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Study of Arsenic Levels in Drinking Water Networks in the Town Of Allato, Huancavelica Peru

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ABSTRACT : *This review shows the importance of Bioadsorption as an alternative of low cost, easy elaboration and application and mainly environmentally friendly (adsorbents of organic sources) for the removal of metallic elements in effluents Miner-Metallurgical. Mining makes it possible to obtain important economic currencies, however, following the development of its activities, many of the environmental legacies are seen in large waste and effluent installations with heavy metal presence. This strong impact caused to the water resource needs techniques to remedy and the existing technologies for it as precipitation, reverse osmosis, precipitation, among others are not feasible because they present excessive costs, generate sub productsas part of their treatment and demand a lot of energy. Therefore, the Bioadsorption that is responsible for the selective catching of heavy metal ions or other molecules by organic biomass whose functional groups have a great affinity to adsorb these elements, turns out to be an advisable option. But it is not only considered a potential mechanism for the removal of metal solutions, but also for the recovery of precious materials. Its main attraction is the profitability compared to conventional technologies, in addition to not generating toxic byproducts for the environment. The materials to be used for some are "organic waste" such as coconut shells, orange peels, banana peels, rice husks, sugarcane bagasse, among others, but for others they are a source of great potential for exploitation; And there are diverse researches that have shown efficiency of these as bio adsorbents of heavy metals.*

KEYWORDS –*Biosorption, Bio adsorbents, Heavy metal,Mining effluents*

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I. INTRODUCTION

Human decisions are of great importance in the distinction between waste and mineral, many of the environmental legacies of metal mining are often dominated by large waste facilities, which can be sources of Acidic drainage and Metalliferous, resulting in both a local contamination and irreversible losses of some of the soluble minerals[1]. The presence of contaminants in the water represents a problem that should occupy the daily agendas as it endangers the survival and advancement of humanity. Therefore, efficient and effectiveelimination of water contaminants has come to be a hot topic [2]

Heavy metals are found in the natural environment and/or appear due to the action of man, caused specifically by mining activities.[3]The presence of these pollutants in the environmental environment, air, water and soil, even in low concentrations are toxic and inevitably impact on the welfare of living beings.[4]

A range of technologies has been developed to eliminate the presence of metal traces in low concentrations of drinking water, including oxidation, coagulation, adsorption by precipitation, flotation of adsorbed flocs, ion exchange and membrane techniques. Many of these techniques are expensive, energy intensive and not continuous [5, 6]. In addition, some of these methods need further treatment processes that are difficult, mostly costly and cause environmental problems.[7]

It is an urgent need for industries, specifically for the mining area to find new methods that do not depend on large investments to treat their effluents, so that they comply with the current regulations. In recent years, some researchers have shown that certain organic materials such as fruit peels (banana, coconut, orange, cocoa and others) have effective adsorbent properties with notable economic benefits by giving it extra use to waste materials.

Biosorption occurs whenever a rigid surface is exposed to a gas or liquid phases and is defined as the enrichment of the material or the increase in the density of the fluid in the vicinity of an interface.[8] What makes this technology interesting is that the waste used is given a high potential for use and is addressed as viable alternatives for development. This mainly because it has functional groups (hydroxyl and carboxyl) able to participate in the retention of metal ions.[9] The complexity of bio adsorbents leads to the intervention of Adsorption Processes, Ion Exchange and also Micro-precipitation.[10]

For *Volesky*, the toxicity and health hazards associated with heavy metals are clearly established.[11] But in terms of choosing the type of metals for Biosorption studies and eliminating their threat to the environment, there are at least three basic considerations: metal toxicity (Direct threat to health), metal costs (Recovery interest) and how representative metal can be in terms of its behavior (Scientific studies). In practice, Biosorption studies focus on anthropogenic sources, mainly:

- Mine acid Drainage (MAD)- Associated with Mining Operations
- Electrodeposition Industry- Waste Solutions (Growth industry)
- Coal-based power generation- (Production of huge amounts of coal)
- Generation of Nuclear Energy- (Extraction/processing of Uranium and generation of special Waste).

As described above, the report seeks to raise awareness of an alternative of low cost, easy elaboration and application and most importantly, environmentally friendly (adsorbents of organic sources) for the removal of metallic elements in effluents Miner-Metallurgical.

II. BIOADSORTION BACKGROUND

2.1 Mining

No doubt the mining sector is a good contributor to the economy not only for industrialized countries but also an important engine for those developing.[12] It´s necessary to understand that together with the notable economic development also have significant environmental costs[13]this being an activity harmful to the environment, because it alters the ecological equilibrium in the places that is exploited;[14] This linked to the rapid development of industries, leads to the production of large quantities of toxic heavy metal ions.[15] Along with the remarkable achievement of rapid economic development, environmental costs are also significantly increasing.

According to *Vargas and Ministry of Environment (MINAM)*,Mining activity in Peru is classified as shown *Table 1* and the Legislative Decree 1105 clearly defined as the illegal mining informal, detailing what following[16, 17]:

- *Ilegal:* Activity exercised by a person or an organized group of people in which they use machinery and equipment not in accordance with the activity, do not comply with the environmental, technical, administrative, and social norms, or they exercise in areas that are Prohibited.
- *Informal:* What differs from the illegal, is that it is already in the process of formalization and its operation is given in areas not prohibited.

Table1- Mining Activity from Peru

Type of Mining		Features
Formal		It is carried out considering necessary requirements and permits in the mining, environmental, social and labor part determined in the current legal regulations.
		Include: Small, Medium and Large-scale Mining and Artisanal Mining
No formal	Informal	Does not comply with permits to execute the activity
		Operates in areas that are not prohibited
		It has a declaration of commitment and is in the process of being formalized.
		Its scale of operation is small
	Ilegal	Does not comply with permits to carry out the activity
		Operates in areas that are banned and/or uses Large-Capacity Machinery
		It is subject to eradication

Source: *(Vargas V, 2008)*

2.2 Heavy metal sources in water

By definition, it is called heavy metals to any metallic chemical element that has a relatively high density (more than 5 g / cm3); Most of them are toxic or carcinogenic even in low concentrations, such as mercury (Hg), cadmium (Cd), arsenic (As) and chromium (Cr).[18] High levels of water contaminants are a global concern. At least 20 metals are classified as toxic and half of these are emitted to the environment in amounts that present risks to human health.[19]

Heavy metals can reach in this medium by natural sources like various anthropogenic activities. One of the examples are the rocks (Igneous, Sedimentary and Metamorphic) that through interactions with the surrounding environment (Erosion, Outdoor) transport and redistribute heavy metals, commonly Nickel, Cobalt, Manganese, Zinc, Copper and others. Another of the means responsible for the storage of heavy metals are the soils (in remains of rocks, insoluble minerals, water and air transported). But it is also important to consider industrial activities as contributors in great proportion to the pollution of the environment by heavy metals. Mining produces large quantities of sterile rock, which still contains heavy metals (As, Cu, Cd, Pb, Hg), which are deposited inside the mine tailings and exposed to the weather and the oxidation conditions that lead to acid drainage.[20]

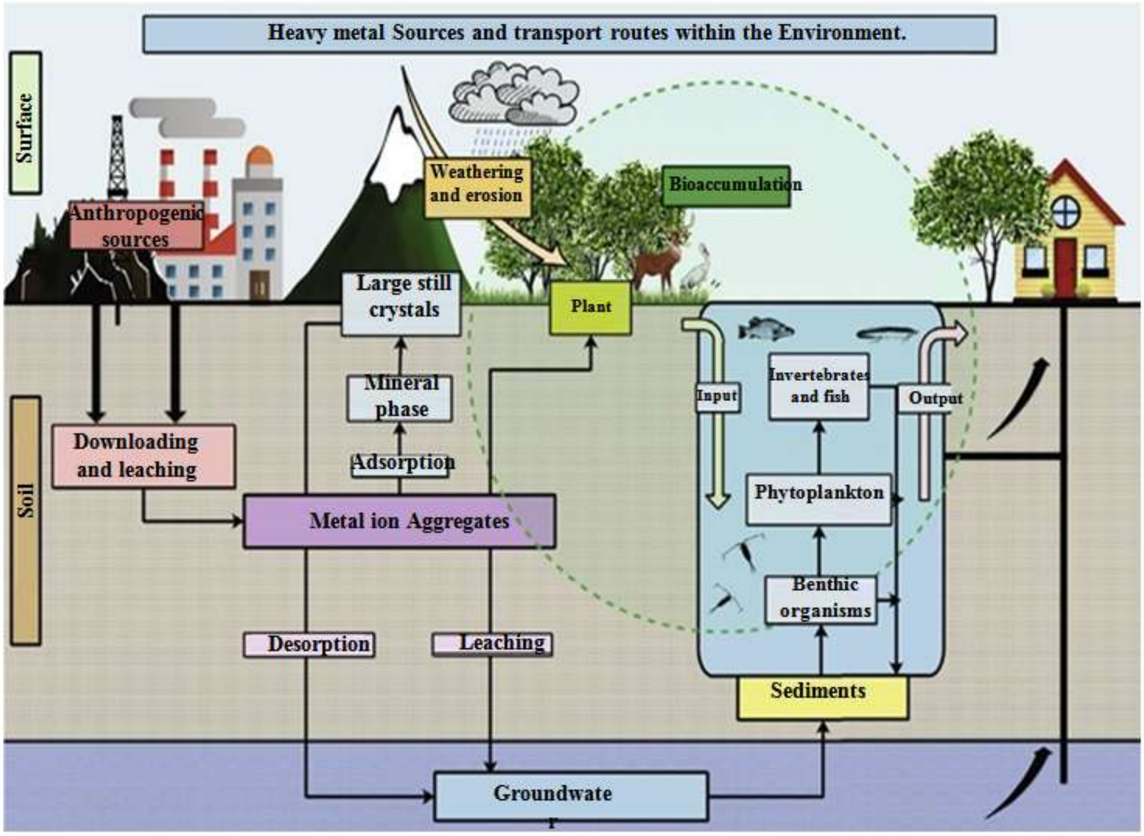

Figure1- Shows how soil, freshwater and groundwater systems redistribute heavy metals of anthropogenic origin. (Source: Adriano D, 2001).

Due to the stability, high solubility and migratory activity of heavy metals in aqueous media, wastewater effluents contaminated with untreated or inadequately treated metals cause a variety of environmental and health impacts when released into bodies of water.[22] Therefore, they must be managed properly (Mainly those metal ions that are considered the most widespread toxic mineral contaminants in soil and water systems such as Cu, Zn, Hg, Cd, Pb, Sn, Fe, Mn, Ag, Cr, Co, Ni, Ace, Al). So that long-term effects are not triggered in man and other living creatures.[23] In fact, Lead, Mercury, Cadmium, Chromium, Zinc and Copper ions have been considered as point pollutants to be removed from wastewater.[24]

2.3 Effects of heavy metals

1.3.1 Environment

Since the advent of the industrial age, the environment has been subject to the emission and deposition of anthropogenic chemical substances, both organic and inorganic.[25] Environmental pollutions by hazardous waste materials, organic pollutants and heavy metals has negatively affected the natural ecosystem of man[26] and is that the rapid industrialization and urbanization makes the environment is continuously exposed to various loads of chemicals from natural and anthropogenic sources.When these groups of omnipresent and nonbiodegradable environmental chemicals,[27] of high, toxic and non-degradable densities[28] enter the environment they can lead to bioaccumulation and bio-magnifications.[29]

The contamination of agricultural soils with heavy metals has serious ecologically and environmentally consequences, as it implies the entry of metals into the food chain, soil deterioration, the suppression of plant growth, reduction of performance and alteration of the microbial community. This is why soils contaminated with metals have become a major concern for scientists around the world.[30]

All metals have the potential to exhibit harmful effects at different concentrations, the toxicity of each metal will depend on the quantity available for the organisms, the absorbed dose, the route and the time that will last the exposure;[31] The action of metals in the soil and plants is then required.

1.3.2 Health

Although concentrations of some metals may be beneficial for the normal functioning of biological cycles, high concentrations become toxic to living beings, causing serious hazards over an extended period of time (Due to its cumulative and non-degradable properties);[32] The toxicity of metal elements for mammalian systems is due to the chemical reactivity of these ions with the structural cellular proteins, enzymes and membrane system.[33]

Heavy metals in the soil pose potential threats to the environment and can damage both human health and affect animals and this occurs through various absorption pathways such as a) respiratory (For gaseous particles); (b) The skin (Chemicals capable of crossing the barrier of the skin); (c) Digestive tract (For food contaminants)[34, 35]

It turns out that the largest edible parts of plants are the main source of heavy metal intake for human consumption, which in the long term are detrimental; The main risk point in human health is because they are persistent in nature and have a tendency to accumulate in biological systems.[36]Consumption of foods contaminated with heavy metals can severely impair some essential nutrients in the body that are also responsible for the reduction of immune defenses, intrauterine growth retardation, associated disabilities With malnutrition and high prevalence of gastrointestinal cancer rates.[37] The following table is presented with some of the important effects of the main metals.

Table 2- Effect to the Main Heavy Metals in Soils and Plants

	Effects of the main Heavy Metals
To the Soils	▪ Heavy metals at high concentrations affect the microbial population of the soil and its associated activities, which can directly influence soil fertility.[38, 39] ▪ Affect the growth, morphology and metabolism of soil microorganisms and any decrease in microbial diversity or abundance can negatively affect the absorption of soil nutrients for the plant.[40] ▪ Toxic effects consequently induce disturbances in terms of diversity, size and general activities of soil microbial populations.[41]
To the Plants	▪ Heavy metals are natural components that can´t be degraded or destroyed biologically and life can not develop and survive leaving metallic ions out because, life is both inorganic and organic; Plants require certain heavy metals (Fe, Cu, Zn, Mn, Mo, Ni, Co) for their growth and conservation, however excessive amounts of these metals can become toxic.[42] ▪ The effect of heavy metal toxicity on plant growth varies according to the particular heavy metal involved in the process.[43] ▪ For example, chromium occurs naturally in the form of crustal rocks but it is also used in several industrial units. This, like other heavy metals, can directly inactivate many proteins that bind to them or displace metals from the active centers of proteins.[44, 45] ▪ That leads to: Death and inhibition of seeds, Changes in enzymatic activity, Oxidative stress and Inhibition of growth

Source: *(Own Elaboration)*

2.4 Conventional treatments applied to the removal of heavy metals

Treating industrial residual effluents is generally difficult because their compositions vary and may include high content of organic material and low biodegradable components.[47] However, there is a wide range of technologies available for disposal, such as chemical precipitation, ion exchange, oxidation, reduction, reverse osmosis, electro-dialysis and Ultrafiltration (Renu, Singh, Upadhyaya, &Dohae, 2017).

Traditional treatment technologies for the elimination of these chemical elements have their inherent limitations as they require considerable capital investment and maintenance costs for infrastructure and reagents[47], produce a large amount of mud, they are less efficient and of delicate operating conditions.[48]

Table 3- Conventional techniques used for the treatment of metallic elements.

Technique	Disadvantages
Reverse osmosis: A semipermeable membrane is used to separate the heavy metal at a pressure greater than the osmotic pressure**.**	High energy consumption due to pumping pressures and the restoration of the membranes
Electrodialysis: A selective ion semipermeable membrane is used to separate heavy metals by applying electrical potential between two electrodes.	The percentage of separation decreased with an increased flow rate.
Ultrafiltration: A porous membrane is used to remove heavy metals by applying pressure	If the surfactant and heavy metals are not eliminated, secondary pollution is generated when generating sludge.
Ionic exchange: From the diluted solution containing the heavy metal, the metal ion is exchanged to the exchange resin for the retained ions by the electrostatic force.	It can be used only with a low-concentration metal solution and is highly sensitive to the pH of the aqueous phase.
Chemical precipitation: Chemical products react with heavy metal ions to form insoluble precipitates.	Generates large volumes of sludge that is difficult to remove.
Coagulation: Elimination of heavy metals by neutralization of particle load.	Heavy metal wastewater can not be completely treated.

Source*:(Das & Osborne, 2018*)

Therefore, it is significant to develop profitable processes for the treatment of contaminated water resulting from industrial processes. In particular, bioadsorption with organic waste has recently been studied and successful results have been found. Agricultural waste usually contains a variety of organic compounds (lignin, cellulose and hemicelluloses) and functional groups (hydroxyl, carbonyl and amino). Both organic compounds and functional groups have a high affinity for the formation of metal ion complexes.[50] Recent biosorption experiments with waste materials from industrial operations have drawn attention, their large surface area, the microporous character and the chemical nature of their surface have turned them into potential adsorbents for the removal of heavy metals from industrial wastewater. Studies conducted aim at the valuation of diverse materials such as coconut husks, rice, peanuts, coconut sawdust, cactus, among others.[51]

2.5 **Bio Adsorption: Alternative treatment**

2.5.1 *Adsorption*

For *Do Nascimento*, depending on the nature of the forces involved, the adsorption can be classified as to its intensity in two types: Physical Adsorption and Chemical Adsorption.

- **Physical adsorption**. Physical adsorption (physisorption) is a reversible method in which there is the attraction of molecules by mechanical forces when the molecules come into contact with the adsorbent. The reversible process basically depends on the force of attraction between the sorbate and the adsorbent. This type of adsorption is multilayer, which means that each layer of molecule is formed in the upper part of the previous one with the layers of numbers that are proportional to the concentration of contaminants.[53] In this type of adsorption, the bonding of the adsorption to the surface of the adsorbent implies a relatively weak interaction that can be attributed to the forces of Van der Waals, which are similar to the forces of molecular cohesion.[52, 54]
- **Chemical adsorption.** It involves the exchange of electrons between the molecules of the poly-sorbate and the surface of the adsorbent, resulting in a chemical reaction. This results essentially in a new chemical union and, consequently, much stronger than physisorption. Chemical adsorption is highly specific and not all solid surfaces possess active sites capable of chemically adsorbing the sorbate. It should be noted that not all molecules present in the fluid can be adsorbed chemically, only those able to connect to the active site. Physical adsorption, unlike chemical adsorption, is non-specific.[52]

2.5.2Bio*adsorption*

The term absorption and adsorption is often mistaken. Absorption is the incorporation of a substance into a state in a different state (i.e. liquids absorbed by a solid or gases absorbed by water); Adsorption is the physical adhesion or the binding of ions and molecules to the surface of the solid material. In this case, the material accumulated in the interface will be called ansorbate and the solid surface will be the adsorbent.[55]Thebiosorption is a subcategory of adsorption, where the sorbent is a biological matrix. It is a process of rapid and reversible bonding of ions based on aqueous solutions in functional groups present in the superficial part of the biomass. Such substances can be organic and inorganic and are soluble or insoluble forms. This process is independent of cellular metabolism.[56]

Bioadsorción is responsible for selective sequestration of heavy metal ions or other molecules in certain biological materials. It is the passive absorption of toxics by dead/inactive biomaterials from highly diluted complex solutions with high efficiency and is considered a potential mechanism for the removal of metal solutions, not only for toxic metals but also for the recovery of precious metals.[57] In the literature, the sorption properties of a wide range of biomasses of natural origin are usually analyzed to treat wastewater, especially when the concentration of contaminants is less than 100 mg L^{-1}, and where the use of other methods of treatment It is ineffective and too expensive.[58]

Crini, states that the adsorption process would be a very attractive technology if the sorbent is ready and ready to use. Therefore, it is necessary to pass through physical and chemical processes such as drying, autoclaving, crosslinking reactions or contact with organic or inorganic chemicals to improve the selectivity and sorption capacity.[60]

- **Bio-adsorption mechanism**

The biosorption process involves a solid phase (biosorbent) and a liquid phase (solvent) that contains species to be absorbed (Metal Ions). The high affinity of the sorbent towards metal ions results in the interaction and binding in the cell wall by different mechanisms. The process continues until the equilibrium between the amount of bound solid sorbate and the remaining sorbate in the solutions is established. Its action is through various mechanisms that take place in the cell wall, where the way to capture pollutants will be carried out depending on the type of biomass. [57]

Bioadsorption can be performed over a wide range of pH values between 3-9 and temperature values of 4 - 90 ° C. As the optimum biosorbent particle size is between 1 and 2 mm, the steady state of both adsorption and desorption It is achieved very quickly. This process does not require a large capital investment, so operating costs are economical. In addition, biological materials are often cheap and can be obtained from agriculture or industrial waste.[60]In the following scheme the treatment process is exemplified: The process includes liquid and solid phase, the process can occur in the same phase of the dissolution or within the same particle.

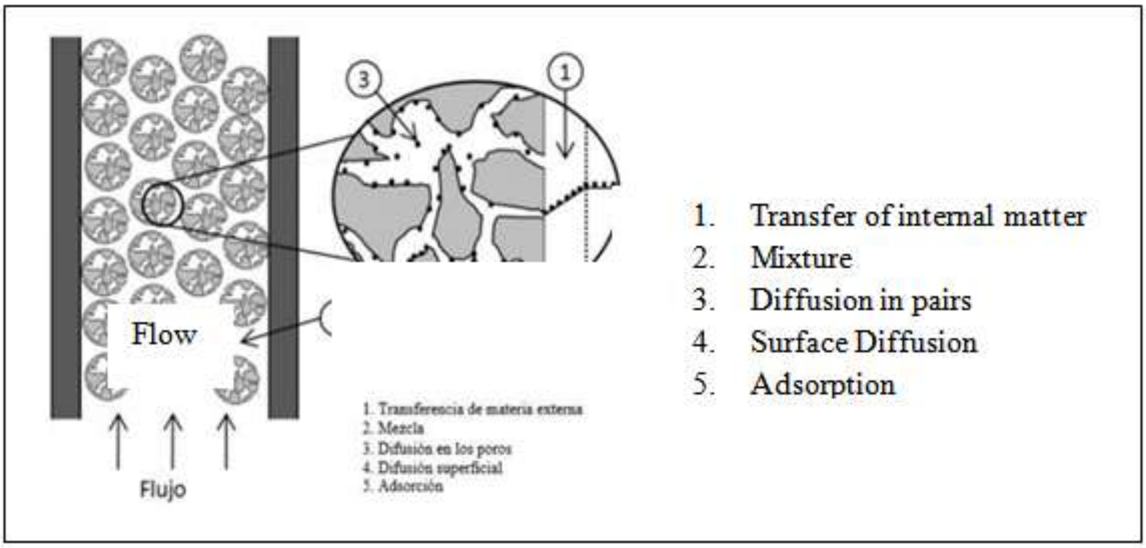

Figure 2- Treatment scheme in the process of bioadsorción in fixed milks(Source: Izquierdo, 2006)

- **Variables that influence the bioadsorption process**

The efficiency of heavy metal bioadsorción depends on the following variables:

A) pH

One of the most significant parameters affecting the process of biosorption is pH.[60] The biosorption is similar to an ion exchange process, i.e. biomass can be considered as a natural ionic exchange material containing mainly weakly acidic and basic groups. Therefore, the pH of the solution influences the nature of the sites of bonding to the biomass and the solubility of the metal; It affects the chemistry of the metal solution, the activity of the functional groups in the biomass and the competence of the metal ions. Metal Biosorption has often proven to be strongly pH-dependent on almost all systems examined, including bacteria, cyanobacteria, algae, and fungi. The competition between cations and protons for binding sites means that the biosorption of metals such as Cu, Cd, Ni, Co, and Zn is often reduced to low pH values.[61, 62]

In some respects, the biosorption is similar to ion exchange, and therefore the pH of a solution has a significant impact on removal of heavy metals. The number of links available the points on the surface of the cells depend on the pH. At low pH, binding points available in a cell bind to Hydrogen cations present in a solution. This leads to limiting the number of stains available and less metallic cations can be adsorbed. However, with the increase in pH, the number of active points with negative charge attracting cations also increases.[63]Some research shows the following charts:

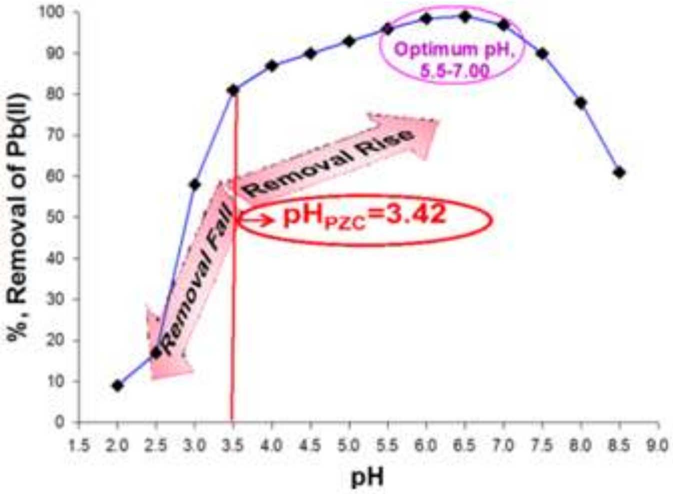

Figure 3- pH behavior with the use of Taro in the removal of Lead (Source: Chowdhuryf, et al., 2017).

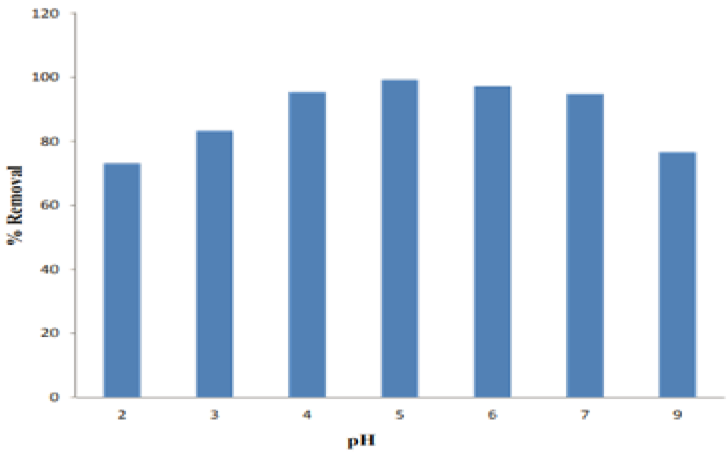

Figure 4- Effect of pH on the elimination of Sr (II) with banana peel (Source: Mahindrakar & Rathod, 2018).

B) Temp erature

The Metallic ions stability in a solution and the stability of metal cellules complex depend of Temperature. However, temperatures between 20 to 35°C don´t affect significantly bio sorption Process. A higher Temperature allow improved the absorption ability to the biomass, but it can become in harmfulBioadsorption material. [64]

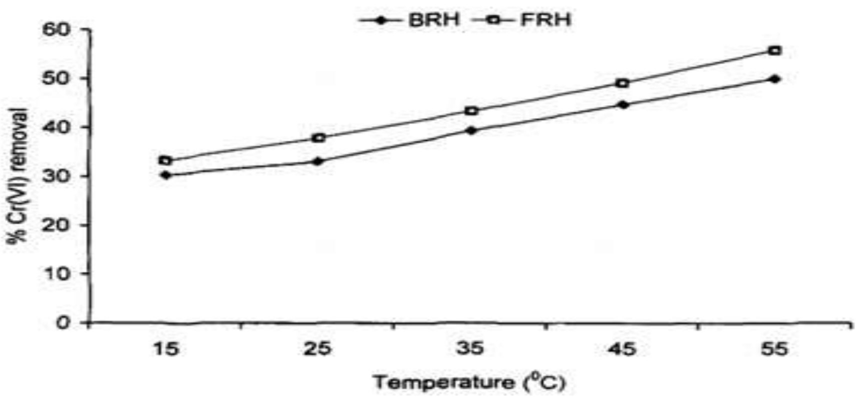

Figure 5- Effect of temperature on the elimination of Cr (VI) by boiled rice husk (BRH) and formaldehyde-treated rice husk (FRH) (Bansal, 2018).

C) Contact Time

The biosorption is also affected by the contact time between biomass and the solution containing metals. Biosorption advances fast and most metals are adsorbed at the very beginning of the process. The equilibrium is reached during the first minutes from the moment of the exposure of biomass to the solution.[64]

The elimination rate of metal percent is higher at first due to a larger surface area of the adsorbent available for the adsorption of metals. The absorption of metal by the surface of the sorbent will be rapid initially, slowing as the competition to decrease the availability of the active sites is intensified by the metal ions that remain in solution.[66]

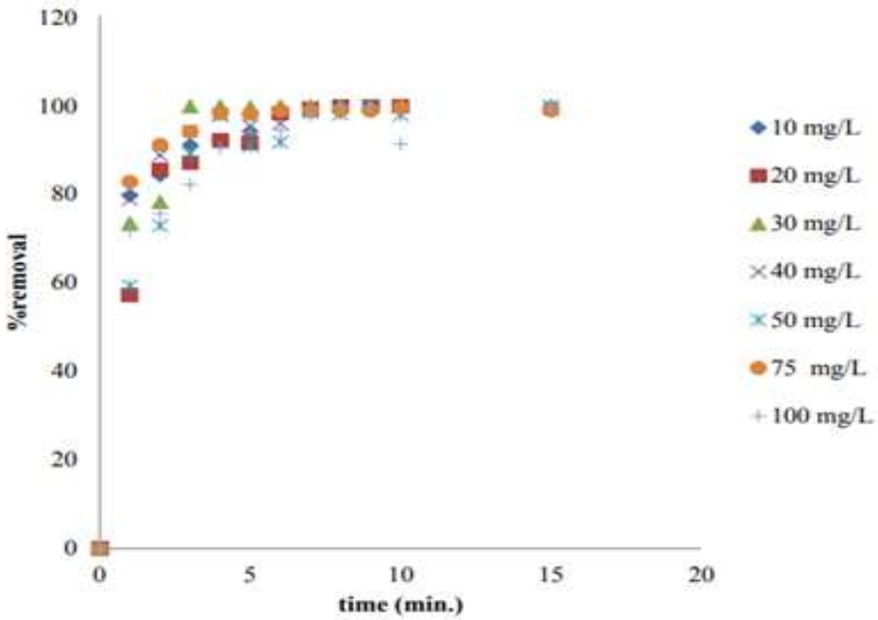

Figure 6- Effect of contact time in the elimination of Sr (II) with banana peel (Source: Mahindrakar & Rathod, 2018).

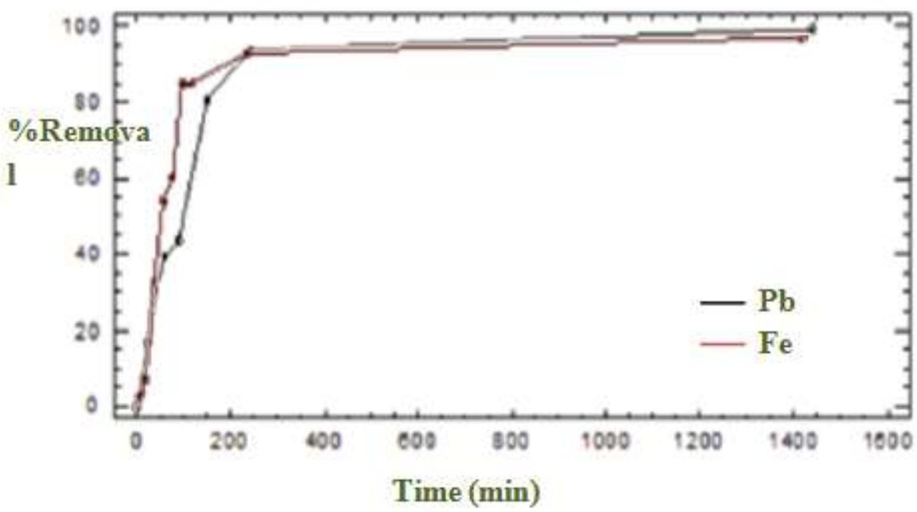

Figure 7- Removal of iron and lead in time function by Sour Orange Husk (Source: Samaniego Leon, Arzamendia, & Ayala, 2016).

D) Initial Metallic Ions Concentrations

Initial Concentration provides an important incentive force to overcome all mass transfer resistors of the metal between aqueous and solid phases.[67] Increased in the amount absorbed metal for biomass will increase with the Initial Metal Concentrations. The optimum percent to Metal removal can be taken at a low initial metal concentration, Therefore, at a given concentration of biomass, the absorption of metal increases with the increase in the initial concentration,[68]and this is usually related to two factors: the high probability of collision between metal ions with the surfaceand the high velocity of metal ions on the biosorbent surface diffusion.[50]

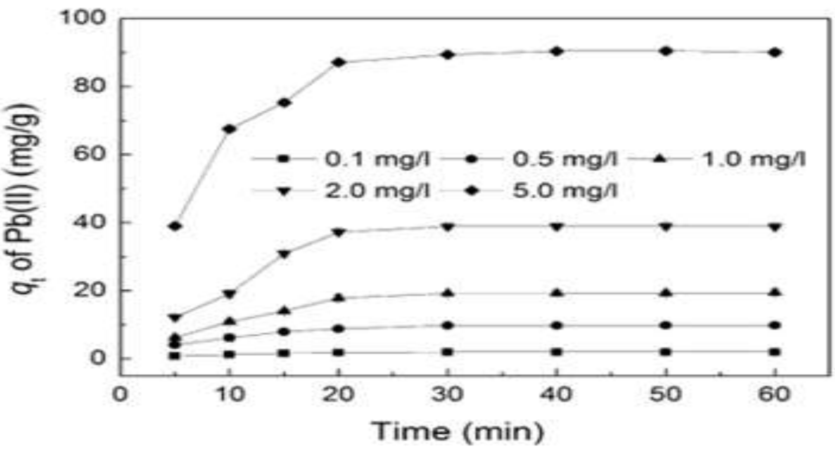

Figure 8- Effect of the initial concentration of Pb (II), pH 7.0 (Source: Wang, Chen, Yang, & Ma, 2013).

E) Dose of the bio-adsorbent

The biomass provides binding sites for the adsorption of metal ions, and therefore its concentration strongly affects the adsorption of metal ions from the solution.[69] The amount of biosorbent used for treatment studies is an important parameter, which determines the biosorbent potential to remove metal ions at a given initial concentration.[70]

For a fixed initial metal concentration, increasing the adsorbent dose provides greater surface area and availability of more active sites, which leads to the improvement of the metal uptake of ions.[71] At low biomass doses, the amount of ions adsorbed per unit weight of adsorbent is high. In the adsorption capacity is reduced when the dose of biomass increases as a result of a lower ratio of adsorbate to binding sites where the ions are distributed in a greater number of biomass binding sites. However, at a higher dose, the adsorbed ions are higher due to the availability of more empty binding sites compared to lower dose which has fewer binding sites to adsorb the same amount of metal ions in the adsorbate solution.[72]

F) Presence of other ions

Wastewater is contaminated with various contaminants, including different types of metals at the same time, which has an effect on the dynamics of Biosorption. The presence of other substances dissolved in a solution can inhibit metal biosorption. This is due to the competitiveness of metal ions that are eliminated and other ions for binding points on the surface of cells.[64]

2.6 Organic Biosorbent

Due to its simplicity and profitability, the adsorption technique is considered suitable for wastewater treatment, since adsorbents are non-toxic, cost-effective, easy to access and can be easily regenerated; In addition, these are found naturally, such as agricultural waste and industrial subproducts.[73]

A wide range of biomaterials available in nature has been used as bio sorbents for the elimination of metal elements. All types of microbial, plant and animal biomass and their derived products have received great interest in a variety of forms and in relation to a variety of substances.[74, 75] However, the attention has been directed towards the agricultural waste materials, polysaccharides and biomaterials of industrial waste in recent years.[76, 77]Among these biomaterials, chitosan, a natural amino polysaccharide, has received ample attention to treat a large percentage of aquatic contaminants due to its high content of amino and hydroxyl functional groups.[78]

In addition to the natural biosorbents mentioned above, in the literature, few other biomaterials have received much interest and they are: rice husk,[79]Coconut bark,[80]Plant barks,[81, 82] sawdust and sugar cane bagasse.[83]

Some biosorbents can join and collect a wide range of heavy metals without a specific priority, while others are specific to certain types of metals.[84, 85] Biosorbents for the removal of metals are classified in different categories, such as Fungi, Bacteria, Industrial Waste, Algae and Agricultural Waste.[74] Profitability is the main attraction of the metal biosorption, and must be maintained.[86] Although many biological materials bind to heavy metals, only those with a bonding capacity to metal and a selectivity for heavy metals high enough are suitable for use in a large-scale biosorption process .[87] The viability and efficiency of a biosorption process depend not only on the properties of Biosorbents, but also on the composition of wastewater.

A large number of biomass types have been tested for their metal fixation capability in various conditions, including agricultural products such as rice straw, coconut husks, residual coffee powder, dried plant leaves, wool, seed shells from Cotton, waste tea, biomass of cork.[88, 89] residual sludge and microbial cells such as bacteria, fungi, algae, yeasts and peat moss .[90] Industrial waste, such as Scerevisiae residual biomass fermentation and the food industry) and other polysaccharide materials, etc,[88]

Table 4- Several Biosorbents used in Sorption.

Bio adsorbents	Metallic Ion	pH	Temperature (C°)	Removal (%)	Reference
Coconut husks	Pb (II), Cu(II) y Fe(II)	5--7	100, 50	94 (+-3.2), 92(+-2.8) y 94(+-1.4)	(Abdulrasaq & Basiru, 2010)
Orange Peels	Pb (II) y Zn (II)	5	50	99	(Cardona, Cabañas, & Zepeda, 2013)
Cocoa Residues	Pb y Cd	6	30	91,32 y 87,80	(Lara, Tejada, Villabona, Arrieta, & Granados, 2016)
Almond shell	Cu (II)	5	25	9,44 mg/g	(Calero, Hernáinz, Blázquez, Dionisio, & Martín, 2011)
Rice husk	Cd y Ni	6	ambient	98 y 96	(Córdoba, Hoyos, Rodríguez, & Uribe, 2016)
Parsley, cilantro and coriander	Pb (II)	3--5	25 (+-2)	>97	(Boontham & Babel, 2017)
Banana Peels	Mn (II)	8	25	94	(Ali, 2017)

2.6.1 Recent studies

Šoštarić, et al., used alkali-modified apricot shells (SHM) as a biosorbent for the removal of Cu (II), Zn (II) and Pb (II) ions from an aqueous solution. *Fig. 9* graphical process model. To calculate the biosorption capacity of the following formula:

$$qe = \frac{V(Ci - Ce)}{m}$$

Where: q: the amount of metal ions adsorbed (mg / g); Ci and Ce: the initial metal and equilibrium concentrations (mg / l), respectively; V: the volume of the solution (L); M: the mass of the sample (g).[98]

The results showed high efficiency in elimination of multiple metal ions. The amounts of Fe, Pb, Cu and Cr ions were reduced by 97, 87, 81 and 80%, respectively, while the amounts of Ni and Zn were reduced by 33 and 14%. In addition, the used biosorbent could be regenerated to be reused or finally disposed of safely.

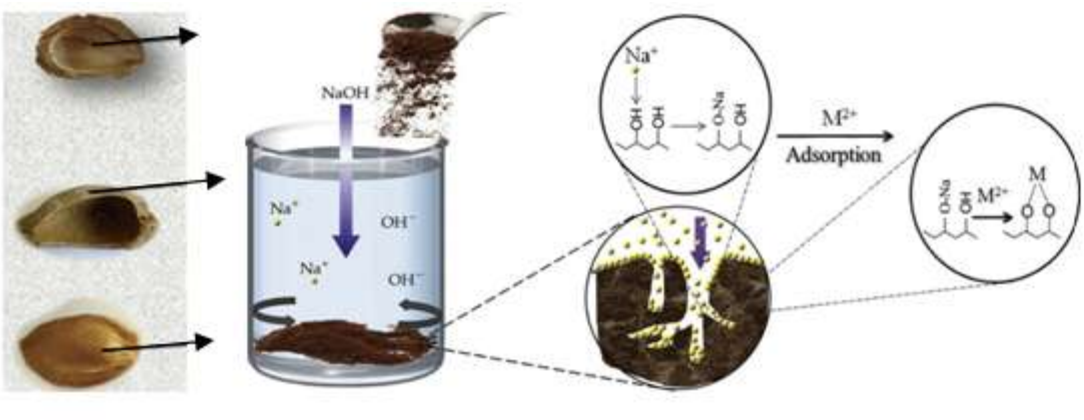

Figure 9- Operating graphical model (Source: Šoštarić, et al., 2018)

Also *Vargas, Cerro, Bandala, Sanchez, & Tellez,* used the bark residues of banana (Musa paradisiac), lemon (Citrus limonum) and orange (Citrus sinensis) for the elimination of Pb and Cu. The authors found that the banana bark had a higher biosorption capacity than the orange and lemon. On the other hand, lemon and orange rind were more efficient in the elimination of Pb and Cu than banana[99] (See *table 5*).

Table 5- Biosorption capacity of different fruit crusts

Biosorbent/ Metal	Pb(mg/g)	Cd(mg/g)	Cu(mg/g)
Banana	65.5	67.2	36
Lemon	77.6	12	70.4
Orange	76.8	28.8	67.2

Source:*(Vargas, Cerro, Bandala, Sanchez, & Tellez, 2012)*

Malik, Dahiya&Lata investigated the Sorption Capacity of coconut husk (Cocosnucifera L.) unmodified in the removal of heavy metal ions (Pb^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) from industrial wastewater. To determine the equilibrium relationships between the adsorbent and the adsorbed, the Freundlich and Langmuir isotherms were used:[100]

- Isormutation of Langmuir (1) and Freundlich (2):

$$q_e = \frac{q_{máx} K_L C_e}{1+K_L C_e} \qquad (1)$$

$$q_e = K_f C_e^{\frac{1}{n}} \qquad (2)$$

Where: **qe**: Equilibrium Desorption Capacity (mg/g); **q_{max}:** Maximum Desorption Capacity (mg/g); **K_L:** Langmuir constant (L/mg); **C_E:** Equilibrium concentration (mg/L);**K_f:**Freundlic constant (mg/g) (L/Mg); **n:** Heterogeneity factor.

The authors showed that the maximum adsorption capture occurred at 443.0 mg/g (88.6%) for Cu, for Ni with 404.5 mg/g (80.9%), 362.2 mg/g (72.4%) for Pb^{2+} and 338.0 mg/g (67.6%) for the ion Zn^{2+} simultaneously. The order of metal elimination is well adjusted to the adsorption order and has been found to be $CU^{2+} > Ni^{2+} > Pb^{2+} > Zn^{2+}$ for most operating conditions, such as initial concentration of metal ions, adsorbent dose, pH, Temperature and Contact Time.

2.6.2 Importance of the use of organic materials as bioadsorbents

According to *Kratochvil&Voleskyand**Aksu, Sag, &Kutsal*, the fascinating features of the bio adsorption on conventional heavy metal removal treatment methods include:[101, 102]

- Use of naturally abundant renewable biomaterials that can be produced economically
- Ability to treat large volumes of wastewater thanks to rapid kinetics.
- High selectivity in terms of elimination and recovery of specific heavy metals
- Ability to handle multiple heavy metals and mixed wastes
- High affinity, reducing residual metals to less than 1 ppb in many cases
- Less need for additional costly reagents that typically cause disposal and space problems.
- Operation in wide ranges of physicochemical parameters (pH, temperature, and presence of other ions)
- Relatively low capital investment and low operational cost
- A highly improved recovery of the United heavy metals from biomass
- Very small volume of dangerous sub-products.

For *Fu & Wang*, the Bio adsorbents have the following characteristics:

- It is an effective technology that also offers Design and Process flexibility.
- In some cases, it is reversible, so the adsorbent used can be regenerated through a proper desorption process.
- Does not require living organisms, manipulation is facilitated.
- Physiological conditions of the medium are less restrictive; no aseptic conditions are required.
- The process can be reversible, recovering the material used and minimizing waste or sludge loaded with chemical or biological compounds.

In addition to the advantages of low cost, high efficiency and non-production of sludge, there is the possibility of recovering metals from biosorbents loaded by the treatment of elution or incineration.[104] But on the other hand the cost advantage of the Biosorption technology would guarantee a strong penetration of the large market of the heavy metal pollutant industries, added to this is that the treatment of wastewater with the presence of heavy metals. It can be carried out by several agro-products, whose structure presents a wide variety of functional groups such as Hydroxyl, Carboxyl, Carbonyl, Amine, Amide, Alcoholic, Phenolic, Thiol and Phosphate.[105]

III. CONCLUSIONS

Mining, despite its economic contribution to a country, is not expeditious to be one of the protagonists of the many environmental problems, because in carrying out its different processes and by the use of some chemical inputs, the effluents discharged present great Contents of heavy metals, mainly Pb, Hg, Zn, Cd and As, causing a progressive deterioration of the ecosystems.

Considering that many of the activities of extraction of precious metals are carried out in an informal manner, without abiding by the regulations in force, and with little interest in the impacts that are generated, punctually in the water resource, whose quality is altered by the Presence of these chemical compounds, it is necessary to look for alternatives of solution that return it to its original state or in any case, allow an improvement of its characteristics before being poured.

Different technologies for the removal of heavy chemical elements emerged from this problem. However, in recent years, special attention has been paid to "Organic Waste" which after being studied proved to be quite efficient as bio adsorbents. What makes it different from conventional methods is its profitability, easy operability and sustainability. Although there are still no cases where it has been applied on an industrial scale, it is expected to continue to be investigated and can be used on a large scale.

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