organic forms may lead to erethism (abnormal irritation or sensitivity of an organ or body part to stimulation), gingivitis, stomatitis, neurological disorders, brain and central nervous system damage, acrodynia (pink disease, characterized by rash and desquamation of the hands and feet) and congenital malformation (Lenntech, 2004; Duruibe *et al*., 2007; Simone *et al*., 2012). Furthermore, exposures to high levels of arsenic can cause death, since it is known to coagulate protein, form complexes with coenzymes and inhibit ATP production during respiration (INECAR, 2000).

Heavy metals are also known to have impacts in soil ecosystems. The impact of heavy metals pollution on soil is mostly felt by plants that grow in such environments. Some of these impacts include decreased seed germination and lipid content, decreased enzyme activity and plant growth, inhibition of photosynthesis, reduction of seed germination, reduction of chlorophyll production and plant growth; which may be caused by cadmium, chromium, copper or mercury, nickel and lead, respectively (Gardea-Torresdey *et al*., 2005). The presence of large amounts of heavy metals in a soil could also lead to the prevention of plants' growth, uptake of nutrients, physiological and metabolic processes, chlorosis, and harm to root tips, minimized water and uptake of nutrients and impairment to enzymes (Sardar *et al*., 2013)

Furthermore, the potential detrimental effects of heavy metal polluted wastewater effluents on the quality of receiving water bodies are numerous, although it may depend on the volume and composition of the effluent that is discharged (Owuli, 2003; Akpor and Muchie, 2011). As an example, in aquatic ecosystems, the concentration and availability of lead can lead to decreased dissolved oxygen, which may make young aquatic organisms, such as young fishes vulnerable to lead than the adult fish. The presence of lead may also cause blackening of the tail region and spiral deformity to young fishes (Peplow, 1999; European Commission DG ENV, 2002).

4. Biological Remediation Processes for Heavy Metal Pollutants in Wastewater

Biological removal of heavy metals in waste water involves the use of biological techniques for the elimination of pollutants from wastewater. It is a selective technique that utilizes the operational flexibility of microorganisms and plants. Microbial remediation may entail ex-situ and in-situ application. In phytoremediation, plants play a great role in the biological process as they break down, reduce, degrade and remove these contaminants using various parts, such as the root, leaves, stomata, cell wall and the shoot (USEPA, 2000; Rajendran *et al*., 2003; Sharma, 2012).

In microbial remediation or bioremediation, microbial communities are of primary importance. The process is cost effective process, with non-hazardous end products (Ahmedna *et al*., 2004). During pollutant removal, the microbe(s) alter the metal chemistry and mobility through either reduction, accumulation, mobilization or immobilization (Faryal and Hameed, 2005). According to Gupta *et al*., (2000) and Dias *et al*., (2002), the major groups of microorganisms that have been implicated in heavy metal remediation are bacteria (such as *Anthrobacter, Bacillus* sp, *Citrobacter, Cupriavidus metallidurans, Cyanobacteria, Enterbacter cloacae, Pseudomonas aeruginosa, Streptomyces* sp, *Zoogloe aramigera, Alcaligenes, Sphinganonas, Rhdococcus, Mycobacterium* and *Arthrobacter*) and fungi (such as *Aspergillus tereus, Penicillium chrysogeum, Candida utilis, Hamsenula anomala* and *Rhodotorula mucilaginosa*). Beside bacteria and fungi, certain protozoa, such as *Euplotes mutabilis* and algae, such as *Oscillatoria* sp, *Chlorella vulgaris* and *Chlamydomonas* sp have been reported to possess metal reducing capabilities (Ramasamy *et al*., 2006).

The microbial remediation of toxic metals is said to occur in two ways: direct and indirect reduction (Sinha *et al*., 2009). Microbial remediation can be in the form of bioaugmentation, biosorption or biosparging. Bioaugmentation entails the introduction of microbial strain, which has high degradation factor to assist the indigenous microbe in the active degradation process of the contaminated environment. It is mostly used in municipal wastewater to restart activated sludge bioreactor (Rajiv *et al*., 2009). In biosorption, there is the immobilization of metals by microbial cells. Its technique involves the sequestration of a positively charged heavy metal ions to the negatively charged microbial cell membranes and polysachharides, which is secreted (Sinha *et al*., 2009). The mechanisms of heavy metal removal from wastewater by microorganisms can be based on microbial precipitation, complexation, ion-exchange and intracellular accumulation (Volesky, 2000; Ademiluyi, 2009). During biosparging, also known as air sparging, there is the injection of air by pressure to the water to enhance the activation of oxygen concentration by the microorganism, which can increase biological degradation of contaminant. Apart from the promotion of aerobic bacterial growth, air sparging also leads to the volatilization of contaminants from the liquid to the vapor phase (Sharma, 2012).

In phytoremediation green plants are employed technique in the in-situ treatment of contaminants. Such plants have the advantage of accumulating and degrading components of such contaminants. The commonest phytoremediation processes are rhizofiltration, phytostabilization, phytoextraction, phytovolitazation, phytodegradation and rhizodegradation (Robert, 1997; Ana, 2009).

During rhizofiltration (phytofiltration), both aquatic and terrestrial plants are used to sorb, concentrate and precipitate toxic metals and organic compound from wastewater effluents. The technique involves the breakdown of organic contaminant by enhanced microbial activity in the plant root zone and is absorbed by the root surface or by the plant root. The technique is based on the effectiveness of a plant root to synthesis chemicals. Both the root exudate and a change in pH of the rhizophere can cause a biogeochemical condition, which may result in the precipitation of this metal to the surface of the root (Vinita, 2006). In phytostabilization (in-placed inactivation or phytoimmobilization), a plant root is used to limit a contaminant mobility and bioavailability by providing a barrier mechanism against direct contact with contaminated soil (Schnoor, 1997). It is indicated that plants that are best suited for phytostabilization include trees, which transpire large amounts of water for hydraulic control and grasses with fibrous roots help to bind and hold (Sinha *et al.*, 2009).

In the case of phytoextraction, metal-accumulating plants are used for the translocation and concentration of metals, radionuclides and non-metals in the root of the plant, before they are translocated to the shoots or leaves (Asha and Sandeep, 2013). The biological processes involved in phytoextraction are metal acquisition and transport and shoot accumulation. In some instances, some heavy metals can be removed by binding to soils and root masses through rhizofiltration, while others may require the addition of chelating agents, such as ethylene diamine tetra acetate (EDTA) to the soil. Sunflower and mustard are examples of plants that have been implicated to have phytoextraction ability for heavy metals (Robert *et al*., 1997). Similarly, in phytovolatilization, a contaminant is removed by transforming it from its original medium to the atmosphere. The technique entails the ability of a plant to take up a contaminant that is water soluble and release it to the atmosphere without the need of harvesting or disposal. Certain metals, such as selenium and mercury have been reported to form volatile molecule, which may be released to the atmosphere by some plants (Ghosh and Singh, 2005).

However, during phytodegradation (phytotransformation), there is the breakdown of organic contaminants taken up by a plant into simpler molecules. The breakdown is carried out by the plant enzymes, which metabolize the contaminant and release it in the rhizosphere, which may then undergo further active transformation (Sinha *et al*., 2009). Also, in phytostimulation (rhizodegradation), the technique involves the release of natural substances by the plant through its roots, thereby supplying nutrients to microorganisms, which may in turn enhance biological degradation. In this technique, the plant may secrete exudate (amino acid, organic acid, fatty acid, sterol, growth factors and other compounds) that can lead to an increase in the number and activities of microorganisms (Meers and Tack, 2004; Akpor and Muchie, 2010).

5. Conclusion

This review, which was aimed at discussing the sources, impacts and remediation processes for heavy metals pollution in wastewater effluents revealed that the two main sources of heavy metals in wastewater are natural and human, with the natural factors being soil erosion, volcanic activities, urban run offs and aerosols particulate while the human factors include metal finishing and electroplating processes, mining extraction operations, textile industries and nuclear power.

The entrance of untreated or inadequately treated heavy metal contaminated wastewater to receiving water bodies pose a variety of health and environment impacts to humans, animals and plants. In aquatic ecosystems, heavy metals greatly depress the number of living organisms. Also, heavy metals have negative effect on the growth of aquatic organisms and can cause serious upsets in biological wastewater treatment plants.

To safeguard the health of living organisms and for environment sustainability a variety of biological treatment processes are employed for the removal of heavy metals from wastewater effluents, with the most common being microbial and phytoremediation. Biological removal of heavy metals in wastewater is a selective technique that utilizes the operational flexibility of microorganisms and plants for the elimination of pollutants from wastewater. Microbial remediation may entail ex-situ and in-situ applications. In phytoremediation, plants play a great role in the biological process as they break down, reduce, degrade and remove these contaminants using various parts, such as the root, leaves, stomata, cell wall and the shoot.

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