

Indira Altynbekova

**REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTIONS
WITH BIOMASS**

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ABSTRACT

Centria University of Applied Sciences	Date June 2020	Author Indira Altynbekova
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<p>Nowadays, heavy metal pollution is considered as one of the most dangerous problems, and the use of biomass for uptake of heavy metals helps the environment and it is a potential alternative for the traditional technologies. In this work nine heavy metals (zinc, lead, mercury, cadmium, chromium, copper, nickel, arsenic, iron) are taken into consideration and their side effects are shown. Two problems reduction of waste and removal of heavy metals from aqueous solutions are covered.</p> <p>As the traditional techniques have some drawbacks, the new method as biosorption has been studied. The several types of biomass such as microbial cells (bacteria and algae) and agricultural waste (rice husk, wheat shell, papaya wood, apricot and peach stones) are included. Different cases for instance the same biosorbent but different metals are considered under conditions such as changing pH, temperature, metal and adsorbent concentrations. All of the conditions showed interesting results depending on the metal and biomass type. Further research is required for the more precise conclusion about the usage of biomass for heavy metals removal.</p>		

Key words

Adsorbent, Biomass, Biosorption, Heavy metals, Waste

CONCEPT DEFINITIONS

List of abbreviations

AWB	Agricultural waste based biosorbent
CO ₂	Carbon dioxide
Cr (III)	Trivalent chromium
Cr (VI)	Hexavalent chromium
FTIR	Fourier – transform infrared spectroscopy
NaOH	Sodium hydroxide
TFW	Tea factory waste

Symbols

C	Initial metal concentration
N_s	Rotation speed
T	Temperature
W	Absorbent concentration
η	Efficiency

ABSTRACT

CONCEPT DEFINITIONS

CONTENTS

1 INTRODUCTION	1
2 HEAVY METALS AND THEIR EFFECT	2
3 TRADITIONAL REMOVAL TECHNIQUES OF HEAVY METALS	9
3.1 Chemical precipitation	9
3.2 Membrane filtration	10
3.3 Ion exchange	11
4 BIOMASS	13
4.1 Microorganisms as biomass	14
4.1.1 Bacteria as biomass	14
4.1.2 Algae as biomass	17
4.2 Agricultural waste	18
5 BIOSORPTION	21
5.1 pH value	22
5.2 Temperature	25
5.3 Initial metal concentration	26
5.4 Adsorbent dose	28
5.5 Contact time and agitation speed	30
6 CONCLUSION	32
REFERENCES	34

FIGURES

FIGURE 1. Membrane filtration process.....	10
FIGURE 2. A scheme of metal binding by functional groups on the cell wall of biomass.....	15
FIGURE 3. The removal of Zn (II), Cd (II), Cu (II) with papaya wood.....	23
FIGURE 4. Effect of pH on Pb (II) adsorption with peach and apricot stones.....	24
FIGURE 5. Effect of temperature on removal of Zn (II), Cd (II), Mn (II) by maize stalks.....	26
FIGURE 6. Initial metal concentration effect on biosorption.....	27
FIGURE 7. Apricot and peach stones effect on Pb absorption.....	29

TABLES

TABLE 1. Essential and nonessential heavy metals.....	2
TABLE 2. Heavy metal types and their effect on human health.....	3
TABLE 3. Biosorption of bacteria with heavy metals.....	16
TABLE 4. Biosorption of heavy metals with algae.....	18

1 INTRODUCTION

The environment receives a considerable amount of harmful impact from the manufacturing processes which produce heavy metals. Due to many industries and industrial products, heavy metals end up in wastewater. Wastewater damages the groundwater and soil reducing the quality of consumption. It is considered as a global problem which leads to deterioration of the ecological system and creation of eutrophication. Moreover, heavy metals are not biodegradable pollutants and they can accumulate in living organisms; consequently, they can cause different diseases and present a high danger to human health. (López-Mesas, Navarrete, Carrillo & Palet 2011.).

The most common methods of heavy metals treatment are chemical precipitation, extraction, ion-exchange, membrane filtration are a part of wastewater pollution removal (Babel & Kurniawan 2003). However, it has its own drawbacks such consumption of energy and a special qualification is required. Therefore, the eco-friendlier way of heavy metals' treatment in wastewater is shown in this thesis.

This thesis aims to show the toxicity of heavy metals and the traditional techniques which are used to remove them from wastewater. The alternative method of heavy metals' removal with biomass is covered. The different types of biomass, its size and its composition are taken into consideration. The factors such as pH value, temperature, initial metal and biomass concentrations are included. The functional groups of biomaterials such as amino groups, carboxylic, phosphates, sulfates are taken into account too because they are the binding sites for complex reactions and ion exchange processes.

The thesis is a literature review, the research about replacement of traditional wastewater treatment with biomass is conducted. No lab work is done but, in this study, a brief summary of the scientific articles is presented.

2 HEAVY METALS AND THEIR EFFECT

Aluminium, arsenic, cadmium, chromium, cobalt, copper, gold, iron, lead, manganese, mercury, nickel, selenium and zinc are considered as heavy metals. The metals with higher than 5 g/cm³ density are considered as heavy metals (Nies 1999). Heavy metals are divided into two types: essential and nonessential metals. Essential metals are needed for daily life and normal cellular growth in low concentrations (nM) (Große, Anton & Hoffmann 2004). While nonessential metals are not known with their biological functions and they are toxic at low concentration, too (Rehman 2006). The most dangerous ones are arsenic, cadmium, chromium (VI), lead and mercury from the eco-toxicological point of view. The table with essential and nonessential heavy metals with the most common oxidation states in wastewater are shown in Table 1.

TABLE 1. Essential and nonessential heavy metals (adapted from Shamim 2018)

CATEGORY OF HEAVY METALS	
Essential	Nonessential
Zinc (Zn (II))	Lead (Pb (II))
Copper (Cu (II))	Mercury (Hg (II))
Nickel (Ni (II))	Arsenic (Ar (III; V))
Iron (Fe (II))	Chromium (Cr (III; VI))

Wastewater containing heavy metals flows due to different industry productions. Leather, mining, milling, tannery, and other metal processing sectors contain a considerable amount of heavy metals. The following industries such as electroplating, electrolysis, milling and anodizing cleaning generate heavy metals such as cadmium, chromium, copper, lead, nickel, silver and vanadium. Printed circuit board manufacturing releases lead, nickel and tin. Arsenic can be released from chromated copper-arsenate treatment in wood processing industries. Also, oil refining produces contaminated chromium, nickel and vanadium because of the catalysts. Heavy metals appear in natural mineral forms as carbonates, oxides, silicates and sulfides. These compounds are mostly insoluble in water, but it can slowly break down by weathering and be a hazard for groundwater and rainfall. Rainwater contains dissolved carbon dioxide (CO₂) and it may attack some rocks. For example, peridotite contains 50 % of magnesium oxide, if rainwater attacks the rock, magnesium can be dissolved with bicarbonate ion.

However, iron oxidizes to ferric hydrate which is highly insoluble even if pH is lower than 2. Also, the other metals, which act as iron, are insoluble in water and precipitate in their oxides. (Dean, Bosqui & Lanouette 2002.). Moreover, metal ions can bioaccumulate and biomagnify through the food chain in the environment. As a result, their toxicity brings more danger for animals and humans in the high trophic levels. (Baysal et al. 2013.). Heavy metal polluted water causes various types of diseases such as anemia, damage to the nervous system, cancer and kidney diseases (Mubarak et al. 2014). If the concentration of metals is above the permissible level, it causes different diseases, even death (TABLE 2).

TABLE 2. Heavy metal types and their effect on human health (adapted from Abbas, Al-Amer, Laoui, Al-marri, Nasser, Khraisheh & Atieh 2016)

Pollutant	The source	Effect on human health	Permissible level (ppm)
Zn (II)	Brass manufacturing, metal plating, refineries, plumping	Skin, nervous system, gastrointestinal damage,	15
Pb (II)	Automobile emission, mining, paint, coal burning, pesticides	Gastrointestinal damage, liver, kidney, diarrhea	0.1
Hg (II)	Batteries, paper and paint industries, pesticides	Nervous system, protoplasm poisoning, eyes and muscles pain	0.01
Cd (II)	Electroplating, pesticide fertilizer, nuclear fission plant	Bronchitis, gastrointestinal damage, kidney damage, cancer	0.06
Cr (III; VI)	Dyes and pigments, chrome plating, leather tanning, and wood preserving	DNA, mutagenesis changes, lung tumors	0.05

TABLE 2 (continued)

Cu (II)	Electrolysis, electroplating, milling and anodizing cleaning	Anemia, kidney and liver damages, respiratory damages	1.3
Ni (II)	Electrolysis, paint formulation, printed circuit board	Gastrointestinal damage, bone, skin, heart, and inhalation	0.01
Ar (III; V)	Fungicides, pesticides, metal smelters	Bronchitis, dermatitis	0.02

Zn (II) is considered as one of the heaviest metals appearing in wastewater. Zn ions can form inorganic salts and stable organic complexes due to the reaction between Zn ions and ionic or neutral compounds. The amount of metal depends on the solubility of formed compounds, pH, temperature, and the general quantity of present Zn and other organic and inorganic compounds in water. (Mubarak, Sahu, Abdullah & Jayakumar 2014.). Zn pollution comes from the petroleum and burning of coal, and 75 % of air is polluted with it (Hubicki & Kołodyńska 2012). Also, the wastewater contains a critical amount of Zn which accumulates in the surface of soil. The toxicity of Zn varies depending on the pH value, Zn is necessary for the human; however, if the dose is higher than 150 mg, it may cause some health problems. Kidneys, liver and gonads can be damaged because of the overdosing. (Hubicki & Kołodyńska 2012.). Workers inhale Zn containing smoke from the industries, and soldiers are affected from the military smoke bombs which contain zinc chloride or zinc oxide (Plum, Rink, Haase 2010).

Pb (II) is one of the most frequently present heavy metals occurring in wastewater. Mostly it can be found in soil, sewage and sediment sludge. Pb, itself, does not bioaccumulate or the concentration of it does not increase in the food chain. Moreover, it is not necessarily needed in plants and animals' lives. However, it can be accumulated in organisms such as mussels or worms. Pb discharges come from plastics, ceramics, finishing tools and some other by-products of steel (Adiana, Juahir, Joseph & Shazili 2017). It has harmful biological effects in high concentrations and it strongly bonds to oil, sediments and sludge particles. (Kennish & Michael 1989; Shaheen, Antoniadis, Kwon, Biswas,

Wang & Rinklebe 2017). Pb can enter human's body through the air, food and water, and it is especially dangerous for men's vital organs. 0.05 mg/dm^3 is allowed concentration of drinking water (Adiana et al. 2017). Excess of lead causes anemia, kidney malfunctioning and brain damage. Loss of appetite, headache, sleeplessness, birth defects, autism, allergies can be caused by excess of Pb at work of place and manufacturing industries. (Martin & Griswold 2009.).

Hg (II) is a unique metal because of its fluidity at room temperature. Moreover, ionic Hg can change to a Hg atom with no charge which is volatile, and it can move by air. Another feature of Hg that it may be biologically and chemically transformed to methylmercury and dimethylmercury which are volatile too. The toxicity of organic Hg forms is higher than inorganic forms. (Baysal, Ozbek & Akman 2013.). Hg is the most toxic heavy metal; it can cause danger for human health and the environment in its simple form and in compounds form. One of the most dangerous compounds is methylmercury which can accumulate very fast. Mercury's concentration is between 0.001 and 0.050 ppm in most of food especially in marine foods. The standards for drinking water are set from 0.001 to 0.002 mg/L by the World Health Organization and Environmental Protection Act. (WHO 2003.). The short-term exposure of mercury affects the nervous system while the long-term exposure is harmful for the immune and reproductive system, and kidneys. (Alalwan, Kadhom & Alminshid 2020.) Moreover, the nervous system is sensitive for all the types of Hg, brain functions and memory problems may be the result of Hg excess (Martin & Griswold 2009).

Cd (II) and its compounds are water soluble; therefore, they are more mobile and bioavailable in soil. Cd is quickly moved by microorganisms and mollusks because of the high bioconcentration factors. Free ionic form of Cd (II) is absorbed by organisms in water and the metal has high solubility in water, and they bioaccumulate fast in soil; consequently, it is counted as a serious pollutant (Qi, Lamb, Naidu, Bolan, Yan, Rahman & Choppala 2018). The toxicity of Cd for organisms in water depends on the ionic metal concentration (Baysal et al. 2013). Humans receive the danger of Cd from food and water, even from the air if there are industrial plants nearby. Cd can be easily absorbed by inhalation, and it goes to the gastrointestinal tract where 10 % of Cd is absorbed. The allowed concentration of Cd in drinking water is 0.003 mg/dm^3 . (Hubicki & Kołodyńska 2012.). Long-term exposure of Cd can cause lung cancer and damages of kidney and bones (Liu, Xiao, Perkins, Zhu, Xiong & Ning 2017). Cd accumulates in intestines, kidneys and glands, changing the metabolism of the necessary elements such as Zn, Fe, Cu, Mn, Se and Ca. The problems with lungs and emphysema, may be caused because

of the fumes and dusts that contain cadmium. Also, the kidney damages develop with the cadmium poisoning. (Hubicki & Kołodyńska 2012.).

Cr appears in many industries such as tanning, paints and dyes manufacturing for plastic; thus, a vast amount of chromium is released to the environment (Kazakis, Kantiranis, Kalaitzidou, Kaprara, Mitrakas, Frei, Vargemezis, Vogiatzis, Zouboulis & Filippidis 2018). Cr occurs most commonly within compounds. It does not generally bioaccumulate and does not increase the concentration of metals in the food chain. Cr has different oxidation states but trivalent chromium, (Cr (III)), and hexavalent chromium, (Cr (VI)), are the most spread ones. There is a difference between the third and sixth oxidation states, especially the effect on the environment. (Baysal et al. 2013.). Cr (III) is needed for human's body for its development and it is an important nutrient for humans, it is needed for insulin's metabolism. Moreover, it is an essential nutrient for animals and plants (Baysal et al. 2013). However, Cr (VI) is not necessary for people, it disturbs DNA synthesis and causes a risk of mutagenous changes (Hubicki & Kołodyńska 2012). Compared to Cr (III), Cr (VI) produces more danger and causes health problems such as cancer, and it is more toxic. The high concentration of hexavalent chromium can infect fish, snails and worms. Small water fleas can be affected by small presence of hexavalent chromium which is equal to 0.01 mg/L. (Baysal et al. 2013.).

Cu (II) compounds can be easily found in the environment and water sources because they are involved in agricultural and industrial activities (Poole 2017). Cu in soil does not move far because it directly attaches to organic materials; thus, mostly it does not reach groundwater. Although Cu can make long distances as a free ion in surface water. (Baysal et al. 2013.). The food and drinks can be contaminated because of the packaging containers which contain copper (Liberti & Pichtel 1997). Cu is the second most toxic heavy metal after mercury, because it can be found in air, in drinking water and in different types of food. Humans absorb Cu daily from breathing, eating and drinking. (Baysal et al. 2013.). Cu is an important substance for human life; nevertheless, large concentrations of it can bring health problems, such as anemia, kidney and liver damages, stomach irritation and it may damage respiratory systems in high doses (Mubarak et al. 2014; Abbas, Al-amer, Laoui, Al-marri, Nasser, Khraisheh & Atieh 2016). Copper is a necessary element for human's blood, and it increases during pregnancy, elderly age and in children. Excess of copper may lead to liver damage and gastrointestinal

problems, inhalation of copper causes diarrhea, chronic lung damage and gastritis. (Hubicki & Kołodzyńska 2012.). The limit of Cu for drinking water is 0.05 mg/dm^3 (Fewtrell, Kay, Jones, Baker & Mowat 1996).

Ni (II) is considered a toxic metal because it is a natural element of the Earth, it comes from natural and industrial activities such as ship cruise industries (Baysal et al. 2013). It is dangerous in high concentrations to humans and animals. The presence of Ni can be found in electroplating industries as well, the concentration of metal reaches 200 ppm (Revathi, Kavitha & Vasudevan 2005). The amount and mobility of nickel in soil, and nickel's concentration in groundwater rise to 0.98 mg/dm^3 with every acid rain. Nevertheless, the limit for nickel in water is 0.02 mg/dm^3 and it is 0.01 mg/dm^3 in drinking water. Nickel damages the gastrointestinal tract, bones, skin and heart, while inhalation of nickel causes breathing problems. (Hubicki & Kołodzyńska 2012.).

As is dangerous because it can be operated under natural conditions. It has four different oxidation states as -3, 0, +3 and +5. All of them have different impacts on the environment and human health. (Baysal et al. 2013.). As rarely occurs in the free state, it is mostly found in complex forms in combination with oxygen, sulfur and iron (Ungureanu, Santos, Boaventura & Botelho 2015). As appears in its inorganic form in aquatic environments. Removal of arsenic is complicated; it must be reduced to the cationic state first because it hardly precipitates as a hydroxide (Higgins & Romanow 1987). Arsenic pollutes the environment under natural conditions but the additional effect comes from the agriculture compounds, the combustion of fossil fuel and mining (Ungureanu et al. 2015). People can receive excess arsenic from groundwater, surface water and rain, and the drinking water may cause the greatest risk (Pan American Health Organization. 2011). The most toxic of arsenic species are arsines and inorganic arsenites, and the least toxic is arsonium compounds and arsenic in elemental form (Anderson, Thompson & Culbard 1986). Arsenic in 3+ oxidation state (arsine, arsenites) is most soluble and mobile; therefore, it is 70 times more toxic than arsenic in other forms (Ungureanu et al. 2015). Consumption of contaminated drinking water with arsenic may lead to cancer and spontaneous abortion in the future (Smith, Marshall, Yuan, Ferreccio, Liaw, Ehrenstein, Steinmaus, Bates, & Selvin 2006).

Fe is a possible toxic metal which can cause heart disease in its excess. Fe compounds can be much more dangerous rather than the element itself. (Alimohammadi, Sedighi & Jabbari 2017.). Fe is the

tenth most abundant element, it takes 34,6 % of the Earth. It is found in its different oxides and minerals. The allowed levels of Fe are between 0.5 and 1.50 mg/L, but it rises to 10 mg/L which is seriously toxic. (Arnarson 2017.). Levels of Fe in drinking water and collected groundwater can be higher than the permissible limits and many people have been consuming excess amounts of Fe (Grazuleviciene, Nadisauskiene, Buinauskiene & Grazulevicius 2009). Fe is a necessary mineral in human organisms and an important part of hemoglobin; hemoglobin is needed for oxygen delivery to all the cells. High level of Fe is toxic, and it increases the hepcidin level, which results in the decrease of iron absorption in the body. Fe toxicity may increase the free ions and it might damage the cells. Early symptoms can be nausea and stomach pain, later the excess of Fe may cause the brain and liver damages. Fe may cause oxidation of DNA molecules which can end as a cancer. (Bhasin, Kauser & Athar 2012.).

3 TRADITIONAL REMOVAL TECHNIQUES OF HEAVY METALS

The methods for heavy metals removal mainly include biological, chemical and physical treatment. The following methods are suggested for removal of metal ions such as filtration, ion exchange, chemical precipitation, electrochemical treatment and membrane technologies. Nevertheless, they have their drawbacks, for example sludge is used in electrochemical treatment and chemical precipitation, when the ion concentration of metal in the aqueous solution is between 1 and 100 mg/L, a considerable amount of sludge is needed for the treatment. Therefore, it can be considered as an inefficient method. Activated carbon adsorption, ion exchange and membrane technologies are expensive for the low heavy metal concentrated wastewater. They cannot be used for wastewater with a large amount of heavy metals in. (Wang & Chen 2009.). All these methods are labor-consuming, expensive and they have a lack of selectivity (Chen, Zeng, Tang, Du, Jiang, Huang, Liu & Shen 2008).

3.1 Chemical precipitation

One of the widely spread methods is chemical precipitation. In this process dissolved metal ions precipitate by chemical reagents and form metal carbonates, hydroxides, phosphates and sulfides. In the result insoluble solid particles can be separated by sedimentation and filtration (Kanamarpudi, Chintalpudi & Muddada 2018). The point of chemical precipitation is adjusting concentrations for ionic constituents that change from a dissolved ionic phase to a solid salt. The salts precipitate fast, and the ionic species remain in a solution depending on the solubility of the solid phases. (Wang, Li & Shammas 2007.). Chemical precipitation is considered as an effective way for wastewater pollutants. Firstly, it operates at normal conditions and it suits the automatic control. (Ojovan, Lee & Kalmikov 2019.). Secondly, the price is reasonable, and most of the required chemicals are available. Also, the maintenance is not complicated, and it does not require many operators, replenishment of chemicals is enough. (Wastewater technology fact sheet: chemical precipitation. 2000.). The method of chemical precipitation involves four main stages which are: reagents' addition and pH adjustment to form the precipitate, flocculation, sedimentation, solid – liquid separation. However, there are some drawbacks such as limited use of chemical precipitation because of the possibility of chemical interference during the mix of wastewater and treatment chemicals (Ojovan et al. 2019). Second drawback

is the conditions must be confirmed in advance because overdosing may minimize the treatment effectiveness. The volume of waste might reach up to 50 % which is not environmentally friendly. (Wastewater technology fact sheet: chemical precipitation. 2000.). Moreover, the complexants and trace organics presence in the waste stream may affect the chemical precipitation. For the elimination of those particles, filtration, microfiltration and ultrafiltration are required. (Ojovan et al 2019.).

3.2 Membrane filtration

Membrane filtration is a physical method where solid and organic compounds can be removed as well as metal ions. It is a pressure-controlled separation process for heavy metals which is based on the size exclusion and suitable chemical materials are needed. There is a layer of membrane which provides contact between two homogeneous phases (Kanamarlapudi et al. 2018). Membrane filtration consists of microfiltration, ultrafiltration, nanofiltration and reverse osmosis (FIGURE 1).

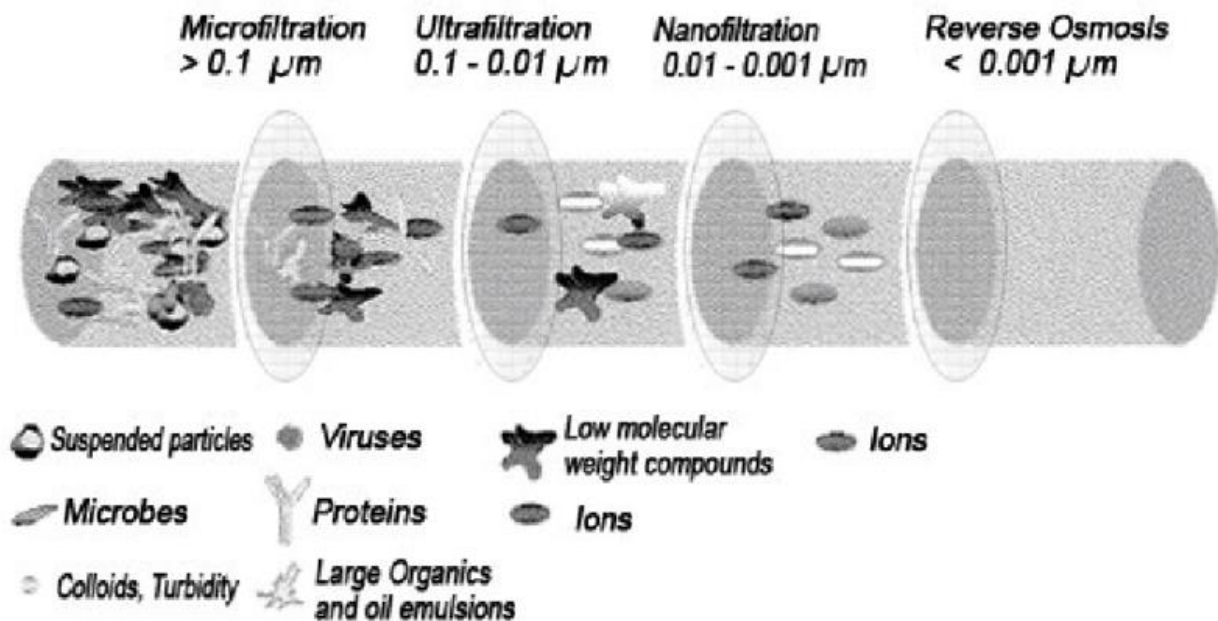


FIGURE 1. Membrane filtration process (adapted from Abdelkader 2017)

Microfiltration is a type of membrane filtration process where a contaminated fluid passes through a microporous membrane to separate suspended particles, bacteria and microorganisms from liquid. The pore size of 0.1 – 10 μm performs microfiltration. The process passes crossflow separation where a feed stream under low pressure is involved. The materials which do not pass through the membrane are rinsed out and mentioned as a concentrate. Another part is ultrafiltration where pressure or concentration gradient is considered as a driven force and it leads to a separation of wastewater treatment with low energy (Sun, Hu, Tong, Zhao, Qu, Liu & Elimelech 2017). The particle with the size of 10 – 100 nm can be removed in this process (Carolyn, Kumar, Saravanan, Joshiba & Naushad 2017). Nanofiltration is a part of membrane filtration and it is similar to the ultrafiltration process. The difference in the particles size, nanofiltration can filter small particles starting from 1nm and up to 10 nm. The advantages of nanofiltration for heavy metals removal is in its effectiveness, in energy saving and in easy operativeness. Reverse osmosis has membrane pore size $< 0.001 \mu\text{m}$ and it uses semi-permeable membranes. The principle of work depends on size exclusion and solution diffusion. The netted structure of the polymer materials membranes allows the water to pass through and escape. The main drawbacks are membrane regeneration, the high-power consumption and maintenance. (Ali Shah, Ashfaq, Hussain Gardazi, Tahir, Pervez, Haroon & Mahmood 2013.). The membrane preparation must be easy and simple to control and the investigation of coexisting ions' effects in the solution should be performed for membrane filtration (Pan & An 2019). However, this separation method is not economically practical due to high maintenance and operational costs.

3.3 Ion exchange

One of the most spread physical methods is ion exchange which is a reversible exchange between liquid - solid phases. Anions and cations from an electrolytic solution exchange in a solid resin and ions of similar charge release (Kanamarlapudi et al. 2018). This technique can remove negligible quantities of ion contaminants from water and give an acceptable product. During this process initial metal concentration, resin dose, pH value on exchange capacities are important. Ion exchangers are popularly used in purification and separation processes, in analytical chemistry, in water treatment and in pollution controls. The ion exchange process occurs between resin which is a solid and water which is a liquid. The desired compounds appear on the resin and they swap the ones which are less desired. In the cation exchange the cations are exchanged with the positively charged ions which are on the surface of the resin. While in the anion exchange process the anions are swapped with the

resin's negatively charged ions. There are different types of resin such as strong base or strong anion, and resin beads which are special for water treatment. (Clifford, Sorg & Ghurye 2011.). Ion exchange is suitable for metal ions' purification with high value but low processing (Hubicki & Kołodyńska 2012). The disadvantage of the ion exchange process is a lack of the heavy metal ions, alkaline and alkali selectivity (Hubicki & Kołodyńska 2012).

4 BIOMASS

Biomass is animal and plant material used for energy production and industrial processes; it refers to the organic material's use. Biomass is carbon based but it also consists of organic molecules including hydrogen, oxygen and nitrogen. Wood and forest residues, food crops waste, animal farming and food processing are considered as biomass. Biomass is a renewable source because its natural energy comes from the sun and it can be grown again in a short time of period. Also waste residues will always exist and forests will always have trees if they are properly managed. For example, biomass inhales CO₂ while it is growing, and it returns it back to the atmosphere as it is burnt. The new growth consumes CO₂ from the atmosphere while it is released by combustion of the previous plants. The level of CO₂ in the atmosphere stays the same; therefore, biomass can be considered as a constantly supplied crop. (Dixit, Dixit & CS 2015.).

Biomass and biowaste are considered as a new biosorbent for heavy metals in the biosorption process. Heavy metals can be bound by several biological materials but the ones with high metal binding capacity is suitable for biosorption (Wang & Chen 2009). The choice of biomass depends on several aspects as it should be cheap, natural and in a high volume. The organism's psychological state, the availability of micronutrients in organisms and the age of the cells are the parameters that affect biosorbents' choice. (Ismail & Moustafa 2016). There is a category of biomass which is called a native biomass which includes agricultural products, such as rice husks, tea waste, papaya wood, apricot and peach stones, wheat shell, cork biomass, and microbial cells as algae, fungi and bacteria, and industrial waste from food industry and fermentation (Romera, González, Ballester, Blázquez & Muñoz 2006; Orhan & Büyükgüngör 1993).

The biosorbents such as bacteria, fungi, and algae have metal-sequestering features and can decrease the heavy metals' concentration from ppm to ppb. It provides a high efficiency in a short time and it is ideal for the large volumes of wastewater. (Abbas, Ismail, Mostafa, Sulaymon 2014.). The biomass may consist of metabolically inactive dead cells and it is more effective to use inactive microorganisms rather than living microorganisms. Living microorganisms require nutrient's supply and the bioreactor system is more complicated. Also, they need special environmental factors such as pH and temperature, and the recovery of heavy metals is limited in living cells because living microorganisms may link cellularly. (Romera et al. 2006.).

Many industries dispose of a growing amount of waste, one of them is a food industry where a considerable amount of waste and byproducts can be found. Also, waste from agriculture which contain functional groups such as amino, alcoholic, carbonyl, phenolic groups have high metal binding and high percentage of cellulose and lignin (Hossain, Ngo, Guo & Setiadi 2012). These functional groups donate a pair of electrons forming complexes with metal ions (Demirbas 2008). Using biomass waste can reduce two problems, reduction of waste on the Earth and treatment of wastewater from heavy metals (Kanamarlapudi et al. 2018).

4.1 Microorganisms as biomass

Microorganisms are used for the heavy metals' extraction. Microorganisms are divided into six main types which are algae, archaea, bacteria, fungi, protozoa, viruses. Bacteria and algae are chosen as biosorbent for heavy metals extraction. They are considered as they have the low cost of production, they cause less environmental pollution rather than other traditional removal methods and high efficiency even if the metal concentration is low. Moreover, microorganisms can be stored for a long period of time without any inverse effect on their sorption; the maintenance and nutrition are not needed. Their performance of binding metal ions depends not only on environmental status and nutrients, but also on the age of cells. (Javanbakht, Alavi & Zilouei 2014.).

4.1.1 Bacteria as biomass

Bacteria are considered as the main responsible organism for toxic waste such as heavy metals and organic matter degradation. Bacteria are versatile microorganisms with simple morphology and with basic shapes as spherical, rod and spiral (Norberg & Persson 1984). The size of the bacteria cell usually varies from 1.1 to 1.5 μm wide and 2.0 – 6.0 μm long. Cell size is important for an organism because it affects a number of cell biological properties. Bacteria with a small cell size provide rapid metabolic processes. (Norberg & Persson 1984.). The cellular components including carboxyl, hydroxyl, sulfate, phosphate, phosphonate, phosphodiester, amino, amide, phenol, carbonyl (ketone) have properties of metal binding (FIGURE 2). Also, most of the microbial surfaces are negatively charged because of the functional groups' ionization which increase the metal binding as well. As

bacteria have a polysaccharide layer and amino, carboxyl, phosphate and sulphate groups, it has high heavy metal absorption. (Vijayaraghavan & Yun.).

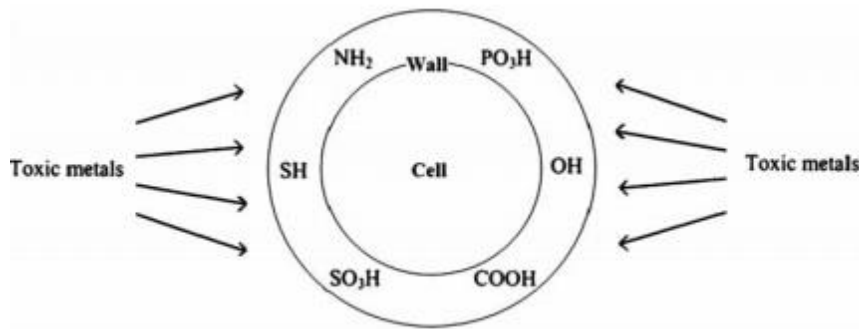


FIGURE 2. A scheme of metal binding by functional groups on the cell wall of biomass (Adapted from Vijayaraghavan et al.)

The main reasons of the bacteria usage are the small size, ability to grow under specific conditions, and they can adapt in any environmental circumstances. In the metal extraction process biomass, which is not chemically and physically treated, is used. The bacteria are washed with the distilled water to remove impurities before the use. (Kinoshita, Sohma, Ohtake, Ishida, Kawai, Kitazawa, Saito & Kimura 2013; Vasudevan, Padmavathy, Tewari and Dhingra 2001.). If bacteria are chemically treated previously, they must be washed with a 10 mL aqueous solution of 0.1 M sodium hydroxide (NaOH), 0.1M hydrogen chloride and 30 % ethanol and left in the solution for 40 minutes and for one day in distilled water. This type of pretreatment may affect the metal removal process. One study showed that the metal extraction efficiency decreases due to the competitive complexation between H^+ and metal cations, and loss of extracellular polymers because biomass was soaked in distilled water for a day. There is a controversial result in the Juan Wu experiment that pretreatment strengthens the metal removal. It is explained as NaOH solution can transform chitosan structure and more active sites to bind the heavy metals can be opened in the biomass. (Huang, Pan & Zheng. 2001.). The bacterial biomass' suspension is added to a pH adjusted metal solution, and it is done at different pH, T, C and W depending on the type of the bacteria and metal (Kinoshita et al. 2013; Vasudevan et al. 2001). There are two stages of heavy metals binding to the surface of a bacterial cell. There is an interaction between heavy metal ions and reactive groups of the cell on the first stage and the second stage involves the deposition of metals in high concentrations. (Iihan, Nourbakhsh, Kilicarslan & Ozdag 2004.).

The bacterial biomass is produced as a by-product waste from industries or it can be particularly spread in large proportions. The absorption capacity of bacteria varies between 0.23 and 0.90 mmol/g; nevertheless, each metals removal capacity is different depending on the bacteria type and given conditions. The conditions such as pH value, temperature (T), initial metal concentration (C), absorbent concentration (W), rotation speed (N_s) and time are shown. The chosen values give the highest efficiency (η) of metal extractions (TABLE 3). (Modak & Natarajan 1995; Mawgoud).

TABLE 3. Biosorption of bacteria with heavy metals (adapted from Abbas et al. 2014)

Metal	Bacteria type	pH	T (°C)	C (mg/L)	W (g/L)	N_s (rpm)	Time (h)	D (%)
Zn	Sulphate-reducing bacteria	6.0	30	10-200	1	-	24	0.56
Pb	Starphy-lococus saprophyticus	4.5	27	100-150	0.2	150	4	100
Hg	Enterobacter cloacae	4	25	100	0.1	240	2	43.23
Cd	Enterobacter cloacae	5	25	300	0.1	240	2	58.9
Cr	Bacillus licheniformis	3.5	28	1200	-	120	48	95
Cu	Enterobacter cloacae	5	25	200	0.1	240	2	78.9
Ni	Pseudomonas sp.	5.5	30	1-10 mmol/L	5	200	-	55.6
Fe	Bacillus licheniformis	3.5	28	1200	-	120	48	52

4.1.2 Algae as biomass

Algae are one of the most auspicious biosorbent types because of their high sorption, and they dwell in enormous quantities in the oceans and seas (Rincón, González, Ballester, Blázquez & Muñoz 2005). Algae have rich biochemical composition, renewable availability and high biosorption capacity; consequently, algae biomass is a conducive material for heavy metals extraction. The algal protein and sugar cells consist of amine, carboxyl, phosphate, sulphate, hydroxyl functional groups which give a selective interaction with heavy metals in the biosorption process. Algae do not require a plenty of nutrients despite this they can produce biomass in a large volume. (Oyedepo 2011.). The adsorption of metals depends on metal's ionic charge, algal species and metal ions' chemical composition (Abbas et al. 2014). There are three groups of algae as red algal, micro-algal (green algae), and macro-algal (brown algae), the latter one is famous with the highest uptake capacity, 0.65 to 1.21 mmol/g (Wang, T. C., Weissman, Ramesh, Varadarajan & Benemann 1998). Algae collected from freshwater and washed with Milli-Q water several times to eliminate the sediments. In the next stage, it is dried at 60 °C in the oven and ready to be used in the extraction. (Cardoso, Costa, Nishikawa, Silva, Carlos & Vieira. 2017.). The process is divided into two stages; heavy metals replace Na, Mg, Ca ions in the ion exchange on the first stage after this the biosorbent's functional groups such as amino, carboxyl, phosphate, and hydroxy interact with the heavy metals. The process is similar to an ion exchange resin because algae cells biosorb the metal ions. Moreover, the covalent bonding and ionic charge are involved here. For example, there can be a covalent bonding between amino and carboxyl groups. (Oyedepo 2011.). However, each metal requires different algae types and conditions. The conditions are shown at what pH, T, C, W, N and time the efficiency is the highest (TABLE 4).

TABLE 4. Biosorption of heavy metals with algae (adapted from Abbas et al. 2014; Shamim 2018).

Metal	Algae type	pH	T (°C)	C (mg/L)	W (g/L)	N _s (rpm)	Time (h)	D (mg/g)
Zn	Green algae	5.0	25	20-350	3	-	1	7.62
Pb	Calotropis procera	4.0	25	25-100	2	150	6	22.8
Hg	Brown algae (Sargassum sp)	4.0	30	-	-	100	-	14.8
Cd	Brown marine macro algae	5.0	25	75-100	2.0	-	1	24-40
Cr	Green algae (Spirogyra spp)	4.0	30	1-25	1-3	180	3	265.0
Cu	Ascophyllum nodosum	5.0	25	10-150	0.5- 1.0	-	2	70.9
Ni	Ascophyllum nodosum	5.0	25	10-150	0.5- 1.0	-	2	50.0
Ar	Spirogyra hyalina	-	25	-	1.0	180	2	9.8
Fe	Brown algae (Sargassum sp)	3.0	30	-	-	150	-	14.6

4.2 Agricultural waste

Extraction of heavy metals from wastewater demands development of new sorbents. A vast range of commercial sorbents as activated carbon and chelating resins are available for metal biosorption; however, their cost is relatively high. In the last few years, low-cost natural materials including agricultural waste such as papaya wood, wheat shell, rice hulls, peach and apricot stones have been found. They

have several advantages as low cost, high adsorption efficiency and regeneration ability. (Alalwan et al. 2020).

Papaya wood does not have any utilities, it cannot be even used as a firewood and it causes environmental degradation. When the papaya tree stops giving fruits and the trunk is felled, it is considered as waste. The papaya trunk is soft and brittle, it is made of fibrous tissue mass, which runs through the trunk cylinder walls, and it looks like a net with longitudinal slits. Therefore, the wood has a wide surface area which suits the metal biosorption. The wood contains 32.39 % of crude fiber which indicates the presence of hemicellulose and polysaccharides. For the metal extraction process the papaya trunk is debarked, small pieces of trunk like 2×2 cm are cut, and it is soaked in boiling water for 30 mins. Later, it is washed by tap water and left in the distilled water for 2 or 3 h. The washed trunk pieces are milled into fibers of diameter 0.05 - 0.2 mm and length of 2.5 mm, dried at 80 °C in the oven and ready to be used for biosorption. (Saeed, Akhter & Iqbal 2005.).

Wheat shell is available agricultural material and it is considered as a byproduct for wheat bread and bakery products, in general wheat production industries. Most of wheat husk is used for cattle feed; nevertheless, the spoiled ones are not available for proper storage, so they are dumped. (Das, Dey & Marik 2012.). It is rich with fiber and contains cellulose, lignin, carbohydrates, and starch. (Basci, Kocadagistan & Kocadagistan 2004). Moreover, it is full of functional groups such as carboxyl and hydroxyl which generate the adsorption possible (Das, Dey & Marik 2012). Wheat shell is collected filtered to remove suspended pieces. Filtered wheat shell is washed with deionised water and dried at room temperature for few days, then it is blended in a mortar and sieved under 5000 μm . The small pieces of wheat shells are mixed with the wastewater and ready to absorb the heavy metals. (Basci et al. 2004.).

Rice hulls are a waste material produced from agriculture. 500 million metric tons of rice is produced around the world yearly, 10-20 % of all the production is rice hulls. The surface morphology and elemental constitutions of the rice hulls are studied by scanning electron microscope and energy-dispersive X-ray spectroscopy. Dry rice husks consist of 70-85 % of organic materials such as cellulose, lignin and sugar. The rest which is 15-30 % contains silica. (Vempati, Musthyala, Mollah & Cocke 1995.). Due to the high proportion of cellulose, 28-36 %, in rice husk, it goes well in the modification with carboxylic acid. Carboxyl groups help to increase the rice husk's sorption capacities. Rice husk can be used as an adsorbent with the use of tartaric acid to carry out lead and copper from aqueous

solution. The several parameters such as adsorbate concentration, pH value, particle size, temperature affect the removal process. (Wong, Lee, Low & Haron 2003.). Rice husk is collected from agricultural product processes and dried under the sun, and the impurities are separated. Later, it is boiled with distilled water for 5 h because this process helps to free them from coloured components. The residue is dried at 80 °C in the oven for 24 h. The dried rice hulls are grinded and sieved under 300 µm. The ready biosorbent is mixed with the wastewater. The rest of materials can be stored in the plastic containers for further experiments. (Bansal et al. 2009.).

Apricot and peach stones which are collected from solid wastes of jam and juice industries can be used as biosorbents. They must be washed several times by tap water and then by distilled water, after all washing stages it has to be dried in the oven at 105 °C for 5 h. The dried samples are burned at 800 °C for 2 h in a muffle furnace and ground by an electric agate mortar. The powder samples are sieved in the sieve series smaller than 63 µm. The powder is mixed with distilled water or 0.1 M NaOH in the proportion of 1:100. The solvents as distilled water and NaOH are chosen because atomic absorption spectrophotometer showed zero percentage of Pb sorption from these adsorbents. (Rashed 2006.).

Tea producers cut the top leaves and they are used for the tea production while some overgrown woody shoots which have six or seven leaves are not treated by the tea factories. They can be called tea factory waste (TFW), 30000 tons of TFW are deposited only near the Black Sea annually. One of the ways to reduce the waste is to use TFW as a biosorbent because it has high insoluble components and high insoluble ignition. Soluble dirtiness and coloured components are removed by washing with distilled water until a colourless solution of TFW is observed at room temperature. Later, it is dried at room temperature for several days and sieved until 0.15 – 0.25 mm. The TFW powder is mixed well with the Cr (VI) solution and the experiment is performed. (Malkoc & Nuhoglu 2007.).

5 BIOSORPTION

Removal of heavy metals from industrial wastewater requires a special qualification and lots of energy. The most common methods like biosorption can be considered as one of the methods of heavy metals' removal. The main function of this method is based on the biological materials' ability which is an accumulation of heavy metals from wastewater with metabolically mediated pathways (López-Mesas et al. 2011). Biosorption has several mechanisms depending on the type and origin of biomass and processing. In the process there is a physico-chemical interaction between microbial surfaces and heavy metal ions (Abbas et al. 2014). There is a presence of high attractive forces between removal materials (compounds and metal ions) and materials of biological origin or biomass (Volesky & Holan 1995). Two phases are involved in the biosorption process, first is a solid phase which are sorbents, adsorbents or biological material. Second is a liquid phase which is a solvent, for example, water. Also, the dissolved species in this process are metals or it can be called sorbets. The substances which need to be removed can be organic or nonorganic and soluble or insoluble (Ahemad & Malik 2012).

The main advantage of biosorption is the low cost and high efficiency, while additional nutrients are not required. Biosorbents are regenerated, recovery of heavy metals and valorization of waste, in this case biomass, are performed. (Valls & de Lorenzo 2002; Volesky 2003.). Moreover, large volumes can be obtained, and multiple heavy metals can be absorbed at the same time. Additional chemicals are not needed; consequently, the toxic materials production is much less, and the waste volume is reduced as well. The results show high affinity and the metal reduction reaches 1 ppb (Sağ, Açıkel Aksu & Kutsal 1998). This process has been known since the early 1900s, but it started to be used in the last four decades due to its low-cost technologies. (Abbas et al. 2014.).

Absorptive capacity is affected by several factors for instance cell age, metal ions' properties in aqueous solutions (radius of ion and valence), cultural conditions such as nutrition supply, growth media composition. The factor affecting the biosorption of heavy metals might be physical and chemical such as pH, temperature, heavy metal concentration, biosorbent dose and size. Understanding the environmental factors on biomass can help to develop the eligible types of biosorbents and to use it in a suitable way for its application. (Nguyen, Ngo, Guo, Zhang, Liang, Yue, Li & Nguyen 2013.).

5.1 pH value

pH value can be considered as the most important parameter for biosorption. pH influences the binding sites and concentration of biomass, because biomass contains weakly basic and acidic groups. (Abbas et al. 2014.). Ionization of heavy metals and metal ion's solubility are dependent on the pH value. Not only the adsorbate's solution is affected but also the functional groups' activity is involved in. (Puranik, Modak & Paknikar 1999). Biosorption process is affected by pH in different ways, mostly the pH range between 5.0 – 6.0 suits most of the processes. However, there is some exceptions, when at lower pH the absorption capacity is higher.

If pH increases, the biosorption of cationic metals raises, respectively there is a decrease in anionic metals sorption (Nguyen et al. 2013). There is an excess of H_3O^+ ions at low pH value; therefore, the hydrogen and metal ions with positive charge start adsorbing on the surface of the biosorbent which is negatively charged. When pH value increases the balance between hydrogen and hydroxide ions becomes more equal; thus, more metal ions are adsorbed. In the result, the rate of metals' removal increases. The solubility of metals decreases and the precipitation appears when pH of the solution is high; thus, the sorption process is more complicated. (Volesky 2003.). At higher pH, the number of H^+ ions are lower, the functional groups are free and as they are negatively charged, they start attracting positively charged metal ions, so the metal ions are not adsorbed on the surface of biomass (Kanamarlapudi et al. 2018). The right chosen pH affects the whole process to figure out the rest of the factors which affect the biosorption.

The binding sites can be changed by adjusting the pH value. For example, pH from 3 to 6 corresponds the biosorption with the bacterial biomass. (Romera et al. 2006). In this case, H^+ ions are released from the bacterial biomass and it decreases the pH of the solution. During the initial period the pH changes rapidly because most of the reaction occurs on the initial stage and it slowly moves to the equilibrium. (Kang, Lee & Kim 2006).

For 10 ppm solution of Zn (II), Cd (II) and Cu (II) the papaya wood is used, the removal of metal from the aqueous solution is studied at different pH values. The biosorption is low at the initial stage, pH 2.0 (11.6 % Zn, 10.3 % Cd, 17.3 % Cu). The low metal absorption at low pH can be explained as there is a competition between H^+ and Zn^{2+} , Cd^{2+} , Cu^{2+} ions. Figure 3 shows the dramatic increase at

pH 4.0-5.0 and there is a decline in the sorption of three metals after pH 6.0 (Saeed et al. 2005). As there is a decrease in the competition between metal ions and protons for the same functional group which results in a low electrostatic repulsion between the metal ions and absorbent surface. (Reddad, Gerente, Andres & Le Cloirec 2002.).

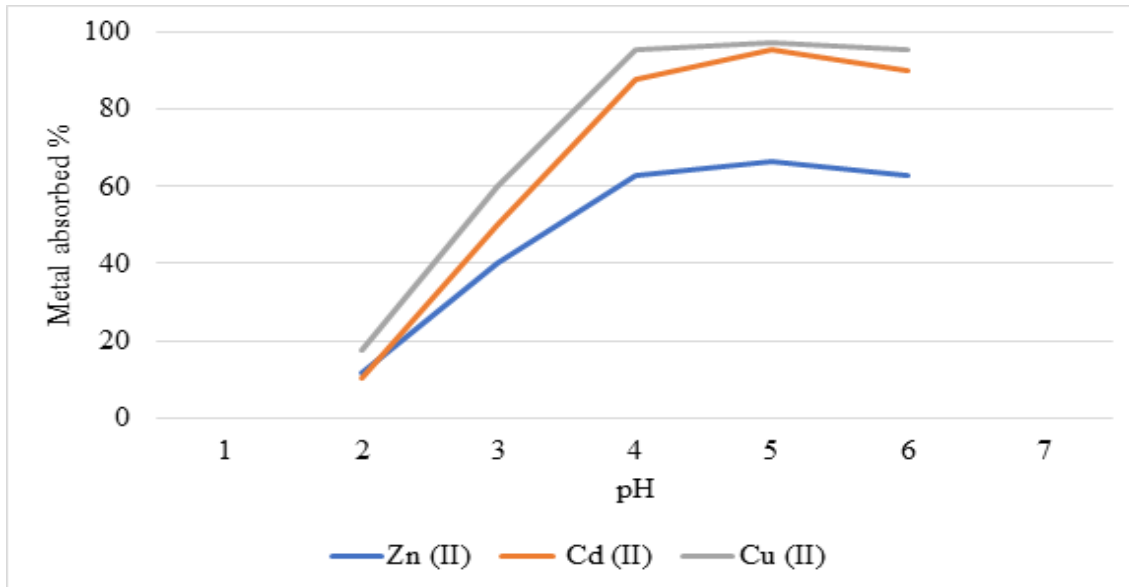


FIGURE 3. The removal of Zn (II), Cd (II), Cu (II) with papaya wood (adapted from Reddad et al. 2002)

The biosorption of Cu ions with wheat shells showed the following results in pH difference. The biosorption efficiency increased from 33 % at pH 2.0 to 95 % at pH 5.0. The highest biosorption was shown at pH value between 5.0 and 6.0. After pH 6.0, the biosorption decreases again. (Basci, Kocadagistan & Kocadagistan 2004.). Similar results are shown in the adsorption of 25 ppm Pb with 1 g/L of peach and apricot stones solution. The pH was observed between 2 and 10, and the highest adsorption was marked at pH 7.0 (FIGURE 4). The range of 2.0 - 3.0 shows low metal removal because there is a competition between H^+ and Pb^{2+} ions for the adsorption (Kadirvelu, Thamaraiselvi & Namasivayam 2001). After pH 8.0 the adsorption decreases as well due to the lead hydroxide precipitation (Rashed 2006). The pH plays an important role here because it affects the surface charge of peach and apricot stones solution, adsorbent speciation and ionization degree. (Weng & Huang 1994.).

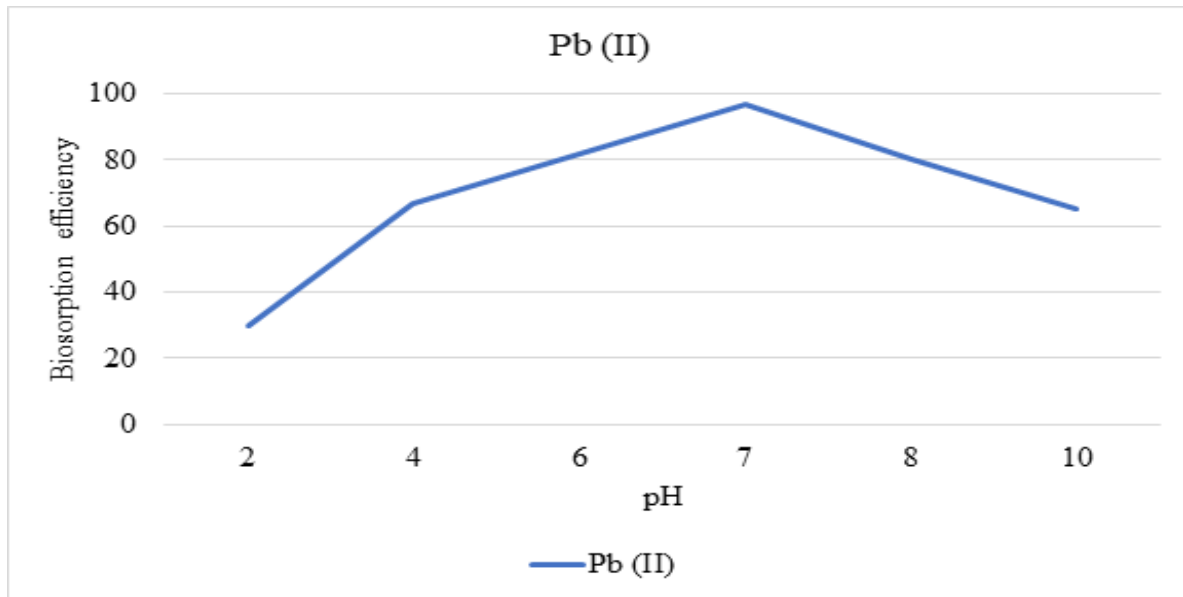


FIGURE 4. Effect of pH on Pb (II) adsorption with peach and apricot stones (adapted from Rashed 2006)

The pH range of 2.0 – 6.0 was carried out in the 100 ppm Ni absorption with the rice husk. At lower pH values there is a competition between metal cations and protons to bind on the adsorbent surface. (Bansal, Singh Garg & Rose 2009). At acidic conditions, the ligands of adsorbent surface are associated with H_3O^+ which reduce the access to ligands by metal ions (Sekhar, Subramanian, Modak & Natarajan 1998). Removal of Ni with rice husk shows the highest removal pick at pH 6.0 which is 51.4 % (Bansal et al. 2009). The higher pH gives more negative charged ligands which attract metal cations. (Sekhar et al. 1998). However, if pH is higher than 6.0, Ni starts to precipitate; therefore, the efficiency decreases (Bansal et al. 2009).

There is a case when absorption is higher at lower pH. The research on chromium (VI) removal by tea factory waste shows the highest adsorption at low pH value. The adsorption of metal is 99 % at pH 2.0 while at pH 5.0 the adsorption is equal to 37 % (Malkoc & Nuhoglu 2007). It can be explained with the fact that at lower pH value the positive charge on the surface of adsorbent in this case tea factory waste increases. In the result, attraction between metal ions and adsorbent particles increases. (Malkoc & Nuhoglu 2007.). Aqueous phase controls the metal speciation and the active functional groups dissociation on the sorbent. Fourier – transform infrared spectroscopy (FTIR) analysis showed that the OH^- groups, SO_3^- , CN^- and C-O stretching are especially involved in Cr (VI) removal with the tea waste. (Malkoc & Nuhoglu 2007.). The positive charge increases on the biosorbent surface,

and hydrogen ions can easily integrate with the amino and carboxyl groups. (Park, Yun & Park 2005.). It leads to the increase of metal adsorption because there is an electrostatic attraction between negative sorbate and positive adsorbent. When pH increases the adsorbent surface becomes more negative; consequently, the adsorption decreases as well. Cr (VI) can be removed at low pH 5 too but the sufficient time should be given. (Malkoc & Nuhoglu 2007.).

5.2 Temperature

Temperature affects diffusion rate of metal ions, the solubility of metal ions and the adsorption capacity because temperature functions with the thermodynamics of the process and the metal ion's kinetic energy (Kanamarlapudi et al. 2018). It can have positive and negative impact on the biosorption. The biosorption process is affected by temperature in different ways, depending on the nature of the process, endothermic or exothermic. In most of the cases biosorption is claimed as an exothermic process, the adsorption capacity is inversely proportional to the temperature (Sahmoune, Louhab & Boukhiar 2011).

In the research of Cd (II) removal from aqueous solution by cashew nutshell, the biosorption of cadmium decreased with the increase of temperature from 30 to 60 °C (Ponnusamy, Subramaniam, Vasanthakumar, Kirupha, Arukkani & Sivanesan 2012). The reason is referred to the decrease of agricultural waste based biosorbents' (AWB) surface activity. The research of Park, Park & Yun about Zn (II), Cd (II) and Mn (II) removal by maize stalks showed the decrease in biosorption with the increase of temperature (Park, Park & Yun 2010). The biosorption decreased from 52 to 28 %, from 34 to 16 % and from 39 to 13 % respectively with the temperature rising from 25 to 55 °C (FIGURE 5). The reason for this trend is explained as the AWB's active adsorption is damaged and the metal ions are broken away from the surface of AWB to the solution (El-Sayed 2011).

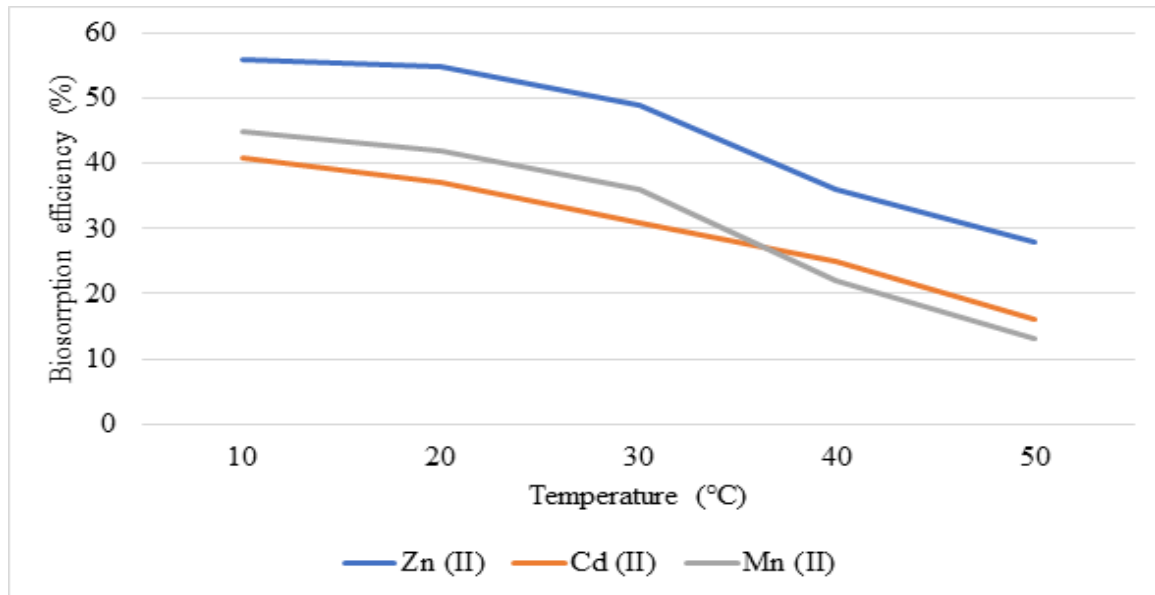


FIGURE 5. Effect of temperature on removal of Zn (II), Cd (II), Mn (II) by maize stalks (adapted from Park et al. 2010)

In the removal of Cr (VI) with the tea waste, the higher adsorption efficiency is registered at higher temperature 60 °C rather than at 25 °C. It can be explained with the increase of the mobility of metal ions at higher temperature. There is a swelling effect in the internal structure of the biosorbent because of the high temperature, and more metal ions can enter. (Malkoc & Nuhoglu 2007.). There is a continuous increase from 46.9 % to 65.4 % in the range of 15-50 °C in the removal of Ni with rice husk (Bansal et al. 2009). In this case, adsorption is an endothermic process and the nature of rice is porous; therefore, there might be a diffusion of adsorbate (El-Shafey 2005). Accordingly, the increase of temperature favors the nickel ions transport in the adsorbent.

5.3 Initial metal concentration

The increase of metal adsorbed by the biomass depends on initial metal concentration. There is a statement when initial metal concentration increases, the maximum adsorption capacity of AWB increases as well. It is explained by collision between AWB and metal ions. However, there is another statement where it says the optimal percentage of metal uptake is recorded at low metal concentration.

(Alalwan et al. 2020.). The constant increase or decrease cannot be followed in this case, the absorption is different depending on the metal and biomass type (FIGURE 6).

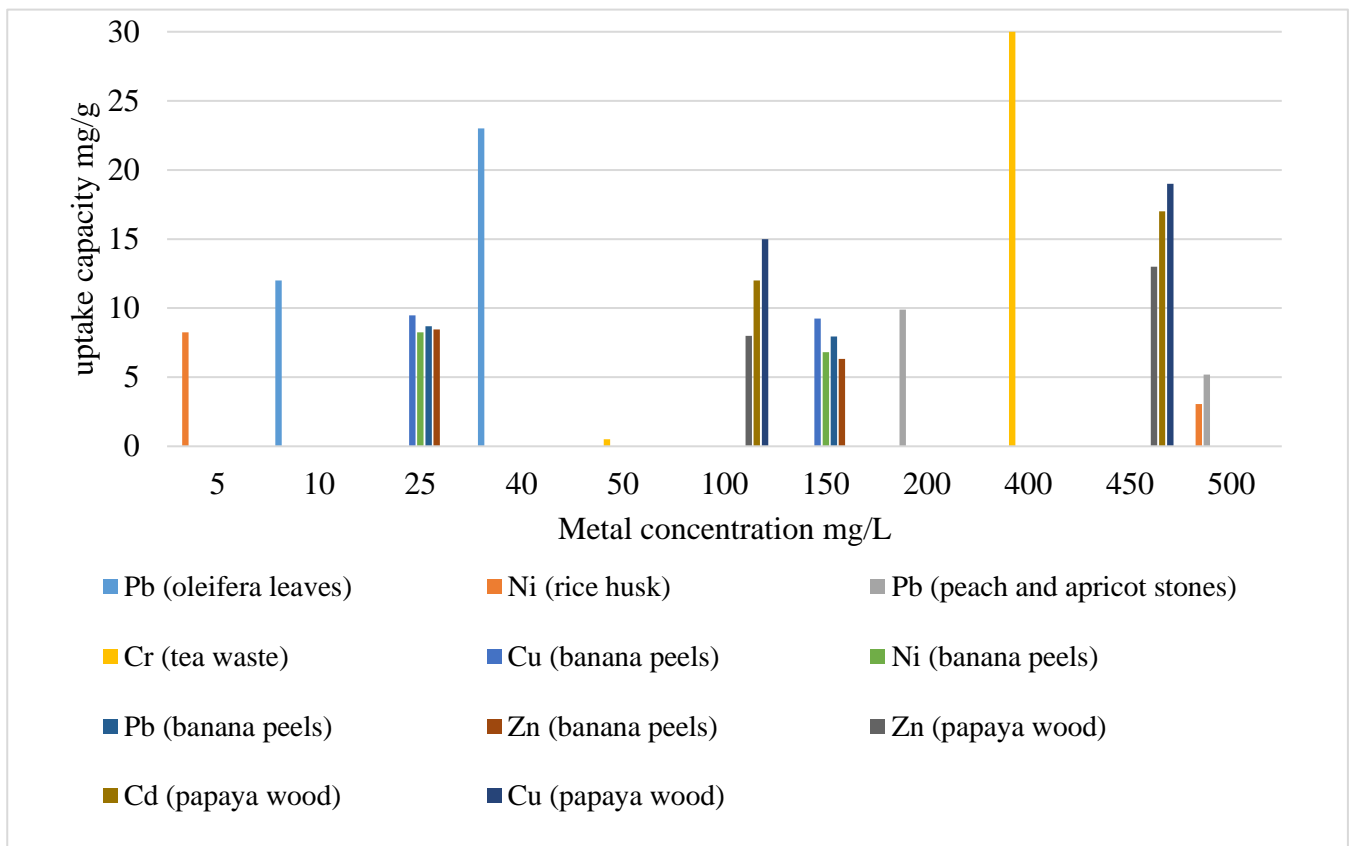


FIGURE 6. Initial metal concentration effect on biosorption (adapted from Reddy, Yapati & Seshaiiah 2010; Bansal et al. 2009; Ashraf, Wajid, Mahmood, Maah & Yusoff 2011; Malkoc & Nuhoglu 2007; Saeed et al. 2005)

The research about Pb removal by oleifera leaves proves the statement. Initial metal concentration is increased from 10 to 40 mg/L likewise the Pb (II) capacity raised from 12 to 23 mg/g (Reddy et al. 2010). In Ni removal with rice husk the low concentration of metal gives higher efficiency of adsorption. Due to the high saturation of adsorbent surface, most nickel cannot be adsorbed at high concentrations of metal. The efficiency decreases from 82.5 to 30.5 % when initial metal concentration rises from 5 to 500 mg/L. At higher metal concentration, most of Ni is left unabsorbed because of the saturation of adsorption sites. The ratio of the sorption surface to metal concentration decreases with the rise of metal ions concentration. (Bansal et al. 2009.). 0.5 g/L of apricot and peach solutions are taken for Pb absorption at different concentrations from 5 to 500 ppm. The adsorption is stable and the highest peak (99 %) is found at 200 ppm then the decrease is observed from 200 to 500 ppm (52

%). The reason is a limitation of available active sites on the surface of adsorbent to take in the metal ions. (Rashed 2006.). Accordingly, the higher absorption occurs at lower metal concentrations.

However, there is a converse statement that the adsorption capacity decreases with the increase of initial concentration. The removal of Cu (II), Ni (II), Pb (II) and Zn (II) by banana peels show at the highest concentration 150 mg/L, the removal efficiencies were 92.52 %, 68.10 %, 79.55 % and 63.23 % respectively. While at the lowest concentration 25 mg/L, the efficiency slightly rises, 94.80 %, 82.36 %, 86.81 % and 84.63 %. (Ashraf et al. 2011.). The biosorption of chromium by tea waste is carried at concentration from 50 to 400 mg/L at pH 2.0, 360 rpm, 10 g/L of adsorbent and 60 min of contact time (Malkoc & Nuhoglu 2007). When the metal concentration increased from 50 to 400 mg/L, the uptake capacity raised from 0.5 to 30 mg/g as well. A higher initial metal concentration provides a driving force to pass through the mass transfer resistances between aqueous and solid phases, so the uptake rises too. (Aksu & Tezer 2005.). Accordingly, the increasing the initial Cr (VI) concentration brings to the higher uptake.

Metals at different concentrations are used in this part of the experiment, 5-500 mg/L of Zn (II), Cd (II), Cu (II) are measured at pH 5.0. The metal absorbance increases with the rise of metal concentration. The metal concentrations raised from 100 to 400 mg/L and the removal capacity of Zn (II), Cd (II), Cu (II) increased from 8, 12, 15 mg/g to 13, 17, 19 mg/g respectively. However, the sorption at low metal concentrations is sufficient, too. Therefore, papaya wood is suitable for wastewater treatment even at low concentrations (<100 mg/L). (Saeed et al. 2005.).

5.4 Adsorbent dose

The electrostatic interaction between the cells is important for metals removal (Abbas et al. 2014). Adsorbent dose is one of the factors affecting the metal removal process. The higher adsorbent dose gives higher efficiency in adsorption because there is more surface available for metals to be adsorbed. The biomass concentration is directly proportional to the metal removal, biomass absorbs more heavy metals ions at low densities. (Gadd & White 1985; Modak & Natarajan 1995.).

In the experiment of Ni with rice husk the concentration of metal kept the same 100 mg/L while the adsorbent dose changes from 4 to 20 mg/L. As a result, the final dose 20 mg/L showed the highest efficiency of removal, 51.8 % (Bansal et al. 2009). When the biosorbent's concentration is low, the ratio of metal adsorbed and the weight of biosorbent is high. Conversely, when the biosorbent's concentration is high, the ratio of metal adsorbed and the weight of biosorbent is low; thus, more metals can be adsorbed. (Kanamarlapudi et al. 2018.). Different doses (5, 10, 15 g/L) of tea waste are added to the 400 mg/L of Cr ions at pH 2.0 and at 360 rpm. The uptake capacity of metal increases with the rise of adsorbent dose due to the higher surface area of adsorbent, more adsorption area is available. The removal of chromium increases from 23.51 mg/g to 48.82 mg/g with the increase of tea waste from 5 g/L to 15 g/L, respectively. (Malkoc & Nuhoglu 2007.).

The adsorption of 25 ppm Pb increases as the amount of peach and apricot stones rises from 0.5 to 4 g/L. This can be explained as the availability of more surface area to bind more metal ions as the dosage of adsorbent is higher (Kadirvelu, Thamaraiselvi & Namasivayam 2001). FIGURE 7 shows the efficiency of apricot and peach stone solutions separately, peach stones have slightly higher efficiency than apricot stones.

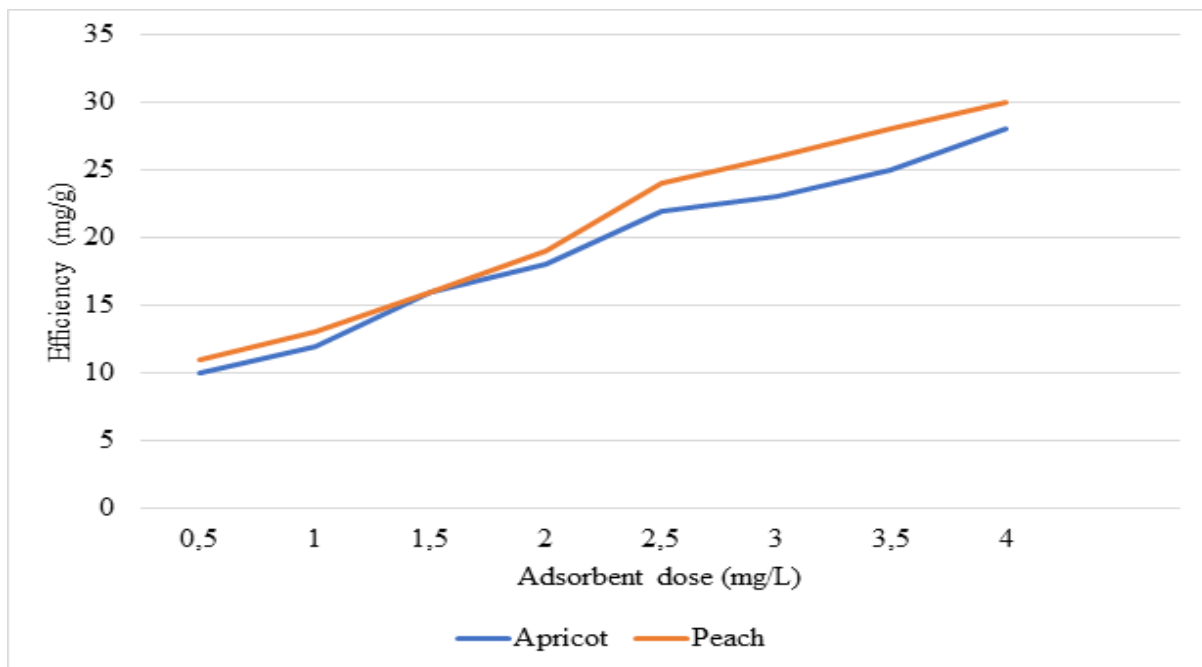


FIGURE 7. Apricot and peach stones effect on Pb absorption (adapted from Kadirvelu et al. 2001)

The rice husk dosage is varied between 4 and 20 g/L for 100 ppm Ni (II) removal, as the highest adsorption, which is 51.8 %, is shown at 20 g/L (Bansal et al. 2009). More surface area is available for metal ions to be adsorbed when the adsorbent dose is high and it increases the rate of the adsorption (Rao, Parwate & Bhole 2002). The amount of papaya wood varies between 0.5 and 20 g/L, but the process is ongoing at pH 5.0 within 60 min of contact time constantly. The highest sorption (66.8 % Zn, 94.9 % Cd, 97.8 % Cu) is shown at 5 g/L, later on it increases little by little until 20 g/L and it reaches the maximum absorption values (72.9 % Zn, 97.9 % Cd, 99.2 % Cu). The ratio of metal ions to biomass concentrations decreases while biomass concentration increases. Therefore, the maximum absorption is at the highest biomass concentration. (Saeed et al. 2005.).

5.5 Contact time and agitation speed

The contact time is important, too, the efficiency increases with the increase of contact time. In Ni removal with *Typha domingensis* leaves the highest efficiency is 51.8 % after 180 minutes of contact between metal ions and adsorbent. (Bansal et al. 2009.). The time needed for the most efficient adsorption depends on the type of biosorbent and metal ion. In the beginning of the process, the rate of biosorption is fast because there is an active space available on the biosorbent surface for metal ions. At the end of the process, the biosorption rate decreases due to the high saturation of metal ions in the solution. (Abdel-Ghani, Hegazy & El – Chaghaby 2009.). The same conditions (50 mL of 25ppm Pb in 0.5 g/L of banana peels as an adsorbate) are obtained to calculate the contact time. The observation is conducted between one and five hours, the highest absorption (96 %) is shown after 5 hours of contact between metal ions and adsorbent. (Ashraf et al. 2011.).

The 100 ppm Ni is in contact with 20 g/L rice husk at 180 rpm for 180 min. The lowest absorption, 30.3 %, is shown at 10 min while the highest absorption is at 120 min. (Bansal et al. 2009.). Later on, after 120 min the absorption becomes constant because in the beginning a high number of vacant sites are available while closer to the end the remaining surface area cannot absorb as much as initially (Gupta & Kumar.2019).

The same conditions (pH 5.0, 10 ppm of heavy metals, 5 g/L papaya wood) as in the previous experiment with papaya wood is repeated, with the change of contact time. The rapid increase is shown at

the first 30 min, and absorption reaches the highest peak (66.6 % Zn, 95.3 % Cd, 97.3 % Cu) at 60 min, it keeps constant the rest 60 min; therefore, further removal of small quantities is not possible. (Saeed, Akhter et al. 2005.). There is a difference in the uptake of the three metals, and it can be explained in terms of difference in the nature and distribution of metals, the ionic size, and the interaction between metal cations and biosorbent. (Sathasivam, Haris & Mas Rosemal Hakim Mas 2010.). The rapid absorbance is due to the sufficient numbers of available active sites on the biomass; nevertheless, the surface of biomass is more occupied that is why the sorption decreases. Also, the mesh and porous structure of papaya wood provides the fast metal removal process. (Saeed et al. 2005.).

Agitation speed affects the biosorption capacity of the biosorbent, the increasing speed leads to the minimization of biosorbent's mass transfer. It may enhance the metal ions' sorption; thus, it may also affect the biosorbent's physical nature. (Chong, Chia & Ahmad 2013.). The biosorption of 400 mg/L Cr (VI) is carried at pH 2.0 with the different agitation speed between 180 and 480 rpm. The adsorption increases from 18 mg/g to 32.5 mg/g with the increase of agitation rate. (Malkoc & Nuhoglu 2007.).

6 CONCLUSION

Heavy metals contaminate the environment, fauna and flora, groundwater and bring health problems. There are metals which are necessary for the biological growth of humans; however, most of the heavy metals are nonessential. Also, excess of any metals cause health problems. The fumes from industries contain a considerable amount of toxic gases, people inhale them and breathing becomes difficult, even lung cancer can be caused. Moreover, food and drinking water contain a variety of toxic metals and excess of them cause problems with health such as gastrointestinal, kidney and liver damages, cancer, or death.

There are the traditional ways of heavy metals removal, such as membrane filtration, ion exchange and chemical precipitation. Nevertheless, they are inefficient and labor-consuming, and they are high-priced. Also, they have a lack of selectivity of needed chemicals, required equipment and conditions. The traditional ways of heavy metals removal have another drawback that all contaminants cannot be removed completely at these processes. The new method, biosorption, is considered as an eco-friendly and reasonable heavy metal removal process. The vast amount of research provides a wide range of information about diverse types of biosorbents and the required conditions. The maximum biosorption is shown under pH value between 5.0 - 7.0, at lower temperature, at high concentration of adsorbent dose, and more contact time and higher agitation speed are the main reasons. However, there are some exceptions which do not follow the above observation. Each metal needs special conditions for each biosorbent. The same biosorbent cannot be used to remove all heavy metals. Therefore, each metal and biosorbent have to be studied separately, because of their different structures.

In nature, there is a diversity of biomass with different specifications, efficiency and types. Also, using biomass waste can help to decrease the existing amount of waste significantly. Biodegradable waste can be used as a biosorbent while non-biodegradable waste can be recycled and used as biomass. Agricultural waste, or products that cannot be consumed by humans can be used as a biosorbent for heavy metals uptake. The agricultural waste materials have various advantages; however, it is not advertised essentially due to the lack of knowledge about engineering of materials. Furthermore, more research is required to discover new biosorbents and the special factors such as pH, temperature, metal and biosorbent concentrations, temperature, contact time, and agitation speed. Future research should

be focused on the gaps such as pre-treatment methods, eco-friendly advantages of the materials in addition industrial scales must be considered.

REFERENCES

- Abbas, A., Al-amer, A.M., Laoui, T., Al-marri, M.J., Nasser, M.S., Khraisheh, M. & Atieh, M.A. 2016. Heavy metal removal from aqueous solution by advanced carbon nanotubes: Critical review of adsorption applications. *Separation and Purification Technology*, 157, 141-161.
- Abdel-Ghani, N., Hegazy, A. & El – Chaghaby, G. 2009. Typha domingensis leaf powder for decontamination of aluminium, iron, zinc and lead: Biosorption kinetics and equilibrium modeling. *International Journal of Environmental Science and Technology*, 6.
- Abdelkader, A.M. 2017. A review of membrane bioreactor (MBR) technology and their applications in the wastewater treatment systems. Available: https://www.researchgate.net/figure/Membrane-filtration-types_fig1_275040060. Accessed 02.05.2020.
- Adiana, G., Juahir, H., Joseph, B. & Shazili, N.A.M. 2017. Tracing the sources of lead (Pb) in Brunei Bay, Borneo by using integrated spectrometry ICP-MS and chemometric techniques. *Marine Pollution Bulletin*, 123(1), 232-240.
- Ahemad, M. & Malik, A. 2012. Bioaccumulation of Heavy Metals by Zinc Resistant Bacteria Isolated from Agricultural Soils Irrigated with Wastewater. *Bacteriology Journal*, 2, 12-21.
- Aksu, Z., Tezer, S. 2005. Biosorption of reactive dyes on the green algae *Chlorella vulgaris*. *Process Biochem*, 40.
- Alalwan, H.A., Kadhom, M.A. & Alminshid, A.H. 2020. Removal of heavy metals from wastewater using agricultural byproducts. *Journal of Water Supply: Research and Technology-Aqua*, 69(2), 99-112.
- Ali Shah, J., Ashfaq, Q., Hussain Gardazi, S.M., Tahir, A., Pervez, A., Haroon, H. & Mahmood, Q. 2013. Waste biomass adsorbents for copper removal from industrial wastewater-A review. *Journal of hazardous materials*, 263.
- Alimohammadi, V., Sedighi, M. & Jabbari, E. 2017. Experimental study on efficient removal of total iron from wastewater using magnetic-modified multi-walled carbon nanotubes. *Ecological Engineering*, 102, 90-97.
- Anderson, R.K., Thompson, M. & Culbard, E. 1986. Selective reduction of arsenic species by continuous hydride generation. Part I. Reaction media. *Analyst*, 111(10), 1143-1152.
- Arnarson, A. 2017. The dark side of Iron - why too much is harmful. Available: <https://www.healthline.com/nutrition/why-too-much-iron-is-harmful#section7>. Accessed 01.05.2020.
- Ashraf, M.A., Wajid, A., Mahmood, K., Maah, M.J. & Yusoff, I. 2011. Low cost biosorbent banana peel (*Musa sapientum*) for the removal of heavy metals. *Scientific Research and Essays*, 6(19), 4055-4064.
- Babel, S. & Kurniawan, T.A. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials*, 97(1), 219-243.

- Bansal, M., Singh, D., Garg, V.K. & Rose, P. 2009. Use of agricultural waste for the removal of nickel ions from aqueous solutions: Equilibrium and kinetics studies. *Int. J. Environ. Sci. Eng.*, 1, 108-114.
- Basci, N., Kocadagistan, E. & Kocadagistan, B. 2004. Biosorption of copper (II) from aqueous solutions by wheat shell. *Desalination*, 164(2), 135-140.
- Baysal, A., Ozbek, N. & Akman, S. 2013. Determination of Trace Metals in WasteWater and Their Removal Processes. *WasteWater - Treatment Technologies and Recent Analytical Developments*.
- Bhasin, G., Kauser, H. & Athar, M. 2002. Iron augments stage-I and stage-II tumor promotion in murine skin. *Cancer Lett*, 183(2), 113–122.
- Cardoso, S.L., Costa, C.S.D., Nishikawa, E., Silva, Carlos, M.G. & Vieira, M.G.A. 2017. Biosorption of toxic metals using the alginate extraction residue from the brown algae *Sargassum filipendula* as a natural ion-exchanger. *Journal of Cleaner Production*, 165, 491-499.
- Carolin, C.F., Kumar, P.S., Saravanan, A., Joshiba, G.J. & Naushad, M. 2017. Efficient techniques for the removal of toxic heavy metals from aquatic environments: A review. *Journal of Environmental Chemical Engineering*, 5(3), 2782-2799.
- Chen, G., Zeng, G., Tang, L., Du, C., Jiang, X., Huang, G., Liu, H. & Shen, G. 2008. Cadmium removal from simulated wastewater to biomass byproduct of *Lentinus edodes*. *Bioresource Technology*, 99(15), 7034-7040.
- Chong, H.L.H., Chia, P.S. & Ahmad, M.N. 2013. The adsorption of heavy metal by Bornean oil palm shell and its potential application as constructed wetland media. *Bioresource Technology*, 130, 181-186.
- Clifford, D., Sorg T. J. & Ghurye G. L. 2011. Ion Exchange and Adsorption of Inorganic Contaminants. In J. K. Edzwald (ed.). *Water Quality & Treatment: A Handbook on Drinking Water*. 6th Edition. American Water Works Association, Denver, CO, 12.1-12.96.
- Das, P., Dey, A. & Marik, P. 2012. Batch removal of chromium (VI) from aqueous solutions using wheat shell as adsorbent: Process optimization using response surface methodology. *Desalination and Water Treatment – Desalin water treat*, 39, 95-102.
- Dean, J.G., Bosqui, F.L. & Lanouette, K.H. 2002. Removing heavy metals from wastewater. Available: <https://pubs.acs.org/doi/pdf/10.1021/es60065a006>. Accessed 10.04. 2020.
- Demirbas, A. 2008. Heavy metal adsorption onto agro-based waste materials: a review. *Journal of Hazardous Materials*, 157(2-3), 220-229.
- Dixit, A., Dixit, S. & CS, G. 2015. Eco-friendly Alternatives for the Removal of Heavy Metal Using Dry Biomass of Weeds and Study the Mechanism Involved. *Journal of Bioremediation & Biodegradation*, 6(3), 1-7.
- El-sayed, G.O., Dessouki, H.A. & Ibrahiem, S.S. 2011. Removal of Zn (II), Cd (II) and Mn (II) from aqueous solutions by adsorption on maize stalks. *Malaysian Journal of Analytical Sciences*, 15 (1), 8-21.

- El-Shafey, E.I. 2005. Behaviour of reduction-sorption of chromium (VI) from an aqueous solution on a modified sorbent from rice husk. *Water, Air, and Soil Pollution*, 163(1-4), 81-102.
- Fewtrell, L., Kay, D., Jones, F., Baker, A. & Mowat, A. 1996. Copper in drinking water--an investigation into possible health effects. *Public Health*, 110(3), 175-177.
- Gadd, G.M. & White, C. 1985. Copper Uptake by *Penicillium ochro-chloron*: Influence of pH on Toxicity and Demonstration of Energy-dependent Copper Influx Using Protoplasts. *Microbiology*, 131(8), 1875-1879.
- Grazuleviciene, R., Nadisauskiene, R., Buinauskiene, J. & Grazulevicius, T. 2009. Effects of Elevated Levels of Manganese and Iron in Drinking Water on Birth Outcomes. *Polish J of Environ Stud*. 18(5), 819–825.
- Große, C., Anton, A. & Hoffmann, T. 2004. Identification of a regulatory pathway that controls the heavy – metal resistance system *Czc* via promoter *czcNp* in *Ralstonia metallidurans*. *Arch Microbial* 182, 109 – 118.
- Gupta, S. & Kumar, A. 2019. Removal of nickel (II) from aqueous solution by biosorption on *A.barbadensis* Miller waste leaves powder. *Appl Water Sci* 9, 96.
- Higgins, T. E. & Romanow, S. 1987. Treatment Processes for Contaminated Groundwater-Three Case Studies. *Haz. Waste Haz. Mater.*, 4, 307.
- Hossain, M.A., Ngo, H.H., Guo, W.S. & Setiadi, T. 2012. Adsorption and desorption of copper (II) ions onto garden grass. *Bioresource Technology*, 121, 386-395.
- Huang, Pan & Zheng. 2001. Removal of heavy metals from aqueous solutions using bacteria. *J. of Shanghai University*. 5, 253- 259.
- Hubicki, Z. & Kołodyńska, D. 2012. Selective Removal of Heavy Metal Ions from Waters and WasteWaters Using Ion Exchange Methods. *Ion Exchange Technologies*.
- Iihan, S., Nourbakhsh, M., Kilicarslan, S. & Ozdag, H. 2004. Removal of chromium, Lead and Copper ions from industrial waste waters by *Staphylococcus saprophyticus*. *Turkish electronic Journal of Biotechnology*, 2, 50-57.
- Ismail, I. & Moustafa, T. 2016. Biosorption of Heavy Metals. *Heavy Metals: Sources, Toxicity and Remediation Techniques*. 131-174.
- Javanbakht, V., Alavi, S.A. & Zilouei, H. 2014. Mechanisms of heavy metal removal using microorganisms as biosorbent. *IWA Publishing*.
- Kadirvelu, K., Thamaraiselvi, K. & Namasivayam, C. 2001. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Biore-source Technology*, 76(1), 63-65.

- Kanamarlapudi, S.L.R.K., Chintalpudi, V. K. & Muddada, S. 2018. Application of Biosorption for Removal of Heavy Metals from Wastewater. *Biosorption*.
- Kang, S., Lee, J. & Kim, K. 2006. Biosorption of Cr (III) and Cr (VI) onto the cell surface of *Pseudomonas aeruginosa*. *Biochemical Engineering Journal*, 36(1), 54-58.
- Kazakis, N., Kantiranis, N., Kalaitzidou, K., Kaprara, E., Mitrakas, M., Frei, R., Vargemezis, G., Vogiatzis, D., Zouboulis, A. & Filippidis, A. 2018. Environmentally available hexavalent chromium in soils and sediments impacted by dispersed fly ash in Sarigkiol basin (Northern Greece). *Environmental Pollution*, 235, 632-641.
- Kennish, M. J. 1989. *Practical Handbook of Marine Science*, Good Hardcover. Jean Blicksilver, Bookseller. Available: <https://www.abebooks.com/9780849337000/Practical-Handbook-Marine-Science-Kennish-0849337003/plp>. Accessed 13.04.2020.
- Kinoshita, H., Sohma, Y., Ohtake, F., Ishida, M., Kawai, Y., Kitazawa, H., Saito, T. & Kimura, K. 2013. Biosorption of heavy metals by lactic acid bacteria and identification of mercury binding protein. *Research in Microbiology*, 164(7), 701-709.
- Liberti, M. & Pichtel, J. 1997. Spatial distribution of trace metals in Delaware county, Indiana, Surface Soils. *Proceedings to the Indiana Academy of Science*, 106, 233 – 245.
- López-Mesas, M., Navarrete, E.R., Carrillo, F. & Palet, C. 2011. Bioseparation of Pb (II) and Cd (II) from aqueous solution using cork waste biomass. Modeling and optimization of the parameters of the biosorption step. *Chemical Engineering Journal*, 174(1), 9-17.
- Malkoc, E. & Nuhoglu, Y., 2007. Potential of Tea Factory Waste for Chromium (VI) Removal from Aqueous Solutions: Thermodynamic and Kinetic Studies. *Separation and Purification Technology*, 54, 291-298.
- Martin, S. & Griswold, W. 2009. Human health effects of heavy metals. *Environmental Science and Technology Briefs for Citizens*, (15), 1–6.
- Mawgoud, Y.A. Enhancement of chromium removal from industrial effluent drain by *Pseudomonas fluorescens* SC106 and *Bacillus subtilis* SC106 consortia.
- Modak, J.M. & Natarajan, K.A. 1995. Biosorption of metals using nonliving biomass. *Mining, Metallurgy & Exploration* 12, 189 – 196.
- Mubarak, N.M., Sahu, J.N., Abdullah, E.C. & Jayakumar, N.S. 2014. Removal of Heavy Metals from Wastewater Using Carbon Nanotubes. *Separation & Purification Reviews*, 43(4), 311-338.
- Nguyen, T.A.H., Ngo, H.H, Guo, W.S., Zhang, J., Liang, S., Yue, Q.Y., Li, Q. & Nguyen, T.V. 2013. Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Bioresource Technology*, 148, 574-585.
- Nies, D. 1999. Microbial heavy – metal resistance. *Appl Microbiol Biotechnol* 51, 730 – 750.

- Norberg, A.B. & Persson, H. 1984. Accumulation of heavy-metal ions by *Zoogloea ramigera*. *Biotechnology and Bioengineering*, 26(3), 239-246.
- Ojovan, M.I., Lee, W.E. & Kalmykov, S.N. 2019. *Treatment of Radioactive Wastes. An Introduction to Nuclear Waste Immobilisation*. Third Edition. Elsevier, 231-269.
- Orhan, Y. & Büyükgüngör, H. 1993. The Removal of Heavy Metals by Using Agricultural Wastes. *Water Science and Technology*, 28(2), 247-255.
- Oyedepo, T. 2011. Biosorption of Lead (II) and Copper (II) Metal Ions on *Calotropis procera* (Ait.). *Science Journal of pure and Applied Chemistry*, 1, 1-7.
- Pan, Z. & An, L. 2019. Removal of Heavy Metal from Wastewater Using Ion Exchange Membranes. 25-46.
- Pan American Health Organization. 2011. *Guidelines for Drinking-water Quality (4^o ED.)*. Available: <http://www.paho.org/en/documents/guidelines-drinking-water-quality-4o-ed-2011>. Accessed 16.04.2020.
- Park, D., Park, J.M. & Yun, Y. 2005. Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp. *Chemosphere*, 60(10), 1356-1364.
- Park, D., Park, J.M. & Yun, Y. 2010. The past, present, and future trends of biosorption. *Biotechnology and Bioprocess Engineering*.
- Plum, L.M., Rink, L. & Haase, H. 2010. The essential toxin: impact of zinc on human health. *International journal of environmental research and public health*, 7(4), 1342-1365.
- Ponnusamy, S.K., Subramaniam, R., Vasanthakumar, S.S.B., Kirupha, S., Arukkani, M. & Sivanesan, S. 2012. Removal of cadmium (II) from aqueous solution by agricultural waste cashew nutshell. *Korean Journal of Chemical Engineering*, 29.
- Poole, K., 2017. At the Nexus of Antibiotics and Metals: The Impact of Cu and Zn on Antibiotic Activity and Resistance. *Trends in Microbiology*, 25(10), 820-832.
- Puranik, P., Modak, J. & Paknikar, K. 1999. A Comparative Study of the Mass Transfer Kinetics of Metal Biosorption by Microbial Biomass. *Hydrometallurgy*, 52, 189-197.
- Qi, F., Lamb, D., Naidu, R., Bolan, N.S., Yan, Y., Ok, Y.S., Rahman, M.M. & Choppala, G. 2018. Cadmium solubility and bioavailability in soils amended with acidic and neutral biochar. *Science of The Total Environment*, 610-611, 1457-1466.
- Rao, M., Parwate, A.V. & Bhole, A.G. 2002. Removal of Cr⁶⁺ and Ni²⁺ from aqueous solution using bagasse and fly ash. *Waste management*. New York, 22, 821-30.
- Rashed, M.N. 2006. Fruit stones from industrial waste for the removal of lead ions from polluted water. *Environmental Monitoring and Assessment*, 119(1-3), 31-41.

- Reddad, Z., Gerente, C., Andres, Y. & Le Cloirec, P. 2002. Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environmental Science & Technology*, 36(9), 2067-2073.
- Reddy, D.H., Yapati, H. & Sessaiah, K. 2010. Biosorption of Pb (II) from aqueous solutions using chemically modified. *Chemical Engineering Journal*, 162, 626-634.
- Rehman, A. 2006. Survey of protozoan fauna surviving in stress conditions industrial wastes and their role in bioremediation. Lahore: University of Punjab. Doctor's thesis.
- Revathi, M., Kavitha, B. & Vasudevan, T. 2005. Removal of nickel ions from industrial plating effluents using activated alumina as adsorbent. *Journal of environmental science & engineering*, 47, 1-6.
- Rincón, J., González, F., Ballester, A., Blázquez, M.L. & Muñoz, J. 2005. Biosorption of heavy metals by chemically activated algae *Fucus vesiculosus*. *Journal of Chemical Technology and Biotechnology*, 80, 1403-1407.
- Romera, E., González, F., Ballester, A., Blázquez, M.L. & Muñoz, J.A. 2006. Biosorption with Algae: A Statistical Review. *Critical Reviews in Biotechnology*, 26(4), 223-235.
- Saeed, A., Akhter, M.W. & Iqbal, M. 2005. Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. *Separation and Purification Technology*, 45(1), 25-31.
- Sağ, Y., Açıkel, Ü, Aksu, Z. & Kutsal, T. 1998. A comparative study for the simultaneous biosorption of Cr (VI) and Fe (III) on *C. vulgaris* and *R. arrizus*: application of the competitive adsorption models. *Process Biochemistry*, 33(3), 273-281.
- Sahmoune, M., Louhab, K. & Boukhiar, A. 2011. Advanced Biosorbents Materials for Removal of Chromium from Water and Wastewaters. *Environmental Progress & Sustainable Energy*, 30, 284-293.
- Sathasivam, K. & Haris, M.R.H.M. 2010. Banana trunk fibers as an efficient biosorbent for the removal of Cd (II), Cu(II), Fe(II) and Zn(II) from aqueous solutions. *Journal of the Chilean Chemical Society*, 55(2), 278-282.
- Sekhar, K.C., Subramanian, S., Modak, J.M. & Natarajan, K.A. 1998. Removal of metal ions using an industrial biomass with reference to environmental control. *International Journal of Mineral Processing*, 53(1), 107-120.
- Shaheen, S.M., Antoniadis, V., Kwon, E.E., Biswas, J.K., Wang, H., Ok, Y.S. & Rinklebe, J. 2017. Biosolids application affects the competitive sorption and lability of cadmium, copper, nickel, lead, and zinc in fluvial and calcareous soils. *Environmental Geochemistry and Health*, 39(6), 1365-1379.
- Shamim, S. 2018. Biosorption of Heavy Metals. *Biosorption*.
- Smith, A., Marshall, G., Yuan, Y., Ferreccio, C., Liaw, J., Ehrenstein, O., Steinmaus, C., Bates, M. & Selvin, S. 2006. Children's Health Increased Mortality from Lung Cancer and Bronchiectasis in

- Young Adults after Exposure to Arsenic in Utero and in Early Childhood. *Environmental health perspectives*, 114, 1293 – 1296.
- Sun, J., Hu, C., Tong, T., Zhao, K., Qu, J., Liu, H. & Elimelech, M. 2017. Performance and Mechanisms of Ultrafiltration Membrane Fouling Mitigation by Coupling Coagulation and Applied Electric Field in a Novel Electrocoagulation Membrane Reactor. *Environmental Science & Technology*, 51(15), 8544-8551.
- Ungureanu, G., Santos, S., Boaventura, R. & Botelho, C. 2015. Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption. *Journal of Environmental Management*, 151, 326-342.
- Valls, M. & De Lorenzo, V. 2002. Exploiting the genetic and biochemical capacities of bacteria for the remediation of heavy metal pollution. *FEMS Microbiology Reviews*, 26(4), 327-338.
- Vasudevan, P., Padmavathy, V., Tewari, N. & Dhingra, S.C. 2001. Biosorption of heavy metal ions. *Journal of Scientific and Industrial Research*, 60, 112-120.
- Vempati, R.K., Musthyala, S.C., Mollah, M.Y.A. & Cocke, D.L. 1995. Surface analyses of pyrolysed rice husk using scanning force microscopy. *Fuel*, 74(11), 1722-1725.
- Vijayaraghavan, K. & Yun, Y. S. Bacterial biosorbents and biosorption. *Biotechnology Advances* 26, 266–291.
- Volesky, B. & Holan, Z.R. 1995. Biosorption of Heavy Metals. *Biotechnology Progress*, 11(3), 235-250.
- Volesky, B. 2003. Biosorption process simulation tools. *Hydrometallurgy*, 71(1), 179-190.
- Wang, J. & Chen, C. 2009. Biosorbents for heavy metals removal and their future. *Biotechnology Advances*, 27(2), 195-226.
- Wang, L., Li, Y. & Shamma, N. 2007. Chemical Precipitation. *ChemInform*. 141-197.
- Wang, T.C., Weissman, J.C., Ramesh, G., Varadarajan, R. & Benemann, J.R. 1998. Heavy metal binding and removal by phormidium. *Bulletin of Environmental Contamination and Toxicology*, 60(5), 739-744.
- Wastewater technology fact sheet: chemical precipitation. 2000. Washington, D.C.: United States Environmental Protection Agency, Office of Water.
- Weng, C.H. & Huang, C.P. 1994. Treatment of metal industrial wastewater by fly ash and cement fixation. *J Environ Eng*, 120, 1470-1487.
- WHO. 2004. Guidelines for drinking-water quality. Sixty-first meeting. Joint FAO/WHO Expert Committee on Food Additives. Available: <http://ftp.fao.org/esn/jecfa/jecfa61sc.pdf>. Accessed 28.04.2020.

Wong, K.K., Lee, C.K., Low, K.S. & Haron, M.J. 2003. Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere*, 50(1), 23-28.