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Heavy metal water pollution: hazards and remediation methods

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Dedication

I want to dedicate my thesis to my parents, Giovanna Bolagay and Marco Negrete, who always gave me their unconditional support, for their teachings, for their effort, for each word of encouragement, and for always trusting me.

To my sister, Johanna Negrete who has always guided me, has corrected me and supports me at all times with the only purpose of being a better person and meeting all the goals that I have set for myself.

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Daniela Alejandra Negrete Bolagay

RESUMEN

Los contaminantes del agua representan uno de los desafíos globales que la sociedad debe abordar en el siglo XXI con el objetivo de mejorar la calidad del agua y reducir los impactos en la salud humana y en los ecosistemas. La industrialización, el cambio climático y la expansión de las áreas urbanas producen una variedad de contaminantes del agua. En este trabajo, discutimos algunos de los hallazgos más recientes y relevantes relacionados con la liberación de metales pesados, los posibles riesgos para el medio ambiente y la salud humana, así como los métodos y materiales disponibles para su eliminación. Las actividades antropogénicas, como la minería, la agricultura y las operaciones industriales basadas en metales, se identifican como las principales fuentes de contaminación producida por metales pesados que se encuentran en los medios acuáticos. Se describen algunos de los peligros para la salud derivados de la exposición a trazas de metales pesados, como plomo, cadmio, mercurio y arsénico. También damos algunas perspectivas sobre varias técnicas que se utilizan para detectar metales pesados, así como sobre los diferentes factores (por ejemplo, pH, temperatura, fuerza iónica) que podrían afectar su eliminación. Las ventajas y desventajas de los métodos de eliminación de metales pesados convencionales y no convencionales se discuten, prestando especial atención a los relacionados con la adsorción, los materiales nano-estructurados y la remediación mediada por plantas.

Palabras clave: aguas residuales, metales pesados, tratamiento de aguas, toxicidad

ABSTRACT

Water pollutants is one of the global challenges that society must address in the 21st century aiming to improve water quality and reduce human and ecosystem health impacts. Industrialization, climate change, and expansion of urban areas produce a variety of water pollutants. In this work, we discuss some of the most recent and relevant findings related to the release of heavy metals, the possible risks for the environment and human health, as well as the methods and materials available for their removal. Anthropogenic activities, such as those related to mining, agriculture and metal-based industrial operations are identified as the main source of the increasing amounts of heavy metals found in aquatic environments. Some of the health hazards derived from repeated exposure to traces of heavy metals, including lead, cadmium, mercury, and arsenic, are outlined. We also give some perspectives about several techniques that are used to detect heavy metals, as well as about the different factors (e.g. pH, temperature, ionic strength) that could affect their removal. The advantages and drawbacks of conventional and non-conventional heavy metal removal methods are critically discussed, given particular attention to those related to adsorption, nanostructured materials and plant-mediated remediation.

Keywords: *wastewater, heavy metal, water treatment, toxicity*

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Chapter 1

1. Introduction

Water is a primary resource for the presence of life on earth and access to clean water is critical for humans and ecosystem. Nonetheless, during the last decades water quality has been negatively influenced by a continuously increasing population, the rapid industrialization, the increasing urbanization and careless utilization of natural resources (Vardhan et al., 2019; Carolin et al., 2017). Additionally, the availability of natural water resources has been decreased because of the influences of climate change and contamination. Climate change can directly affect the water cycle, causing in several countries the reduction of river flows, affecting the availability and quality of water for flora and fauna and the intake of drinking water. Rising sea levels have a severe effect on coastal aquifers, an important source of water supply for cities near the coast and for regional water supply systems (WWAP, 2009). Organic matter, nutrients, pharmaceutical and personal care products, poly- and perfluoroalkyl substances, biocides, heavy metals, dyes, radionuclides, plastics, nanoparticles and pathogens are among the pollutants of major concern (Villarín and Merel, 2020). Heavy metal ions are among the most released contaminants, and for this reason they are particularly worrisome (Azimi et al., 2017). Heavy metals are elements presenting an atomic density greater than 4 g/cm^3, therefore include copper (Cu), cadmium (Cd), zinc (Zn), lead (Pb), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), niquel (Ni), manganese (Mn) iron (Fe) and platinum (Pt) group elements (Ahmad et al., 2020; Duruibe et al., 2007). These metallic toxic elements are daily released into the water from diverse natural and anthropogenic sources, since they can enter into the aquatic environments through industrial discharges, mining and agricultural runoffs, and consumer wastes, or even from aerosols and acidic rains (Vardhan et al., 2019; Carolin et al., 2017). In several places around the world, the average concentrations of Cr (413.27 µg/L), Mn (2562.15 µg/L), Fe (1654.05 µg/L), Co (3994.82 µg/L), Ni (945.86 µg/L), As (3981.78 µg/L), and Cd (180.88 µg/L) found in surface water bodies are well above the maximum allowed values for drinking water (Kumar et al., 2019). This represents a big concern for the public, local governments and international organizations.

Heavy metals are not biodegradable, therefore they tend to bioaccumulate, which is their overtime increase of concentration in living organisms (Fu and Wang, 2011). They are also persistent and can directly or indirectly affect various organisms due to biomagnification. Heavy metal ions, such as Cr, Pb, As, Cd and Hg, have been classified as carcinogens or toxic, because in very low concentrations they can induce damage in multiple organs. Cr^{6+} exposure increases the risk of gastric cancer (Jaishankar et al., 2014), cancers of skin, liver, prostate, kuffer cell were associated with As (Kim et al., 2015). Long term-exposure to these metallic elements may result in slowly progressing neurological, muscular and physical degenerative processes, eventually leading to cancer (Aldaz et al., 2020; Jaishankar et al., 2014). The Cd and Pb enhance the mortality risk of several cancers, including lung, esophageal, and gastric cancer (Yuan et al., 2016). This damage is originated through a series of mechanisms that produce an unbalance reactive oxygen species that can induce oxidative stress and affect the main metabolic processes in the human body (Fu and Xi, 2020). Metals can also affect aquatic organisms (e.g. phytoplankton, zooplankton, and fish), accumulating in several organs and causing oxidative damage, endocrine disruption, and depression of the immune system, which can also affect survival and growth (Le et al., 2019). These effects, as well as the potential ecological impacts of heavy metals, require the development of technologies to efficiently remove them from water.

Multiple approaches for the remediation of polluted water, specifically heavy metal pollutants have been tested (Ahmad et al., 2020; Lee et al., 2019; Bethke et al., 2018; Carpenter et al., 2015). Conventional treatments such as chemical precipitation, ion exchange, and electrochemical removal for heavy metal removal from inorganic effluents can be used. However, these technologies present many disadvantages including incomplete removal, high-energy requirements and production of toxic sludge (Barakat, 2011). Some additional difficulties could be associated with the capital and technical requirements for installation, operation, and maintenance, which can result in an inadequate application of these technologies, particularly in decentralized contexts where the main challenge is the choice of the type of treatment system to be used from small communities, buildings and homes in remote areas and developing countries. Thus, the scientific community has increased their attention on the search of renewable and environmentally friendly solutions (Bravo, 2014).

This review attempts to summarize the main sources of heavy metals, their critical issues, and health effects on humans. We also discuss the techniques that can be used to detect these pollutants, and the factors that affect the removal process from contaminated waters. This is followed by a discussion about the main treatment technologies, which are categorized in primary, secondary and tertiary according to their features.

Chapter 2

2. Motivation

2.1. Problem statement

During the last decades, environmental concerns progressively escalate worldwide since the number of pollutants has significantly increased following the development of chemical and biological compounds being used in association with a series of resources and technologies (Patel et al., 2018). These pollutant products include pharmaceuticals and personal care products, endocrine disruptors, illicit drugs, heavy metals, gasoline additives, and many other pollutants (Verlicchi et al., 2010). Heavy metals are considered highly dangerous due to their toxicity, accumulation, non-biodegradable nature, and resistance. Once introduced into aquatic environments can represent an alarming concern for both the environment and human health. For this reason, we urgently require treatment processes to eliminate heavy metal water pollution as (Lim and Aris, 2014). It is essential to develop treatments with high removal capacity, ecological and economic viability, overcoming the disadvantages presented in conventional treatment methods. (Vardhan et al., 2019).

2.2. Objectives

General objective

To study the pollution generated by heavy metals in water resources, to understand the different sources of pollution, the influence of heavy metals on human health and the various technologies used for the detection and removal of heavy metals to date.

Specific objectives

1. To evaluate the main sources of heavy metals, to understand the main natural and anthropogenic activities that generate pollution in water, and the effects that each heavy metal has on human health.

2. To evaluate water pollution by heavy metals in Ecuador, and to bring up to date the current situation of the heavy metals in the context of the main production activities in Ecuador.

3. To identify the methods used in the detection of heavy metals in the aquatic environments and to understand the advantages and limitations of each method.

4. To analyze the different types of treatments for the removal of heavy metals from wastewater and to understand the advantages and limitations of each treatment in order to identify the most promising ones.

Overview

This study consists of 4 chapters, which are structured as follows:

Chapter 1 describes the contamination generated by heavy metals in aquatic systems, the possible effects that this pollutant presents, and the importance of seeking removal treatments for heavy metals from aquatic environments.

In Chapter 2 provides the background on the problems associated with heavy metals in the different water resources is indicated, as well as the objectives set for this study and its scope.

Chapter 3 contains a bibliographic review of all the topics considered in this study, the main sources of contamination of heavy metals, their toxicity, and the health problems they cause in humans are presented; in addition, some of the methods of detection and treatment of heavy metals are pointed out along with their limitations and advantages that each one presents; a review of the pollution generated by heavy metals in Ecuador and its impact is also presented.

Chapter 4 contains the conclusions that summarizes the overall study.

Chapter 3

3. Theoretical Framework

Water is one of the most important natural resources for the planet, it allows the well-being and socio-economic development of human beings, in addition to maintaining a balance between the ecosystem and its various components. Water represents 71% of the Earth's surface, but the percentage of freshwater that can be consumed by humans is around 2.5% (Azdiya Suhada et al., 2016). The United Nations Organization states that the growth of the planet's human population has increased at an accelerated rate, generating a direct increase in freshwater consumption. According to Boretti and Rosa, (2019) "Water scarcity currently affects 7.7 billion people. In 2050 when the world population reaches between 9.4 and 10.2 billion, a 22 to 34% increase, the strain on the water system will collapse" (Boretti and Rosa, 2019). This increase raises several doubts and precautions about the available water sources, which can be used for human consumption and their activities in the industries, agriculture, and farming (Vasantha and Jyothi, 2020). According to Sophia & Lima, (2018) "Humans use about 70% of fresh water for irrigation, 20% for industrial use and 8% for domestic use." However, the availability of various water sources is threatened due to the contamination generated in recent decades by pollutants (Sophia and Lima, 2018).

According to Bolisetty et al., (2019), it is estimated that approximately 2 million tons of industrial, and agricultural waste are discharged into the oceans, lakes, rivers, and groundwater worldwide. This generates several outcomes regarding the environment and human health because according to reports, the consumption of this type of water has killed 14,000 people every day (Bolisetty et al., 2019). Water pollutants mainly consist of organic, inorganic, biological, and microscopic pollutants. Heavy metals are one of the main inorganic pollutants found in waters, with alarming exponential growth in recent decades (Carolin et al., 2017). The heavy metals are the main pollutant at 31%, following by mineral oil at 20% (Bolisetty et al., 2019).

3.1. Sources of water pollution

The sources of heavy metals in the environment can be classified into two categories: natural and anthropogenic. Natural sources of heavy metals in the environment include collecting metal-containing rocks and volcanic eruptions (Ali et al., 2019). Anthropogenic activities such as industry (e.g., mining, fossil fuel combustion, metal processing), agriculture (pesticides), and domestic activities (e.g., medical devices, garbage, detergents) (Vareda et al., 2019; Azimi et al., 2017; Carolin et al., 2017). Figure 1 summarizes the major sources of heavy metal pollution. Most of the heavy metal ions are introduced into the environment by anthropogenic activity such as mining, agriculture smelters, and other metal-based industrial operations, which accumulates in their given chemical form or in combination with other metals, making it difficult to remove them from water.

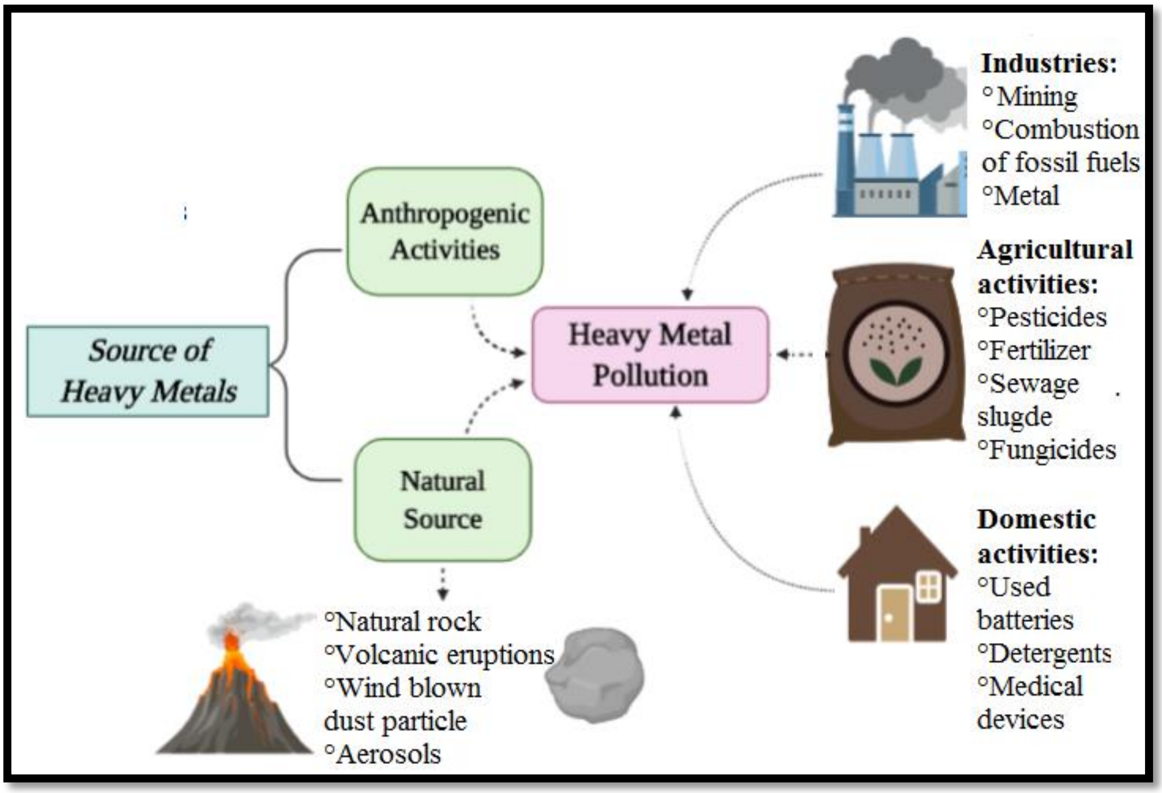


Figure 1. Illustration of sources of heavy metal pollution in the environment. Adapted from: Vareda et al., 2019; Azimi et al., 2017; Carolin et al., 2017.

Industrial activities are the main source of water pollution. The wastes produced during the manufacturing processes contain a different concentration of pollutants that are directly discharged into water sources. Among the main industries that generate organic and inorganic pollutants are those that in their manufacturing processes include working with paper and pulp, textiles, chemicals, cooling towers, and boilers, among other factors. This composition and the various combinations of products and machinery produce a number of contaminants of greater or lesser proportion, in addition to a greater presence of toxicity depending on the material used (Carolin et al., 2017). According to World Water Assesment Programme, (2017), "Approximately 80% of all industrial and municipal wastewater in the developing world is released into the environment without any prior treatment" (WWAP, 2017). The result is continuous deterioration in water quality with direct effects on human health and ecosystems.

The mining industry theatres a crucial role in the economies of both developed and developing countries. For example, countries like China, the United States, and Russia are largely dedicated to mining (Vélez-Pérez et al., 2020). This activity generates a large presence of heavy metals that are eliminated due to the extraction of the mineral and transported through nearby rivers and streams. The metals are present in such aquatic systems as dissolved-metal species in the water or as part of the sediments. These metal species tend to be stored in river sediments or seep into groundwater, generating further pollution (Duruibe et al., 2007). Heavy metals cause scarcity and contamination of water due to its requirement in mining processes, prevent the growth of crops due to soil erosion, cause serious health problems on animals and members of the local human communities (Birn et al., 2018).

3.2. Toxicological effects of heavy metals

The discharge of heavy metals into water sources can lead to different physical, chemical, and biological disorders. The nature and degree of change depend largely on the concentration of heavy metals in the water (Vardhan et al., 2019). Heavy metals once released into water sources become hydrated ions that are highly toxic. These hydrated ions interrupt the enzymatic process (Mokarram et al., 2020).

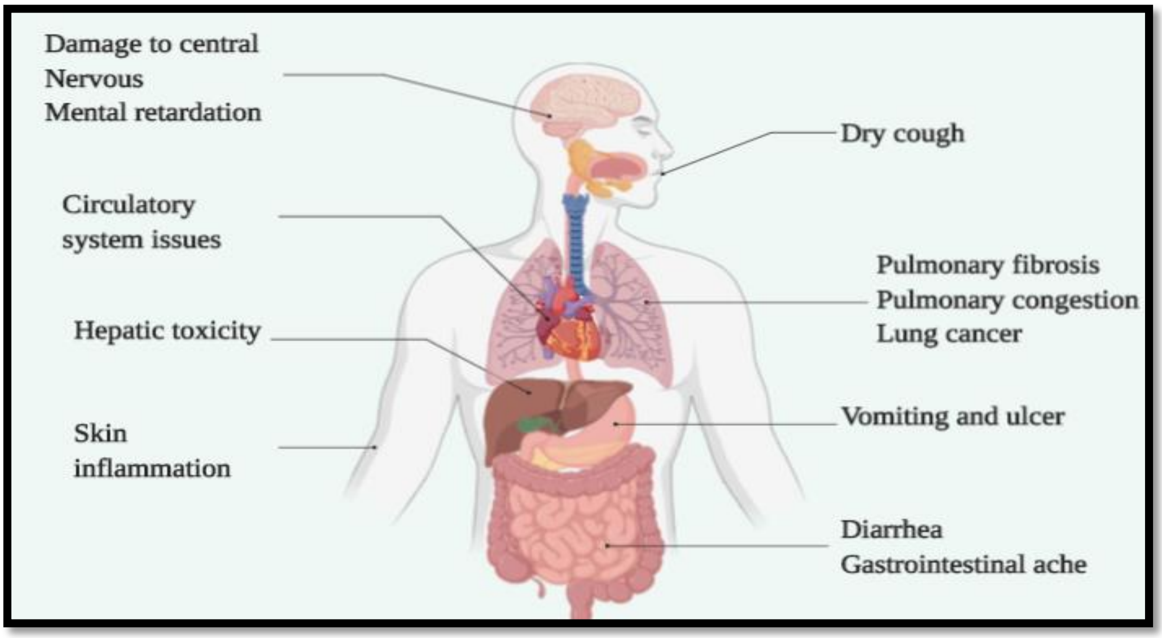


Figure 2. Toxicity effects of heavy metals on the human health. Adapted from: Fu and Xi, 2020.

There is also the presence of heavy metals that are considered essential for living beings because living beings require certain trace levels for their metabolic activities. In this regard, metals such as Co, Cu, Cr, Fe, Mg, Mn, Mo, Ni, Se and Zn are essential nutrients for some biochemical and physiological functions (Tchounwou et al., 2012). Nevertheless, an excess concentration of these heavy metals can lead to serious problems in human health such as muscular, physical and neurological degenerative processes (Azeh Engwa et al., 2019). As and its inorganic forms (arsenite and arsenate) are considered lethal for the environment and living beings. The sources of As are natural, industrial, and domestic, among others (Jaishankar et al., 2014). Around 140 million people in 50 countries regularly drink water that contains high levels of arsenic according to value references (10 mg/L) establish by the World Health Organization (WHO) (Bolisetty et al., 2019). Heavy metal toxicity can lead to various human health-related problems that can range from damage or decreased central nervous and mental activities, damage to the lungs, liver, kidneys, blood compositions, and other key organs. Figure 2 shows some effects of heavy metals in human health. Long exposure periods to toxic heavy metals have been associated with muscular dystrophy, Alzheimer's disease, different types of cancer and multiple sclerosis (Fu and Xi, 2020). The effects of heavy metals on humans along with their toxicity as reported by the WHO, Food and Agriculture Organization (FAO), and United States Environmental Protection Agency (USEPA) are shown in Table 1.

Table 1. Concentration, sources, toxicity metrics, and effects of heavy metals.

Heavy Metal	**Anthropogenic Source**	**Maximum Concentration Level in water µg L^{-1}**			**Toxicity**		**Adverse effect on human health**	**References**
		WHO[b]	**FAO**[c]	**USA**	**Tolerable daily intake (mg/per day)**	**Lethal dose mg kg^{-1} bw**[a]		
Lead (Pb)	-Metal purifying -Pesticides -Vehicular emissions -Fertilizers -Coal -Gasoline	10	5000	15	0.025-0.052	94-158	Kidney and nervous system damage, mental retardation, and cancer to the human body	Wani et al., 2020; Vareda et al., 2019; Carolin et al., 2017; Pratush et al., 2018; Guerra et al., 2012; Fu and Wang, 2011; World Health Organization, 2010; Jones et al., 1979
Cadmium (Cd)	-Electroplating industries -Metallurgical industries -Petroleum products	3	10	5	0.018-0.052	4.4-6.2	Hepatic toxicity, lung cancer, and diseases respiratory system, kidney, liver, and reproductive organs	Vardhan et al., 2019; Vareda et al., 2019; Carolin et al., 2017; Guerra et al., 2012; World Health

	-Insecticides -Synthetic chemicals							Organization, 2010; Jones et al., 1979
Mercury (Hg)	-Fossil fuel combustion -Electronics industries -Plastic industries -Paper and pulp industries	6	------	2	0.03	5.1-10.0	Kidney, brain, reproductive and respiratory system damage.	Joseph et al., 2019; Vareda et al., 2019; Suhada et al., 2016; Fu and Wang, 2011; World Health Organization, 2010; Jones et al., 1979
Zinc (Zn)	-Metal alloys pigments -Electroplating -Industrial waste -Mining -Coal combustion	------	2000	------	15-20	16.1-25.3	Pain, skin inflammation, fever, vomiting, anemia	Vareda et al., 2019; Pratush et al., 2018; Carolin et al., 2017; Fu and Wang, 2011; World Health Organization, 2010; Jones et al., 1979
Nickel (Ni)	-Metal alloys -Battery plants -Electroplating industries -Pulp and paper mills -Fertilizers	70	200	------	0.089-0.231	------	Chest pain, breathing problem, nausea, diarrhea, skin eruption, pulmonary fibrosis,	Vareda et al., 2019; Pratush et al., 2018; Carolin et al., 2017; Suhada et al., 2016; Guerra et al., 2012; Fu and Wang, 2011; World

	-Petroleum refineries						gastrointestinal ache, renal edema.	Health Organization, 2010
Chromium (Cr)	-Leather industries -Tanning industries -Textile industry -Electroplating industries -Industrial Sewage -Anticorrosive products	50	100	100	0.013-0.099	------	Skin inflammation, liver and kidney damage, pulmonary congestion, vomiting and ulcer.	Vareda et al., 2019; Pratush et al., 2018; Carolin et al., 2017; Guerra et al., 2012; Fu and Wang, 2011; World Health Organization, 2010
Copper (Cu)	-Mining industries -Metallurgy -Chemical manufacturing -Steel industries -Electroplating industries -Fertilizers -Pesticides	2000	200	1300	10	4.0-7.2	Hair loss, anemia, kidney problems, and headache.	Vardhan et al., 2019; Vareda et al., 2019; Pratush et al., 2018; Carolin et al., 2017; Fu and Wang, 2011; World Health Organization, 2010; Jones et al., 1979

Arsenic (As)	-Electronics production -Pesticides -Livestock manures -Composts -Sewage sludge -Fly ash -Irrigation with municipal wastewater -Industrial wastewater	10	100	10	0.03	41	Skin damage, Circulatory system issues, and increases the risk of getting cancer	Joseph et al., 2019; Vareda et al., 2019; Srivastava et al., 2017; Ullah et al., 2017; Azimi et al., 2017; World Health Organization, 2010

[a] Bodyweight
[b] World Health Organization (2017)
[c] United States Environmental Protection Agency (2018)

3.3. Factors affecting heavy metals removal

Considering that each heavy metal has different properties and behaviors, it is necessary to analyze its interaction with factors such as pH, temperature, content of natural organic matter (NOM), and ionic strength, since it has been shown that they influence the removal of heavy metals from water sources. The purpose is to guarantee the removal of heavy metals with a high-efficiency index (Joseph et al., 2019). The following section describes the influence on pH, ionic strength, temperature, and NOM on the heavy metals and the interaction with water, consequently their elimination from domestic wastewater effluent, groundwater, rivers, and lakes. Figure 3 shows the effects that occur in the removal of heavy metals in water sources and their interaction with the factors of pH, temperature, ionic strength, and NOM.

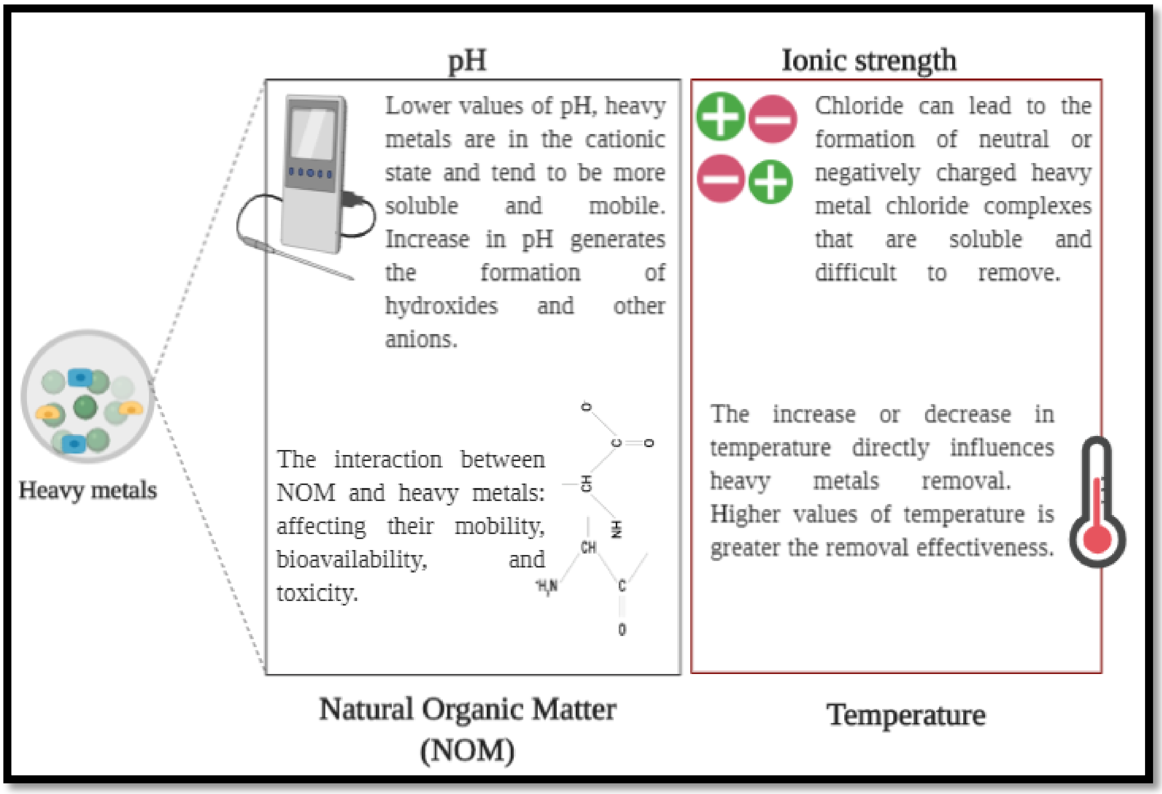


Figure 3. Factors influencing heavy metals removal: pH, temperature, ionic strength, and natural organic matter.

3.3.1. Influence of pH on heavy metals removal

The removal of heavy metals from the water can generate changes in the pH due to the addition of chemicals used by the treatment or due to biological instability that can alter the characteristics of the contaminated water source. Changes in pH have the potential to change the matrix of the water source to be treated and the properties of the surface of the medium, which affects the process of removing heavy metals (Ncube et al., 2018). According to Taşar et al., (2014), at neutral to lower pH values, heavy metals are in a cationic state, generating greater mobility and solubility of heavy metals present in water, which gives rise to new forms of metal ions. On the other hand, higher pH values generate the formation of hydroxides and other anions in the water, affecting the oxidation state of the heavy metal (Taşar et al., 2014).

In terms of treatment alternatives, Es-Sahbany et al., (2019), studied the elimination or reduction of heavy metals (Ni^{2+}) in wastewater by means of the adsorption technique with natural clay as a mineral adsorbent. Their work demonstrated that the variation in removal efficiency and adsorption capacity of Ni^{2+} ions depend upon the effect of pH. That is, nickel removal efficiency increases with increasing pH, in this study the pH ranged from 1 to 9. The results shows that from the pH to 7, the elimination rate of Ni^{2+} ions has a percentage of 75% of metal ion removal (Es-Sahbany et al., 2019). Moreover, several studies reported the influence of pH on the chemical reaction of heavy metal ions by forming precipitation of hydroxides in an aqueous solution. Metal ions such as Zn^{2+}, show a greater removal efficiency at pH ranging from 9 to 10, however the optimum pH was from 7 to 11 for the removal of the Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+}, allowing to easily form hydroxide precipitation and remove it from wastewater (Zhao et al., 2016).

3.3.2. Influence of temperature on heavy metal removal

Temperature is a parameter that in several studies has shown its influence on the removal process of heavy metals (Almomani et al., 2020; Joseph et al., 2019; Chen et al., 2010; Badmus et al., 2007). The increase or decrease in temperature directly influences heavy metals and their subsequent elimination from water sources. Among the tests carried out with different types of treatments, it has been identified that there is a greater removal effectiveness when the temperature is higher (Chen et al., 2010). For example, a study focused on the removal of heavy metals (Cd, Cu, Pb, and Ni) employing plants (*Fatsia japonica*, *Hovenia acerba and Pterocarya stenoptera*), this plants have potential to bind with metal cations. The results show that the removal efficiency of metals increases when the temperature reached the maximum level at 55 °C obtaining a removal percentage of 58.19% for Cu, 74.19% for Cd, 45.97% for Pb and 25.72% for Ni (Xu et al., 2020).

The effect of temperature on the adsorption capacity of Cu^{2+} and Pb^{2+} on hydrogels was investigated at different temperature conditions (22 °C, 30°C, 35 °C, and 40°C). The maximum adsorption capacity on hydrogels was reached at 30 °C for Pb^{2+} and 35 °C for

Cu^{2+}. An increase in temperature up to 40ºC increased slightly the removal outcome (Tirtom and Dinçer, 2020). Moreover, in a study using biomass from fungi *(Penicillium chrysogenum and Aspergillus ustus)*, the removal efficiency of heavy metals was tested at different temperatures 10, 20, 30, 40, 50 and 60 °C. As the temperature increased from 10 °C to 60 °C, the biosorption efficiency of the fungal biomass increased due to a higher affinity of the active sites of the biomass substrates leading to a higher attraction of heavy metal ions (Alothman et al., 2020).

On the other hand, a slightly increase in temperature has also been shown to lead to a decrease in the heavy metal efficiency of removal. The synthesis of a new magnetic iron oxide nanoparticle was used in the removal of Ni, Cu, and Al. The increase in temperature from 20 to 30 °C for Ni, shows a reduction in removal efficiency by 11% (92.8 to 82.3). (Almomani et al., 2020). In the case of Al, the results showed a 5% reduction as the temperature increases from 20 to 30 °C, and a 20% reduction as the temperature increases to 40 °C. The increase in temperature from 20 to 30 °C and then to 40 °C showed a reduction of 6 and 10%, respectively for Cu removal (Almomani et al., 2020). The obtained behaviors can be related to the fact that at higher temperatures the rate of the chemisorption mechanisms did not allow the heavy metals to reach new active sites on the nanoparticles (adsorbent) surface to improve the removal of metal. Also, the temperature can change the size of the pores of nanoparticles resulting into a less adsorption (Almomani et al., 2020). For instance, Sari et al., (2008), studied the adsorption of Cr onto red algae (*Ceramium virgatum*), the results showed that with increasing temperature in the algae the removal efficiency decreased from 90 to 78% (Sari et al., 2008).

3.3.3. Influence of ionic strength on heavy metal removal

The ionic strength is the total concentration of ions in the aqueous solution, as well as the chemical charge of these ions. This ionic strength influences the removal of heavy metal from water. According to Joseph et al., (2019) "The presence of chloride can lead to the formation of neutral or negatively charged heavy metal chloride complexes, which are soluble and difficult to remove from water" (Joseph et al., 2019). This was confirmed by a study in which a relationship was established between ionic strength and removal efficiency. The results showed that as the ionic strength increased, the removal efficiency for Cu^{2+} and Ni^{2+} decreased (Villaescusa et al., 2004). Due to a greater formation of chloride complexes of heavy metals which had low affinity for adsorption in water (Villarín and Merel, 2020; Kwiatkowska-Malina, 2017; Wang et al., 2016).

The adsorption process is affected by this factor because it can cause the inactivation of the ion exchange mechanism between heavy metal ions and the adsorbent. The adsorption capacity of Cu^{2+} using carboxylated alginic acid revealed a high removal efficiency; however, the ionic strength only had a slight effect on the Cu^{2+} removal capacity. This is due to the strongly bonded metals, such as the Cu^{2+}, that can be less affected by ionic strength (Jeon et al., 2005). The same occurred in a study using a porous magnetic material for the removal of Cr^{2+}, Pb^{2+}, Zn^{2+} and Cu^{2+} which concluded that an increase in the concentration of NaCl decreased slightly the magnetic material adsorption on metal ions (Hu et al., 2020).

The potential of bentonite for adsorption of Cu^{2+} and Ni^{2+} ions has been also investigated under various conditions including ionic strength. For instance, the sorption of Cu^{2+} and Ni^{2+} on bentonite increases with decreasing ionic strength at pH 5.5, maintaining a maximum adsorption value at NaCl concentrations lower than 0.05 M. (Musso et al., 2019). At high ionic strength, Ni^{2+} was more affected compared to Cu^{2+}, having a decrease in the removal efficiency (Musso et al., 2019). According to Le et al., (2019); Musso et al., (2019), this is due to an increase in ionic strength that can reduce the electrostatic repulsion of the molecules, increasing the aggregation of particles which reduces the amount of available binding sites in the system and decreases the sorption. On the other hand, a study conducted on an adsorbent compound (magnetic graphene oxide/chitosan composite beads) for the removal of heavy metals (Ni^{2+}) from aqueous solution showed that Ni^{2+} adsorption increased when the saline solution was highly concentrated (NaCl from 0.01 to 1). This is due to the reduction of the electrostatic repulsion between Ni^{2+} ions at high concentrations of salts in water (Le et al., 2019).

3.3.4. Influence of natural organic matter (NOM) on heavy metal removal

Natural organic matter (NOM) contains mainly humic and fulvic acids derived from the decomposition of terrestrial and aquatic animals and plants. The interactions between the hydrologic cycle, biosphere and geosphere produce that the water sources contain NOM (Fontmorin and Sillanpää, 2015). The influence of NOM on heavy metals can generate an alteration in the reactivity of heavy metals, affecting their mobility, bioavailability, and toxicity. However, it is not possible to determine exactly the degree of influence that this interaction can generate in the removal process of heavy metals of water source (Merdy et al., 2006).

In the case of Pb, this can form complexes with NOM in natural waters or wastewater, making it more mobile and more difficult to eliminate using conventional processes such as chemical precipitation, coagulation/flocculation. In a study conducted with powder activated charcoal supported titanate nanotube (TNTs@PAC) for removal Pb^{2+} show that the adsorption capacity of TNTs@PAC is influenced by dissolved organic matter due to the formation of complexes and weak interactions between nanotubes and organic matter (Ma, 2017). Lin et al., (2017) investigated the effect of NOM on the elimination of metal cations (Cd, Cu, Ni and Pb) using reverse osmosis in synthetic solutions using treatment solids of drinking water. The results show that a large amount of NOM affects the adsorption capacity, causing less removal of metals in the aqueous solution. In the case of Cd and Ni, the removal efficiency was slightly reduced in the presence of NOM, due to ionic competition, complex formation, and simultaneous chelation between metals and NOM. Cu and Pb were almost completely removed by sorption and precipitation (Lin et al., 2017).

3.4. Pollution by Heavy Metals

Pollution of various ecosystems has been caused by a constant and increasing emission of harmful substances, which are highly toxic. This increase has been associated with the industrial revolution. Approximately 40 % of the lakes and rivers of the planet have been polluted by heavy metals, mainly from human activities (Andino, 2020). Heavy metals are a source of contamination that in recent decades has increased, therefore taken research of effective treatments have been proposed to eliminate them as well as reducing any effects on human health. Many developing and developed countries must find a way to reduce the concentration of heavy metals from water environments. Moreover, for developing countries, the limitations are greater around this problem. The main limitation is a narrow economic capacity to develop and apply remedial technologies to eliminate heavy metals from their nations (Chowdhury et al., 2016). Research around this topic has been approached globally. The presence of heavy metals has been reported by different studies, where anthropogenic activities, urbanization, and the progress of countries represent key factors in increasing the concentration of these pollutants around the world. Roychowdhury et al., (2003), reported that in India, the concentration of As in drinking water was 107 μg/L. This result is approximately 11 times higher than the reference values reported by WHO (Roychowdhury et al., 2003). Fernandez-Luqueño et al., (2010) conducted an investigation on the presence and exposure to As in Latin America, approximately 4.5 million people in Latin America are exposed to a high level of As that were in levels greater than 50µg/L (Fernández-Luqueño et al., 2013). Likewise, Xu et al., (2017) reported that in 9 coastal rivers of the Laizhou Bay basin, there was the presence of various concentrations of Cd (6.26 mg/L), Cu (2755.00 mg/L), and Zn (2076.00 mg/L) in drinking water (Xu et al., 2017). Moreover, Sanchez et al., (2008) investigated in the Cuyuni river basin (Venezuela) an artisanal gold (Au) mining extraction that has resulted in significant Hg contamination in rivers due to the excessive use of Hg during the Au amalgam processes (Sanchez et al., 2008).

In developing countries, anthropogenic activities are playing a major role has generated concerning the accumulation of heavy metals in this nation. Leventeli et al., (2019) conducted an investigation to evaluate water pollution in the Antalya, Turkey. The city, in urban development, due to the increase in population and settlements. The presence of various heavy metals such as Sr, Fe, Al, Mn, As, Ni, Cu, Pb and Cr were found in two main rivers of the city (Leventeli et al., 2019). Specifically, the concentrations of Sr and Al exceeded the allowed values of Standard specification for reagent water D1193-77. The authors identified as the cause of such heavy metal contamination was anthropogenic activities including industrial development and urbanization (Leventeli et al., 2019).

The following section describes the presence of various heavy metals in Ecuador, a country rich in flora y fauna biodiversity, which has been negatively affected by anthropogenic activities that are constantly present on the Ecuadorian geography.

3.4.1. The incidence of heavy metals in Ecuador

Ecuador is located the western extreme of South America. The country's geographic borders are to the north with Colombia, to the south and east with Peru and to the west with the Pacific Ocean. The total surface of Ecuador is 256,370 km^2, its land is divided into coastal and Andean regions, Amazonia and Galapagos Islands. Ecuador is one of the countries with the highest biodiversity worldwide, due to the number of species per unit area and the natural environments or ecosystems present. This biodiversity is given by various factors such as the presence of the Andes, the inter-Andean alley, the oceanic currents (Humboldt Current and the warm currents of the north), and volcanic activity. Factors that favor the growth and abundance of flora and fauna (Bravo, 2014).

Ecuador is a developing country; however, it is still behind from being a developed nation in several aspects of vital importance such as the contamination found in the soil and water due to the lack of an adequate waste management system (Zach, 2000). Given the biological wealth of Ecuador and the threats that revolve around biodiversity, it has been shown that agricultural activity, oil extraction, and mining are the main industries that pose a risk to the biodiversity in Ecuador. These industries are the major polluters to the water in the country (Sánchez-Mateos et al., 2020). Figure 4 highlights the main sources of heavy metal contamination in aquatic environments in Ecuador that include the petroleum, agriculture and mining industries.

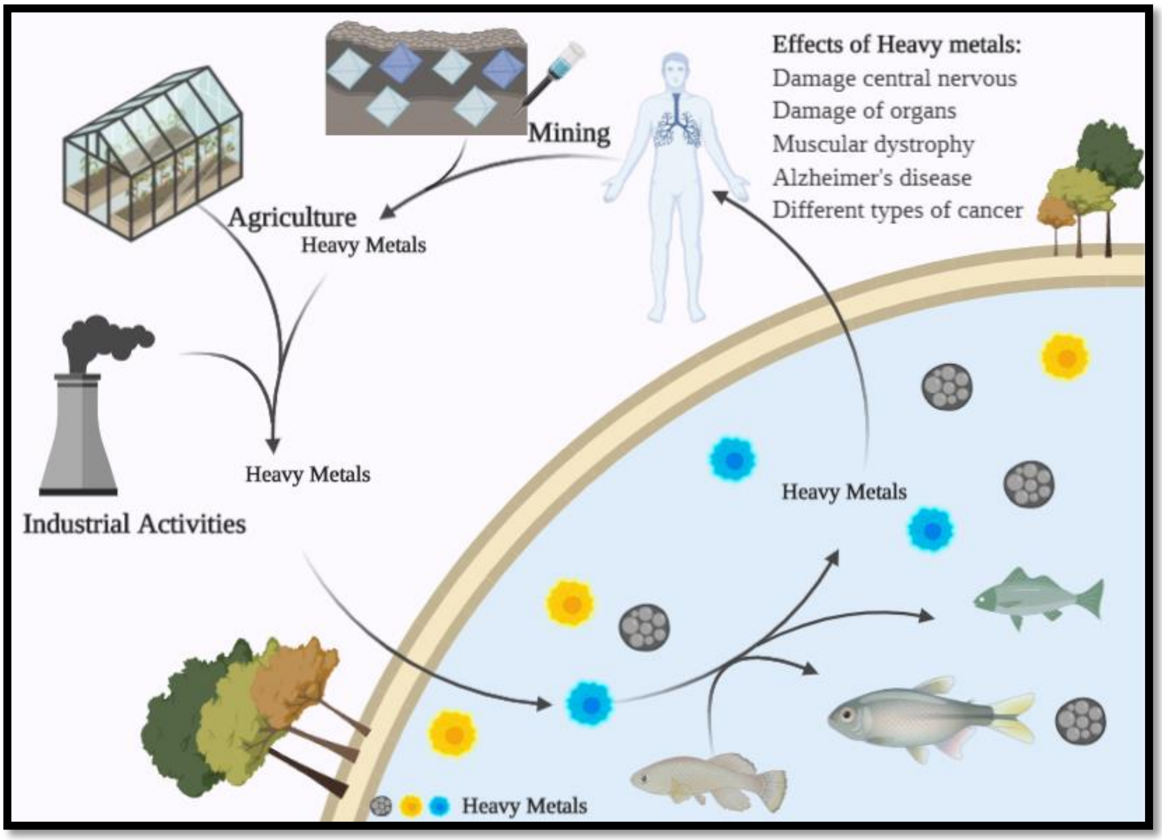


Figure 4. Petroleum, agriculture, and mining industries as the main sources of heavy metal pollution in Ecuador. Adapted from: Sánchez-Mateos et al., 2020.

Agricultural Activity

Agriculture is the main source of economic income for the country. This activity uses water from rivers and canals to irrigate crops. Contamination passes from the water to the soil and from there to the food cultivated on it, which will later be introduced to the market for consumption; its concentration increases as it goes through the food chain with the resulting increase in health risk (Sánchez-Mateos et al., 2020). A study in the provinces of Cotopaxi and Tungurahua, where the main activity is agriculture, was conducted to determine the concentration of heavy metals (As, Cd, Cr, Pb, Hg, and Ni) from the rivers. The results showed that the highest levels were Ni (<0.005mg/L), Cr (22.2 and 30.2 mg/L), Cd (0.23 mg/L), As (0.062 - 0.067 mg/L), Pb (0.2 - 0.18 mg / L), and Hg (0.0084 mg/mL). The authors concluded that all metals except Ni exceeded the limits established by Unified Text of Secondary Environmental Legislation (TULSMA) (Sánchez-Mateos et al., 2020).

The depletion of surface water sources has generated the exploitation of groundwater to satisfy various economic sectors, being agriculture one of them. In the La Peaña area, El Oro province, a study was conducted to determine the concentration of heavy metals in the groundwater wells from several banana farms (Castillo-Herrera et al., 2019). The heavy metal levels found for Hg between (1.10 - 0.10) μg L, Pb at ≤ 5.00 μg/L, Cd at ≤ 0.80 μg/L, and Mn between (1240 and 0.06) μg/L. However, the presence of these metals did not exceed the maximum limits established by USEPA (Castillo-Herrera et al., 2019). Another investigation conducted in the Yahuarcocha Lake, Imbabura province, where there are several anthropic activities such as agriculture, livestock, hotels, sports, and recreation activities that, together with inappropriate environmental practices and the lack of collaboration of the population, increase the contamination of this body. Causing the eutrophication of the lake, which produces a decrease in the water mirror and the expansion of aquatic plants (Andino, 2020). In this study, the concentration of Pb and Cr was quantified in roots of T. Latifolia (aquatic plant that is hyper-accumulator of heavy metals), sediments, soil, and water samples during the dry and rainy seasons. In the plant roots the concentration Pb were 4 - 5 ppm in the dry period, 1 - 2 ppm in the rainy season, while for Cr the concentration were 5 - 1 ppm in the dry season and 0.1 - 0.2 ppm in the rainy season (Andino, 2020). The concentration of Pb and Cr in soil samples, Pb at 56-112 ppm in the dry season and 35 - 42 ppm in the rainy season; while, Cr at 3 - 12 ppm in the dry season, and 1 - 2 ppm in the rainy season. The concentrations of Pb and Cr in the sediments, Pb at 64 - 133 ppm in the dry season and 24 - 93 ppm in the rainy season and Cr at 5 - 29 ppm in the dry season and 2 - 13 ppm in the rainy season. The concentration of Pb in water was at 6 - 20 ppb and 2 - 3 ppb in the dry and rainy seasons, respectively (Andino, 2020). Cr in water was in the range of 4-14 ppb in the dry season and 1-4 ppb in the rainy season. The Pb concentrations in water samples exceed the permissible values according to United States regulations (0.0015 ppm), however, according to current environmental regulations in Ecuador (Acuerdo 097A-2015), the permissible values permitted ranges a little higher (0.2 ppm) (Andino, 2020).

Mining

According to various historians, mining activity dates from the Inca period to the present day. Precious metals, including gold, have been mined in Ecuador. This traditional mining process has caused an increase in contamination in various parts of the country (Pesantes et al., 2019; Garcia et al., 2012). The mining area of Ponce Enríquez, in the province of Azuay, focused on the extraction of gold, was the subject of study to determine the presence of various metals such as As, Cd, Cu, Pb, and Zn in the rivers Fermín Norte, Guanache, and Villa (Pesantes et al., 2019). Approximately 10,000 tons of mining waste is discharged annually into the rivers of this area. The results showed that the concentration of these heavy metals exceeded the referential values for metals established by the Canadian guidelines. The results were Cu (483.7-687.8) ppm, the reference value is 18.7ppm; Pb (20.3-31.0) ppm, the reference value is 35 ppm; Zn (132.5-98.7), the reference value 123 ppm; Ni (42.6-5960.9), the reference value 21 ppm; As (842.8-589.03), the reference value 5.9 ppm; and Cd (0.73-9.3), the reference value 0.7 ppm (Pesantes et al., 2019).

The Puyango river basin, in southern Ecuador, is a region with primary small-scale gold and silver mining activities. Specifically, 110 processing-mining plants are located on the riverside, which generate significant contamination in river. In this study, a seasonal comparison was made (dry and rainy season) of the concentrations of metals in surface waters, sediments, and particles of the various river tributaries (Garcia et al., 2012). The study determined the presence of As, Hg, Mn, and Pb. The highest concentration levels in the river were for Pb and Mn, reaching 159 μg/L and 63 μg/L, respectively. Moreover, Mn reached 970 μg/L in the rainy season, similar to Pb with 510 μg/L, while As with 153 μg/L (Garcia et al., 2012).

Petroleum Industry

In Ecuador, the main oil sites are in the provinces of Sucumbíos, Pastaza, Morona Santiago, Santa Elena and Napo. The areas of greatest influence for oil exploitation are the Santa Elena Peninsula and the Amazon region (Galeas Bolaños, 2013). The oil activity has been performed since 1924 by the company Anglo Ecuadorian Oilfields Ltda., but it was not until the end of the 1960s that the heyday of oil began in the Amazonian sites.

The incorporation of oil in Ecuador became the main engine of economic growth in the country, representing the main source of public revenue (Domínguez Pazmiño, 2010). However, this activity has generated environmental pollution in both flora and fauna, as well as directly affecting the ecosystems of indigenous populations. In the oil industry, all phases of operation have negatively impact on the environment, because they result into deforestation and contamination of soils and rivers (Galeas Bolaños, 2013).

In a study conducted in the basins of the Aguarico, Napo, and Esmeraldas rivers, sites of oil influence in Ecuador, the concentration of some elements (K, Mg, Na, Fe, Mn, and Al) was determined in a fine fraction of sediments found in rivers, because they constitute a danger to aquatic biota and human health of local communities (Pérez Naranjo et al., 2015). The concentration ranges of the elements found were (18-49) mg / g for Fe, (26-59) mg/g for Al, (3-15) mg/g for K, (3-13) mg/g for Mg, (1 -11) mg/g for Na and (0.38-0.89) mg/g for Mn. In this study, it was concluded that the Fe concentrations exceeded by 15% the permissible limits established by the USEPA. In the case of the Mn exceed the maximum permissible levels by 23.95% according to National Oceanic and Atmospheric Administration (NOAA) (Pérez Naranjo et al., 2015).

3.5. Detection of heavy metals

The heavy metal removal process requires examining several essential factors such as contact time, dosage, temperature, pH and the concentration of heavy metals, to be carried out efficiently. Before this removal process, it is necessary to establish or search for an available technique that allows us to detect and quantify the concentration level at which the metal is present in the water source. Several methods for the detection and quantification of heavy metals have been developed; however, these must meet certain criteria, such as being cost-effective, environmentally friendly, selective, and having adequate sensitivity to detect traces of heavy metals with good precision (Malik et al., 2019). A technique that meets all these criteria has not yet been developed; however, the evolution and combination of various techniques have allowed the determination with major efficiency of the concentration of heavy metals in water sources or other anthropogenic sources of contamination.

3.5.1. Methods of detection of heavy metals in aquatic systems

The rapid and accurate detection of heavy metals in water samples has been developed in the last decades. The following section describes the heavy metal detection techniques divided into three categories; the classification was based on spectroscopic, electrochemical, and optical techniques. The detection limits of different heavy metals in aquatic environments, according to the several techniques that may be used, are shown in Table 2.

Spectroscopic detection

The spectroscopic detection are developed in complex sample matrices such as natural and wastewater, food, air, and soil. This category include atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray fluorescence spectrometry, inductively coupled plasma optical emission spectrometry (ICP-OES) (Buledi et al., 2020; Malik et al., 2019; Bansod et al., 2017), ion chromatography ultraviolet-visible spectroscopy (IC-UV vis), and atomic fluorescence spectroscopy (AFS) (Chen et al., 2018; Gumpu et al., 2015). The advantages that these techniques include the simultaneous determination of the concentration of heavy metals, low detection limits in the femtomolar range. Nevertheless, these techniques are expensive, need trained personnel, and complex equipment (Kaur et al., 2016). All the mentioned techniques are limited to laboratory use; if they are in portable field versions, they have an inadequate sensitivity, the results that are obtained have less accuracy performance from the environmental sample (Kurup et al., 2017).

The ICP-MS technique employs solid, liquid, and gaseous samples, it is able on detecting multiple metals at the same time and allow to detect extremely low detection limits ranging from part per billion (ppb) to trillion (ppt). Combined with techniques such as laser ablation or chromatography, detection limits can be optimized. The results obtained have greater precision regarding the concentration of the heavy metal in the sample (Voica et al., 2012). For instance, ICP-MS was used for analyzed rainwater samples collected from Palestine were analyzed for the content of different trace heavy metals (Malassa et al., 2014). The study found the concentration of Cr (22.6–165.5), Mn (4.56–552.3), Co (0.34– 4.93), Ni (9.15–87.28), Cu (21.93– 925.5), Zn(22.19–302.98), Mo (6.17), Ag (149.7), Cd (2, 19), Pb (12.94–486.4), and Bi (1.33–96.52)(µg/L) (Malassa et al., 2014). AAS technique has the ability to identify multiple heavy metals simultaneously from a single pattern in the emission spectrum associated with the elements present in the sample (Zhong et al., 2016). AAS determined Cu^{2+}, Pb^{2+}, and Cd^{2+} ions in water. This technique detection limit has been reported were between (0.2 – 3) µg/L. (Shirkhanloo et al., 2011). The main advantage of XRF is the non-destructive analysis of solid and liquid samples. Portable XRF equipments also available, but they have high detection limits, so not very useful for trace detection (Kodom et al., 2012). Moreover, XRF allows the detection of Cu and Pb in polluted water Langshan area, China; however, it was established that the minimum detectable concentration of the method in the samples collected was 21 ppm for Cu and 28 ppm for Pb (Zhou et al., 2018).

Electrochemical methods of detection

Electrochemical techniques can undergo various changes in their electrical parameters due to the interaction of heavy metals with water. These include changes in current, voltage, electrochemical impedance, charge, and electroluminescence. Among the main techniques included in this detection method are potentiometric, amperometric, voltammetric, coulometric impedance, and electrochemiluminescent (Pujol et al., 2014). Several of these techniques have had a broader development such as voltammetric and potentiometric when combined with nanomaterials that allowed the improvement of the techniques resulting in linear sweep anodic voltammetry (LSASV), square wave anodic sweep voltammetry (SWASV), differential pulse anodic sweep voltammetry (DPASV), cyclic cathodic sweep voltammetry (CSV), cyclic voltammetry (CV) and chronopotentiometry. Another area under development is the electrochemical biosensors together with the combination of metallic nanoparticles such as nanowires, nanorods and nanospheres are helpful in the detection of heavy metals in samples of aquatic systems (Gumpu et al., 2015).

In general, electrochemical techniques are inexpensive, easy to use, and reliable, they also have a short analytical detection time and a higher limit of detection (LOD). These techniques allow fabricating small circuits in the form of portable devices for monitoring contaminated samples *in situ* (Bansod et al., 2017). Nevertheless, electrochemical techniques have limitations, because the polluted environments are always contaminated with a combination of various heavy metals, competition between the pollutants in water must be considered, which makes these methods not, a good alternative when other metal cations coexist in the sample because they will be generating less detection sensitivity in the sample (Chen et al., 2018).

Optical methods of detection

Optical sensors or test strips for heavy metals in aqueous solutions have been developed. Among the techniques, there is the application of fluorophores or indicator dyes that can be quenched or undergone a binding reaction, biosensor tests or the combination of an ionophore with a pH indicator (Mayr, 2002). With the development of technology, research has begun on portable optical enzymatic biosensors with disposable chips for enzymatic bioassays. Lukyanenko et al., (2019) developed a device with the integration of disposable microfluidic chips. The results indicated that the device can be used for a detection limit of Cu^{2+} of 2.5 mg/L in water samples (Lukyanenko et al., 2019).

Optical detection methods have several limitations including expensive and complex equipment, high precision, and not suitable for field applications. Therefore, the development of fast, low-cost, simple and reliable techniques suitable for spot and *in situ* measurements of heavy metal ions is an area of ongoing research (Malik et al., 2019; Bansod et al., 2017).

Table 2. Detection of heavy metals in aquatic systems as reported by various techniques.

Heavy Metal	*Technique*	*Limit of detection*	*References*
Lead (Pb)	AAS ICP-MS ICP-AES Potentiometry Amperometric SWASV CV	1 µg/L 0.02 µg/L 0.0091 µg/mL $1x10^{-6}$ mol/L 1.9×10^{-8} mol/L 1.8×10^{-9} mol/L $9x10^{-8}$ mol/L	Bobaker et al., 2019; Malik et al., 2019; Tan et al., 2018; World Health Organization, 2010
Cadmium (Cd)	ICP-MS AAS ICP-AES Potentiometry Amperometric	0.01 µg/L 2 µg/L 0.0010 µg/mL $1x10^{-7}$ mol/L $1.78x10^{-7}$ mol/L	Malik et al., 2019; Tan et al., 2018; World Health Organization, 2010
Mercury (Hg)	AAS	0.05 µg/L	

	ICP	0.6 µg/L	Malik et al., 2019; World Health Organization, 2010
	AAS	5 µg/L	
	Potentiometry	7x10 $^{-8}$ mol/L	
	Amperometric	1.8x10 $^{-8}$ mol/L	
	CV	1x10 $^{-9}$ mol/L	
Nickel (Ni)	ICP-MS	0.1 µg/L	
	AAS	0.5 µg/L	
	ICP-AES	10 µg/L	
Chromium (Cr)	AAS	0.05–0.2 µg/L	
	ICP-AES	0.0024ug/mL	
Copper (Cu)	ICP-MS	0.02–0.1 µg/L	
	ICP–optical emission spectroscopy	0.3 µg/L	
	AAS	0.5 µg/L	
	ICP-AES	0.0047 µg/mL	
	Amperometric	7.4x10^{-6} mol/L	
Arsenic (As)	ICP-MS	0.1 µg/L	
	AAS	2 µg/L	

3.6. Removal of heavy metals from aquatic systems

The removal of heavy metals from wastewater has a different process depending not only on the metal to be removed but also on the multiple interactions with the environment, which were mentioned in a previous section. Due to all these interactions, various methods have been established, each with a different degree of success (Carolin et al., 2017). However, each technology has certain advantages and disadvantages that limit whether these methods can be completely effective for pollutant removal. Among the main deficiencies from these methods are the production of secondary waste, high cost of operation and maintenance to mention a few. For these reasons, it is crucial to develop ecological-economic and feasible alternatives for the removal of heavy metals from various water sources (Vardhan et al., 2019).

3.6.1. Primary, secondary, and tertiary, water treatment technologies

Several of the water sources are contaminated by heavy metals, each with a different level of contamination. For this reason, several treatment processes are usually employed together (Quach-cu et al., 2018). Wastewater treatment technologies have been classified into three stages: primary treatments, secondary treatments, and tertiary treatments. Depending on the purity standards and the number of contaminants present in the water source, wastewater treatment plants can employ one or more of these technologies at each treatment stage (Ince and Kaplan Ince, 2020; Yenkie et al., 2019). Figure 5 describes the main technologies involved in each treatment stage and their application to different classes of pollutants (e.g., organic, inorganic, and biological).

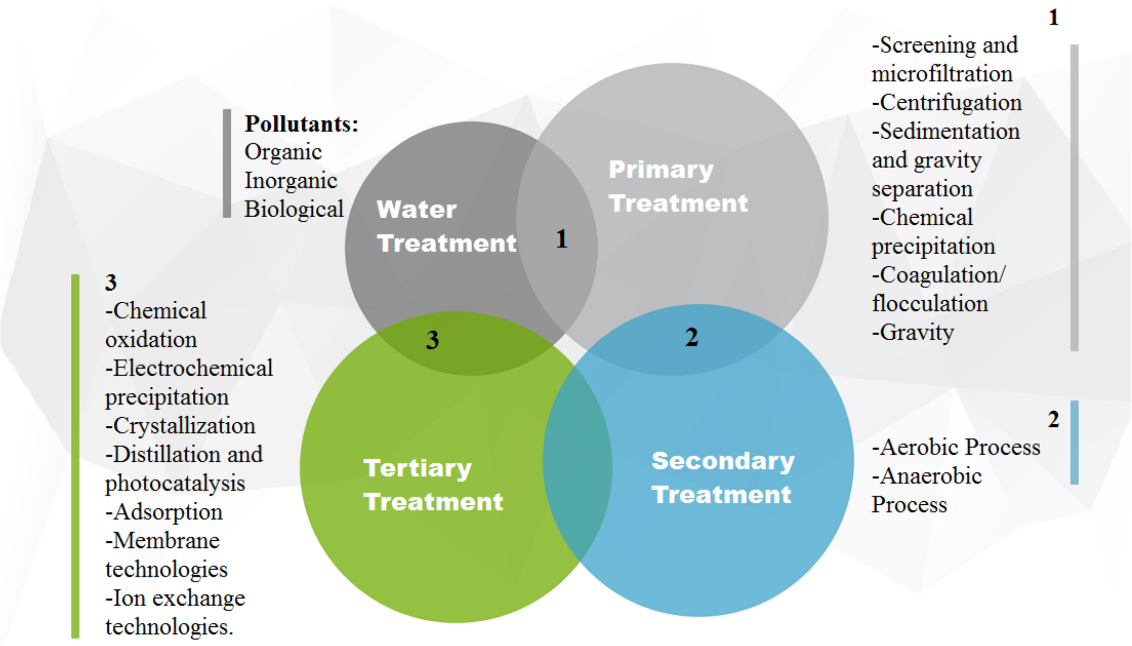


Figure 5. Water Treatment Stages and Technologies for pollutant removal. Adapted from: Ince and Kaplan Ince, 2020; Yenkie et al., 2019

Primary treatment focuses on the removal of organic matter and suspended solids from wastewater through physical and chemical processes, which include methods of screening and microfiltration, centrifugation, sedimentation and gravity separation, chemical precipitation, coagulation, gravity, and flocculation. In the case of water contaminated with high concentration heavy metals, microfiltration, chemical filtration, coagulation, and flocculation are the important primary technologies (Bolisetty et al., 2019; Yenkie et al., 2019). Secondary treatments are based on natural microorganisms capable of converting organic and inorganic contaminants into simpler and safer substances, which allow greater removal efficiency. This type of treatment is divided into two categories: anaerobic and aerobic treatments. In this area, microorganisms are used as bioadsorbents, microbes, and bacterial biofilms, among others. The microbial effectiveness to eliminate metals is still under development, but results have shown high removal rates (Bolisetty et al., 2019). Finally, tertiary treatment processes include chemical oxidation, electrochemical precipitation, crystallization, distillation and photocatalysis, adsorption, membrane technologies, and ion exchange technologies. In this stage, the wastewater is converted into good quality water, removal efficiencies that reach up to 99% can be obtained, when the tertiary treatments are adequately combined with primary and secondary treatments (Ince and Kaplan Ince, 2020; Bolisetty et al., 2019).

3.7. Conventional treatments for removing heavy metals from wastewater

Conventional processes for removing heavy metals from wastewater include a wide variety of treatments such as chemical precipitation, flotation, ion exchange, electrochemical and membrane technologies, coagulation, among others (Gunatilake, 2015; Barakat, 2011). This section describes some conventional methods together with their active principle, as well as the advantages and disadvantages that these treatments present in terms of the efficiency of removing heavy metals. Table 3 summarizes the main advantages and limitations of some conventional treatments presented in this study. Figure 6 describes the main conventional treatments with their corresponding process.

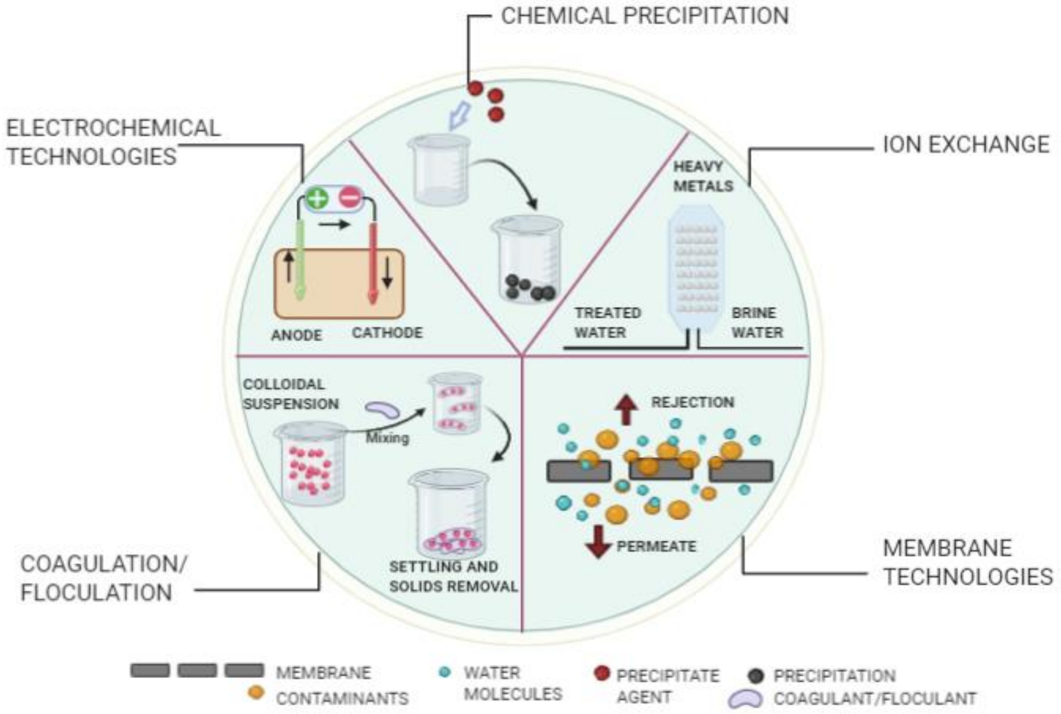


Figure 6. Conventional treatments for removing heavy metals from wastewater.

3.7.1. Chemical precipitation process used on the removal of heavy metals from wastewater

The chemical precipitation process is considered an effective technique, due to the capacity to removed heavy metals from wastewater discharged mainly from the paper production and electroplating industries. In this process, chemical precipitants (e.g. alum, lime, iron salts, and other organic polymers) react with the heavy metals, resulting into insoluble precipitates (Azimi et al., 2017; Joshi et al., 2017; Singh et al., 2017), through this reaction that occurs between the metals dissolved in the solution and precipitant metals can be removed more easily Figure 7 describes the process of chemical precipitation in water. The percentage of heavy metal removal and its removal efficiency can be improved by optimizing pH, temperature, and concentration (Gunatilake, 2015). The mechanism of the removal of heavy metals by chemical precipitation is described by the following Eq. (1) (Barakat, 2011; Kurniawan et al., 2006).

$$M^{2+} + 2(OH)^{-} \leftrightarrow M(OH)_2 \text{ Eq. (1)}$$

Where M^{2+} is the metal ion and OH^{-} represents the precipitant used, and $M(OH)_2$ is the result of the reaction of an insoluble metal hydroxide (Barakat, 2011).

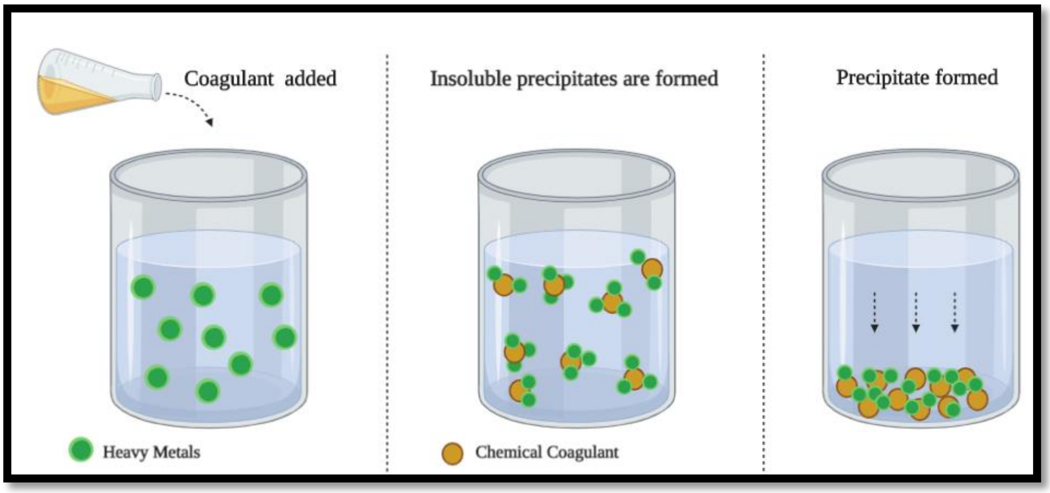


Figure 7. Chemical precipitation process used on the removal of heavy metals from wastewater. Adapted from: Peng and Guo, 2020.

Chen et al., (2018), investigated the chemical precipitation process with three chemical precipitants: lime (Ca $(OH)_2$), sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2S) for the removal of three heavy metals Zn^{2+}, Cu^{2+} and Pb^{2+} from aqueous solutions. The lime precipitation achieved an effective removal for copper and zinc between 99.65% and 99.99%; however, the maximum removal of lead only reached 76.14% (Chen et al., 2018). Carbonate showed similar results to those of the precipitation with lime. Removal efficiencies of 99.96% and 99.81% were obtained for Zn^{2+} and Cu^{2+}, respectively. A higher efficiency was obtained for Pb^{2+}, reaching 97.79% removal. Finally, the precipitation of sulfides was the most efficient method to treat heavy metal solutions. The removal efficiency was ranked as Cu> Zn> Pb. The results indicated that the removal of lead ions was less effective with the three precipitants investigated (Chen et al., 2018). One study investigated the removal of Cr^{6+} with lead sulfate, with direct precipitation (Peng and Guo, 2020). The Cr^{6+} was removed as $PbCrO_4$. The results obtained were the reduction of the Cr^{6+} concentration from 0.2 mol / L to 0.0015 mmol / L with an optimum pH of 13.90. However, this process could not be scale up the industrial level due to the use of lead, which is a well-known poisonous metal (Peng and Guo, 2020). Magnesium hydroxycarbonate was used as a precipitation agent for the elimination of certain heavy metals ($Cr^{3+}$and Fe^{3+}). The removal efficiencies of heavy metals were improved by increasing the dose of magnesium hydroxycarbonate, achieving a removal efficiency of 99.9% (Zhang and Duan, 2020). Verma and Balomajumder, (2020) conducted a study for the reduction of Cr^{6+} to Cr^{3+}, reducing agents such as sodium metabisulfite and ferrous sulfate were used. It was observed that 99.86% and 99.97% of Cr^{6+} was reduced using

1100 mg/L of ferrous sulfate and 100 mg/L of sodium metabisulfite, respectively (Verma and Balomajumder, 2020). For the Cr^{3+} precipitation reaction, the combination of $Ca(OH)_2$ + NaOH was used, obtaining a maximum elimination efficiency of 98.2% (Verma and Balomajumder, 2020).

3.7.2. Coagulation/ flocculation process used on the removal of heavy metals from wastewater

Coagulation-flocculation is a highly efficient physicochemical method for the removal of heavy metals (Xu et al., 2019). The objective of this process is to agglomerate fine particles and colloids into larger particles to reduce pollutants present in wastewater. This process consists of two different stages (Teh et al., 2016). The first is coagulation, a chemical reaction that occurs when a chemical or coagulant is added to water (Lakherwal, 2014). Among the most widely used coagulants are aluminum sulfate, ferric sulfate, polyaluminum chloride (PAC), polymeric ferric sulfate (PFS) and polyacrylamide (PAM) (Xu et al., 2019). The coagulant stimulates the heavy metals in the water to coalesce into small aggregates (flocs). The second part of the process is the flocculation, which allows the agglomeration of these particles by gentle agitation. Finally, the flocs are allowed to settle and are then disposed of as sludge (Teh et al., 2016; Lakherwal, 2014). Figure 8 describes Coagulation/Flocculation process used on the removal of heavy metals in wastewater. This process is used as a pre-treatment, post-treatment, or main wastewater treatment due to its versatility (Teh et al., 2016).

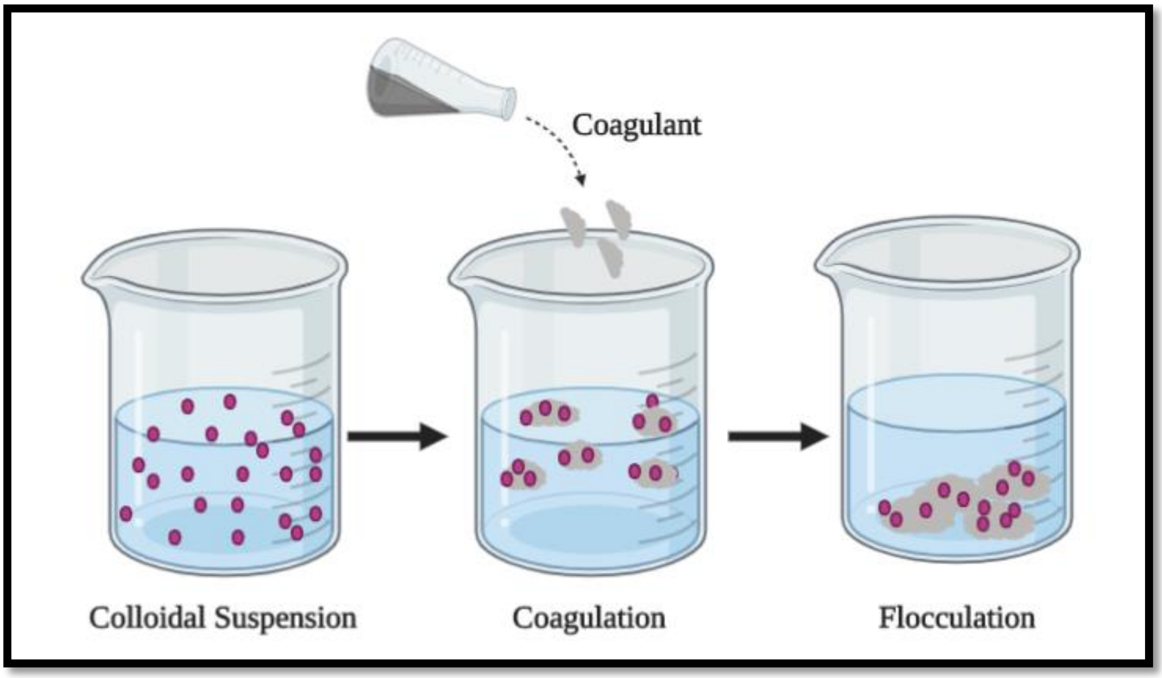


Figure 8. Process of Coagulation/Flocculation used on the removal of heavy metals from wastewater. Adapted from: Choumane et al., 2017

Hargraves et al, (2018) conducted a study on the removal of certain metals (Cu, Pb, Ni, and Zn) using the Coagulation/Flocculation process. For this purpose, ferric chloride ($FeCl_3$), polyethyleneimine synthetic polymer (PEI), and biopolymers (chitosan and flocculant) were used. The results of removal capacity were for Chitosan and PEI around 35%. $FeCl_3$ removed 48% of Cu, 56% of Pb, and 41% of Zn (Hargreaves et al., 2018). Furthermore, Marzougui et al, (2018) studied the removal of Pb, Cr, Zn, Cu, and Ni, using two types of coagulants (aluminum sulfate and ferrous sulfate). The results showed that aluminum sulfate increased the removal efficiency of all heavy metals, Pb (100-98.26%), Cr (93.54-82.08%), and Zn (94.74-81.56%), except for the Ni that achieved a rate elimination (41-34%). However, the results of the ferrous sulfate treatment were Pb (74.41- 20.78%), Cr (78.94-43.65%), Zn (89.86-12.12%), Ni (69.71-2.31%), results lower compared to obtained with aluminum sulfate (Marzougui et al., 2018).

3.7.3. Ion exchange process used on the removal of heavy metals from wastewater

Ion exchange is a stoichiometric chemical reaction (Bashir et al., 2018). The process consists of ion exchange between the solid and liquid phases, an insoluble substance (resins) removes the ions from an electrolytic solution and releases other ions with a charge chemically equivalent (Kurniawan et al., 2006). Therefore, the physicochemical interactions that occur during the removal of metals can be expressed in Eq. (2) (Azimi et al., 2017; Kurniawan et al., 2006):

$$nRSO_3^- - H^+ + M^{n+} \leftrightarrow nRSO_3^- - M^{n+} + nH^+ \text{ Eq. (2)}$$

resin solution resin solution

where RSO_3^- represents the reaction that occurs between the anionic group and resin and and M^{n+} metal cation, n is the oxidation state of the metal ions.

Selecting the right, ion exchange resin can provide an effective and economical solution to contamination control requirements (Al-Enezi et al., 2004). The removal performance of IRN77 and SKN1 resins in a synthetic solution was investigated in the presence of Cr^{3+} (Kurniawan et al., 2006). The results were the complete elimination of Cr^{3+} was achieved. The resins allowed to obtain a higher removal efficiency with a smaller amount of it (Kurniawan et al., 2006). Dong et al., (2018) use of spent activated carbon (AC) in the ion exchange process for the removal of Pb^{2+} and Cd^{2+}. The study found that spent ACs had an adsorption capacity of more than 95% and 86% for Pb^{2+} and Cd^{2+}, respectively (Dong et al., 2018). The ion exchange potential of a double exchange chelating resin (Na^+ / H^+) to remove nickel ions from wastewater was investigated. The results demonstrated that the resin contains functional groups of iminodiacetic acid (IDA) that can lead to the capture of heavy metal ions (Ma et al., 2019). However, it is necessary to set adequate pH conditions and ratio of Na^+: H^+, because too much Na^+ results in precipitation of nickel hydroxide obstructing the ion exchange columns, while too much H^+ in the solution leads to competitive protonation, reducing Ni^{2+} ion absorption (Ma et al., 2019).

3.7.4. Membrane technology process used on the removal of heavy metals from wastewater

A membrane acts as a barrier that inhibits the passage of certain compounds while allowing the passage of others, in other words, it is a selective barrier. The mechanism by which this type of treatment works is governed by the size exclusion or steric hindrance mechanism, the Donnan exclusion effect (charge-charge repulsion), and the adsorption capacity of specific contaminants (Abdullah et al., 2019). Figure 9 describes the membrane technologies mechanism. According to the material used in their manufacture, these membranes are classified as organic or inorganic. Organic membranes are made from synthetic organic polymers (e.g., polyethylene, polytetrafluoroethylene, polypropylene, and cellulose acetate). Inorganic membranes are made of materials such as ceramics, metals, zeolites, or silica (Obotey Ezugbe and Rathilal, 2020).

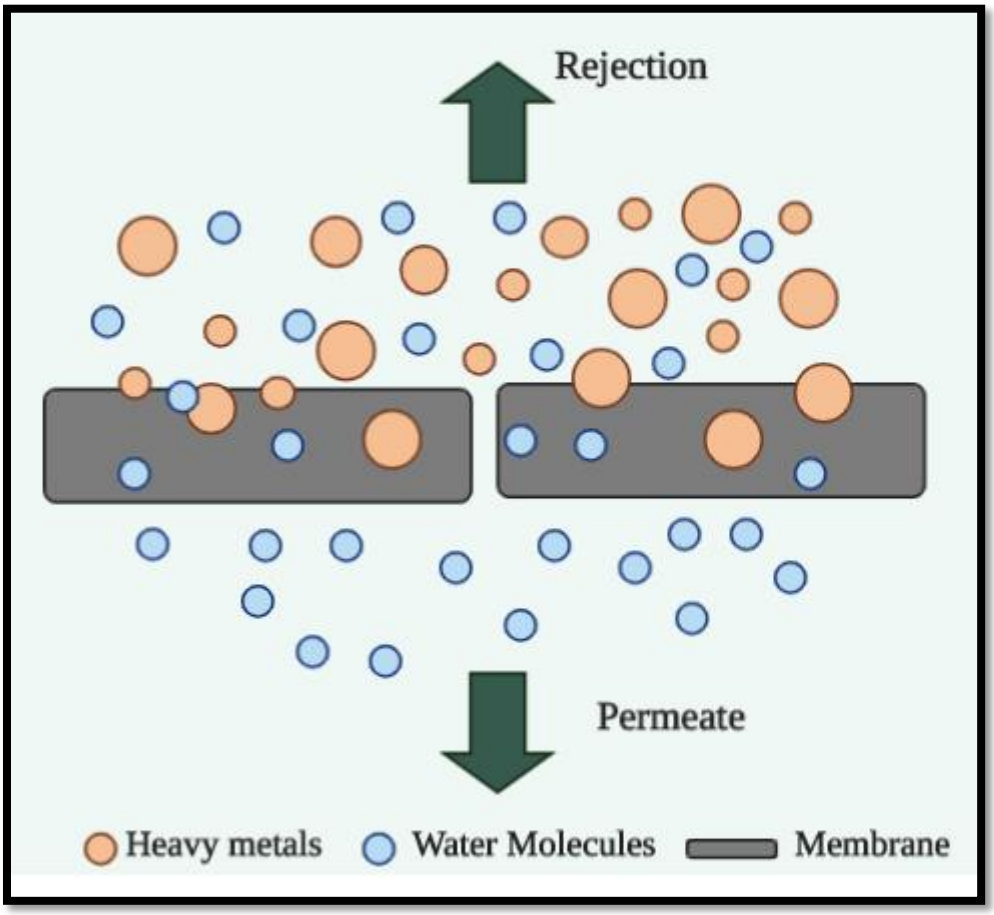


Figure 9. Membrane technologies mechanism used on the removal of heavy metals from wastewater. Adapted from: Abdullah et al., 2019.

Membrane processes can be classified according to the force applied in the process, among these we have: driven by low pressure (microfiltration (MF), ultrafiltration (UF), distillation), driven by high pressure (nanofiltration (NF) and reverse osmosis (RO)), and by osmotic pressure (e.i., direct osmosis (DO), electrodialysis (ED) and liquid membrane (LM)) (Abdullah et al., 2019). MF, UF, NF, and RO are methods mainly used in the treatment of water pollution, specifically for removing heavy metals (Gunatilake, 2015). Factors such as the size and distribution of the pores, the surface charge, the degree of hydrophilicity, the flow of the solution, and the presence of functional groups, must be considered because they significantly affect the general performance of the membrane in terms of removal (Abdullah et al., 2019). RO membranes, for example, TFC-ULP (Koch), allow 99% of arsenic to be removed from groundwater, while DK2540F (Desal) membranes retain between 88% and 96% of the contaminant (Bodzek, 2015). RO and NF were used for removal Cu and Cd ions. The results obtained demonstrated the efficiency of RO with removal percentages of 98% and 99% for Cu and Cd, respectively. However, the NF was able to remove more than 90% of the existing Cu ions (Abu Qdais and Moussa, 2004). Shukla et al., (2018) investigated the removal of As, Cr, Cd, Pb, and Zn from synthetic water using a polyphenylsulfone nanofiltration membrane incorporated with carboxylated graphene oxide. The performance of the nanofiltration was shown that the maximum removal rates of heavy metal ions were between 98% and 80%. The nanocomposite membrane demonstrated high efficiency for this process (Shukla et al., 2018).

3.7.5. Electrochemical technologies used on the removal of heavy metals from wastewater

Electrochemical methods are known as wastewater treatment methods that are effective in removing heavy metal ions from water sources. These methods involve the recovery of metals in their elemental metal state (Fu and Wang, 2011), through anodic and cathodic reactions in an electrochemical cell (Vardhan et al., 2019). Electrochemical treatments include electrodeposition, electrocoagulation, and electroflotation (Maarof et al., 2017).

Electrocoagulation is a process that originates from conventional chemical coagulation (Drogui et al., 2008). The coagulant is generated in situ by electrolytic oxidation. This process is based on the charged ionic metal is removed from the wastewater by allowing it to react with the anion in the effluent. The simultaneous cathodic reaction allows the removal of contaminants either by deposition on the cathode electrode or flotation (Gunatilake, 2015; Drogui et al., 2008). The method of electrodeposition, its electrochemical mechanism for metal recovery is based on cathodic reduction. It is extensively used in the recovery of toxic metal ions from wastewater (e.g., Pb, Cd, Cu, Ni, Zn, and Cr, to mention a few) from industrial effluents or to recover precious metals (e.g., Ag, Pt, Au, etc.) from solutions. Electroflotation can be used for the removal of heavy metals (e.g., Pb, Cu, Zn, Ni, and Fe) from wastewater. The process is based on the solid-liquid separation that allows the metals to float on the surface of the water through small bubbles of oxygen and hydrogen gases, a reaction that occurs through the electrolysis of water. The bubbles adhering to the pollutants and the resulting pollutant-bubble complexes moved up on the surface of liquid where foam can be periodically skimmed off. The polluted foam is wiped with the scraper from the surface of the flotation tank (Vardhan et al., 2019; Drogui et al., 2008).

Table 3. Advantages and disadvantages of conventional treatments employed on the removal heavy metals from wastewater.

Conventional Treatment	**Advantages**	**Disadvantages**	**References**
Chemical Precipitation	Low capital investment, simple operation, and easily automated treatment method.	Produce a large amount of sludge containing toxic compounds that require further treatment, large number of chemicals, slow precipitation, poor settling, and the long-term environmental impacts.	Dula and Duke, 2019; Azimi et al., 2017; Joshi et al., 2017; Barakat, 2011; Kurniawan et al., 2006
Coagulation/Flotation	Relatively economic and simple operation.	Incomplete heavy metals removal, production of sludge, high operational cost	Abdullah et al., 2019; Kurniawan et al., 2006
Membrane Technologies	Higher removal efficiency, saves energy consumption, no need for chemical additives, no phase change involved, no secondary pollution, ease of fabrication, environmentally friendly, and remove organic and inorganic compounds.	High operational cost, membrane fouling, and lower permeate flux	Bolisetty et al., 2019; Vardhan et al., 2019; Bashir et al., 2018; Azimi et al., 2017

Ion Exchange	High removal efficiency, fast kinetic, effective to treat inorganic effluent, no sludge disposal, convenience for fieldwork, less time-consume, low-cost materials, and resin can be re-generated.	Nonselective, highly sensitive to the pH, fouling of metal ions, only suitable for low concentration of metals, and the capital and operational cost is high.	Abdullah et al., 2019; Bashir et al., 2018; Joshi et al., 2017; Barakat, 2011; Fu and Wang, 2011; Kurniawan et al., 2006
Electrochemical Technologies	Simple and environmentally friendly, less labor and can save significant energy.	High large capital investments, expensive electricity supply, and low removal capacity when metal ion concentrations are low.	Bolisetty et al., 2019; Bashir et al., 2018; Azimi et al., 2017

3.8. Non-conventional treatments used on the removal of heavy metals from wastewater

The development of treatments for the removal of heavy metals from water has presented great advances to overcome the disadvantages of conventional treatments. This section describes the main non-conventional methods such as adsorption and their different types of adsorbents, microbial fuel cells, nanotechnology, and Fenton like reactions, together with their own processes. Figure 10 describes the main non-conventional treatments with their corresponding process.

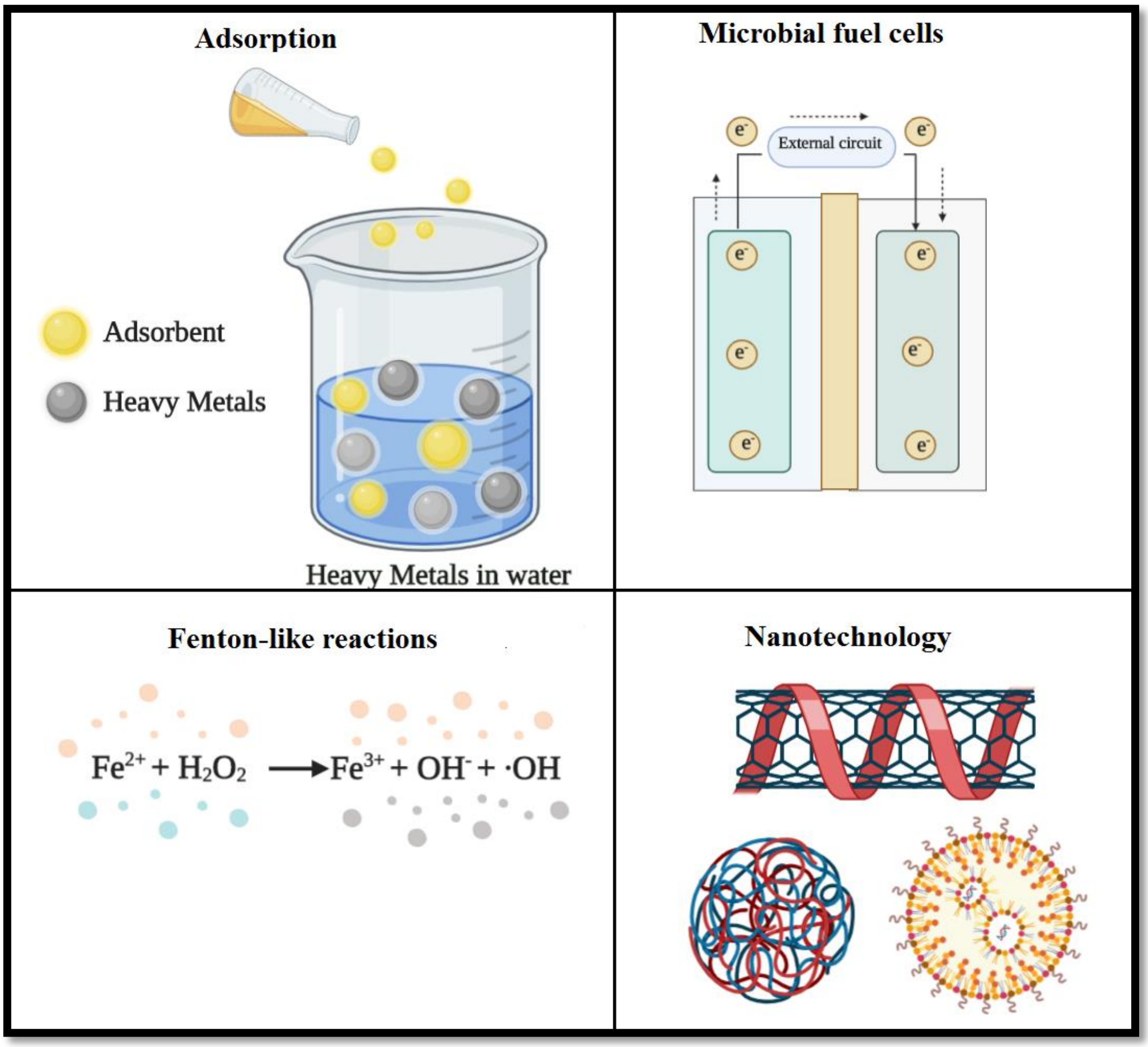


Figure 10. Non-Conventional treatments for removing heavy metals from wastewater.

3.8.1. Adsorption process used on the removal heavy metals from wastewater

Adsorption is one of the best methods to remove a wide variety of contaminants from water, including heavy metals. Among its advantages we can highlight a high removal capacity, relatively low energy consumption and technical requirements for operation, and the possibility of avoiding major secondary pollution (Burakov et al., 2018). Activated carbon (AC), polymer-based materials, biomaterials, agricultural and industrial residues, and biological materials are among the most used adsorbents for adsorption of heavy metals from wastewater effluents. Figure 11 describes the process of adsorption and the main types of adsorbents used for treating water.

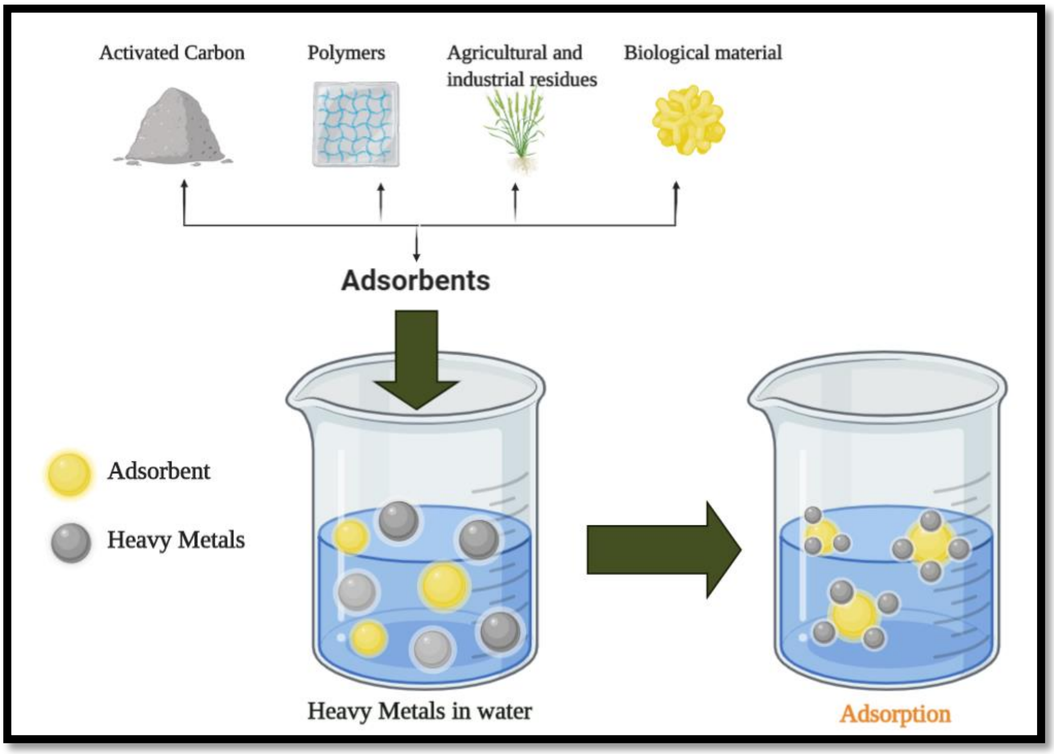


Figure 11. Adsorption removal of heavy metals from idealized aqueous solutions. Adapted from: Burakov et al., 2018

Activated Carbon used on the removal of heavy metals from wastewater

Carbon-based materials are among the most extensively researched, developed and used adsorbents for removal heavy metals from aquatic systems. AC is the most prominent of the group, but others including biochar, carbon nanotubes and graphene-based materials have shown to be very promising as efficient adsorbents. AC is a black adsorbent with a porous surface, large specific surface area, high mechanical strength, good thermal stability, controllable morphology and high adsorption capacity. Materials such as fly-ash, wood, coal, lignite, petroleum pitch, and agricultural residues are among the main raw materials used to obtain AC. The selection of the precursor is performed considering its availability, cost, renewable nature, and purity, manufacturing process and intended use (Kosheleva et al., 2019). It is usually used as a powder or as granules forms. AC is produced by pyrolysis/carbonization of carbon-containing raw materials, followed by an activation process, can be carried out in three ways: chemical activation; physical or thermal activation or the combination of these two methods (Marsh and Rodríguez-Reinoso, 2006). Chemical activation is preferred in several cases because of the lower temperature and shorter processing time, higher yield, and a better development of the porous structure. The porous structure considerably enhance the performance of ACs in the adsorption capacity of pollutants by trapping into the porous structure. Alternative processes, such as microwave activation, have also been developed while aiming to improve the quality of the final AC and the energy efficiency of the methods used (Ao et al., 2018).

Even though AC is very effective for heavy metal sequestration, in some cases it can be modified to improve its affinity for certain pollutants. Different oxidation, sulfuration, and nitrogenation treatments have been studied, as well as processes in which AC is functionalized with a series of coordination ligands. These treatments change the surface area, pore volume and surface chemistry of the modified AC (Rivera-Utrilla et al., 2011). Different raw materials such as palm kernel shell, sugarcane bagasse, rice husk, oil palm shell, and coconut shell, processing parameters and removal conditions have been studied, focusing on reducing the cost of treatments using AC, increasing its adsorption capacity, developing environmentally friendly activation processes, improving the operational life and recyclability to mention a few. Adsorption capacities as high as about 900 mg/g have been reached for Cr^{3+} removal from clean water using an agroindustrial residue as precursor for AC (Yunus et al., 2020). In a search for better adsorbent quality, performance and novel features, AC has also been combined with many other materials, to elaborate composites. For instance, magnetic nanoparticles (Fe_3O_4) have been impregnated on AC was synthesized from pistachio shell resulting in a magnetic adsorbent that can be easily recovered from an aqueous medium using a magnetic field and the characteristics of the resulting surface have modified so that there are a large number of active sites that can increase the chemisorption (Nejadshafiee and Islami, 2019). Moreover, biological macromolecules such as chitosan and alginates can be used to functionalization AC resulting in a composite with high affinity for several pollutants such as pharmaceuticals, dyes, nitrate, phosphate, and organic substances other than heavy metals. The resulting composites well interact with the pollutant via the functional groups on the Ac and also properties such as high mechanical strength, improved durability and better hydraulic properties will be present on the material (Quesada et al., 2020).

Polymer-Based Materials used on the removal of heavy metals from wastewater

The development of novel polymer-based materials have been increased during the last decade due to the wide range of applications that they could have as well as a great variety of physico-chemical properties (Liu et al., 2011; Zhang and Cheng, 2011; McKeown and Budd, 2010). Many studies have tested the adsorption capacities of polymer-based materials for remediation applications such as heavy metal removal from water (Aldaz et al., 2020; Guerra et al., 2018; Liu et al., 2011; McKeown and Budd, 2010). For instance, Liu et al., (2011) have shown that Pb^{2+} imprinted polymer has a selective adsorption on Pb^{2+} ions. Moreover, many of these polymer-based materials are malleable and easy to functionalize. McKeown and Budd, (2010) reported the modification of polymers into microporous polymer-based materials would enhance significantly their adsorption properties, being suitable composites for water remediation. Certainly, these types of polymers have a lot of benefits and advantages over other materials. However, governments and industries have put special attention on environmentally friendly materials (Aldaz et al., 2020).

There are many natural polymers that have been effective for decontamination of water such as alginate, silk, lignin, chitosan, and cellulose (Aldaz et al., 2020). For instance, Wang et al. (2018) described in detail biocompatible, nontoxic, and cost-effective properties of different alginate-based composites for the removal of various pollutants, since they exhibited good removal capacity of dyes, heavy metals, and other water pollutants (Wang et al., 2018). Similarly, Campagnolo et al. (2018) demonstrated that silk-based biocomposites presented high adsorption capacity for methylene blue dye, which is a common water pollutant. Regarding lignin-based materials, many outstanding results on adsorption of heavy metals have been reported in the literature (Campagnolo et al., 2018). Nasser et al., (2019) demonstrated the use of lignin as adsorbent to remove Cr^{3+} from water. The lignin was obtained from black liquor. The removal efficiency was more than 90% (Naseer et al., 2019). Likewise, chitosan and cellulose-based materials are extensively utilized for water remediation. They have been used successfully for various water treatments to remove dyes, oil, and heavy metals in polluted water. Polymeric materials provide high stability and process ability, polymeric matrixes provide specific bindings to target pollutants (Lofrano et al., 2016). Indeed, Zhao et al.,

(2016) demonstrated that carboxylate chitosan composite beads, allowed the adsorption of Cu^{2+} ions in contaminated water (Zhao et al., 2016). Chitosan is also a very promising material for biomedical and environmental remediation applications, including heavy metal removal. On the other hand, numerous studies have shown that cellulose fulfills the expectations of a suitable agent for water remediation (Peng et al., 2020; Abiaziem et al., 2019; Ma et al., 2017; Thakur and Voicu, 2016). As a matter of fact, Cellulose is the most abundant available natural polymer worldwide, presenting a huge variety of unique biological and physico-chemical properties. Thereby, biopolymers emerge as the most suitable materials for remediation applications such as heavy metal removal from water. In Figure 12 the main natural sources of biopolymers for remediation of water pollution are schematized.

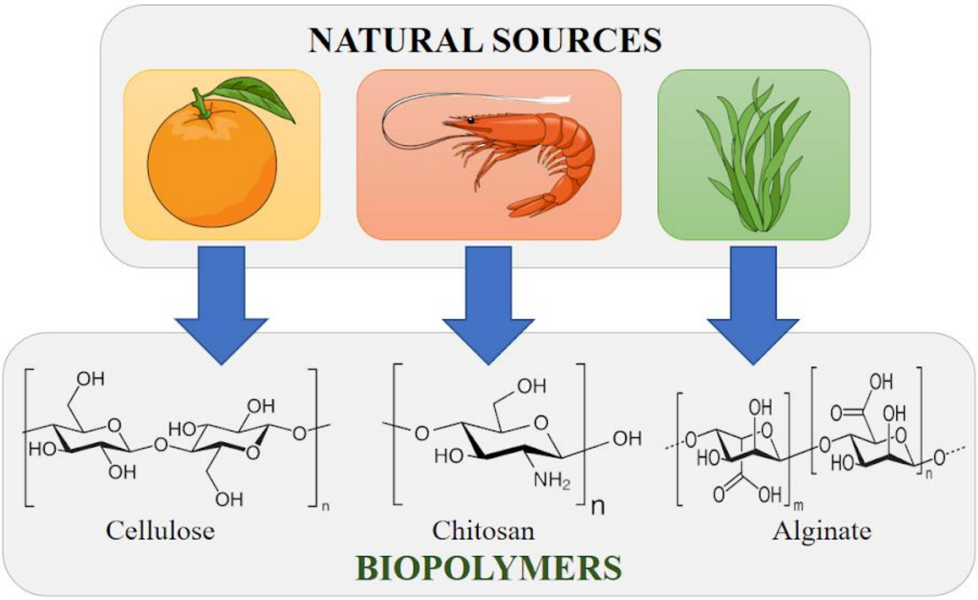


Figure. 12. Main natural sources of biopolymers for remediation of water polluters

Agricultural residues used on the removal heavy metals from wastewater

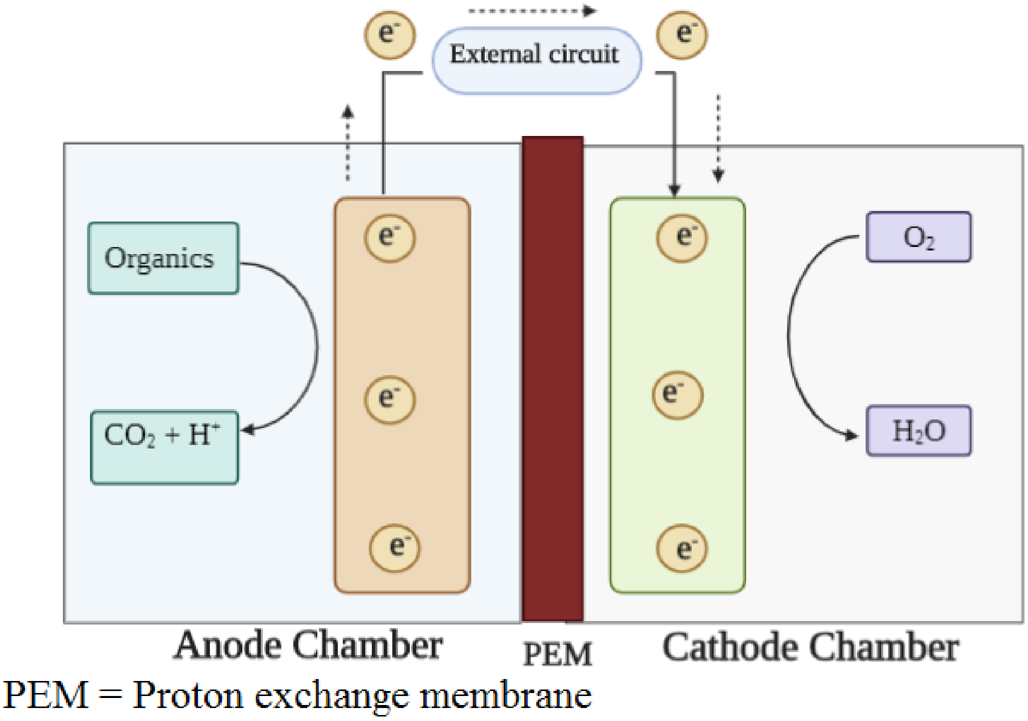
Agricultural residues are currently exploited for heavy metal remediation since they are highly efficient, low cost and renewable source of biomass. The basic components of these residues include hemicellulose, cellulose, lignin, starch, which are biopolymers showing strong exceptional adsorption capacities (Sud et al., 2008). The working principle of heavy metal removal using byproducts or agricultural residues is based on biosorption. Biosorption describes the elimination of heavy metals from water solution by a non-living material such as cellulose, chitosan and alginate (Sala et al., 2010). Moreover, biosorption compared to conventional technologies for removal of heavy metal in aqueous solutions (e.g., chemical precipitation, ion exchange, RO) is less expensive, exhibits higher efficiency, minimization of chemical or biological sludge. These materials will also serve for the regeneration of biosorbents besides the possibility of metal recovery. In addition, one of the main advantages of the biosorbents is that they can be readily modified to enhance their adsorption capacities and their adaptability at industrial scale (Sud et al., 2008).

Numerous studies have demonstrated that agricultural residues or their byproducts present positive results for heavy metal removal from aqueous solutions (Ghasemi et al., 2014; Hameed and Ahmad, 2009; Garg et al., 2008; Dubey and Gopal, 2007; Mohan and Singh, 2002). For instance, Garg et al., (2008) showed that sugarcane bagasse, Jatropha oil cake and maize corncob are potential biosorbents for cadmium. In fact, these agricultural waste materials are able to remove Cu^{2+} from aqueous solutions. Since these agricultural residues are capable to remove cadmium ions from contaminated aqueous solutions. However, the optimal values of these parameters may vary since the experiment carried out by Aksu and Isoğlu, (2005) shows that sugar beet pulp exhibited the highest adsorption capacity at pH of 4 for Cu^{2+}. Hence, it is evident that agricultural wastes residues are excellent for removing heavy metal ions from water and their effectiveness depends on parameters such as pH, temperature, adsorbent dose and concentration of heavy metals (Aksu and İşoğlu, 2005).

3.8.2. Microbial fuel cells used on the removal heavy metals from wastewater

The microbial fuel cell (MFC) is considered a promising technology, capable of removing water pollution and becoming an alternative renewable energy source because it uses organic matter present in wastewater to produce electricity via biocatalysts such as microbes (Jayakumar et al., 2020). The mechanism of MFC consists of two half cells, an anode cell (anaerobic) and a cathode cell (aerobic) separated by a proton exchange membrane (PEM) connected by an external circuit. In the anaerobic cell, oxidation occurs by microorganisms in the anode part. The second half of the cell is where the reduction reaction (cathode) occurs. The microbes produce protons and electrons on the anode side and transfer the protons through PEM and the electrons through the external circuit to the cathode. At the cathode, the final electron acceptor oxygen closes the circuit and reduces to water due to its high redox potential (Jayakumar et al., 2020; Vélez-Pérez et al., 2020). Figure 13 shows the mechanism of MFCs.

According to Bagchi et al., (2020), heavy metal removal using MFC allows heavy metals with higher redox potential than the anode electrode to be removed and recovered in the cathode chambers of an MFC (Bagchi et al., 2020). For example, Wu et al., (2017) conducted an investigation for remediation *in situ* rivers contaminated by heavy metals using microbial fuel cells. The results showed removal of 97.3% Hg^{2+}, 87.7% Cu^{2+} and 98.5% Ag^{+} after 60 days of MFC operation (Wu et al., 2017).



PEM = Proton exchange membrane

Figure 13. Schematic mechanism of Microbial fuel cells used on the removal heavy metals from wastewater. Adapted from: Jayakumar et al., 2020

3.8.3. Nanotechnology applied on water treatment

Nanotechnology has also been at the forefront for water treatment and some good examples are being currently exploited in several countries. As highlighted in the precedent sections, traditional methods of water remediation exhibit several limitations such as high-energy requirements, incomplete removal, and generation of toxic sludge. That is why, at present is of paramount importance to produce innovative, more efficient and less energy consuming technology for treatment of wastewaters. The nanotechnology-based treatments rely on the fact of using nanomaterials. Specifically, nanomaterials can be defined as those at which at least one of their main components exhibit dimensions smaller than 100 nm (Saikia et al., 2020; Upadhyay et al., 2020; Gehrke and Somborn-schulz, 2015; Bhattacharya et al., 2013). These innovative materials had gained special attention the in last decades for the wastewater treatment because they show unique and different properties than their bulk counterpart materials. These properties include high surface-to-volume ratio, electronic, optical, and magnetic properties to mention a few promoting huge improvements in the final performances in pollutant remediation. Nanotechnology also offers to manipulate in a controlled way the specific properties of the materials, such as the surface area, the morphology and sizes, the chemical affinity, the surface charge density and the electron transfer ability making it possible to fabricate tailored nanocomposites for specific needs (Borji et al., 2020). While these Nano-based technologies are by far much better than other conventional techniques used in water treatment, the lack of information about the environmental and health effects due to their toxicity is considerably inadequate and imped their full exploitation in many day to day applications. The environmental concerns and toxicity of nanomaterial are critical topics in the choice of the adequate materials for heavy metal removal and water purification. The difficulty presented by these materials lies in their complex structure that could make them unsustainable and impractical, more research is needed to obtain materials that are economically viable and ecological. Among the most used nanotechnology processes for heavy metal removal is the nanofiltration based on nanocomposites fabricated from a variety of efficient, eco-friendly and cost-effective nanomaterials. Moreover, low dimensional structures such as nanocarbon, single or multi metal oxides, magnetic nanoparticles or clay are the most used for the purification, disinfection, removal of heavy metals from water (Borji et al., 2020; Kang et al., 2019). Figure 14 shows the common nanomaterials used for remediation of water polluters. Metal and non-metal oxides are commonly used for pollutant removal from wastewater. These materials are abundant in nature accompanied by its low-cost synthesis process. The most used for heavy metal removal are based on ferric oxide nanoparticles mainly due to its large surface charge, high redox potential, and its reusability. Other oxides such as manganese oxide (MnO), zinc oxide (ZnO) and magnesium oxide (MgO) are also effective for the removal of heavy metals such as arsenic, zinc, cadmium. All these nanostructures exhibit highly reactive and extensive surface areas. Similarly, nano assemblies, nanoplates, microspheres with nano-sheets and hierarchical ZnO nano-rods have been used for wastewater treatment. In this context, many examples on filtration systems based on aluminum oxide fibers (nanoalumina) or those fabricated by combining with micro glass with high positive charge can readily retain negatively charged particles and thus being highly efficient for removing via chemisorption process the dissolved heavy metals (Borji et al., 2020).

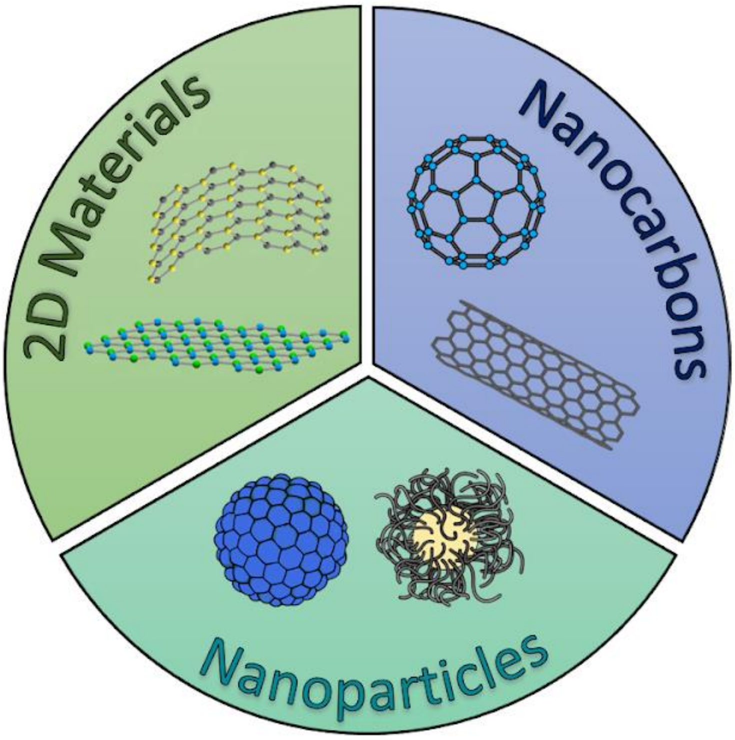


Figure 14. Common nanomaterials used for remediation of water polluters

Nanocarbon (carbon nanotubes, graphene and other carbon derivatives)

Carbon is one of the most versatile materials used as adsorbent for removing pollutants from wastewater including heavy metals from aqueous solutions (Borji et al., 2020; Kang et al., 2019). The size-reduced form as nanocarbon, either carbon nanotubes, graphene or its derivatives, is used currently in water remediation as highly efficient adsorbents. In this context, carbon nanotubes (CNT) are very promising for heavy metal remediation. Its carbonaceous nature accompanied by its highly reactive surface area may allow direct interaction with the pollutants through hydrophobic interaction, π-π interaction, covalent interaction, hydrogen bonding and electrostatic interactions (Hasnain and Nayak, 2019). CNTs exhibit a huge aspect ratio due to its nanometric dimension with typical diameter between 0.5 and 30 nm and length from few nanometers to few micrometers. CNTs can be classified according to their inner walls such as single, double, and triple and multiwall (SWCNT, DWCNT, TWCNT and MWCNT) (Hasnain and Nayak, 2019). Structurally

SWCNTs possess 3 types of arrangement of carbon atoms, providing the Zig-Zag, Arm-Chair and Chiral structural configurations defining its intrinsically dimensions and concomitant physical-chemical properties. Moreover, its rod-like and hollow shape make them exceptional for water remediation, offering several possibilities for where adsorption could take place. SWCNTs surface can be easily modified through acid treatment, metals impregnation and functional molecules/group grafting. The latest, allows the control of the nanotube surface area, surface charge, dispersion and hydrophobicity and their concomitant adsorption potentials. For heavy metal removal, typical nanotube acid functionalization by hydrochloric, nitric, or sulfuric acid, introduces oxy functional groups which are highly effective for the removal of heavy metals ions such as cadmium, copper, lead and mercury from wastewater (Hasnain and Nayak, 2019). The graphene performance as adsorbent is associated with its unique two-dimensional nature and associated electronic band structure which can be easily modified for custom made functionalities (He et al., 2018; Dresselhaus et al., 2010). Chemical oxidation of graphene is readily achieved through acid functionalization producing hydrophilic and carboxylic acids which increase dramatically its adsorption of heavy metals. Features such large surface area and presence of surface functional groups on their most common graphene derivative materials make them highly attractive as adsorbent for water purification (Borji et al., 2020; Vázquez-Núñez et al., 2020). Other graphene derivatives as its reduced form (RGO) are being used successfully for water treatment (Saikia et al., 2020; Upadhyay et al., 2020). For example, Lingamdinne et al., (2016) reported the removal of copper ions Cu^{2+} from water using graphene oxide (GO) composites. The authors used batch adsorption methods to elucidate their removal efficiency, and they found the maximum adsorption of Cu^{2+} in a pH range from 5.0 to 8.0. Moreover, the authors performed FT-IR, XPS, and SEM in GO and concluded that the adsorption of Cu^{2+} onto GO occurred through oxygen-containing –C–O and –C=O or –C=C (π–π bond electrons) surface functional groups of GO (Lingamdinne et al., 2016). As highlighted by Wang et al. (2020) graphene flakes are not the only efficient nanostructures for heavy metal remediation. In fact, various 3D graphene-based macrostructures (3DGBMs) have gained attention in the last decade due to their potential in water treatments (Wang et al., 2020). These innovative structures offer a large surface area and porous network, accompanied by high electronic mobility, excellent chemical active sites, and ultra-lightness, making them promising materials for heavy metal removal and water purification through adsorption mechanisms. These structures can also serve as scaffolds to immobilize nanomaterials which significantly broadens their potential applications in heavy metal remediation or any water treatment (Wang et al., 2020). Barik et al., (2020) reported the fabrication of a mesoporous silica 3D scaffold doped with graphene oxide flakes (GOFs) and showed its potential for removal of Pb^{2+} and As^{2+} ions from groundwater samples. These GO-based mesoporous materials showed surface dependence adsorption and were capable of being recycled four times without any effective loss in activity. Moreover, when combined GO with other nanoparticles its adsorption properties can be dramatically enhanced. Thus, hybrid nanocomposites based on magnetic nanoparticles (MNP) are being fabricated and combined with the intrinsic properties of the graphene with those from the MNP to produce highly efficient nanocomposites for heavy metals removal (Barik et al., 2020). As example, graphene/magnetite hybrid nanoparticles RGO-MagNPs and GO-ferric hydroxide composites were successfully used for the removal of arsenic from water. These hybrid materials based on graphene derivatives, both RGO and GO, showed higher binding capacity and improved adsorption for pollutants compared to those without nanoparticles (Zhang et al., 2010). The hybrid systems benefit not only from the extraordinary properties of nanocarbons with nanoparticles, but also the magnetic properties allow for affordable and easy use separation methods which lead to more efficient and reducing cost in the water treatment process.

3.8.4. Fenton-like reactions used on the removal heavy metals from wastewater

The Fenton reaction is an advanced, naturally occurring oxidation process, a method that has been developed in recent decades for the degradation of various contaminants (Farinelli et al., 2020). According to Zhu et al., (2019) the hydroxyl radicals that are generated from a mixed solution of H_2O_2 and ferrous ions have oxidizing properties, which allow efficient oxidation of many organic compounds in inorganic forms. Examples of this process are the conversion of carboxylic acids, alcohols, and esters into H_2O, CO_2 and other substances, which are less harmful and can be eliminated more easily (Zhu et al., 2019). The general Fenton reaction is described in Eq. (3) which is based on the first reaction proposed by the Haber-Weiss mechanism (Farinelli et al., 2020; Zhu et al., 2019).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \quad \text{Eq. (3)}$$

In the Fenton reaction, soluble iron cations interact with H_2O_2 to generate • OH, which allows the degradation of complexes of metallic organic matter. However, this technique has certain disadvantages in its operation, they work within a narrow pH range, generating large amounts of iron residues, with high operating costs and low water volume treatment capacity (Zhu et al., 2019).

The development of this technique has been an ongoing research, which has resulted into an optimization of the technique. For example, for the removal of Ni^{2+} from NiEDTA wastewater, a new process called Fenton / Fenton-type reaction hydroxide precipitation (FR-HP) was developed (Fu et al., 2009). This process turned out to be an economic and ecological process to remove metal from wastewater, obtaining removal efficiency greater than 90% (Fu et al., 2009). The use of combined methods allows improving the efficiency of this method because it allows a greater selectivity of reaction and formation of • OH, decreases the reaction time and activation energy, in addition to allowing the simple reaction (Zhu et al., 2013; Fu et al., 2009). The combination of Fenton reactions and other methods has demonstrated to be a stable option to achieve the desired remediation results in polluted water. According Pathak et al., (2009) "Bioleaching is the solubilization of metals from solid substrates either directly by the metabolism of leaching bacteria or indirectly by the products of metabolism" (Pathak et al., 2009). Bioleaching in combination with Fenton reaction was investigated for sludge treatment in terms of heavy metal removal. The combined process led to very high improvement in sludge dewatering (Fontmorin and Sillanpää, 2015). Moreover, Li et al., (2019) conducted an industrial wastewater treatment study to remove thallium (Tl) by combining hydroxide precipitation, Fenton oxidation, and sulfide precipitation. The results were a Tl removal (>95%) (Li et al., 2019). The Fenton reaction alone has demonstrated not to be sufficient for wastewater treatment, as it does not meet established standards to be an industrially scalable method. However, the combined use with other processes allows overcome these limitations. The disadvantages of this treatment are: works within a narrow pH range, generating large amounts of iron residue, having high operational costs and low water volume treatment capacity. This method requires further research to produce an improvement and optimization in process to reduce its economic burden (Zhu et al., 2019).

3.8.5. Plant-mediated remediation of heavy metals

Many methodological procedures or techniques to remediate heavy metal pollution in ecosystems (e.g. terrestrial, aquatic-marine, aerial or mixed) have been developed and applied (Deb et al., 2020; Haldar and Ghosh, 2020; Zubair et al., 2016). Among these techniques, the plant-mediated remediation, better known as phytoremediation, is one of the most used so far. This plant-based technology uses raw or genetically modified plant species. They are often combined with other living organisms (bacteria, fungi, algae, biofilms, plants), other external processes (thermic, physical, chemical, electrical) or inputs (soil amendments, macro-micro nutrients, fertilizers, plant-litter, nanocomposites, biosurfactants, emulsifiers, sorbents, gels, hydrogels, ceramics, clays, water, aeration, etc.), to remediate contaminated ecosystems (Abdel Maksoud et al., 2020; Ojuederie and Babalola, 2017; Zubair et al., 2016).

Phytoremediation has been successfully used for several decades; however, its efficiency depends not only on technical factors, but also on logistics, infrastructure, time and costs. This technique benefits from the use of plant interactions in polluted areas to minimize the toxic effects of pollutants (Deb et al., 2020; Devi and Kumar, 2020; Schück and Greger, 2020; Chibueze et al., 2016). Many works have been reported so far about this topic, where the emerging complementary processes and methods to enhance the efficiency of this technique are discussed, as well as those used to overcome current drawbacks. The advantages of using plants to remediate water pollution are recovering metal bioaccumulate in the plant (phytomining process), low cost, environmentally friendly, large-scale operation, low installation, and maintenance cost, prevention and contributions to local employment (Gholami et al., 2020; Azubuike et al., 2016).

A heavy metal plant-mediated remediation framework could be summarized in 4 phases (Figure 6). These 4 stages are: 1) Preliminary considerations, 2) processes, 3) state-of-the-art phytoremediation and 4) final disposal of heavy metals.

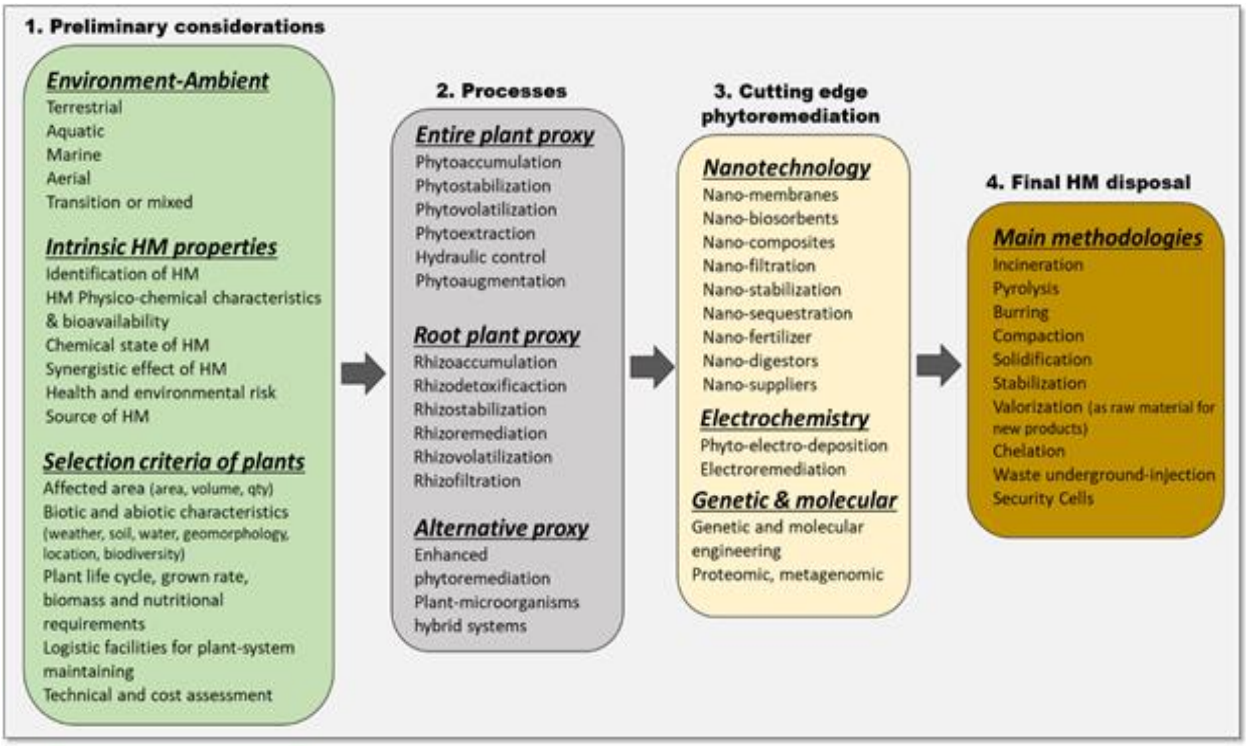


Figure 15. Heavy metals (HM) integrated plant-mediated remediation framework. This conceptual framework consists of 4 phases: 1) Preliminary considerations, 2) Processes, 3) Cutting edge phytoremediation, and 4) Final heavy metal disposal. Adapted from: Deb et al. 2020; Gholami et al. 2020; Shirani Bidabadi 2020; Abdullah et al. 2019; Muthusaravanan et al. 2018; 2020; Zubair et al. 2016; Marques, Rangel, and Castro 2009.

The first phase refers (Figure 15-1) to the preliminary considerations which are mandatory for any remediation action. The main aspects to be addressed include: a) identifying the specific ecosystem polluted; b) the heavy metals biophysics and chemical characteristics, including volume, surface, interactions with other chemical compounds and their environment; c) the selection criteria to choose the plant and the living organisms' association (Deb et al., 2020; Devi and Kumar, 2020; Muthusaravanan et al., 2020).

The second phase (Figure 15-2) involves a variety of plant-mediated remediation processes. Once the magnitude of the pollution is assessed, it is necessary to choose the process that could be affordable to remediate it. It is important to highlight that depending on what component of the plant is used, the process can be identified by a specific term, so there are two major proxies used in plant-mediated remediation:

1) The "entire plant proxy" which considers the plant as a single and global entity, the process could be differentiated in phytoaccumulation, phytostabilization, phytovolatilization, phytoextraction, phyto-augmentation (Azubuike et al., 2016; Marques et al., 2009). 2) The "root plant proxy" which clearly separates the belowground

component or system (roots) from the entire plant. This proxy are based on the underground interactions between plant roots, microorganisms, nutrients, and water dynamics. This proxy considers the microorganisms residing over the rhizosphere which have the capability to catalyze metal uptake in a symbiotic relationship with the roots (Schück and Greger, 2020; Mishra et al., 2017; Zubair et al., 2016; Marques et al., 2009). 3) The "alternative proxy", that we use to describe some hybrid methodologies to improve both phyto- and rhizoremediation processes. There are many reports about this kind of mixed systems that is able to potentiate the efficiency of the original method by using other supplies, living organisms, and in general, by adding external inputs or raw materials. It is also known the complementary use of mechanical, physical or chemical procedures to increase the speed and removal level of heavy metals (Deb et al., 2020; El-nour, 2020; Muthusaravanan et al., 2020; Martino et al., 2019; Yuan et al., 2019; Agnello et al., 2014). The phase 2 thus, permit to define the best specific strategy to apply an efficient phytoremediation process.

In phase 3 cutting-edge technologies are used (Figure 15-3), many of which are based on knowledge and applications of nanotechnology. For example, nanotechnology can be used in the process of eliminating heavy metals. In this case, the plants that absorb pollutants from the environment could use their metabolic processes to reduce them to nanoparticles and store them in their stem, leaves, and estate. Thus, in this process, the plants known as Phyto-tolerant or Phyto-accumulators allow the reduction of contamination.

During the last phase (Figure 15-4), the final disposal of heavy metals, their subproducts, and residues could be efficient and economically viable if the post-harvesting technologies employed are properly chosen and applied. Some routes are based on incineration, chelation, pyrolysis, compaction, solidification, stabilization, valorization, burring-landfill, waste underground-injection, and security cells. From these options, valorization of residues or materials with high content of heavy metal has received special attention worldwide, due to the positive results not only in technical and environmental aspects but also from the economic point of view (circular economy-sustainable development). A recent study addressing this topic demonstrated that the combination of biosorbents with catalytic technologies provided new ideas for the follow-up research direction of biosorbents (Deb et al., 2020; Huang et al., 2020; Sas-Nowosielska et al., 2004).

Chapter 4

4. Outlook and Conclusion

The pollution of water sources with heavy metals is a major issue worldwide, being one of the most critical environmental challenges nowadays. The interest on this topic lies on the fact that the current human activities are causing dramatic raise of heavy metals in the environment, making toxicity and real risks to human health. Thus, it is of highly important to develop efficient and affordable technologies to remove heavy metals from water sources. Future investigation must pursue global challenges such as (i) to improve the conventional methods of water use and its treatment and (ii) to produce innovative technologies considering non-conventional methods, including nanotechnology.

Ecuador's main problem lies in the absence of laws to control waste generated by industrial activities, where the lack of control by the authorities due to lack of human, physical and financial resources and the non-application of sanctions to offenders have contributed to increasing pollution in various water sources for the country. To achieve sustainable development, it is necessary to establish a regulation that allows the compliance, control, and permanent supervision of wastes management in the country

Eliminating heavy metals demands the ability of detecting their presence in the environment and determining their concentration. For this reason, we have discussed some of the characteristics of the spectroscopic, electrochemical and optical methods available for quantifying these pollutants. In this regard, the appropriate selection of a measurement technique offers the possibility of choosing an adequate treatment and evaluating its effectiveness. Heavy metal removal from aquatic systems can be achieved by using a variety of technologies which take advantage of mechanisms that allow capturing and degrading these pollutants. We have shown primary, secondary and tertiary treatments, emphasizing on the need of using methods that are highly efficient, environmentally friendly and cost effective.

Conventional and non-conventional treatments have been explored and we have focused on the materials used and the efficiencies achieved. Even though there are several mature methods and technologies available for heavy metal removal, there are also several research and development needs and opportunities. The adsorption process is considered the most convenient method for the removal of heavy metals from aquatic environments. Several investigations carried out around this technique indicate the advances that it has achieved. The main advantage of this process is the diversity of materials that can be used to be used as adsorbents. The novel methods based on nanocomposites seem to be very promising due to the capacity to control the final performance of the material by tuning the morphology, size, type, and functionalities depending on the specificity of the pollutants to be removed. Nano carbon-based nanocomposites also offer huge possibilities as starting materials that can be used as low-cost, safe, and effective adsorbents. However, more research is still necessary to firstly understand the mechanisms involved in the treatment and remediation process. Plant-mediated remediation represents an option of advancing in the development of robust, environmentally responsible, and efficient methodologies to remove heavy metals and/or restore polluted ecosystems/sites.

Performing studies using real instead of synthetic waters, evaluating the toxicity of the advanced materials currently researched, and working at scales beyond the laboratory level are some of the opportunities for future research. This research should allow improving the conventional methods for water treatment and to create safe, innovative, efficient and affordable technologies exploiting residues, natural materials, nanotechnology and improved detection and quantification methods.

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