Doctoral Thesis

An Insight into the Mechanism of Metal Biosorption by Algae Biomass

Department of Civil and Environmental Engineering, Graduate School of Engineering

TOHOKU UNIVERSITY

García Cáceres Irina Giselle

(ID No. B6TD6002)

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Acknowledgments

Pursuing a PhD must have been one of the biggest challenges I have ever faced so far. From the selection of the research topic, the long hours of reviewing what has been done so far (trying to find that novel idea), the making of a research plan, the execution of the research plan, analyzing the results (sometimes obtaining many unexpected results) to the defense and explanation of what you have done and the summarizing of the whole in a dissertation. However, at the same time it has been one of the most rewarding experiences in my life, helping me grow professionally and personally.

A friend of mine always told me, doing a PhD is like a long ultra-marathon rather than a speed race, you need a lot of patience and perseverance to get all the way to the finish line, now I believe it more than ever.

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> “Science is a way of life. Science is a perspective.
> Science is the process that takes us from confusion to understanding in a manner that's precise, predictive and reliable - a transformation, for those lucky enough to experience it, that is empowering and emotional.
>
> –**Brian Greene**

Abstract

Heavy metals have been widely used in different industries. Consequently, they have negatively affected our ecosystems, especially our water sources. Biosorption was developed and improved as a water treatment method over the past decades. Biosorption is the removal of pollutants from water, using dead organic biomass as an adsorbent. Commonly used biosorbents are algae, fungi, bacteria and agricultural waste. Algae is typically used as a biosorbent because of its high binding capacity. However, their biosorption mechanisms are not fully understood yet. Comprehending the mechanism of biosorption will lead us to its industrial application under the most optimum conditions. Since more reliable mathematical models based on the actual mechanisms could be employed to predict the influence of the parameters affecting it. This study aims to investigate the adsorption mechanism of green and red algae. For this purpose three algae, hitoegusa (green algae), funori and ogonori (red algae) were selected and their removal affinity towards Cd(II), Pb(II), Zn(II), As(III), As(V) and Se(IV) was examined. Initially, the biosorption of Cd, Pb, Zn, As, and Se was reviewed in a meta-analysis. The maximum adsorption capacity data of 71 different biosorbents was analyzed. Results shows that cationic metals are easier to be removed with biosorption when compared with anionic metals. The biosorption of anionic metals is a more selective process. A reduced amount of biomass show affinity towards these contaminants. Next the metal removal capacity by the three chosen algae was evaluated and the main parameters (pH, contact time and biomass dosage) were studied through batch experiments. None of the algae were capable of removing the anionic metals (As and Se). On the other hand, when it came to the cationic metals: the maximum biosorption capacity of Cd(II), and Zn(II) by hitoegusa was 67.1 mg/g and 61.2 mg/g, by funori 59.3 mg/g and 58.2 mg/g and by Ogonori 30.2 mg/g and 20.3 mg/g. Lead removal by hitoegusa and funori was 67.4 mg/g and 78.0mg/g. Under conditions of 4 g/L of biomass dosage, pH 5 and contact time of 60 min. The biosorption process by all algae for all three metals was rapid (15mins) and its kinetics followed the pseudo-second order

model. Finally, several analytical techniques such as chemical modification of the functional groups, potentiometric titrations, FTIR, SEM-EDX and the quantification of desorbed metal were applied to determine the biosorption mechanisms of the Cd(II), Pb(II) and Zn(II) on funori, hitoegusa and ogonori. Metals were removed with funori predominantly by an ion exchange process through the release of Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} into the solution phase. The carboxylic groups of hitoegusa and funori played a major role in the biosorption of all three metals. On the other hand, the amine group is a fundamental component of ogonori for the removal of metals. Because of it, ogonori is highly alkaline favoring the removal of metal through precipitation too. The chemisorption was determined through the changes in frequency of the biosorption spectra before and after. Results shows that the removal of cationic metals by hitoegusa, funori and ogonori biomass were due to (i) ion exchange and chemisorption (ii) ion exchange (iii) cation exchange and precipitation. Since cation exchange played a key role in the uptake of metal the removal of As and Se was not favored when using these algae. Our results revealed that all three algae could be employed as an effective and low-cost biosorbent for removal of Pb(II), Zn(II) and Cd(II) from contaminated water sources.

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Chapter 1

Introduction

1.1. Background

Heavy metals have been part of our lives for several centuries. Their application in almost any industry had influenced their distribution around the world and their concentrations in water, air and soil. Unfortunately, besides all the benefits link to them, there are also many adverse effects connected to their presence in high concentrations in water. The negative health effects, their slow elimination, and complex degradation make heavy metals particularly dangerous contaminants. The reported numbers about the water pollution issue are alarming. According to the non-profit organization *One Drop*, currently, 663 million people lack access to safe water, and this amount of people is equal to the combined populations of the United States, Russia, Japan, France, Italy, and Canada. At this rate, by the year 2025, it is estimated that on the one hand there might not be enough water to satisfy the demand of 1.8 billion people, while on the other hand two-thirds of the global population could experience water stress. The World Health Organization (2012) estimated eight million deaths in low and middle-income countries due to exposition to pollutants in the air, water, and soil.

Considering water is a non-renewable resource and an essential substance for the life of the all living beings, its conservation, remediation, and sustainable usage should be a top priority. Over the years, not only have our water consumption multiplied but also the generation of wastewaters have increased at the same rate. Fortunately, along these years researches have also succeeded in the development of many techniques to remove heavy metals from water. However, due to their high expenses and complex methodologies, many of those technologies are only suitable for high-income countries. While actually, developing countries are more affected by severe pollution of their water because of a lack of appropriate control regulations and remediation protocols.

With the acceleration of the production processes and the growth of the population the disposal of solid wastes adds up to the current environmental concerns. Biosorption emerged as an answer to these problems, recycling bio-waste to eliminate important pollutants from the water sources. Biosorption as a treatment technique have been extensively studied. Many diverse pollutants (heavy metals, dyes and phenolic compounds) have been successfully removed with vast amount of biosorbents (algae, bacteria, fungi, agricultural wastes, sludge wastes, and natural residues to mention some). Seaweeds are considered a promising alternative due to their natural origin, great diversity, overall cost-effective ratio, and effectiveness against a broad pollutant range.

So far very few efforts have been oriented to understand the mechanism controlling the biosorption process. By understanding the mechanism, the biomaterial selection process becomes more effective and cheaper. Also this helps to establish better and more appropriate enhancement methods according to the specified conditions.

Therefore the main questions arise regarding biosorption were

- How do biosorbents adsorb metal? What is the biosorption mechanism of the red and green algae?
- Why some biosorbents adsorb cationic metals only? Why some biosorbents adsorb only anionic metals? Why some biosorbents adsorb both metals?
- Is biosorption really a suitable technique for the removal of arsenic?

1.2. Objectives

The main purpose of this research is to study the adsorption mechanism of green and red algae. It also aims to find general characteristics from each type that can contribute to a better selection process of a biosorbent without facing a costly trial and error process.

The specific objectives of this study are:

a) To evaluate the adsorption properties of funori (*Gloiopeltis furcata),* hitoegusa (*Monostroma nitidum)* and ogonori (*Gracilaria* sp.) to remove o Cd, Pb, Zn, As, and Se from aqueous solutions, considering single system.
b) Define a relation between the functional groups contained in funori, hitoegusa, and ogonori, and their adsorption capacity of metals.
c) To determine the binding mechanism of Cd, Pb, Zn ions onto funori, hitoegusa and ogonori by the application of a combination of different analytical techniques.

1.3. Scope

This study focuses on the removal of a single metal from a synthetic aqueous solution through the temporary addition of certain amount of dried algae biomass.

The conditions limiting this research are:

a) The vast complexity and uniqueness of the molecular structures of the biomaterials (representativeness of each sample)
b) The chemistry and speciation of the metal elements and their great dependence on the different conditions (pH, oxygenation, organic content, etc) in an actual aqueous system.
c) The different behavior in a more complex system of binary, tertiary or multi elemental matrix as freshwater samples that typically contain more than one contaminants at the same time.

1.4. Outline of the Content

The thesis presents a comprehensive analysis of the biosorption process of heavy metals by three seaweeds, from the red and green types. **Chapter 1** provides the justification for the scientific and environmental significance of this study. The chemistry, toxicology and current situation of cadmium, lead, zinc, arsenic, and selenium in water sources are summarized in **Chapter 2**. This chapter also presents an overview to the state of the art techniques use in the removal of heavy metals, and the important role of biosorption among them. A critical review of the limitations of biosorption as a

treatment technology is included as well. **Chapter 3** includes a statistical review of the findings regarding biosorption capacity from previous biosorption studies. Also discusses previously proposed biosorption mechanisms of heavy metals by different biomaterials. An evaluation of the biosorption capacity of the five representative heavy metals by the selected biomass (funori, hitoegusa and ogonori) was investigated in the **Chapter 4**. The effects of certain parameters in the sorption capacity was also discussed. The results obtained in this chapter highlighted the great difference of the biosorption abilities and mechanisms between anionic (arsenic, and selenium) and cationic metals (cadmium, lead, and zinc). Consequently, in order to explain this big discrepancy among anionic and cationic metals, the mechanism of biosorption was studied in **Chapter 5**. Here, the morphological characteristics of the used algae, the characterization of the functional groups in their cell wall structure and their influence in the biosorption are presented. **Chapter 6** summarizes and discusses the results of this thesis, and the potential future routes to follow in the context of this research.

Chapter 2

Literature Review: An Overview of Heavy Metals Issue, Their Current Remediation Technologies and Biosorption Technique

Abstract

Heavy metals (most of them cataloged toxic) occur naturally in the earth crust. And since they are a key element in almost all industry, pollution of water by them have been an issue for many years. Traditional water treatments are expensive and most of them generates large amounts of toxic waste. Biosorption is a promising technique. It is a rapid simple process that does not required the adjustment of different conditions. Commonly used biosorbents are algae, fungi, bacteria and agricultural waste. And since they are applied in their inactivated forms no nutrients are necessary to maintain them. Despite all the advantages biosorption possess, still there is a lot to be done regarding its mechanism. Immobilization seems as the most adequate next logical step to improve the biosorbents. Additionally, more pilot studies are require in order to obtain all the necessary information to apply this technique on an industrial scale.

Keywords:

Heavy Metals, Biosorption, Algae, Fungi, Bacteria, Agricultural waste,

2.1. Introduction

This next chapter presents a summary of the available research regarding the characteristics of some representative anionic and cationic heavy metals, their occurrence, their chemistry, their harmful effects on human health and the current technologies used to remove them from water. Also is a brief overview of concepts like biosorption and biosorbent. The limitations of this technique, and the existing approaches used to unveil the binding mechanisms of the biomaterials are also discussed.

2.2. Heavy Metals Issue Worldwide

Scientists have been using the term "heavy metals" for over 60 years without reaching a generalized consensus about the meaning of the expression (Hawkes, 1997)(Duffus, 2002)(Järup, 2003). For our purposes, heavy metals will be those elements with a specific gravity of 5 or higher (Passow et al., 1961), also including the semimetals with this same physical characteristic like Arsenic, Antimony, and the less commonly recognize as metalloid: Selenium, etc but however more importantly, **those sharing common chemical properties and similar toxicological effects**. Heavy metals can be found in nature as mineral ores, however, throughout time they have also been widely used in multiple industries. As a result, day by day their impact on the ecosystems have been increased, affecting the air, soil, and water, jeopardizing the life of different species of animals and of the human beings too. Mining, electroplating, tannery and manufacturing industries along with refining and smelting processes are typical sources of metals pollution in water. Because of the great role that the heavy metals have in our lives the generation of wastewaters containing them is far from being stopped. And although can be and is decreasing, heavy metal pollution will still be a major environmental problem for around the upcoming half-century.

When they are in aqueous solutions the majority of the usual metals can be found as cations (positively charged) like the case of Pb, Hg, Cd, Cu, etc (Naja and Volesky, 2011). However, this solubility is restricted by oxides precipitation process as the pH increases near or above the neutrality (they become more insoluble), whereas in comparison most

of the negatively charged metals can persist in solution at relatively elevated concentrations at this same pH conditions. Therefore, elements such as As, V, Mo, Cr, etc are most commonly found as groundwater contaminants (Smedley and Kinniburgh, 2002).

The following section describes the origin, the speciation, the toxicological characteristics and some other important information of our study targeted metals: arsenic, chromium, selenium, chromium, cadmium, lead and zinc.

2.2.1. **Arsenic**

Arsenic is virtually found everywhere: in rocks, in the soil, in the air, in water sources. Under natural conditions, Arsenic is very mobile (easily lixiviate from rocks and minerals) which causes many environmental problems. However, the human beings are also responsible for increasing the amount of released arsenic into the water, through many different activities such as mining, smelting, the combustion of fossil fuels and the usage of pesticides, herbicides and wood preservatives (Manju et al., 1998)(Bissen and Frimmel, 2003a)(Rahaman et al., 2008)(Vaclavikova et al., 2008)(Shankar et al., 2014). Several incidents of arsenic contamination have been reported all around the world as a result of inappropriate industrial waste management.

Japan: Matsuo (1920-1962) well water was contaminated with residues of calcinated ores from white arsenic production, Nakajo (1960) an arsenic sulfide factory affected a neighboring well. India: Behala, Calcuta (1969-1989) in the sites near an industrial area, concentrations of underground water were in the range of 0.05 to 58 mg/L. Thailand: Ronphibun (1987) the arsenic level in the water was in between the 0.4 to 5 mg/L in many areas. Philippines: Mindanao Island (1992) arsenic was released into the streams as a consequence of the construction of a thermal plant, concentrations of up to 0.1 mg/L were detected (Mandal and Suzuki, 2002). More recently in China, in 2006, Xinqiang river, a drinking water source for a community of around 100,000 inhabitants reached concentrations 10 times higher than the local permissible limit, after three chemical factories discarded their wastewaters there. And only two years later, lake Yangzonghai which is the main source of drinking water for 20,000 residents also reported alarmingly high levels of arsenic.(Miao et al., 2015).

The main sources of drinking water are surface water (rivers, lakes, ponds), rainwater and groundwater (Basu et al., 2014). The minimum detected concentrations of arsenic in river waters are low (in the region of 0.1–0.8 μg/L and up to approximately 2 μg/L) and in lake waters the concentrations are almost the same or even lower than those found in the river water. In surface waters, high concentrations are only found usually when affected by geothermal water and by mining activity (Smedley and Kinniburgh, 2002)(Järup, 2003). Arsenic is a lethal poison, especially when ingested in large doses. However, a prolonged and continuous ingestion of low concentrations of it can also lead to an intoxication. So even though, the concentrations of the water bodies used as drinking water supplies can be considered low in some cases, they still pose a threat to the health of those who consume it. (Kartinen and Martin, 1995). At the same time, in the last two decades, groundwater containing high concentrations of Arsenic have been reported all over the world: Argentina, Bangladesh, Chile, China, Hungary, Mexico, Taiwan, Vietnam, and West Bengal (India) (Smith et al., 2000)(Nordstrom, 2002)(Smedley and Kinniburgh, 2002)(Mandal and Suzuki, 2002)(Shankar et al., 2014)(Basu et al., 2014). The fact that both surface water and groundwater (primary sources of water consumption) represent a threat due to the presence of arsenic is undoubtedly a global worrisome panorama and one of the environmental challenges of the 21st century.

Although both organic and inorganic arsenic exists in nature in numerous ways, As(III) and As(V) are the most common oxidation states in water. From these As(III) is (around 60 times) more poisonous and complex to remove(Bissen and Frimmel, 2003a) (Pokhrel and Viraraghavan, 2006) (Ranjan et al., 2009).That is why traditionally when removing arsenic, As(III) is oxidize to As(V) (Bissen and Frimmel, 2003b).

Even though there is no evidence to consider arsenic as a necessary nutrient for humans or animals, exposition to arsenic generally happens through water and food (besides the occupational hazard). In food, organic arsenic can be consumed in fish and crustaceans. Also, regular consumption foods prepared with water as a base (soups or similar) contribute to a higher arsenic ingestion rate. The gastrointestinal tract is capable of quickly and easily digest inorganic arsenic compounds (WHO, 2017).

Inorganic arsenic has been classified as a carcinogenic element to humans (Group 1) according to (IARC, 2012). Also, the ATSDR categorizes substances in a priority list based on their frequency of occurrence, toxicity, and potential for human exposure. In 2017, arsenic was ranked as the top number one concern of the aforementioned list.

Researchers agree that the main health risks associated with a prolonged exposure to arsenic are: skin lesions (pigmentation problems and hyperkeratosis), lung, bladder, kidney, and skin cancer. Also, other effects, nonrelated with carcinogenic issues as vascular and pulmonary diseases (Järup, 2003)(Yoshida et al., 2004)(Pal et al., 2009) (IARC, 2012) (WHO, 2017).

2.2.2. **Selenium**

Selenium is widespread around the world in the soil, the rocks, the water and, the air, and because of its chemical nature, it exists in combination with different elements (Fernández-Martínez and Charlet, 2009) (Santos et al., 2015). Elemental selenium, ferric selenite ($Fe_2(OH)SeO_3$), calcium selenate (CaO_4Se) and organic selenium (produced by the decomposition of plants and animals) are generally present in soils (Kapoor et al., 1995). And in the water, is available in the form of Se(II) (selenite) and Se(VI) (selenate), unlike the elemental selenium and Se(-II) (selenide) which are insoluble in an aqueous system. The main natural source of selenium in water is the weathering of the soil and rocks that contain it. Though its recent increase in water bodies is also related to the amount of wastewater released from industrial processes. Selenium is a versatile material used in electronics for the fabrication of photocells, rectifiers and xerographic tools, and in the manufacturing of glass, as a pigment. (Kapoor et al., 1995) (Tuzen and Sari, 2010). As a coating for stainless steel and copper. In mining, fossil fuels production and agriculture (in insecticides) (Lemly, 2004). The concentrations of Selenium in the water coming from the industrial discharges are in the range between 1 µg/L and 7,000 µg/L (Kapoor et al., 1995), while the mining wastewaters are in between 3 µg/L up to as high as 12,000 µg/L (Wasewar et al., 2009). The average concentration of selenium reported in freshwater (around the world) is 0.02 µg/L (Fernández-Martínez and Charlet, 2009). The selenium concentrations in the groundwater tend to be higher than in the surface water because of its constant contact with rocks (Santos et al., 2015). Like in the case of the USA, where the surface water and the groundwater content of

selenium are generally in the interval of 0.06 µg/L to 400 µg/L, nevertheless in some regions, the concentration in groundwater can be as high as 6000 µg/L. Samples taken from the tap water of diverse public supplies around the world showed concentrations lower than the 10 µg/L or surpassing the 50 µg/L (WHO, 2011a). Although most of the selenium intake is believed to be through food ingestion, the WHO has provided 40 µg/L as a provisional guideline value in drinking water.

Selenium is a vital micronutrient. 1 mg of selenium per kg of body is the recommendable consumption intake for human beings when these levels are exceeded it turns poisonous (Tuzen and Sari, 2010). The ingestion of 50 to 200 mg of selenium meets the humans' daily nutritional requirements regarding selenium. Consuming more than the needed, over the 400 mg, can lead to an acute intoxication better known as selenosis. The reported symptoms of selenosis are gastrointestinal and neurological issues, fatigue, deformities, and loss of hair. The excess can also cause liver issues as cirrhosis and pulmonary edema and consequently death (Hasan et al., 2010). Selenium poisoning due to a prolonged exposure has been observed in China. People who consumed it for an extended period of time even in small amounts presented hair breakage and deformations in the nails. In the more severe cases also gross motor skills issues (movement of arms and legs)(Barceloux, 1999)(ATSDR, 2003).

The problems concerning pollution of mercury, lead, and cadmium, pesticides, air pollutants, and some others have outshined the environmental impact of selenium for a long time. In the past years, very few scientific efforts have been dedicated to the research about water treatments for selenium-containing sources, however recently more interest about adsorption studies have emerged (Santos et al., 2015). The relevance of selenium became more visible due to the expansion in the range of the substances covered by the current water pollution monitoring programs. It also became noteworthy how rarely, a contaminant possess such a capacity of affecting the aquatic ecosystems the way selenium does, so extensively and with such a complex mobility scheme around the components of a habitat (Lemly, 2004).

2.2.3. **Cadmium**

In minerals cadmium is naturally found in combination with zinc lead and copper (Järup,

2003). As a minor component of zinc ores, it is frequently recovered as a by-product of the zinc refinery (Hem, 1972). Like most metals, its presence in water is partly due to the weathering of the minerals and rocks that contain it. In the water is soluble as the hydrated ion or when with different organic or inorganic ligands it forms ionic complexes. For example, cadmium chloride and cadmium sulfate are highly soluble compounds. The soluble forms are very mobile, unlike the insoluble ones which accumulate into the sediments (ATSDR, 2012).

With the intensification of the production and usage of cadmium in the last 100 years also came a great increase in its release in the atmosphere. This has been aggravated by the lack of recycling and treatment protocols for products containing cadmium, thus they are usually disposed with the domestic waste and end up dangerously getting incinerated (Järup, 2003).

Industrial wastewaters are a typical source of cadmium in water. Mining, the refining of petroleum, metallurgical processes like smelting (especially lead, zinc, and cadmium smelters), manufacturing of alloys and electroplating are a usual source of these polluted streams (Aksu, 2001) (Vilar et al., 2006)(Vinok K. Gupta and Rastogi, 2008). Pesticides, phosphate fertilizers and cadmium-containing pigments also contribute to its dispersion along with the burning of fossil fuels, the incineration of waste, and the melting of scrap metals (Friberg et al., 1974) (ATSDR, 2012).

The concentration of cadmium in natural surface water and groundwater is <1 μg/L (ATSDR, 2012). The maximum permissible concentration of cadmium in wastewater is of a 0.1 mg/L (Vinok K. Gupta and Rastogi, 2008), almost 34 times higher than the admissible concentration for drinking water of 3 μg/L according to the WHO. The effects of Cadmium on the human health have been detected and studied for almost a century. In the 1940's, residents from the Miyagawa village (Toyama Prefecture, Japan) presented symptoms of a painful disease very similar to rheumatic illnesses, what will be known later as Itai-Itai disease (Itai is the Japanese interjection used to express pain or displeasure, equivalent to "ouch" in the English language). A link between the Jintsu River and the disease was observed: the crops irrigated by this water were being affected by the discharges of the Kamioka mine. The rice and fish of the area were proven to contain high concentrations of heavy metals particularly cadmium (Friberg et al., 1974).

Despite now there is a continuous increasing awareness about the immense damage caused by heavy metals. Mining and water pollution by heavy metals still a concern. In January, 2012, Guangxi Longiang River located in Guangxi province at the southeast of China was heavily contaminated with the wastewater from the Jinhe Mining Corporation and Hongquanlide Powder Material Plant. The companies released around 18,000 Kg of cadmium into the water. The enormous leak of cadmium caused a massive death of fish (1.33 million baby fish and 40,000 kg of adult fish) and also affected the water supply and consumption habits of a large number of people (3 million residents) (Miao et al., 2015). By 2015, 5 million people in 150 sites around the world were estimated to be at risk of exposure to cadmium (Pure Earth & Green Cross Switzerland, 2015).

As for the non-occupational related sources of cadmium, after smoking, its intake in food is the primary route of exposure to this metal. Especially in the crops harvested in agricultural fields contaminated by industrial waste (Pure Earth & Green Cross Switzerland, 2015). Which causes dietary intakes of around 10 to 35 µg per day. A very high amount when compared with the intake through drinking water that is even lower than 2 µg per day (WHO, 2011b). Cadmium is considered one of the most hazardous metals for people's health and the environment. It affects greatly the ecosystems because it accumulates in living beings causing poisoning and easily moving through the food chain (Vinok K. Gupta and Rastogi, 2008). When entering the human body, cadmium tends to gather and stay in the kidneys and the liver for numerous years. Only small quantities of it can be slowly eliminated, through urine and feces (ATSDR, 2012). Kidney failure, deterioration of the bones, respiratory failure, liver damage, anemia, and hypertension are some of the negative effects of this metal on the health of people that have been exposed to it (Vinok K. Gupta and Rastogi, 2008) (Ding et al., 2012). It has also been defined as carcinogenic by the US Department of Health and Human Services (Sheng et al., 2004).

2.2.4. **Lead**

Lead is a heavy, low melting, and bluish-gray metal. Naturally, is extensively dispersed (even when is not a major constituent of the earth crust) in rocks and soils at low concentrations (Hem and Durum, 1973).

For that reason, its contribution to the lead in the environment is smaller against the amount coming from anthropogenic activities. As most of the metals, lead is a key component in nearly every industry that has provided our daily life products for many years. Typically wastewaters from the manufacturing of batteries, pigments, photographic materials, and printing processes contain high volumes of unwanted lead (Jalali et al., 2002) (Vilar et al., 2005)(Martins et al., 2006). Mining and smelting of ores are also associated with lead discharges in water as acid mine drainage (Ucun et al., 2003). It is largely extracted when silver is mined from galena (lead sulfide) (Flora et al., 2006). Other common sources are processes like the combustion of leaded petrol (V. K. Gupta and Rastogi, 2008) and the recycling of acid lead-batteries.

Unlike other metals, the presence of lead in drinking water is not only related to its content at the source. High levels have been detected in the tap water (the point of consumption) as a result of the corrosion of the plumbing systems. For centuries, lead pipes have been widely used as household distribution system because of their flexibility, and endurance (Flora et al., 2006). This particular feature turns lead into a unique hazard since a lot of effort needs to be invested in the improvement of the distribution lines (installation of lead free connections) and the application of corrosion control protocols besides the traditional water treatments (WHO, 2017).

In industrial wastewaters, lead can be mainly found as divalent lead or as organic complexes like lead tetraethyl. While the water quality standards for wastewaters demand divalent lead concentrations to be around the range of 0.05 to 0.10 mg/L, its concentrations are considerably higher oscillating in between the 200 to 500 mg/L (Ucun et al., 2003).

Estimations of the NGO Pure Earth for the year 2015, calculated 26 million people living in risk of exposure to lead globally. The organization has also identified at least 800 sites where the conditions increase the odds of being exposed to this metal. In between November, 2007 and March, 2008, the seriousness of the lead issue became more evident when 18 children died after suffering an acute lead poisoning in Dakar, Senegal. The route of exposure was the contact with contaminated soil. One of the most important economic activities of the community, the recycling of used lead-acid batteries, led to the accumulation of this dangerous metal in the soil of the area.

Similarly, a study in Pakistan revealed that the clothing of lead recyclers is likely to be the reason for the high exposure rate of their children to this pollutant (Pure Earth & Green Cross Switzerland, 2015).

Just a few years ago, in 2014, a terrible crisis of water contaminated by lead occurred in the USA endangering the lives of thousands of people. As a cost-saving measure, the city of Flint, Michigan changed its drinking water source from Lake Huron to Flint River.

At that time corrosion control protocols were not being applied to Flint River's water. The more corrosive water is, the more easily metals like lead can be dissolved. And since the water from Flint River was 19 times more corrosive than the one in Lake Huron, this apparent small change increased dramatically the concentrations of lead in the household water after its leaching from the old distribution system of the city. In more than the 90% of the houses where the lead concentration was measured, values of 25 µg/L were reported and in some cases even exceeded the 1000 µg/L. Between 2013 and 2015, the occurrence of blood lead levels above the 5 µg/dl (the reference value) in children, increased from 2.4% to 4.9% (Bellinger, 2016)(Hanna-Attisha et al., 2016).

As for its toxicology, possibly no other metal have been as broadly investigated as lead has (Jalali et al., 2002).

Unlike zinc or selenium, lead doesn't has any function in our bodies. Perhaps for this reason, any level of lead exposure is considered dangerous. Lead is absorbed much more easily through drinking water than when it is contained in food. When this element is in the water, an adult can take in around 35% to 50% of all the lead drunk. Compare to adults, children are more endanger by it since they absorb even more than the 50% (Flora et al., 2006).

The maximum permissible concentration in drinking water established by the U.S. Environmental Protection Agency (USEPA) is of 15 µg/l. If it is consumed above this allowable concentration, various negative effects may occur. Effects like anemia, encephalopathy (brain dysfunction), hepatitis, and nephrotic syndrome (loss of lot of protein as a result of the inflammation of the kidneys)(Lo et al., 1999) (Martins et al., 2006) (Deng et al., 2006)(Vinod K. Gupta and Rastogi, 2008). In their National Priorities List (NPL) the USEPA enumerates the most hazardous waste sites around the territory

of the United States. In 2007, lead was considered a concern in at least 1272 sites, out of 1684 included in the NPL (ATSDR, 2007). EPA has also classified lead as a probable human carcinogen (Choi and Yun, 2004).

2.2.5. **Zinc**

Zinc is one of the most common elements in the Earth's crust. Hence, is widely used in diverse industrial processes. Like in the manufacture of viscose rayon (yarn, fiber, etc.), photographic paper, rubber (accelerator for vulcanization), fertilizers, pigments, and batteries. However, the most substantial contribution comes from the acid mine drainage, the waste of metal processing industries, and the process of coating iron or steel(Martins et al., 2004) (Al-Rub, 2006) (Lu et al., 2007). For example, the drainage of abandoned copper mines in Montana, U.S.A reported concentrations of zinc above the 620 mg/L (Lu et al., 2007).

Normally, the surface water concentrations of zinc are beneath the 0.01 mg/L, and as for the groundwater ones are around the 0.04 mg/L. Similarly to the case of lead, zinc content in tap water tend to be much higher as a result of its dissolution from the pipes (WHO, 2017). Even though most of the zinc in the lakes or rivers precipitate to the bottom. A small quantity stays present in solution with the water and in the form of small suspended solids. This dissolved zinc in water may also increase, as the pH of the water decreases (an increase of acidity).

Zinc is an essential element needed by our bodies in small doses, and exits in almost every food and even in potable water (as salts or inorganic complexes). On the other hand high doses of it can be dangerous (Sheng et al., 2004). Besides the dose ingested through diet, about 150,000 people are exposed to levels higher than the average through occupational sources (ATSDR, 2005).

The current levels of zinc found in drinking water have yet not considered being a concern. And that is why a guideline value has not been established yet. However when zinc is present in water at concentrations above the 3 mg/L, it may become iridescent and a greasy film can be observed after boiling it, making it not acceptable for human consumption (WHO, 2017).

Overconsumption of zinc can cause irritability, muscular stiffness, loss of appetite and nausea (Afroze et al., 2016). It has also been classified as one of the 129 pollutants from wastewaters that represent a major threat by the U.S.EPA (Al-Rub, 2006).

2.3. Current Removal Processes

As for now an extensive variety of water treatment techniques have been developed and many more are in current development. And since many of these treatment technologies can be suitable for the removal of one or many pollutants, when deciding their treatment process, several criteria like technical complexity, cost, and local circumstances should be considered. For instance, membrane technology can effectively remove a wide range of contaminants, however, there are other techniques (cheaper and simpler) that are capable of removing those same chemicals (WHO, 2004).

Table 2.1 summarizes some of the most relevant techniques traditionally used to remove heavy metals from water. It highlights the benefits and downsides of each method.

Table 2.1 Advantages and disadvantages of different techniques used for the removal of metals from water.

Method	Advantages	Disadvantages
Chemical Precipitation	• Fairly easy and rapid process • Inexpensive • Simultaneous removal of several contaminants	• Large amount of waste sludge is produced • Elevated maintenance cost • pH sensitive process (adjustment required)
Coagulation	• Favor the elimination of bacteria as well • Used chemicals are readily available • Good sedimentation	• Generates big volumes of toxic sludge • Requires large amounts of chemicals
Membrane filtration	• Generates low quantities of toxic sludge	• High initial cost

	• Requires low amounts of chemicals • High efficiency • Requires small physical space	• Elevated maintenance cost • Is limited to low flow-rates.
Ion exchange	• Ion specific • High regeneration of the metals	• Elevated maintenance cost • Lack of selectivity • Sludge disposal problems
Adsorption	• Covers a wide variety of contaminants • Relatively fast process • Metal selective	• The efficiency highly depends on the adsorbent. • Generates toxic solid waste

Source: Modify from (O'Connell et al., 2008)

2.3.1. **Precipitation**

Precipitation has long been the primary method of treating wastewaters containing metals. Metals precipitation from contaminated water involves the conversion of soluble heavy metal salts to insoluble salts that will precipitate. The precipitate can then be removed from the treated water by physical methods such as clarification (settling) and/or filtration. Most of metals can be treated by precipitation with the addition of calcium hydroxide (Ghimire et al., 2008).

2.3.2. **Coagulation**

Coagulation is a process used to neutralize pollutants charges (the forces that keep them apart) and destabilize the solution by the addition of a coagulant (typically a metallic salt), resulting in a particles collision that creates a mass large enough to settle or be trapped in a filter.

2.3.3. **Membrane Filtration**

Membranes provide a physical barrier that effectively removes solids, viruses, bacteria

and other unwanted molecules. Different types of membranes are used for softening, organic removal, desalination and bacteria elimination of wastewater.

These membranes permit the passage of materials only up to a certain size, shape or character. There are four pressure-driven and pore size membrane separation processes currently employed for liquid/liquid and liquid/solid separation: ultrafiltration (UF), reverse osmosis (RO), nanofiltration (NF), and microfiltration (MF).

2.3.4. **Ion Exchange**

Ion exchange technology has been used in the chemical and environmental engineering fields for a long time. The ion exchange uses a resin that removes charged inorganic contaminants (like arsenic, chromium, nitrate, radium, uranium and fluoride) by exchanging them for harmless charged ions on its surface. Eventually, the resin becomes "filled up"; because all or most of the "exchange sites" that were loaded with harmless ions become loaded with arsenic or other anions.

2.3.5. **Adsorption**

Absorption is the usage of solids to remove substances from gaseous or liquid solutions. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption operations employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters (Martínez et al., 2006).

2.3.6. **Biosorption**

2.3.6.1. What is Biosorption?

Studies using biological materials to uptake pollutants have been reported since 1900, far before even the biosorption term was coined (Park et al., 2010). It was not until the end of the 70s and the beginning of the 80s that research papers discussing biosorption started to appear (Gadd, 2009). Biosorption could be interpreted as an adsorption process that concentrates the contaminant in a natural, biological adsorbent. However,

from the appearance of the first biosorption studies up to now, there has been a lot of confusion on the application of this concept. Mainly because it was not clear if it also included metabolically active processes. Throughout this time, many research publications have referred to this active process as bioaccumulation. Both terms, biosorption, and bioaccumulation have been used inconsistently as if they are interchangeable when they are not.

Most of the authors have reached an agreement that biosorption is a passive uptake process of pollutants (metal ions or organic compounds) from an aqueous solution through its biding on the surface (cell wall) of non-living biomass (Gadd, 1993)(Dursun, 2006)(Vijayaraghavan and Yun, 2008) (Vinod K. Gupta and Rastogi, 2008) (Lesmana et al., 2009) (Wang and Chen, 2009) (Sameera et al., 2011)(Fomina and Gadd, 2014). Consequently, the capacity of biosorption is given primarily by the affinity between the adsorbent and the adsorbate, as a cellular metabolism-independent process (Davis et al., 2003)(Volesky, 2007)(Pehlivan et al., 2008)(Michalak et al., 2013) (Dadwal and Mishra, 2017). The functional groups present in the structure of the cell wall are believed to have a crucial role in the biosorption process.

Biosorption is a fairly rapid and reversible process (it is possible to recover the adsorbed metal ion) (Dursun, 2006)(Michalak et al., 2013). It is also a relatively simple procedure as it does not need many controlled conditions (normal pressure and temperature conditions are sufficient)(Gabr et al., 2008). Due to these features biosorption is one of the best options when treating large volumes of wastewaters containing multiple complex contaminants in low concentrations (Tsezos, 2001).

Other important advantages are that since the used biomaterial is dead, no nutrients are necessary to keep the biomass (Vinod K. Gupta and Rastogi, 2008). They typically show a high efficiency at a low cost with a minimal generation of chemical sludge (Nirmal Kumar et al., 2009).

The long disagreement in what is categorized as biosorption have led to an extensive amount of publications that includes the word biosorption but that are not truly dealing with it. This makes the analysis of the data, and the screening of accurate information from previous studies a slow tiresome process. Especially since many of the articles and

reviews that can be access used the concepts of biosorption and bioaccumulation interchangeably. A realistic comparison between biosorbents is already complicated considering that the testing conditions among studies tend to be very different, it becomes even more problematic if the bioaccumulation variable is added. Metabolic processes are extremely complex and different from a passive adsorption. When searching for the most effective biosorbent, comparing living organism capacities against dead ones is not only imbalanced, but it also does not reflect a correct information about their capacities.

2.3.6.2. Representative Biosorbents

The selection of the most appropriate biosorbent from the vast existent inventory of potential biomass still is one of the biggest challenges when it comes to biosorption (Kratochvil and Volesky, 1998). Since any type of biological material is capable of removing a metal or several ones (and even other types of contaminants), we could say the options are unlimited (Gadd, 2009). An important aspect to be taken into account in the process of selecting a biosorbent it is its source. Suitable biomass can be easily available in nature in big quantities without any cost or it can also be provided by industry in the form of an unwanted by-product (Vieira and Volesky, 2000). Organisms especially cultivated for biosorption are not recommended as an option. This not only represents rising the acquisition costs but also intensifies the difficulty of keeping a steady supply of the needed biomass for the remediation process (Vijayaraghavan and Balasubramanian, 2015). Also, when choosing a biosorbent it makes little or no sense to go for biomaterials that may possibly never be used on an industrial level, e.g. pathogenic bacteria and fungi, nutritionally-fastidious extremophiles, rare or endangered plants, macroalgae, macrofungi and lichens (Gadd, 2009).

In general biosorbents tend to be group in the following categories: algae, bacteria, fungi and agricultural waste (fruits or plants waste) and natural residues (seafood waste) (Park et al., 2010) (Dadwal and Mishra, 2017). For the purposes of this study, we followed the formerly mentioned classification with the modifications of considering natural residues in the same group as agricultural waste, and by analyzing the algae group subdivided as macroalgae (brown, green and red) and microalgae (green).

Algae possess high metal binding capacities, because of the polysaccharides, proteins or lipid on the surface of their cell walls (Deng et al., 2006). And apart from its compatibility with almost all heavy metal ions, its macroscopic appearance, rigidity and easy availability are the important factors which make seaweeds an ideal candidate for heavy metal removal in both batch and column operations (Senthilkumar et al., 2007).

Macroalgae have played an important role in the research and development of new biosorption materials due to their high uptake capacities, similar to commercial ion-exchange resins and their availability in nearly unlimited amounts from the ocean (Luo et al., 2006). However, it should be noted that algae are not regarded as wastes; in fact, algae are the only source for the production of agar, alginate and carrageenan. Therefore, utmost care should be taken while selecting seaweeds for biosorption process (Vijayaraghavan and Balasubramanian, 2015).

(Romera et al., 2006a) and (Santos et al., 2018) presents detailed reviews about the biosorption by algae.

Bacteria on the other hand, are the most abundant and versatile of microorganisms and constitute a significant fraction of the entire living terrestrial biomass (Wang and Chen, 2009). The evaluation of bacterial metal-sorbing properties has aroused some controversy. Most of the experiments done with metals and bacteria have really concerned metabolically mediated bioaccumulation, while the basic principle of biosorption is the use of dead biomass (Vieira and Volesky, 2000). Inactivated bacteria species such as *Bacillus*, *Pseudomonas, Streptomyces*, *Escherichia*, and *Micrococcus* have been tested for uptake metals or organics (Wang and Chen, 2009).

Cell wall of bacteria is broadly classified into two types: gram positive and gram negative. The names are given to the reaction of the cells to gram staining. The gram positive bacteria have a thick cell wall and is made up of many layers of peptidoglycan and teichoic acids. The gram negative bacteria have thinner cell walls, and is made up of few layers of peptidoglycans and is surrounded by a lipid membrane containing lipopolysacccharides and lipoproteins

(Vijayaraghavan and Yun, 2008) provides an extensive comparison of biosorptive capacities of various types of bacterial biosorbents.

Fungi are ubiquitous in natural environments. They are found in a wide range of morphologies, from unicellular yeasts to polymorphic and filamentous fungi, many of which have complex macroscopic fruiting bodies. Three groups of fungi have major practical importance: the molds, mushrooms and yeast. Their most important roles are as decomposers of organic materials (Wang and Chen, 2009). The most important yeasts are members of the genus *Saccharomyces*, which are not usually a waste, but a commercial commodity used in bakery and brewery (Vieira and Volesky, 2000). *S. cerevisiae* has been extensively studied and it has succesfully removed different metals (Wang and Chen, 2006). For a further insight in to the fungi characteristics and their adsorption capacities towards different metals (Sağ, 2001)(Dhankhar and Hooda, 2011) can be consulted.

Natural materials and certain **wastes from agricultural operations** have potential to be used as low cost adsorbents. Wide variety of agricultural wastes studied as adsorbent for decontaminating industrial/domestic wastewaters from toxic metals, include walnut waste, apple waste, maize cobs, peanut shell, cassava waste, jackfruit peels, fluted pumpkin waste, olive pomace, wheat bran, coconut shell, coir pith, rice husk and bagasse. Some reviews about this type of biosorbent are (Sud et al., 2008)(Johnson et al., 2008)(Abdolali et al., 2014).

2.3.6.3. Biosorption Mechanisms

It is naturally expected that the mechanism explaining the biosorption process to be as complex as the structure of the used biological materials. The cell wall structure of the biosorbents plays a key role in the removal of pollutants considering that biosorption is a surface process. Typically, a cell wall contains a great diversity of functional groups (e.g. carboxyl, phosphate, hydroxyl, amino, thiol, etc.) that can interconnect with the metals in very different ways depending on the parameters of the system (Gadd, 2009). That is why the efficiency of the biosorption process can be so different between the various biosorbents, and also why usually it happens through a combination of different mechanisms. According to the current literature, the mechanisms involved in the biosorption process can include physisorption, chemisorption, ion exchange, and micro-precipitation (Robalds et al., 2016).

- **Physisorption** is a process by which molecules adhere to solid surfaces. This definition implies no mechanical aspects of the nature of binding. The attraction may often be based on electrostatic charges. Negative adsorption is the adsorption of positive species by negative adsorption sites and vice versa for positive adsorption. While the term adsorption implies a surface phenomenon, the actual sequestration may take place based on either physical phenomena (physical adsorption) or through a variety of chemical binding means (chemisorption).
- **Chemisorption** is a kind of adsorption in which the adsorbed substance is held by chemical bonds.

  The metal removal from solution takes place by a complex formation on the cell surface. A complex compound is a polyatomic molecule that consists of one or several central atoms (usually metal cations) surrounded by and attached to ligands (other atoms or groups, usually of negative or neutral charges) (Javanbakht et al., 2014). The number of molecules known to undergo, or are potentially capable of, ligation is extremely large apart from inorganic systems, most organic molecules can either act as ligands directly or else are able to be converted into other molecules that can do so. The key to an atom or molecule acting as a ligand is the presence of at least one lone pair of electrons (Lawrance, 2010). A metal complex is a particular kind of a coordination compound. The most common metal complexes occurring in aqueous solutions are aquated metal ions or aquocomplexes. Metal chelates are metal complexes where there is an organic compound bound to the metal by at least two available sites (Naja and Volesky, 2011).
- **Ion exchange** is the interchange of ions which are formed by molecular or atomic species either losing or gaining electrons(Naja and Volesky, 2011). The term ion exchange does not explicitly identify the mechanism of heavy metal binding to biomass, because the precise mechanism(s) may range from physical binding (i.e. electrostatic or London– van der Waals forces) to chemical binding (i.e. complexation)(Javanbakht et al., 2014).
- **Micro-precipitation** of metals results when the solubility of the sorbate reaches its limit. The term micro-precipitation describes the accumulation of

electrically neutral material (micro-precipitate) which does not involve the release of a stoichiometric amount of previously bound ions. The metal micro-precipitate becomes collected by the solid phase and thus immobilized and separated from the solution itself. The precipitation takes place locally at the surface of the biosorbent. The limited solubility (i.e. an interaction between the solute and solvent) represents the main driving force. In micro-precipitation, the metal cation and an anion itself often a metabolic product of certain biomass types, form insoluble aggregates (salts, complexes) such as sulfides, carbonates, oxides, oxalates and phosphonates (Naja and Volesky, 2011).

The factors that may influence the mechanisms behavior will be discussed in detail in a subsequent section of Chapter 4.

The study of the biosorption mechanisms is relatively new. This only became possible with the developing of more powerful tools that have allowed us to investigate in more detail the characteristics and behavior of the biomass. Technologies like: SEM-EDX, FTIR, ICP, and XPS have been used for this purpose.

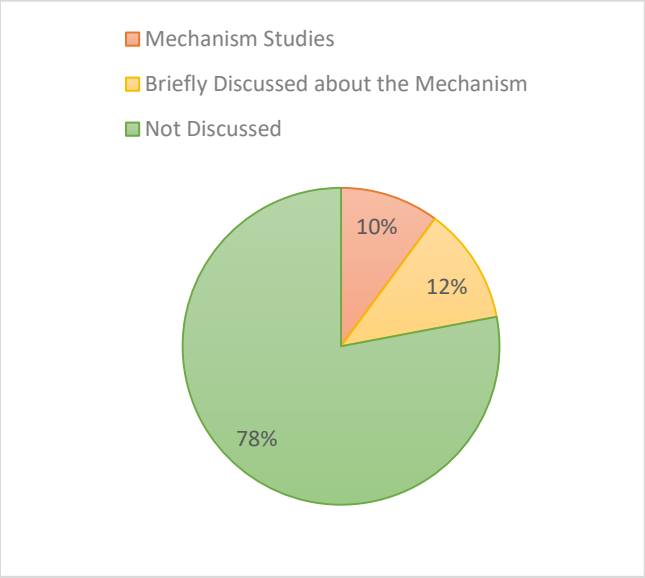

Figure 2.1 Percentage out of 109 publications from 1990 to 2017 with a brief and a detailed discussion about the potential biosorption mechanisms and the ones without this information.

When we look into the trends of the published papers regarding biosorption the amount of research dedicated to unveiling the mechanism it is few when compared to kinetic

and equilibrium studies (**Figure 2.1**).

That it is why the adsorption mechanism of some representative biosorbents has not been completely clarified yet. For biosorption to become an actual applicable technology in the remediation field, first it is imperative to understand how biosorption occurs.

2.3.6.4. Biosorption Limitations

Besides the numerous advantages that biosorption technique may have. Just like other treatment technology, there are still certain conditions affecting its performance and application. Some of the disadvantages of biosorption are:

- The selection of the most appropriate biosorbent (in terms of efficiency and cost) from the infinite possible options stills a main hindrance (Kratochvil and Volesky, 1998) (Gadd, 2009).
- The lack of comprehensive biosorption models (Gadd, 2009) that include more realistic conditions and more complex scenarios (Park et al., 2010).
- The poor mechanical resistance of the biomass (Michalak et al., 2013)

These maybe some of the reasons why despite being a widely studied technique it has not been as extensively applied on an industrial level as it would be expected.

For instance, some pilot plants have been implemented in USA and Canada. With this experience they realized that at a commercial level, a *reliable and steady supply* of waste biomass is crucial. The cost for producing the required biomass for the sole purpose of transforming this biomass into biosorbents was shown to be too expensive. Also logistical problems related with the immobilized *biomass distribution, regeneration and re-use* were detected (Tsezos, 2001).

Problems with the low mechanical strength, the regeneration, and the successive deterioration of the biosorbent may limited its industrial application too (Iqbal and Edyvean, 2004). However some authors have proposed the application of suitable immobilization methods to overcome these issues (Michalak et al., 2013).

Discarding the metal loaded biomass creates another environmental concern. The elution of the adsorbed metal can help solve this issue. This operation would allow both

the recovery of metal solutions at higher concentrations for reducing their reactivity and the recycling of the biosorbent for succeeding uses (Martínez et al., 2006).

2.4. Conclusions

The purpose of this review was to highlight the current state of the heavy metals issue around the world, view the existing trends in the treatment for water and see how biosorption technology has evolved and its future. It is clear that heavy metals have been affecting our ecosystem for a long time now. Heavy metals are extremely hazardous materials that not only represents an immense threat for the human kind but also to all the living beings that are being in contact with them. Due to their high toxicity and extended application in industry arsenic, selenium, cadmium, lead, and zinc are recognized as top priority pollutants.

It is also quite evident that researchers have made great efforts trying to address this ecological issue by developing different technologies such as precipitation, coagulation, membrane filtration, ion exchange, adsorption, and biosorption. Among these, biosorption has emerged as a valuable option to clean water sources without damaging our environment. Algae, bacteria, fungi and agricultural waste are the typically used biomaterials as sorbents of diverse contaminants. The developing and application of the biosorption technique implies a low-cost investment, while it can remove pollutants at a fast rate with a wide application range. Further studies regarding immobilization techniques, the adsorption mechanism, and computational modeling are required to start applying this technology at a larger scale under real conditions.

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Chapter 3

Biosorption Capacities Meta-analysis

Abstract

The biosorption of cadmium, lead, zinc, arsenic and selenium was reviewed. The data of their maximum adsorption capacity using 71 different biosorbents (17 agricultural waste products, 4 bacteria, 7 fungi, 1 green microalgae, 3 blue-green algae, 21 green algae, 10 brown algae, and 8 red algae) was statistically analyzed. In average, maximum adsorption capacity values fluctuated from 1.2 mmol/g for zinc and up to 1.7 mmol/g for arsenic. Brown seaweed exhibited the best overall cadmium, lead and zinc removal from the different type of algae. It was noted that fungi was capable of removing a large variety of metals both cationic and anionic. Significant research indicates that ion exchange tend to be the dominant metal mechanism in biosorption. Further investigation is needed regarding the influence of the surface area and the activity property in the biosorption process.

Keywords:

Biosorption, Biosorption Capacity, Mechanism, Surface Area, Activity Coefficients

3.1. Introduction

The treatment of polluted soil and water with biological methods has been successfully applied in sewage plants and artificial wetlands. For this reason, biosorption has been extensively studied as an alternative technology to remediate water sources. During this time, a large number of biomass types have been investigated, collecting a sufficient amount of quantitative information on the removal of pollutants through biosorption. Despite various bio-materials are able to remove heavy metals, only those with sufficiently biosorption capacity and metal selectivity are suitable for use in a full-scale biosorption process (Wang and Chen, 2009). There seems little justification in examining yet more different biomass for remarkable novel properties since so many representative biomaterials have already shown optimum removal capacities. It is expected that future research should be oriented towards the enhancement of this high-efficiency biomass (Gadd, 2009). However, because the acquisition of the biomaterial is somehow related to their location many times this high-efficiency biomass become difficult and expensive to procure. For example, the brown seaweed kombu (*Laminaria japonica*) that have been proven capable of eliminating cadmium and zinc (Liu et al., 2009) would be a high-cost alternative to apply in a treatment plant at the American continent, since is typically found or harvest in Asia. Selection of a biomass still a critical step

The published work on evaluating the performance of biosorbents offer a good basis for looking for new and potentially feasible metal biosorbents. By making a numeric comparison of their capabilities it may be possible to establish a pattern between the desired structural characteristics of a biomaterial against the metal to be removed.

Many review articles have shown a compilation of detailed information about the characteristics of the diverse biosorbents, their metal binding capacity and how these are applied in the removal of different heavy metals (Bailey et al., 1999) (Babel, 2003)(Demirbas, 2008)(Johnson et al., 2008) (Sud et al., 2008)(Yadanaparthi et al., 2009) (Abdolali et al., 2014)(Kumar Gupta et al., 2015) (Santos et al., 2018). But very few have comparatively evaluated the available data in a quantitative and statistical way. This work presents a comparative analysis of the heavy metal removal efficiency of several biosorbents according to results found in the literature. With this, the affinity between

a specific biomass and a target metal can be roughly identified. It also discusses the importance of the particle size in the biosorption, how the metric units are critical when comparing biosorbents, and how the concept of activity affects biosorption in an aqueous system. It also aims to identify a pattern between the biosorption mechanism of certain biosorbents and a specific metal.

3.2. Methodology

3.2.1. Screening of Articles

The compilation of the data used for this analysis was performed using Google Scholar and Scopus search engines. Papers published from 1990 to 2017 with the keywords *heavy metals*, *biosorption*, *biosorbent*, *cadmium*, *lead*, *zinc*, *arsenic* and *selenium* were investigated. Under these criteria 1,120 results were obtained. From which firstly only research articles written in English were selected (excluding e.g. dissertations, proceedings papers, etc.). Next a quick selection was done based on the articles titles (excluding review papers) and on their respective abstracts (excluding other pollutants and/or metals beside As, Cd, Pb, Se and Zn). The biosorption process can be quantified through the adsorption isotherms. Hence the biosorbents can be compared by their respective q_{max} values which quantifies the maximum metal uptake by the biomass and are calculated from fitting the Langmuir isotherm model to the actual experimental data (if it fits). Finally, only papers that included information regarding exclusively dead untreated biomass, with an q_{max} (maximum adsorption capacity) data that properly fit the Langmuir model were considered (R^2>0.96).

For more detailed information about the parameters used (concentration range, dosage, pH, temperature and equilibrium time) in these studies and their respective references please refer to tables A-1.1 to A-6.2 from the appendix section.

3.2.2. Evaluation of the Biosorption Capacities

The biosorption capacity of the different biosorbents was analyzed using the values of Q_{max} (mmol metal/g biosorbent) and then applying a boxplot analysis to the data. This to measure the spread of the data. The box plot uses the median, the approximate

quartiles, and the lowest and highest data points to convey the level, spread, and symmetry of a distribution of data values. Range can be easily calculated by substracting the maximum value from the lowest one. The interquartile range (IQR) is the difference between the upper (Q3) and lower (Q1) quartiles. An additional advantage of this tool is that values deviating from the rest or values that maybe erroneous can be detected. These atypical values are known as outliers. An outlier is a data point that lies outside the overall pattern in a distribution. In this study outliers were calculated following the formulas: low outliers were below Q1-1.5*IQR and high outliers were above Q3+1.5*IQR.

Afterward, in order to compare the available data for different types of biomass (agricultural waste, bacteria, fungi, brown, red and green macroalgae, green microalgae and blue-green algae), average values of Q_{max} were calculated for each group. And were represented in a bar chart to evaluate the highest efficient type of biomass.

3.3. Discussion

3.3.1. Adsorption Capacity

Firstly, an analysis of the maximum biosorption capacities of algae, bacteria, fungi and natural materials in single metal aqueous system was performed.

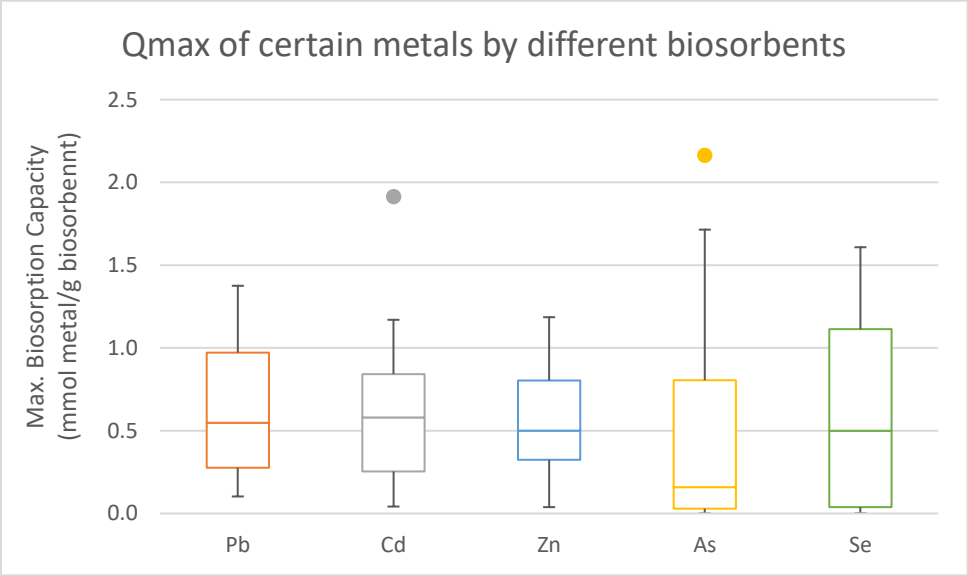


Figure 3.1 Distribution of the maximum biosorption capacity values of different biomass for Pb, Cd, Zn, As and Se. The symbol (●) represents atypical values.

Figure 3.1 describe how similar or varied the set of observed maximum capacities are for a particular metal.

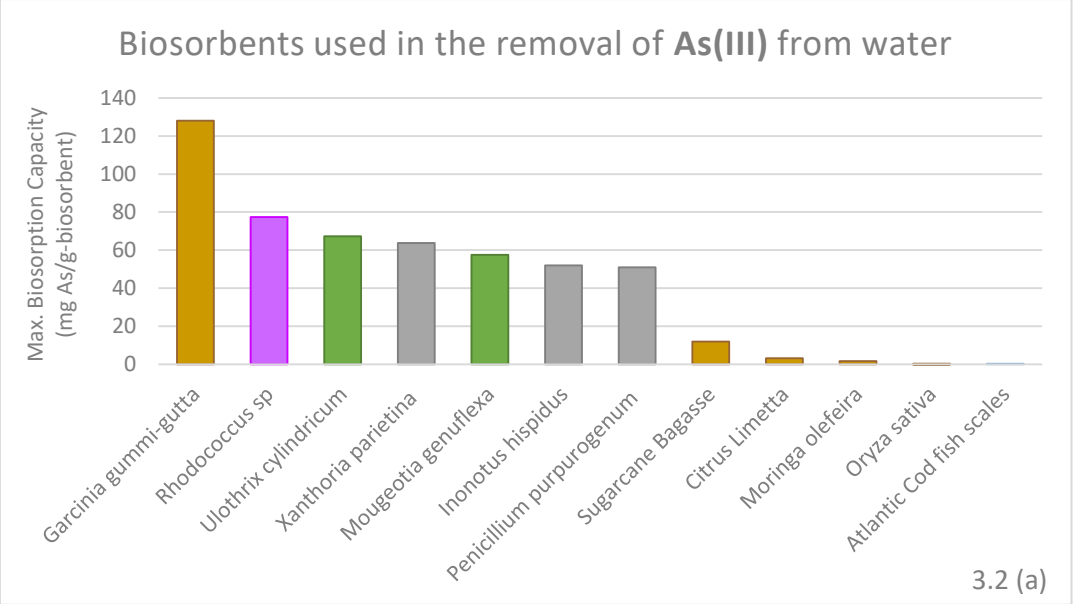
There are a 1.71 and 1.61 mmol metal/g biosorbent spread between the lowest and the highest biosorption capacities of arsenic and selenium respectively. The spread or in other words the range of adsorption capacities it is wider than the one of the cationic metals (Cd, Pb, Zn). For arsenic and selenium at least 75% of the biosorbents reported adsorption capacities higher than 0.03 mmol metal/g biosorbent. While on the other hand, at least 75% of the biosobernts reported maximum adsorption capacities of lead, cadmium and zinc higher than 0.3 mmol metal/g biosorbent. Meaning that inside those 75% even the biosorbent with the lowest adsorption capacity for cationic metals showed a capacity 10 times higher that the biosorbent with the lowest one from the anionic metals. The figure also show that the biosorbents in general responded in almost the same way to all the cationic metals and selenium. The distance from the lower and upper quartiles to the median are very similar which suggests that the described distribution is rather symmetric. However, lead seems to be the metal most consistently removed by biosorbents. Highest and lowest biosorption values of lead are both higher than ones of cadmium and zinc, and the median figure is also higher. Similarly the interquartile range (the box size) is larger for lead.

From the box plot of the arsenic data, we see that the distance from the lower quartile to the median is significantly smaller than the distance from the upper quartile to the median. This suggests that its distribution is skewed to the higher biosorption capacity values.

Odd values were indetified for the seaweed *Ascophyllum nodosum*-Cd and the plant *Rhazya stricta*-As systems.

Figure 3.2 to **Figure 3.8** are a graphical summary of the maximum adsorption capacities of arsenic (III and V), selenium (IV), cadmium, lead, and zinc by different biosorbents calculated using the Langmuir model.

In the case of arsenic (III), researchers have invested most of their efforts in testing untreated biomaterials from agricultural waste. However, according to **Figure 3.2(a)**, their removal capacity is quite low.



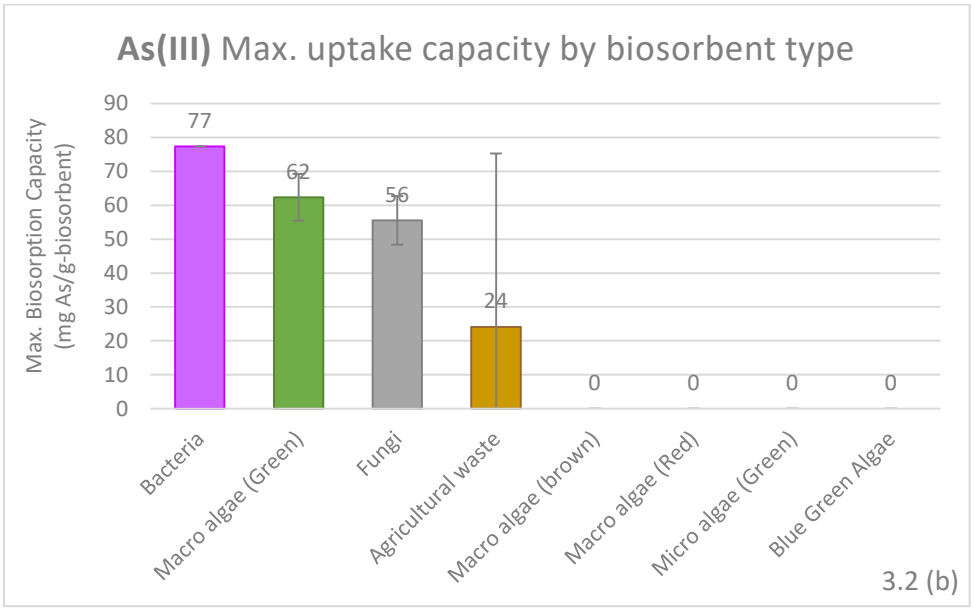
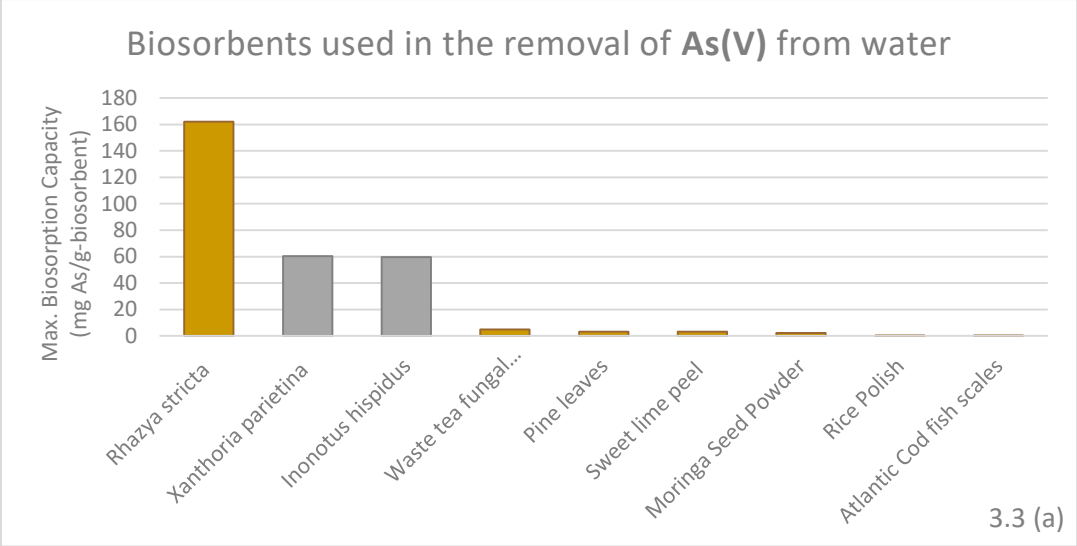


Figure 3.2 Comparison of the maximum adsorption capacities of **arsenic (III)** by **(a)** different biosorbents **(b)** the average of those biosorbents classified according their type.

And even though the tropical Indonesian fruit *Garcinia gummi-gutta* reported a very high adsorption value (Kamala et al., 2005), in average natural materials not necessarily represent the best option for an arsenic biosorbent. It seems that green macroalgae can be more recommendable.

The studies about arsenic (V) are fewer and much less varied. Like for arsenic (III), the most used biomass were agricultural wastes and fungi.



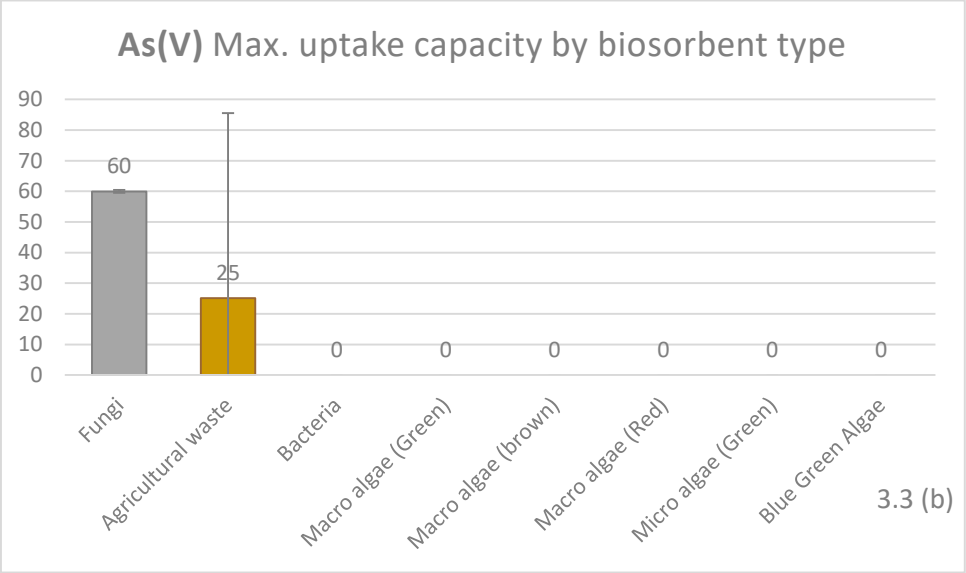


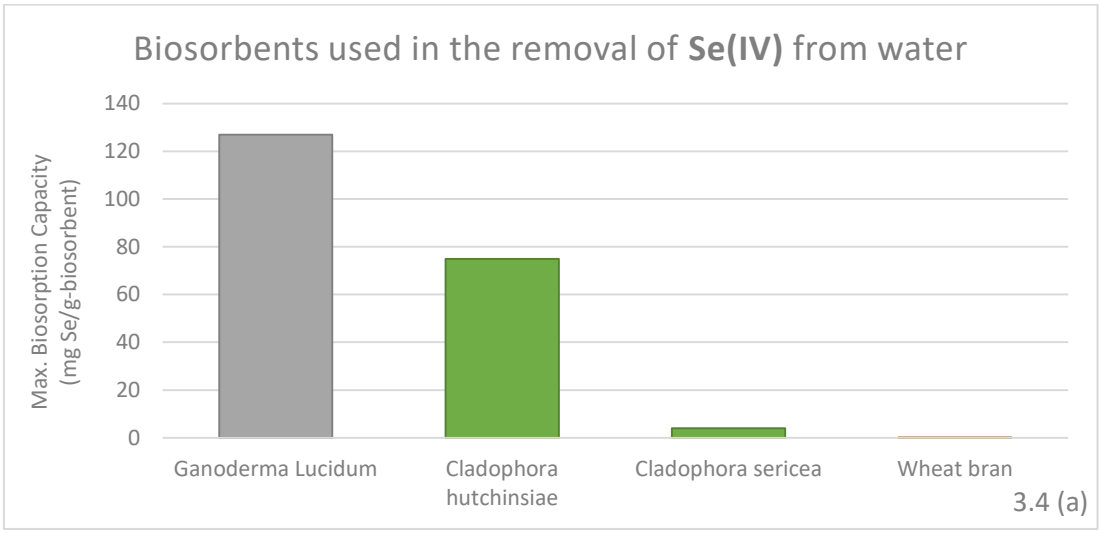
Figure 3.3 Comparison of the maximum adsorption capacities of **arsenic (V)** by **(a)** different biosorbents **(b)** the average of those biosorbents classified according their type.

Being *Rhazya stricta*, a native plant of Afghanistan the biosorbent with the highest removal ratio (Badr and Al-Qahtani, 2013). Then again when compared with the other biosorbents obtained from natural materials it is almost as if it is too high. And yet still the average of the agricultural materials is quite low when measured up with the Fungi.

Xanthoria parietina fungi performed better since Rhazya stricta maximum capacity was far from the general pattern of distribution of biosorbents. By using the average as comparative value it was avoided that greatly deviated value of the Rhazya stricta plant

influenced the comparison of the different type of biomass.

Very scarce information is available on the adsorption of As(III) and As(V) by bacteria and macroalgae.



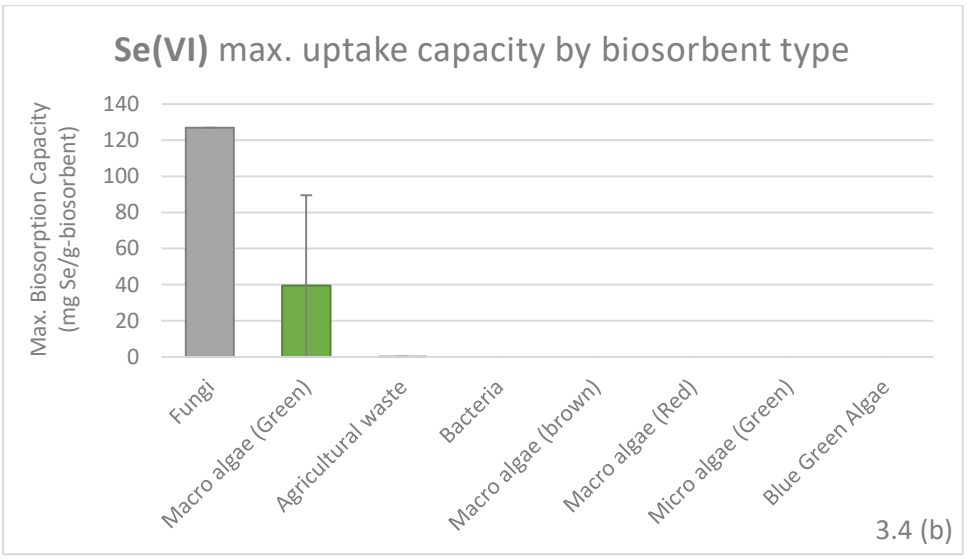
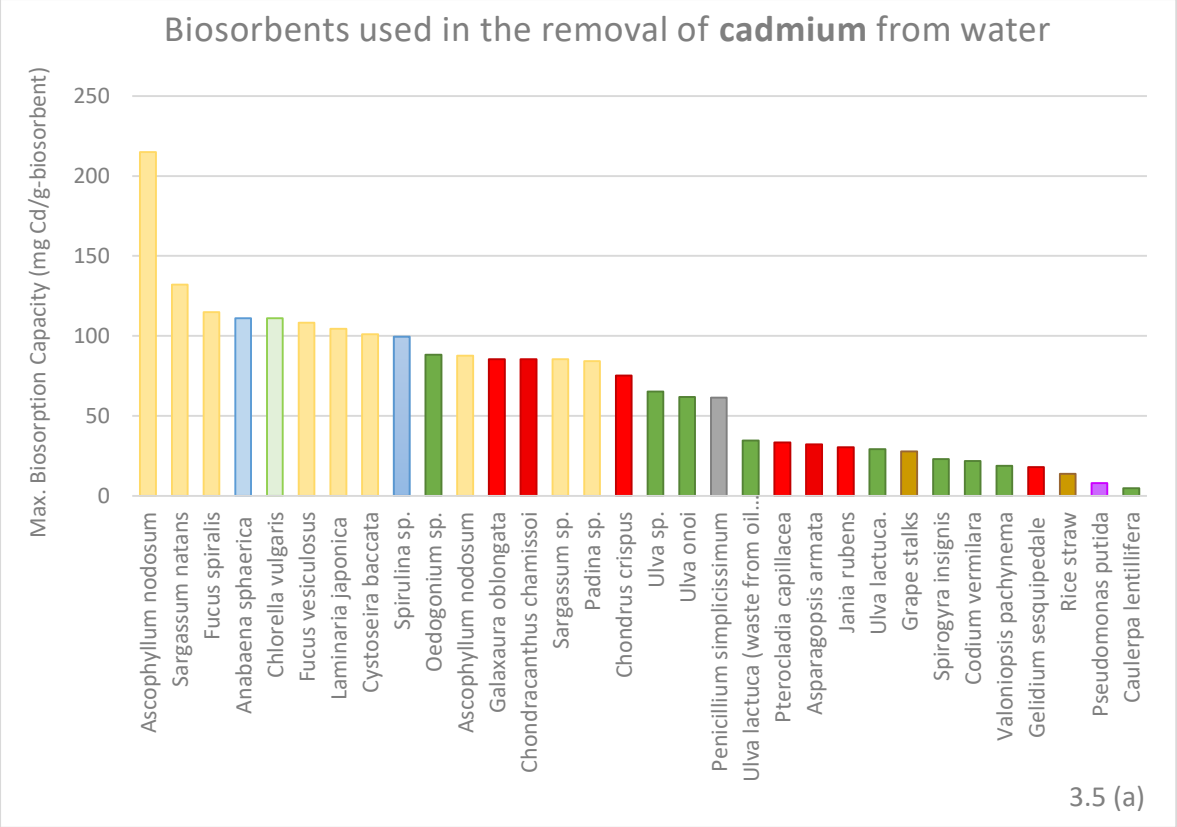


Figure 3.4 Comparison of the maximum adsorption capacities of **selenium (IV)** by **(a)** different biosorbents **(b)** the average of those biosorbents classified according their type.

The majority of the selenium (IV) removal studies with biosorption have been carried out using pretreated biomass (El-Shafey, 2007a)(El-Shafey, 2007b)(Rajamohan and Rajasimman, 2015). In the same way, as for arsenic species, the fungi biomass showed the highest affinity for selenium (IV). Green macroalgae also reported promising results.



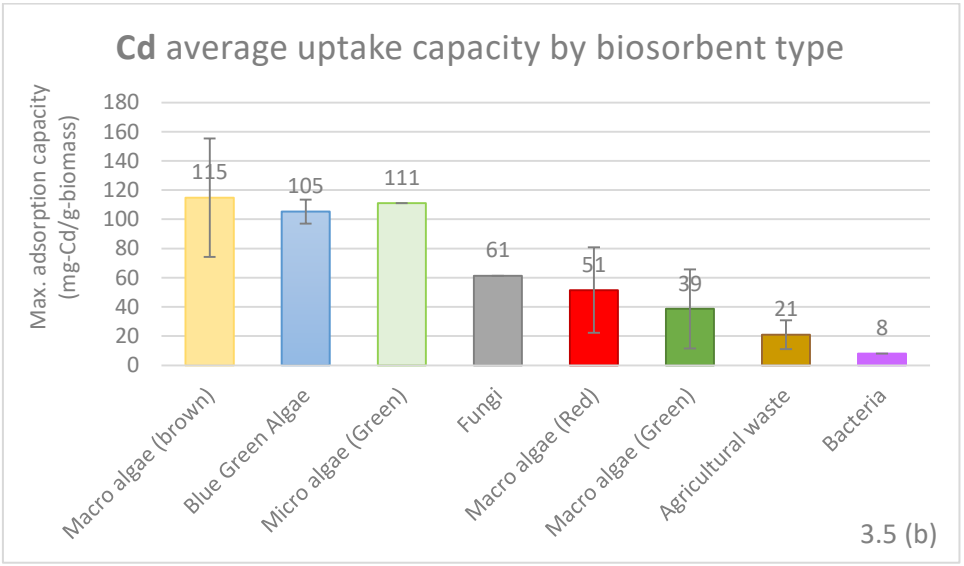


Figure 3.5 Comparison of the maximum adsorption capacities of ***cadmium*** by **(a)** different biosorbents **(b)** the average of those biosorbents classified according their type.

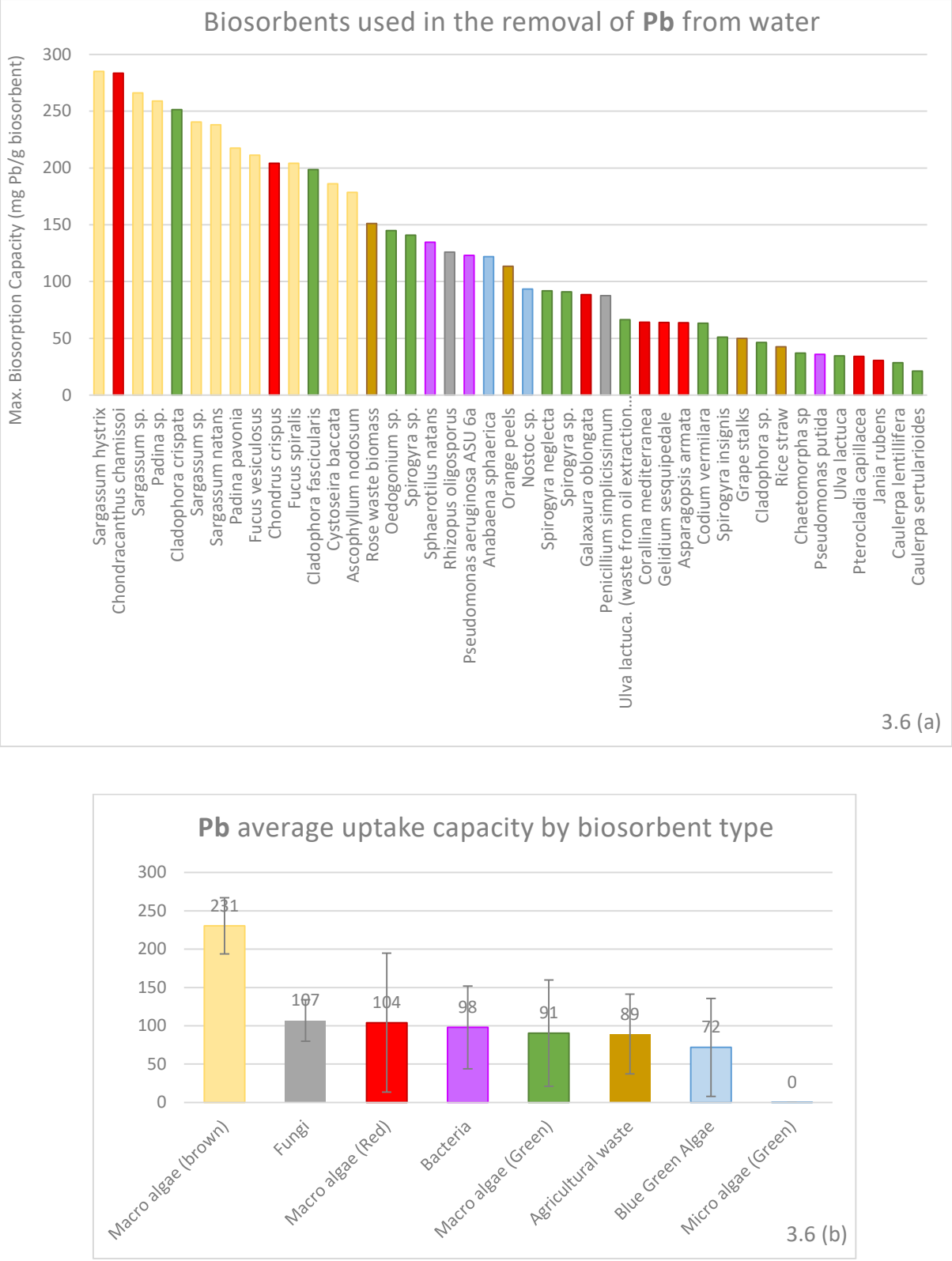
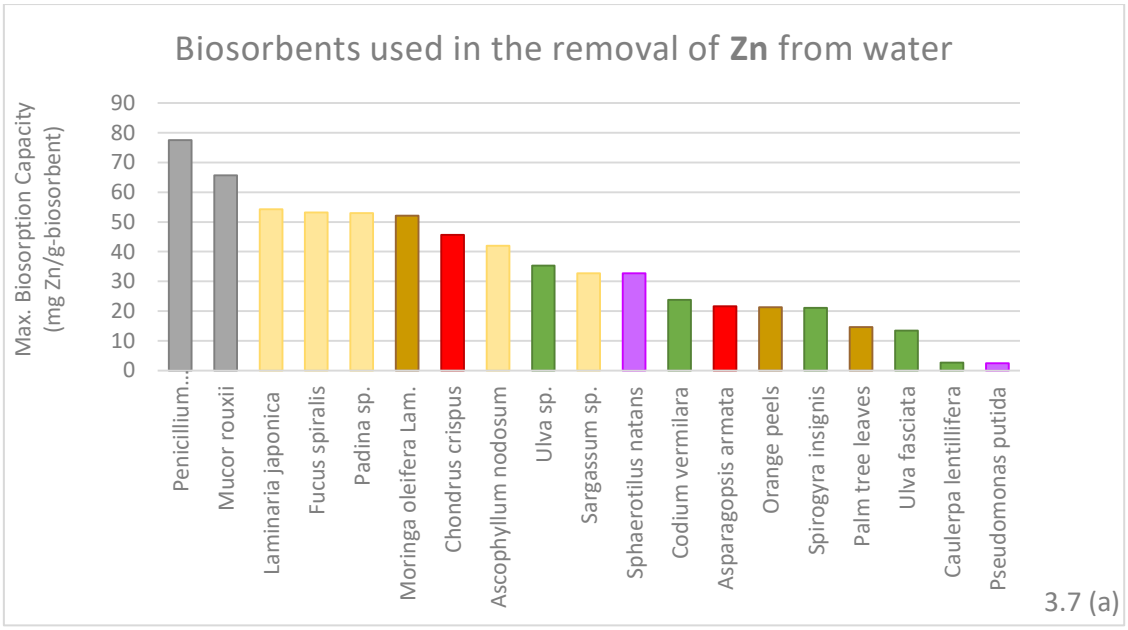


Figure 3.6 Comparison of the maximum adsorption capacities of ***lead*** by **(a)** different biosorbents **(b)** the average of those biosorbents classified according their type.



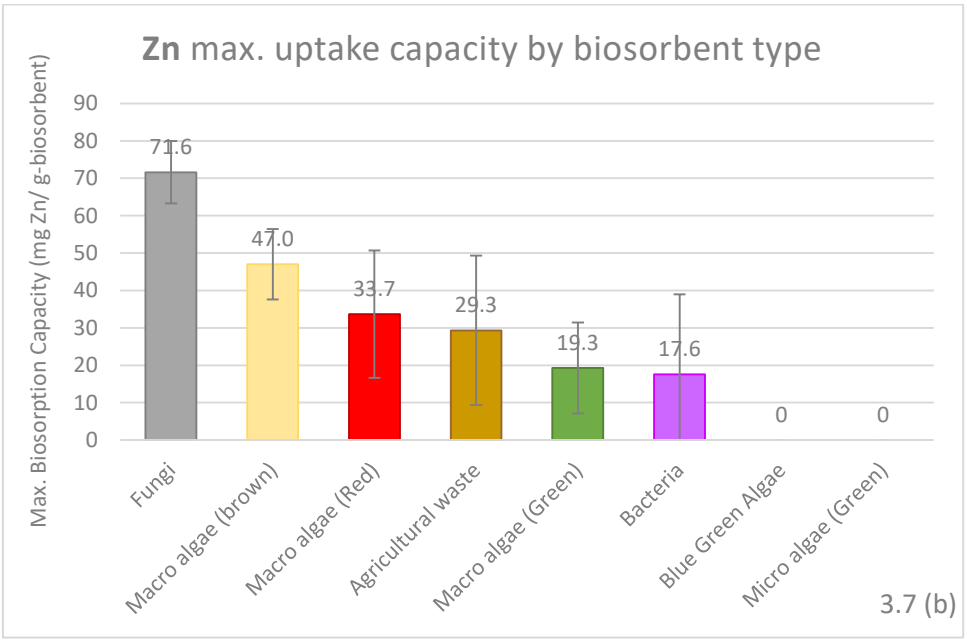


Figure 3.7 Comparison of the maximum adsorption capacities of ***zinc*** by **(a)** different biosorbents **(b)** the average of those biosorbents classified according their type.

For cadmium, lead and zinc the most used biomaterials are brown and green algae. **Figure 3.5 (a)** shows *Ascophyllum nodosum* algae as the superior biosorbent. If we eliminated this deviated data point the biomass with the highest affinity still is a brown algae (Sargassum natans) which is in accordance with the obtained results from **Figure 3.5(b)**. Green microalgae *Chorella vulgaris* and blue-green algae *Anabaena sphaerica* are almost equally efficient.

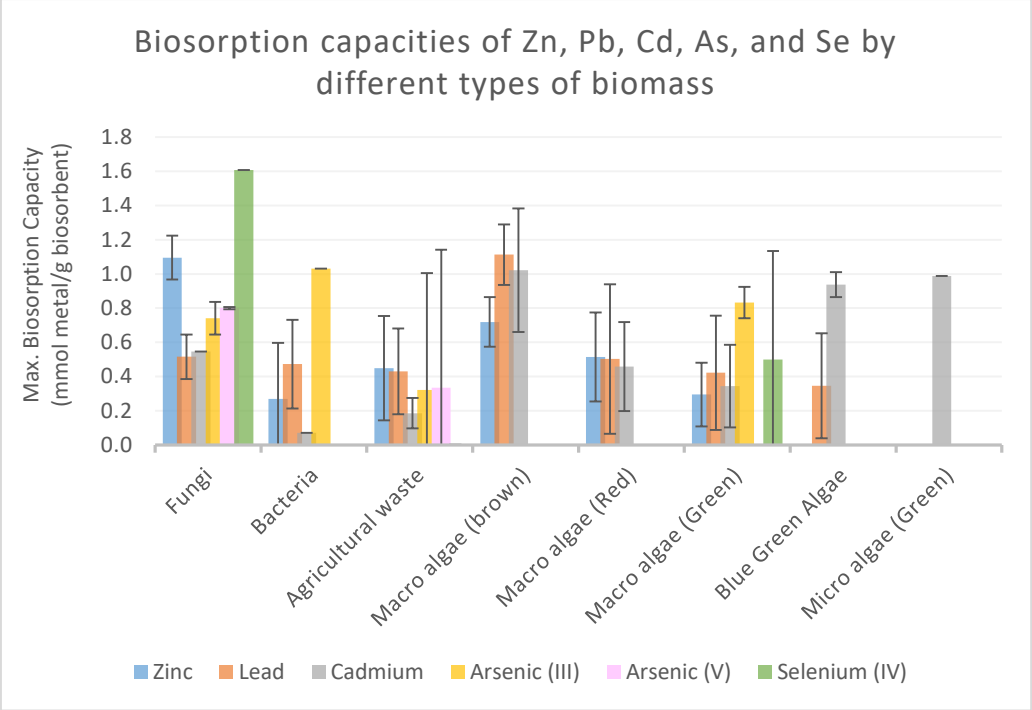


Figure 3.8 Comparison of the average removal performance of Zn, Pb, Cd, As and Se by different biomass

Table 3.1 Summary chart of the affinities between different biomass and different metals according to previous studies.

	Cd	Pb	Zn	As(III)	As(V)	Se(IV)
Fungi	✓	✓	✓	✓	✓	✓
Bacteria	✓	✓	✓	✓	X	X
Agricultural Waste	✓	✓	✓	✓	✓	X
Brown Algae	✓	✓	✓	X	X	X
Red Algae	✓	✓	✓	X	X	X
Green Algae	✓	✓	✓	✓	X	✓
Blue-green Algae	✓	✓	X	X	X	X
Micro Green Algae	✓	X	X	X	X	X

Note: (✓)= the biomass was capable of removing this contaminant. The symbols highlighted in blue indicate which biomass have reported the maximum biosorption capacity of the respective metal.
(X)= the biomass was NOT capable of removing this contaminant.

As for lead, brown algae stand out as a very good biosorbent. Reporting twice the amount of the removal by all the other types of biosorbents **Figure 3.6 (b)**.

From the summaries in **Figure 3.8** and **Table 3.1** it can be concluded that according to the available literature, cadmium can be removed by any type of biomass followed by lead and zinc (from which the biosorption capacity of green microalgae and blue-green algae remains unknown). While on the contrary, the anionic species showed a tendecy to be adsorbed only by certain type of biomass (fungi, agricultural waste and macro green algae).This proves that cationic metals have a higher probability to be removed with biosorption when compared with anionic metals.

It seems like the net charge of the cell surface of most of the biosorbents is negative at neutral pH, and this maybe why cationic metals can be absorbed more efficiently than anionic ones.

On the other hand, fungi seems to be the most adequate biomass to remove a wider range of metals (both cationic and anionic). In average it was not only capable of removing all metals, at the same time showed the highest removal capacity towards zinc, arsenic (VI) and selenium (IV).

Is the lack of data about the removal of arsenic and selenium with macro and microalgae genuinely because researchers have not shown interested in testing them (**Table 3.1**). Or is it because they have tried without success, obtaining data that has not been published?. The latest means that truly the removal of anionic metals requires a very specific type of biomass. However, since the information only appears to be scarce we can barely speculate about this particular.

3.3.2. Adsorption Units

Traditionally, the adsorption capacity has been measured as the relation: weight of contaminant per dry weight of the biomass, expressed by the units: mg/g. However, the application of the units must be done with caution. When comparing the capacity of two or more metals by one same biosorbent, molar terms should be preferred (e.g. µmol/g, nmol/mg, etc) since it also considers relation between the molecules of the metal and the adsorption sites. Only a certain number of molecules can be adsorbed per gram of the biosorbent. This means the amount of metal we can accommodate in the

same amount of biosorbent will depend on its molar mass. The usage of mg-metal/g-biosorbent can mislead over the relative sorption efficiencies for different metals (Gadd, 2009). A metal with a high molar mass may seem to have a better uptake but actually we can collect fewer molecules. Whereas when comparing between biosorbents which removes a certain metal from water more efficiently, the maximum adsorption capacity can be expressed in mg-metal/g-biosorbent. In this case all the data from the different biosorbents it is related to one same molar mass, therefore adsorption values in weight terms will equally differed as the values in molar terms. We are only quantifying the relation of how much metal can be contained in the totality of the biomass.

At the same time, unless the evaluated biosorbents have the same particle size their comparison by mg-metal/g-biosorbent or mmol-metal/g-biosorbent neglects the effect of the surface area in the biosorption. Particle size and surface area are important, because surface area is the means by which a solid interacts with its surroundings. As the particle size decreases, the surface area per unit volume (or mass) increase.

The greater the surface the more amount of metal molecules can be store (Mameri et al., 1999)(R and Abraham, 2001)(Vijayaraghavan et al., 2006). However, the selection of the particle size should be done with the utmost care since that the grinding of the biosorbent to reach small-size particles can induce damages to reactive groups that decrease their availability and activity (Yipmantin et al., 2011).

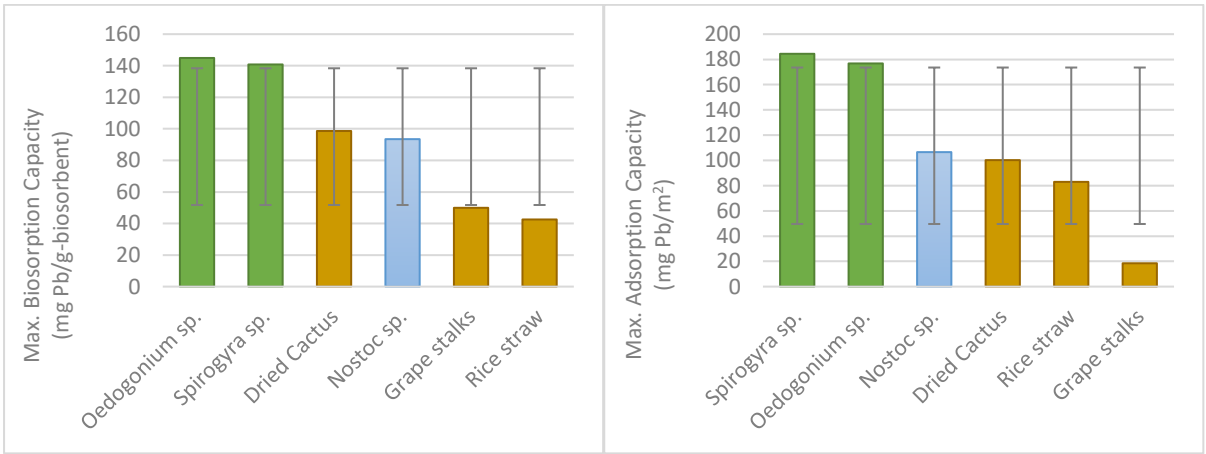


Figure 3.9 Comparison of the maximum adsorption capacities of lead by different biosorbents in (a) mg Pb/g-biosorbent (b) mg Pb/m^2

In cases where we assume the biosorbent is covered with a monolayer of the specific metal ion (fit the Langmuir model) maybe units such as mg-metal/m² or mmol-metal/m² can be more suitable when comparing the removal efficiency of several biosorbents, and hence consider the influence of the particle size and consequently the surface area too. This is illustrated by **Figure 3.9** which presents the case of lead's maximum adsorption capacities of certain biosorbents expressed in traditional units and the change of tendency when expressed in units of mg/m². The information concerning their parameters are shown in **Table 3.2**.

From the figure 3.9 we can see that when consider the surface area in the quantification of the adsorption capacity, the trend of the biosorption efficiency changes. Biomass with more available area it is expected to accommodate more metal in this case Spirogyra sp. However the area is not the only measure that determines the adsorption rate, this can be seen as the rice straw is the biomass with the highest SSA but the one with the highest removal capacity.

Table 3.2 Experimental parameters of selected biosorbent used to remove lead from water

Biomass Name	Biomass Type	pH	qmax (mg/g)	Particle size (mm)	SSA (m²/g)	References
***Oedogonium* sp.**	Green algae	5.0	145.0	0.063-0.105	1.22	1
Spirogyra sp.	Green algae	5.0	140.8	0.063-0.105	1.31	2
Dried Cactus	Agricultural waste	3.5	98.6	<0.1	1.02	3
***Nostoc* sp.**	Blue-green algae	5.0	93.5	0.063-0.105	1.14	1
Grape Stalks	Agricultural waste	5.5	49.9	1-1.5	0.37	4
Rice Straw	Agricultural waste	5.5	42.6	0.075-0.15	1.95	5

1 (Vinod K. Gupta and Rastogi, 2008), 2 (V. K. Gupta and Rastogi, 2008), 3 (Barka et al., 2013), 4 (Martínez et al., 2006), 5 (Amer et al., 2017)

Since the information regarding the specific surface area in the biosorption field is scarce it is hard to conclude whether quantifying the metal per area is a more suitable option than the traditional measure by weight of metal per weight of dried biomass.

Which highlights the need for more studies that discuss the effect of the surface area in the biosorption process.

3.3.3. Mechanism

Biological materials accumulate heavy metals from wastewater through a passive physicochemical uptake. Due to the interaction of several factors on specific biosorbents, it is almost impossible to propose a general mechanism, therefore the actual mechanism of metal biosorption is still not fully understood (Arief et al., 2008). In this section, an overview of the available information of the biosorption mechanisms by selected biosorbents is included.

Table 3.3 Main biosorption mechanisms of several heavy metals from different types of biosorbents

Biosorbent	Type	Target metal	Mechanism	Functional Groups	References
Rhizopus arrhizus	Fungus	U	Complexation, micro precipitation	nd	(Tsezos and Volesky, 1982)
Ganoderma lucidum	Fungus	Cu(II)	Ion exchange	nd	(Muraleedharan and Venkobachar, 1994)
Rhizopus oligosporus	Fungus	Pb(II)	Ion exchange, micro precipitation	nd	(Ariff et al., 1999)
Sargassum vulgaris	Brown macroalgae	Cd(II) Ni(II) Pb(II)	Cd: chelation, Ni: ion Exchange, Pb: ion exchange, chelation, micro precipitation	carboxyl, amino, sulfhydryl, and sulfonate	(Raize et al., 2004)
***Spirulina* sp.**	Blue-green algae	Cr(III),Cd(II),Cu(II)	Ion exchange, physisorption	Carboxyl, phosphate and hydroxyl	(Chojnacka et al., 2005)
Chlorella miniata	Green microalgae	Cr(III)	Complexation	Carboxyl, phosphate and amine	(Han et al., 2006)
Mucor rouxii	Fungus	Pb(II), Cd(II), Ni(II), Zn(II)	Ion exchange	Carboxylate, phosphate and amine	(Yan and Viraraghavan, 2008)
Microcystis	Blue-green algae	Sb(II)	Physisorption, complexation	Carboxyl, hydroxyl and amino	(Sun et al., 2011)

Auricularia polytricha	Fungus	Cd(II), Cu(II), Pb(II)	Ion exchange, complexation	Carboxyl, amine/hydroxyl, amino, phosphoryl	(Huang et al., 2012)
Rice Straw	Agricultural waste	Cd(II)	Ion exchange and complexation	Carboxyl and Hydroxyl	(Ding et al., 2012)
Green Tomato Husk	Agricultural waste	Fe(III), Mn(II)	Ion exchange and complexation	Carboxyl, hydroxyl, amides	(García-Mendieta et al., 2012)
Soybean Meal Waste	Agricultural waste	Cr(III), Cu(II)	Ion exchange, coordination and precipitation	Carboxyl and hydroxyl	(Witek-Krowiak and Harikishore Kumar Reddy, 2013)
Agave Bagasse	Agricultural waste	Cd(II), Pb(II) and Zn(II)	Ion exchange and complexation	Carboxyl, hydroxyl, sulfur and nitrogen	(Velazquez-Jimenez et al., 2013)

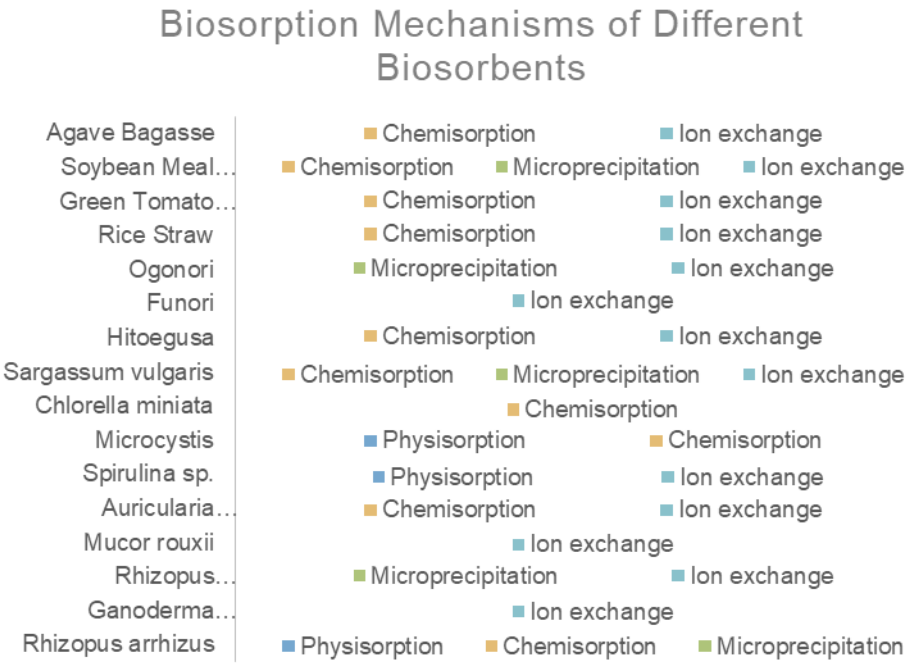


Figure 3.10 Metal biosorption mechanisms ratio of different biosorbents

Table 3.3 describes in detailed the metals removed by the studied fungi, blue-green algae, green microalgae, and brown algae and their characteristic structural groups.

The results from these investigations confirmed the predominant function of carboxyl,

hydroxyl and amino groups in the bonding of heavy metal ions. They also showed how diverse the mechanisms are even between biomass of a same type. Like in the case of blue-green algae, *Spirulina* sp. was able to eliminate cationic metals through an ion exchange process (Chojnacka et al., 2005) and anionic metals were removed by a chemical bonding to the biomass of the cyanobacteria *Microcystis* (Sun et al., 2011).

Regardless of the type of biomass or the metal to be removed, a significant amount of research results indicate that ion exchange tends to be the dominant metal mechanism in biosorption (**Figure 3.10**). The fact that this phenomenon is in most cases reversible offers an attractive possibility of effective wash-release of the deposited metal, and reuse of the biosorbent in several cycles. Despite this, the great influence of the chemisorption process cannot be denied.

3.3.4. Activity

Biomass particles contain different chemically active groups, which are partially ionized in aqueous solution. The resulting interactions of these ionized groups with their surroundings can be rationalized from a wide perspective in the framework of electrochemistry. Biosorption depends on speciation in solution. In addition to temperature and solvent, a factor influencing speciation, through its effect on the equilibrium constant, is the **activity** of species in solution according to equation:

$$K^T = K^* \cdot Q(\gamma) \qquad (1)$$

where the thermodynamic constant, K^T, for each equilibrium, can be expressed as the product of stoichiometric constant, K^*, times the activity coefficient quotient $Q(\gamma)$ (Lodeiro et al., 2007).

An **activity coefficient** is a factor used in thermodynamics to account for deviations from ideal behavior in a mixture of chemical substances. In the case of an aqueous liquid mixture having thermodynamic properties which are ideal, the mole fraction of water is a direct measure of its activity. In other words the standard state (pure water), is the state for which the activity of the component is unity (Blandamer et al., 2005).In other words, activity coefficients can be used to examine the ionic strength effects on the biosorption process.

The influence of this property in the removal of metals have been already studied by (Ucun et al., 2009)(Moghaddam et al., 2013).

3.4. Conclusions

- Cationic metals are easier to be removed with biosorption when compared with anionic metals.
- The biosorption of anionic metals is a more selective process. A reduced amount of biomass show affinity towards these contaminants.
- When selecting a new biosorbent, it is recommended to use fungal biomass, since this has shown high affinity towards both cationic and anionic metal. Nevertheless, a deeper outlook to the available data about fungi is necessary to determine if all the type of fungi is equally effective (filamentous, yeast, etc.).
- Identical uptake values in weight terms may be very different uptake values in molar terms.
- Biosorption studies should include surface area measurements, since this factor directly affects the uptake hence the biosorption efficiency.
- So far, ion exchange seems to be the main removal mechanism of the various biosorbents.
- More non ideal solution models should be study considering the electrochemistry of the system (activity cofficients).

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Chapter 4

Biosorption of Anionic and Cationic Metals

Abstract

Biosorption is a helpful technique in the bioremediation of water sources containing diverse pollutants. The algae biomass has shown a great removal capacity for different heavy metal ions. In this study, three macroalge, hitoegusa (green algae), funori and ogonori (red algae) were examined to remove Cd(II), Pb(II), Zn(II), As(III), As(V) and Se(IV) ions from aqueous solutions. The parameters affecting the biosorption process such as pH, contact time and biomass dosage were studied through batch experiments. None of the algae were capable of removing the anionic metals (As and Se). On the other hand, when it came to the cationic metals: the maximum biosorption capacity of Cd(II), and Zn(II) by hitoegusa was 67.1 mg/g and 61.2 mg/g, by funori 59.3 mg/g and 58.2 mg/g and by Ogonori 30.2 mg/g and 20.3 mg/g. Lead removal by hitoegusa and funori was 67.4 mg/g and 78.0mg/g. Under conditions of 4 g/L of biomass dosage, pH 5 and contact time of 60 min. The biosorption process by all algae for all three metals was rapid (15mins) and its kinetics followed the pseudo-second order model.

Keywords:

Heavy Metals, Biosorption, Hitoegusa, Funori, Ogonori, Kinetics, Equilibrium Studies

4.1. Introduction

Water pollution represents one of the biggest concerns because affects all the living beings. With the increase of the population, the production demands have also increased which leads to a higher generation of wastewaters. Water bodies are damaged by the discharge of industrial wastewaters containing a high amount of heavy metals (Fu and Wang, 2011)(Tchounwou et al., 2012)(Jaishankar et al., 2014). When dissolved in aqueous solutions most of the metals can be found as positively charged cations like the case of Pb, Hg, Cd, Cu, etc (Naja and Volesky, 2011). However, because of their nature, some elements occur in negative ionic species to a lesser degree. Due to their extensive application in the mining, metallurgy, and metal finishing industries, recently, more and more attention is been direct towards these anionic metals such as As, Se, V, Mo, etc (Niu and Volesky, 2003). Because anionic metals usually represent a particular challenge regarding their toxicity and separation (Volesky, 2007), a great percentage of the current research is dedicated to the treatment of cationic metals and the information available in respect of the anionic ones is limited (Pokhrel and Viraraghavan, 2006). **Figure 4.1** shows us the percentage trend of the current investigations regarding on the metal element. We can see that the amount of studies dedicated to anionic metals (approx. only 0.3%) is extremely small when compared with the available information about cationic metals.

The biosorption of anionic metals and metalloids may require a chemical pretreatment of the solution or a physicochemical upgrade of the biosorbents to assure the binding of the targeted anionic metal or at least of neutral molecules (Brierley, 1990). Hence, there is a need of developing and enhancing more methods to remove of anionic metals (without treatments). However, because both species are highly toxic and represent a major health threat worldwide, developing effective removal techniques for both is equally important.

The selection of arsenic, selenium, cadmium, lead and zinc as our metals of interest was done based on their chemotoxicity and importance as a pollutants, which was extensively discussed in **Chapter 2** and is summarized in **Table 4.1**. Just between the five selected metals, there is already a wide range of chemical properties and very

different chemical speciation that is important to understand for obtaining a better comprehension of their removal processes.

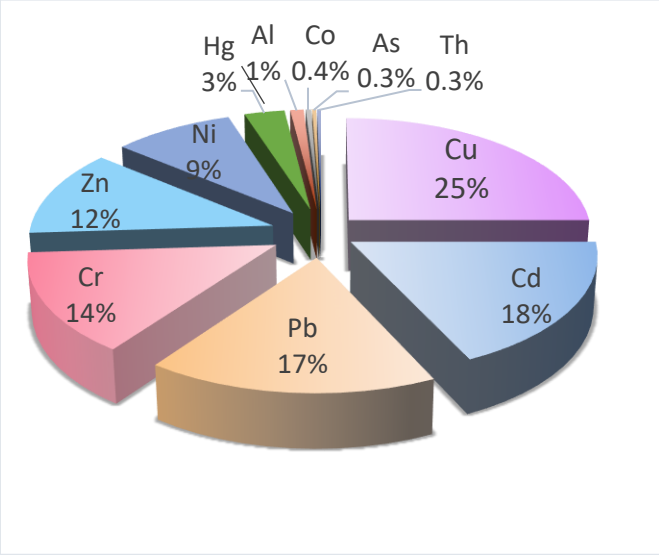


Figure 4.1 Current trends in research about biosorption. Source: Adapted from (Chojnacka, 2009).

Biosorption have been selected as removal method because of its high promising potential. Among the biomaterials typically used as biosorbents, algae have proved to possess high metal binding capacities (Das and Guha, 2007), due to the presence of polysaccharides, proteins or lipid on the surface of their cell walls containing some functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals (Gupta and Rastogi, 2009).

Table 4.1 Sources, detected concentrations in water, minimum permissible levels and toxicological effects of arsenic, selenium, cadmium, lead and zinc.

Metal	Pollution source	Toxicological effects	Detected conc. in water (µg/L)	Standard guidelines (µg/L)	References
As	Mining, smelting, the combustion of fossil fuels and pesticides, herbicides and wood preservatives	Skin lesions. Lung, bladder, kidney, and skin cancer.	Freshwater: <2	WHO:10	(Vaclavikova et al., 2008)(Shankar et al., 2014) (Järup, 2003)
Se	Manufacturing of photocells, rectifiers and xerographic tools,	Gastrointestinal and neurological issues, fatigue,	Industrial discharges: 1-7,000.	WHO 40* provisional further	(Kapoor et al., 1995) (Wasewar et

	and in the glass, as a pigment industry.	deformities, and loss of hair.	Mining waste: 3- 12,000. Freshwater: 0.02	investigation is required	al., 2009) (Hasan et al., 2010)
Cd	Mining and metallurgical processes. Pesticides, phosphate fertilizers and pigments.	Kidney failure, bones issues, respiratory failure, liver damage, anemia, and hypertension.	Fresh and groundwater: <1	WHO:3	(Vilar et al., 2006) (ATSDR, 2012) (Ding et al., 2012)
Pb	Manufacturing of pigments, photographic and printing processes. Silver mining. Recycling of acid lead-batteries.	Anemia, brain dysfunction, hepatitis, and nephrotic syndrome.	Wastewaters: 200-500 (mg/L)	WHO:10 EPA: 15	(Martins et al., 2006) (Ucun et al., 2003) (Deng et al., 2006)
Zn	Manufacturing of viscose rayon, photographic paper, rubber, fertilizers, and pigments.	Irritability, muscular stiffness, loss of appetite and nausea.	Surface water: <10 Groundwater: <40	N.D.	(Lu et al., 2007) (WHO, 2017) (Afroze et al., 2016)

A review of the top three biosorbents with the highest adsorption capacities of arsenic (in its both common states, III and V), selenium (IV), cadmium, lead and zinc, show how different species of algae have the highest affinity towards these metals. From the brown type: *A. nodosum*, S. natans, *F. spiralis*, *S. hystrix, Sargassum* sp., *L. japonica*. From the green type: *C. Hutchinsiae*, *C. sericea*, *U. cylindrica*. And *C. chamissoi* from the red type **Figure 4.2**.

Also, algae are almost ubiquitous throughout the world. They are found in all coastal areas and climatic zones, distributed from tropical to polar zones (Santos et al., 2018). Despite that it have been less used as biosorbent material than other kinds of biomass, especially fungi and bacteria (15.31% in the former case and 84.69% in the second), according to biosorption statistics (Wang and Chen, 2009).

Therefore algae were selected as potential biosorbent based on their surface characteristics. Two algae from the same phylum (Rhodophyta) and even the same subclass (Rhodymeniophycidae) and a third one from a different phylum (Chlorophyta)

were used. This to compare how the difference between species affects their biosorption process.

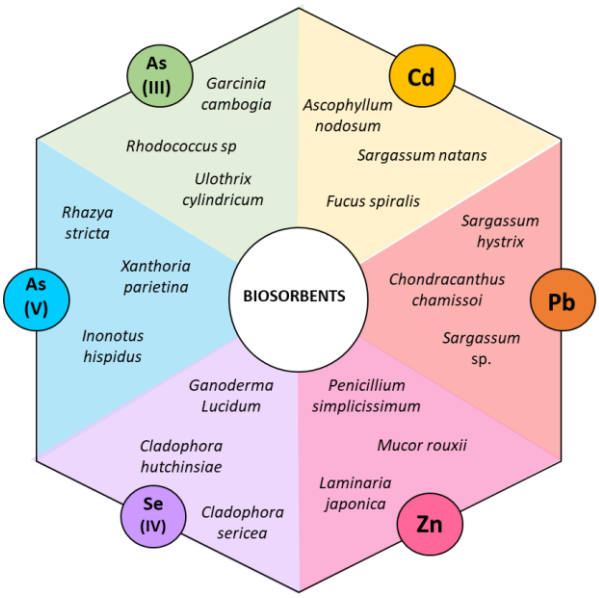


Figure 4.2 Summary of the three biosorbents with the highest adsorption capacities of Cd, Pb, Zn, As (III and V), and Se(IV).[1]

As for green algae *Monostroma niditum* commonly known as **Hitoegusa** was selected. It belongs to the class of Ulvophyceae, therefore it is expected to possess a somewhat similar structure as *Ulothrix cylindrica* and *Cladophora hutchinsiae* both also belong to the formerly mentioned class, which have been proven to be effective in the removal of arsenic (Tuzen et al., 2009) and selenium (Tuzen and Sari, 2010) from water, respectively. **Funori** (*Gloiopeltis furcata*) have a high content of calcium, characteristic which can also favored the adsorption process through the ion exchange process. Red algae also contain cellulose, but their interest in connection with biosorption lies in the presence of sulphated polysaccharides made of galactanes (agar and carragenates)(Romera et al., 2007). Throughout the biosorption data it has been observed that data of algae from the same phylum and even the same class showed different adsorption capacities. **Ogonori** (*Gracilaria* sp.) was chosen because it has been previously studied, reporting a relatively low removal capacity of cadmium, lead and zinc when compared with other algal biomass (Sheng et al., 2004). Thus, ogonori can be used to compare its adsorption

[1] The respective references are shown in the appendix tables A-1.1 to A-6.2.

characteristics and capacity with funori (both from the same subclass) to comprehend what are the critical features that make a biosorbent better than others.

Because the potential to remove metals of the proposed biosorbents (hitoegusa and funori) have not been investigated yet, the next chapter presents a detailed analysis on their biosorption properties and efficiency when in contact with an aqueous solution containing different metals. The same aspects were also studied for ogonori, despite similar information already exists in the literature in an attempt to replicate the results obtained in the original research.

We expect that the comparison of different biosorbents with different removal capacities can provide important information about how their structures (functional groups) greatly influence their efficiency.

4.2. Objectives

a) To determine the metal biosorption (As, Se, Cd, Pb, and Zn) capacities of hitoegusa, funori and ogonori.
b) To investigate the influence of different parameters on the biosorption process.

4.3. Materials and Methods

4.3.1. Chemicals

All used chemicals were analytical grade from Kanto Chemical unless stated otherwise. Arsenic and selenium solutions were prepared by the dilution of 1000 mg/L standards. For the cationic metals low concentrations solutions (up to 2 mg/L) and the ICP solutions were also prepared from 100 mg/L standards. For the isotherm experiments stock metal solutions of different concentrations were prepared by dissolving lead nitrate, cadmium nitrate, and zinc sulfate. Adjustment of pH was done with solutions of concentrations between 0.1 to 3 M of NaOH and HCl.

4.3.2. Equipment

The glassware was properly cleaned before use with a hydrochloric acid solution and then washed several times with tap water and deionized water. Teflon beakers were

soaked overnight in a solution of nitric acid and then wash with tap water and deionized water. All the solutions were prepared with deionized water obtained from a Milli-Q reference purification system. The particle size of the biomass was measured with a laser diffraction instrument Malvern Panalytical Mastersizer 3000. The pH measurements were made using a pH Meter HM-30R. Samples for kinetic and equilibrium experiments were agitated in a TAITEC SR-2DS shaker. In preparation for the filtration process, samples were centrifuged in a tabletop centrifuge Kubota 4000. The residual metal solutions were analyzed by inductively coupled plasma mass spectrometry (8800 Triple Quadrupole ICP-MS, Agilent Technologies).

4.3.3. Biosorbents

4.3.3.1. Genetic Confirmation of the Algae Genus

A genetic DNA test through polymerase chain reaction (PCR) technique was performed at Bioengineering Lab. Co., Ltd., Japan in order to confirm the genus of the used algae.

Funori was successfully identified as *Gloiopeltis furcata* and ogonori as *Gracilaria chorda* with a 100% match. In contrast, hitoegusa reported unclear results, of which only the phylum could be confirmed as Chlorophyta.

Hence, we also observed "hitoegusa" on the microscope **Figure 4.3**. The cross sectional view showed one cell layer, the typical characteristic shape of the *Monostroma* genus.

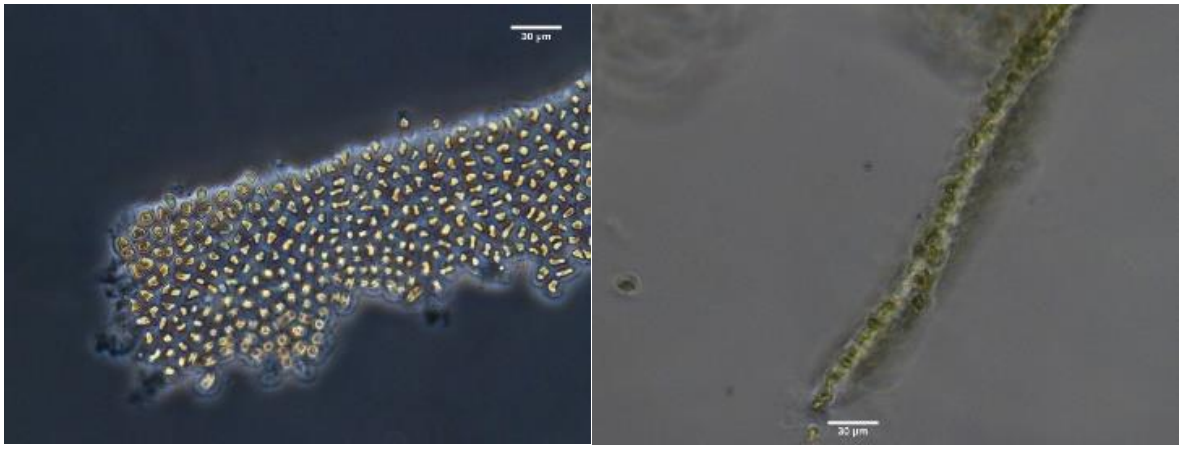


Figure 4.3 Microscopic cross sectional view of "hitoegusa" (a) front (b) edge

Since not only its micro but also its macroscopic shape matches the typical shapes of the alga *Monostroma* sp., we considered it as *Monostroma nitidum* despite the result of the genetic study.

4.3.3.2. Main Features of *Monostroma nitidum* (Hitoegusa)

Monostroma nitidum, depicted in **Figure 4.4** is classified in the **Chlorophyta** phylum, is a green seaweed with thin-layer cells that grows off the coasts of Taiwan, Japan, Korea, and parts of China (the upper part of the intertidal zone) (Chang and Wu, 2008). In Japan it is widely cultivated to use as food resources at Mie and Okinawa (Lee et al., 2010). The mucilage of hitoegusa also possess certain emulsifying and thickening properties (Chang and Wu, 2008).

The cell wall mucilage of seaweeds are known to be rich in sulfated polysaccharides, as for hitoegusa it has been verified that contains a large amount of bioactive-sulfated polysaccharides (Maeda et al., 1991). The sulfated wall constituents of certain green algae are uronic acid-rich polysaccharides also containing rhamnose, xylose, and sometimes galactose (Domozych et al., 2012). Hitoegusa specifically has rhamnan sulfate which is a soluble polyrhamnose saccharide that is composed by rhamnose and sulfated rhamnose. *M. nitidum* is comprise approximately by 50% rhamnan sulfate (Tako, 2017). Rhamnan is a substance similar to fucoidan, a polysaccharide present in brown algae.

Figure 4.4 Hitoegusa growing in Kanagawa prefecture, Japan.
Source: (Suzuki, Date Accessed: 2018-12-03)

4.3.3.3. Main Features of *Gloiopeltis furcata* (Funori)

Gloiopeltis furcata, commonly known as glueweed, jelly moss and **fukuro-funori** (Japan), is a red macro algae that is widely distributed in the North Pacific Ocean, along the shorelines of China, Taiwan, Korea, Japan, and the Pacific shores of Russia; and from the Aleutian Islands south to Baja California. Red seaweeds of the phylum **Rhodophyta** are loosely defined by their color, and subsequent classification has been based on chemical structure and origin. This algae thallus can vary between rusty red to golden yellow color and gets up to 5 cm tall. The thallus grows from a perennial basal crust each spring. This growth has a tufted appearance. It possess smooth rubbery cylindrical branches rarely split (Fretwell et al., 2014)(**Figure 4.5**). After the tide recedes the funori begins to dry out, it first has an almost rubbery consistency, but eventually dries to a brittle hardness. When they are dried the thallus darkens looking almost black (In Klinkenberg, 2017).

For commercial proposes the funori seaweed is cultivated on rocks in Japan and is produced year-round. It is first recorded been used in Japan since the 1600s in papermaking and textile manufacturing and even as a cement for tiles and building materials (Swider and Smith, 2005).

Figure 4.5 (a) Tufted appearance of Funori (b) shape of the cylindrical branches of Funori.
Source: (AlgaeBase, Date Accessed: 2018-12-03)

In recent years, stills widely used in funoran production (a polysaccharide mucilage, similar to carrageenan), silk industry, and extraction of medicinal anticarcinogenic products (Tang et al., 2016).

The basic components of the polysaccharides of the red algal genus *Gloiopeltis* are 3,6-anhydro-a-L-galactose (3.0 e34.4%) and b-D-galactose-6-sulfate, indicating the basic funoran backbone. The sulfur content of the funorans isolated by hot water extraction process is 4.7-7.0%, notable quantity of uronic acids (up to 4.9%) and acetylated residues are present in the cold water extracted funoran preparations (Tuvikene et al., 2015).

4.3.3.4. Main Features of *Gracilaria* sp. (Ogonori)

The genus *Gracilaria*, in the Phylum **Rhodophyta** (also a red seaweed), contains over 100 species found around the world, and many are wild harvested and cultivated for food and the phycocolloid agar. Known as ogo or ogonori in Japan and Hawaii, Gracilaria is a popular ingredient in salads, usually sold fresh or salted. Agar is a gel-forming polysaccharide extracted from the cell walls of *Gracilaria* species, and is especially important in the food and microbiological industries. *Gracilaria* is a warm water seaweed, usually preferring temperatures in the 20-30°C range. It is an ideal candidate for aquaculture due to its warm-water growing season, ease of propagation, relatively high growth rates, high tolerance to a range of environmental conditions, and its existing and potential commercial value.

Figure 4.6 Appearance of wet ogonori. Source: (Suzuki, Date Accesed: 2019-06-08)

Gracilaria has a variable morphology or structure, which differs by species, strain, and growing conditions. It is a bushy, branching seaweed, comprised of rounded branches. Blades are usually red, but can be brownish, green, or almost black.

4.3.3.5. Biosorbents preparation

All biosorbents were commercially acquired. There was no available information about the environmental conditions of the algae growing sites and neither on the industrial process suffered that led to this final product. Hitoegusa and Funori algae were obtained dried, from Mie prefecture and the Sanriku region of northern Japan respectively. Ogonori was obtained dry after collected on the Chilean cost. The biosorbents were pulverized using an osaka pulverizer to a particle size of 0.5mm. They were properly stored in plastic bottles, in a large desiccator cabinet until they were used for the experiments.

The specific surface area of the algae was determined by applying the BET (Brunauer, Emmet, Teller) method using nitrogen gas. In this method the external surface area can be determined from the quantity of gas adsorbed to form a monolayer over the surface of the solid.

4.3.4. Biosorption studies

The biosorption features of Hitoegusa, Funori and Ogonori were investigated as a function of contact time, initial pH, and initial heavy metal concentration through batch wise experiments. **Figure 4.7** shows the general procedure followed for the biosorption experiments. For ogonori only cadmium, lead and zinc studies were performed.

The following measures were implemented to assure the quality of the performed experiments. A blank sample was prepared. This blank contained only distilled water, the same amount of biomass used in regular samples and all the reagents that normally are in contact with a sample during the entire analytical procedure. This blank sample was used to determine the contribution of the reagents and the preparative analytical steps to an error in the measurement. Likewise, initial concentration control solutions (distilled water and metal ion) followed the same analytical protocol as the rest of the samples, this to quantify potential errors regarding contamination of the used material, impurities in acids and reagents or removal of the sorbate by evaporation (during digestion), deposition or precipitation phenomena. Finally, duplicates (sometimes triplicates) of each sample were carried out and the data presented are the average values.

4.3.4.1. Kinetic experiments

The kinetics were obtained from experiments, using 50mL polyethylene centrifuge tubes containing 30mL of heavy metal solutions of an initial concentration of 2mg/L. An amount of 0.3 g of biomass was added to this solution (dosage: 10g/L). The initial pH value was adjusted to the required values (Se and Pb:5, Zn:5.5, As:6, Cd:6.5) with 0.1M HCl or 0.1M NaOH. The samples were stirred at a constant controlled speed of 230 rpm in a horizontal shaker for a specific time, while they were kept at room temperature (25°C). After a certain time (30 mins, 1, 6, 12, and 24 hours), samples were centrifuged at 3000 rpm for 5 min on a centrifuge. Next, aliquots of approximately 7mL (hitoegusa and funori) and 10mL (ogonori) were taken from the supernatant and filtered through a 0.45 µm nylon-membrane syringe filter.

Generally samples containing organic matter required a pretreatment (to eliminate potential interferences) before spectroscopic analysis. Therefore the samples were digested with acid before carrying out the measurement with the ICP. We followed the method 3030E of the 22nd edition of the Standards Methods with the modifications explained below.

The 7mL and 10mL samples were transfer to Teflon beakers. 2.2 mL and 3mL of concentrated nitric acid were added to hitoegusa/ogonori and funori samples respectively.

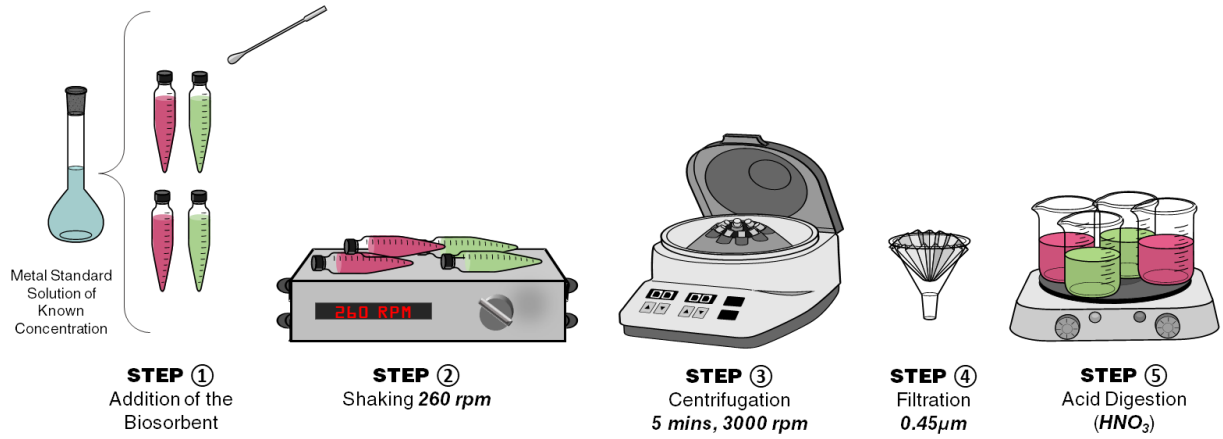


Figure 4.7 Scheme of the batch experiments

After this, samples were heated in a hot plate at a temperature of approximately 90°C. Without letting the samples to get completely dried, they were heated until the digestion was completed. A complete digestion can be determined by the observation on the change of the solution color to a lighted or soft yellowish color. To reach this point, the addition of more acid and Milli Q water can be necessary depending on the sample. The addition of acid and heating process were carried out inside the fume hood. After digestion is complete, the remaining solution is return to a centrifuge tube, the used Teflon beakers were washed with miliQ water recovering this washing solution until the volume is again 7mL and 10mL.

Hereafter, when we talk about acid digestion will refer to the procedure and the respective conditions previously explained. Finally, the content of the metals in the pretreated solution was analyzed with the ICP.

4.3.4.2. pH influence

For the experiments related with the influence of the pH, 0.16 g of biomass was added to 40mL of metal solution (Cd, Zn, and Pb) of an initial concentration of 2mg/L contained in a 50mL polyethylene centrifuge tube. The initial pH value was adjusted with 0.1M HCl or 0.1M NaOH from 3 to 7 (below 2, the high proton concentration minimizes metal sorption, and above 7 metal precipitation is favored). The range of the pH was selected based on the analysis of the chemical speciation of the metals in water, this is discussed in detail in **section 5.2.** of **Chapter 5**. After, the samples were stirred at a constant controlled speed of 230 rpm in a horizontal shaker for 1 hour, while they were kept at room temperature (25 °C). Aliquots of approximately of 10mL were taken and filtered through a 0.45 µm nylon-membrane syringe filter. Samples were digested with 2.2 and 3mL of pure nitric acid for hitoegusa/ogonori and funori respectively.

4.3.4.3. Isotherms experiments

Batch experiments were carried out to determine the isotherms of cadmium and zinc onto 0.16 g of hitoegusa and funori samples added to 30 mL of aqueous solution containing the metals. The concentrations of the solutions varied from 2mg/L to 300mg/L. The best way to calculate q_{max} is to reach saturation by using appropriate amounts of adsorbate (metals), **that's why even if the used concentrations are often**

too high in comparison with environmental ones, we considered those "high" pollutant amounts. On the contrary, if the biomass is not saturated due to low concentration, the calculated q_{max} will be very speculative.

The initial pH for the metal solution was of 5. The polyethylene tubes were shaken at a constant rate of 230 rpm in a shaker, for 1 hour, sufficient time to reach the equilibrium. It was assumed that the applied shaking speed allows all the surface area to come in contact with the ions over the course of the experiments. The study was performed at room temperature of approximately 25 °C. After this, samples were centrifuged, filtrated and digested as explained in the **section 4.3.4.2**.

4.3.4.3.1. Isotherms models

Since sorption processes tend to be exothermic and since the sorption performance may vary with temperature, constant temperature during the sorption process is a basic requirement (Volesky, 2004). When adsorption it is expressed as batch equilibrium isotherm curves, these can be used to compare the pollutant uptake capacities of different types of biosorbents. Adsorption isotherms curves are plots between the uptake (qe) and the final equilibrium concentration of the residual adsorbate remaining in the solution (Ce). These can be modeled by empirical equations which do not reflect the mechanism, but can reflect the experimental curves (Park et al., 2010).

The equilibrium value of sorbate uptake (q_e) is calculated as follows:

$$q_e = \frac{V(C_i - C_f)}{W} \quad (1)$$

V is the volume (L) of the solution contacted with the sorbent; Ci and Cf are initial and equilibrium (final) concentrations of the sorbate (mg/L); W is the amount of biosorbent usually expressed as dry weight.

The Langmuir isotherm was derived originally from studies on gas adsorption to activated carbon. This model contains a number of assumptions which include that (a) all binding sites possess an equal affinity for the adsorbate, (b) adsorption is limited to formation of a monolayer, and (c) the number of adsorbed species does not exceed the total number of surface sites, i.e there is a 1 : 1 stoichiometry between surface adsorption

sites and adsorbate. It is likely that none of these assumptions apply in biological systems. Still, the Langmuir and Freundlich models have been the most commonly used ones, with a high rate of success (Febrianto et al., 2009). The Langmuir isotherm model can be illustrated as Equation (2):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

Where q_m (mg/g) is the maximum adsorption of adsorbate, K_L (L/mg) is the affinity parameter. Ce (mg /L) is the concentration of the absorbate in solution and qe is the corresponding adsorption capacity (mg /g), both at the equilibrium.

The Freundlich isotherm defines adsorption to heterogeneous surfaces. It is the earliest known relationship describing the non-ideal and reversible adsorption, which can be applied to multilayer adsorption. Is an empirical equation. It does not indicate a finite uptake capacity of the sorbent and can thus only be reasonably applied in the low to intermediate concentration ranges (Volesky, 2004). Freundlich model is:

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where Ce (mg /L) is the concentration of the absorbate in solution and qe is the corresponding adsorption capacity (mg /g), both at the equilibrium. K_F and n are the constants, which measure the affinity and intensity; respectively.

Data is usually fitted to the logarithmic form of Equation (3):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

4.4. Results and Discussion

Neither funori nor hitoegusa were capable of removing the anionic metals in any degree. So far, in the literature, there is no information about any untreated red algae that have successfully removed arsenic or selenium.

However, several green macro algae have been proven capable of As and Se removal (Tuzen and Sari, 2010)(Filote et al., 2017)(Tuzen et al., 2009) and (Sari et al., 2011).

Unfortunately, there is insufficient information about their cell wall structure, or how they adsorbed the As and Se. With the available data it is difficult to conclude what are the relevant characteristics of *Cladophora hutchinsiae*, *Cladophora sericea*, *Ulothrix cylindricum* and *Mougetia genuflexa* that differ from hitoegusa that made these algae suitable biosorbents for As and Se. **Table 4.2** shows a summary of some of the characteristics proposed by the authors of the studies.

Table 4.2 Reported biosorbents capable of removing As or Se from water

Algae	Target metal	Max. Adsorption Capacity	Characteristics	References
Cladophora hutchinsiae	Se	74.9	From D–R model, the calculated biosorption energy indicated chemical ion-exchange.	(Tuzen and Sari, 2010)
Cladophora sericea	Se	4.0	Showed a positive surface charge in almost the entire pH range, the surface properties are electrostatically more favorable to the uptake of anionic species from solution.	(Filote et al., 2017)
Ulothrix cylindricum	As	67.2	From D–R model: chemical ion-exchange. The results indicated an ion-exchange between the metal ions and the H atoms of COOH, OH, and amide groups.	(Tuzen et al., 2009)
Mougetia genuflexa	As	57.48	From D–R model: chemical ion-exchange. The results indicated an ion-exchange between the metal ions and the H atoms of COOH,OH, and amide groups.	(Sari et al., 2011)

That is why the following results presented from now on, only contain data regarding cationic metals (Cd, Zn and Pb).

4.4.1. Effect of contact time

Figures 4.7 to 4.10 shows the result obtained from the kinetic experiments of Cd, Pb, and Zn conducted to determine the equilibrium time required for their uptake by the various biomass.

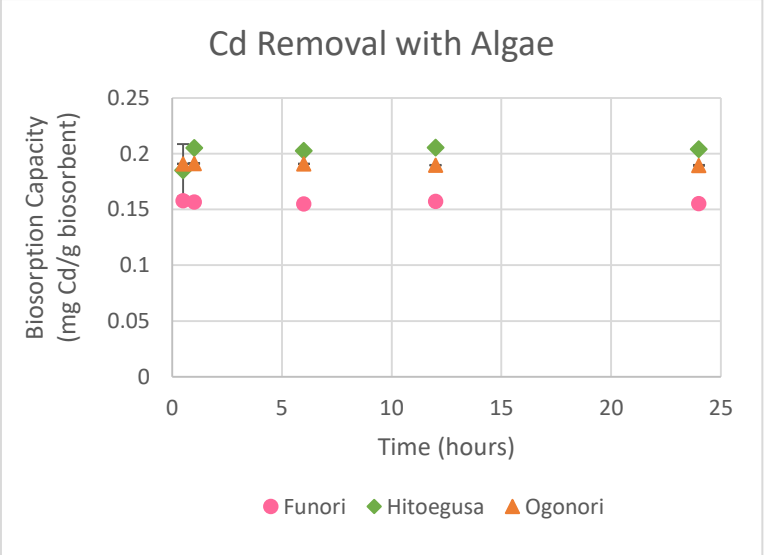


Figure 4.8 Effect of contact time on Cd biosorption capacity.
Co: 2mg/L, Initial pH: 6.5, Temp: 25°C, Dosage: 10g/L

The algae removed all the metals efficiently within the half hour. After this fast step, no significant enhancement of removal efficiency was noted even past 24 hours. Consequently it was demonstrated that the biosorption equilibrium of all three algae was reached rapidly at approximately 15 min and in subsequent equilibrium experiments, 1 h was estimated more than sufficient to establish equilibrium.

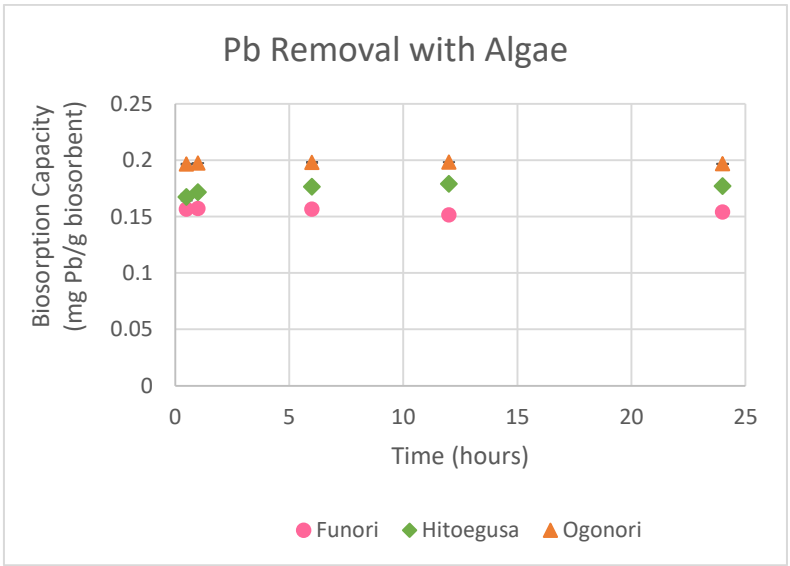


Figure 4.9 Effect of contact time on Pb biosorption capacity.
Co: 2mg/L, Initial pH: 5, Temp: 25°C, Dosage: 10g/L

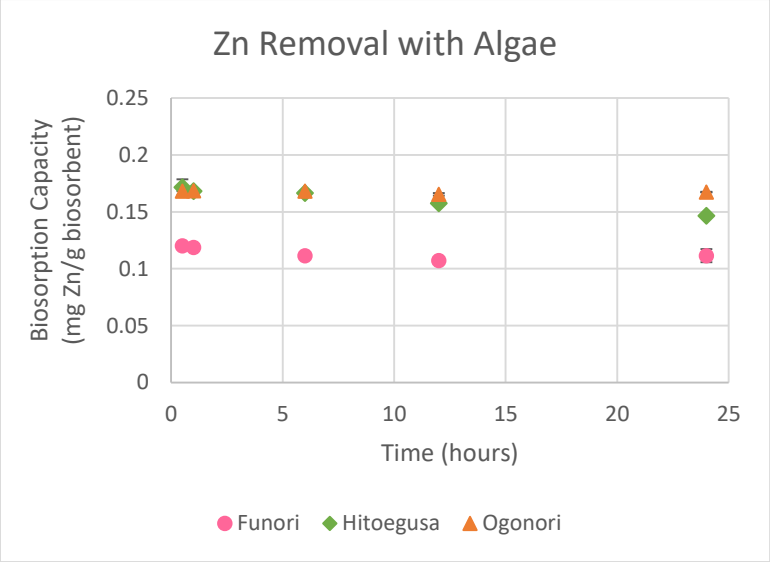


Figure 4.10 Effect of contact time on Zn biosorption capacity.
Co: 2mg/L, Initial pH: 5.5, Temp: 25°C, Dosage: 10g/L

In general, about 90% of the total metal ion sorption was achieved within 30 min for hitoegusa and ogonori. And for funori an 86% of cadmium and lead was removed and about 62% of zinc in the same time interval.

The results are in accordance of the typical two-stage kinetic behavior of biosorption systems: a very rapid initial sorption over a few minutes, followed by a long period of much slower uptake. At the beginning of the sorption process, the rapid uptake of metals may be due to the availability of unoccupied active sites on the surface; however, with time the active sites started to get saturated by the heavy metal ions; therefore, the sorption rate became slower (Amer et al., 2017) (Wang et al., 2018).

On the other hand it can be potentially related to the fact that rapid mass transfer on the outer surface of the adsorbent has taken place first, subsequently a slower internal diffusion process started to occur.

The very fast biosorption of the algal biomass make this material suitable for continuous flow water treatment systems (Bulgariu and Bulgariu, 2012).

From these preliminary results, we can see that funori is the biomass with the lowest biosorption capacity when compared with the other algae. The algae showed a greater affinity towards cadmium and lead, followed by zinc.

The contact time data was fitted using Lagergren pseudo first order model and the pseudo second order model (Javed et al., 2007). The linearized form of first order Lagergren equation is given as Eq. (5):

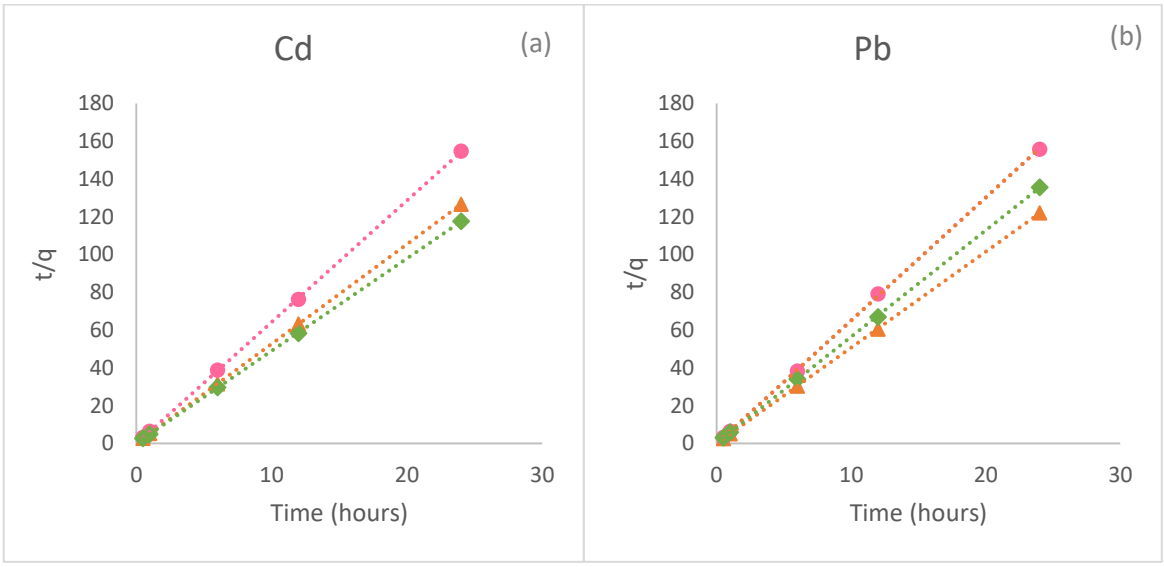
$$\log(q_e - q) = \log q_e - \frac{K_{1,ads}t}{2.303} \quad (5)$$

The pseudo second order equation Eq. (6) is (**Figure 4.11**):

$$\frac{t}{q} = \frac{1}{k_{2,ads}q_e^2} + \frac{t}{q_t} \quad (6)$$

where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t the mass of metal at time t (min.), $k_{1,ads}$ the first order reaction rate of adsorption (per min.), $k_{2,ads}$ the pseudo second order rate constant of adsorption g/(mg*min).

Since the data did not fit at all the pseudo first order model, only results concerning the pseudo second model are shown. The calculated parameters related to the pseudo second order kinetic model are tabulated in **Table 4.3.**.



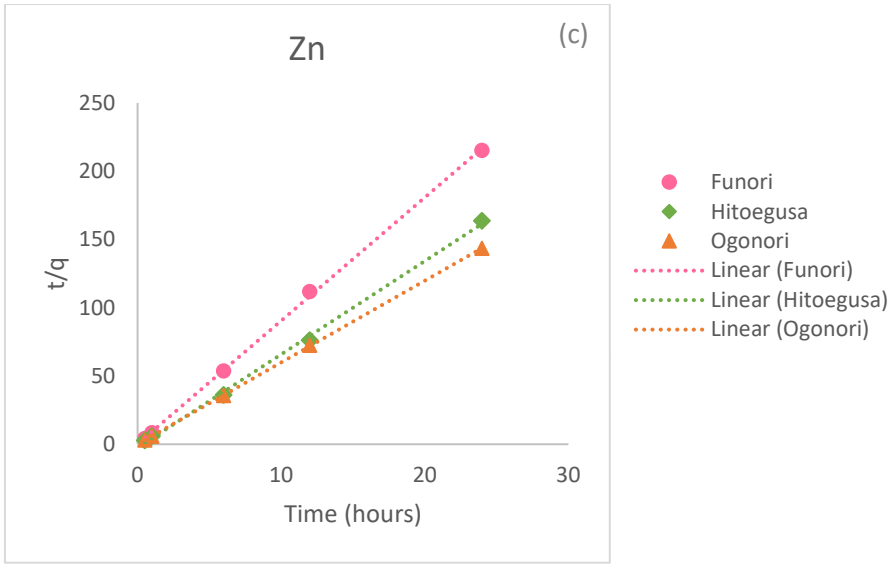


Figure 4.11 Estimated qe, adsorption rate constants and coefficients of correlation associated to the Lagergren pseudo-second order kinetic model of (a) Cd(II) (b) Pb(II) and (c) Zn(II)

Table 4.3 The pseudo-second order kinetic models constants of Cd(II), Pb(II) and Zn(II) on hitoegusa and funori

	Biosorbent	**$q_{e,exp}$ (mg/g)**	**q_e (mg/g)**	**$k_{2,ads}x10^3$ g/(mg*min)**	**R^2**
Cd(II)	Hitoegusa	0.206	0.204	310.7	1.000
	Funori	0.158	0.155	237.4	0.999
	Ogonori	0191	0.189	309.8	1.000
Pb(II)	Hitoegusa	0.179	0.177	570.6	0.999
	Funori	0.157	0.154	519.0	0.999
	Ogonori	0.198	0.197	224.6	1.000
Zn(II)	Hitoegusa	0.172	0.146	18.64	0.998
	Funori	0.120	0.111	414.9	0.999
	Ogonori	0.169	0.167	953.4	1.000

The obtained kinetic data suggest that the sorption of cadmium, lead and zinc ions followed the second kinetic model which relies on the assumption that biosorption may be the rate limiting step. The model predicted values of biosorption capacity at

equilibrium very close to the equilibrium capacities obtained experimentally.

The basic data of chemical kinetics are then the concentrations of the reactants and products at different times after the reaction has been initiated. Reaction rates depend on the concentration of reactants, and of products, which it is directly related to the reaction mechanism. Kinetics can provide important insights regarding the chemical mechanism and tries to describe in detail what takes place at each stage of an overall chemical reaction. Hence, kinetic models are not enough to describe the complex adsorption process.

The early works of pseudo-second-order model used the sorption of metallic ions with adsorbents that could form complexes with the metallic ions. In this case, the sorption process should be the formation of covalent bond between the adsorbate and the adsorbent. However, this specific case of a pseudo-second-order kinetic model being followed does not imply that the every sorption process is a chemisorption (Lima et al., 2015). That is why it is very common in the adsorption literature that the authors attribute that a mechanism of adsorption is chemisorption based only on the fitting parameters of kinetic data.

To establish if an adsorption process is chemical or physical, it is necessary to prove the formation of some chemical bonds using some analytical techniques (FTIR, Raman spectroscopy, TGA, and so on) and/or combined with thermo dynamical data of changes in enthalpy (ΔH) and changes in entropy (ΔS)(Tran et al., 2017).

4.4.2. Effect of the pH

The removal of the different metal under different pH conditions was investigated.

The dependence of metal uptake on pH is related to both the surface functional groups on the cell walls of the biomass and the metal chemistry in solution. The influence of the pH value was very similar for the three algae employed.

The biosorption of cadmium did not show great changes despite the adjustment of different pH (**Figure 4.12**). Extremely slight changes were also observed in the biosorption for lead and zinc (**Figure 4.13** and **Figure 4.14**). Apparently, extreme acidic conditions seem to have a slight influence in the removal of the metal ions for any of

the used biomass. The coefficients of variation (CV) between the metal biosorption capacities obtained at each pH of all the biomass were calculated to evaluate the magnitude of the changes among the data. In the case of cadmium CV values oscillated between 0.23 to 0.37%, for lead between 0.48 and 0.61% and finally for zinc in the range of 0.84 to 4.25%. These variations are so small they can be considered insignificant. Hence, we can say for all algae, a change in the pH did not influence the biosorption process of the three cationic metals.

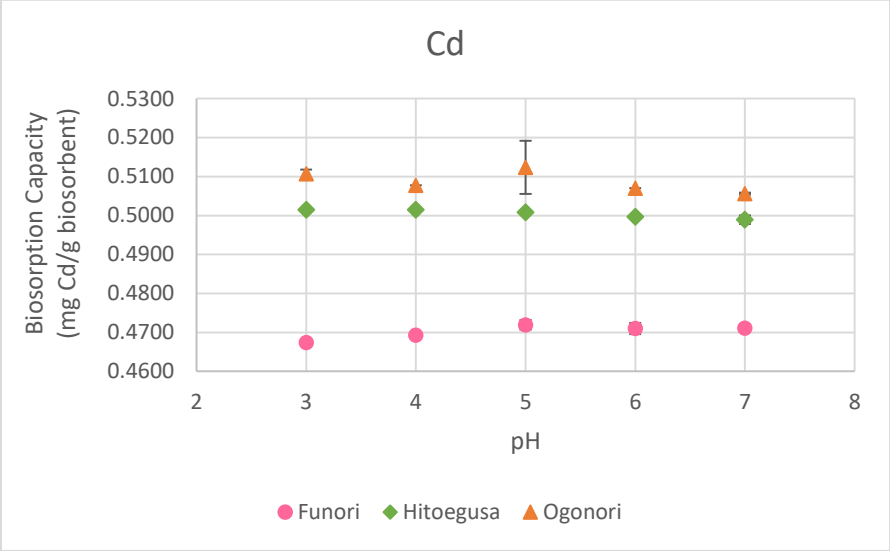


Figure 4.12 Effect of pH on Cd biosorption capacity.
Co: 2mg/L, Contact time: 1h, Temp: 25°C, Dosage: 4g/L

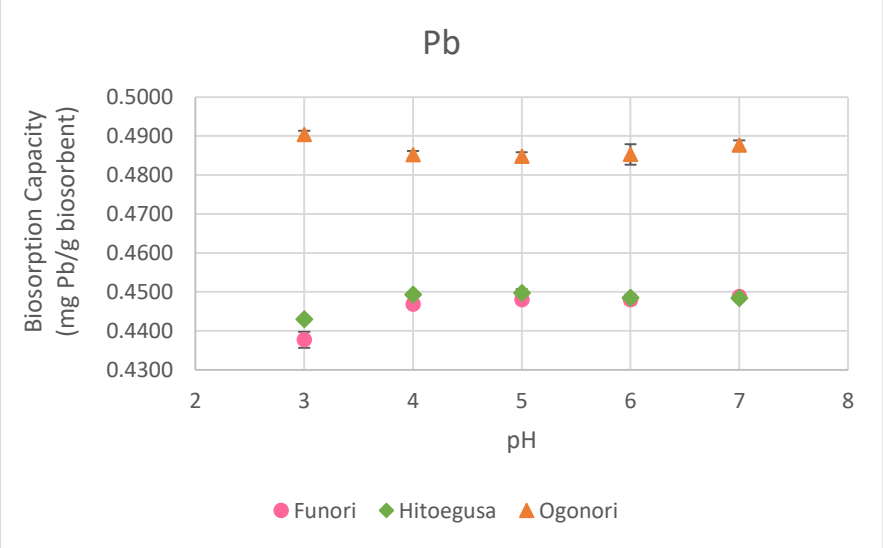


Figure 4.13 Effect of pH on Pb biosorption capacity.
Co: 2mg/L, Contact time: 1h, Temp: 25°C, Dosage: 4g/L

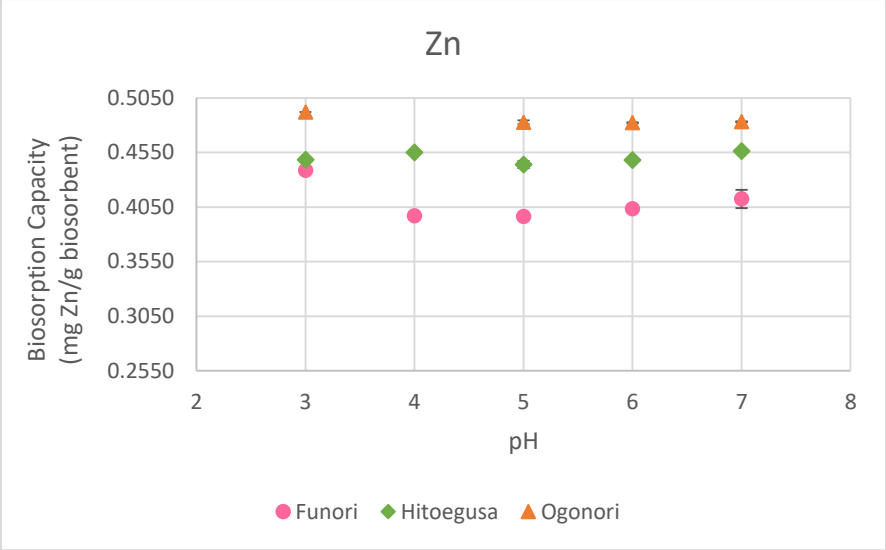


Figure 4.14 Effect of pH on Zn biosorption capacity.
Co: 2mg/L, Contact time: 1h, Temp: 25°C, Dosage: 4g/L

Ideally, solution pH should be kept constant during biosorption. Which means it has to be continuously monitored during the whole process and could also imply the addition of acid and/or alkali to assure its stability. From a practical view, in a large scale application this is not only laborious but also means higher costs. Thus, the pH experiments were carried out by adjustment of an initial pH just before the addition of the biosorbent. The final pH of the solution after it was exposed to the biomass was also recorded.

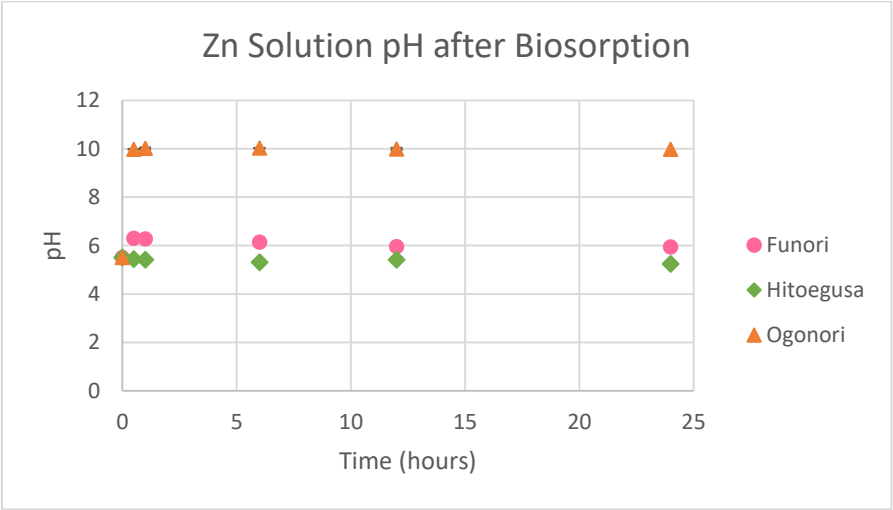


Figure 4.15 Final pH of Zn solution after biosorption with funori, hitoegusa and ogonori.
Co: 2mg/L, Initial pH: 5.5, Temp: 25°C, Dosage: 10g/L

Figure 4.15 shows the evolution of the pH as a function of time using funori, hitoegusa and ogonori in the removal of zinc. The variance of the data was illustrated with error bars, it is so small that is covered by the markers points.

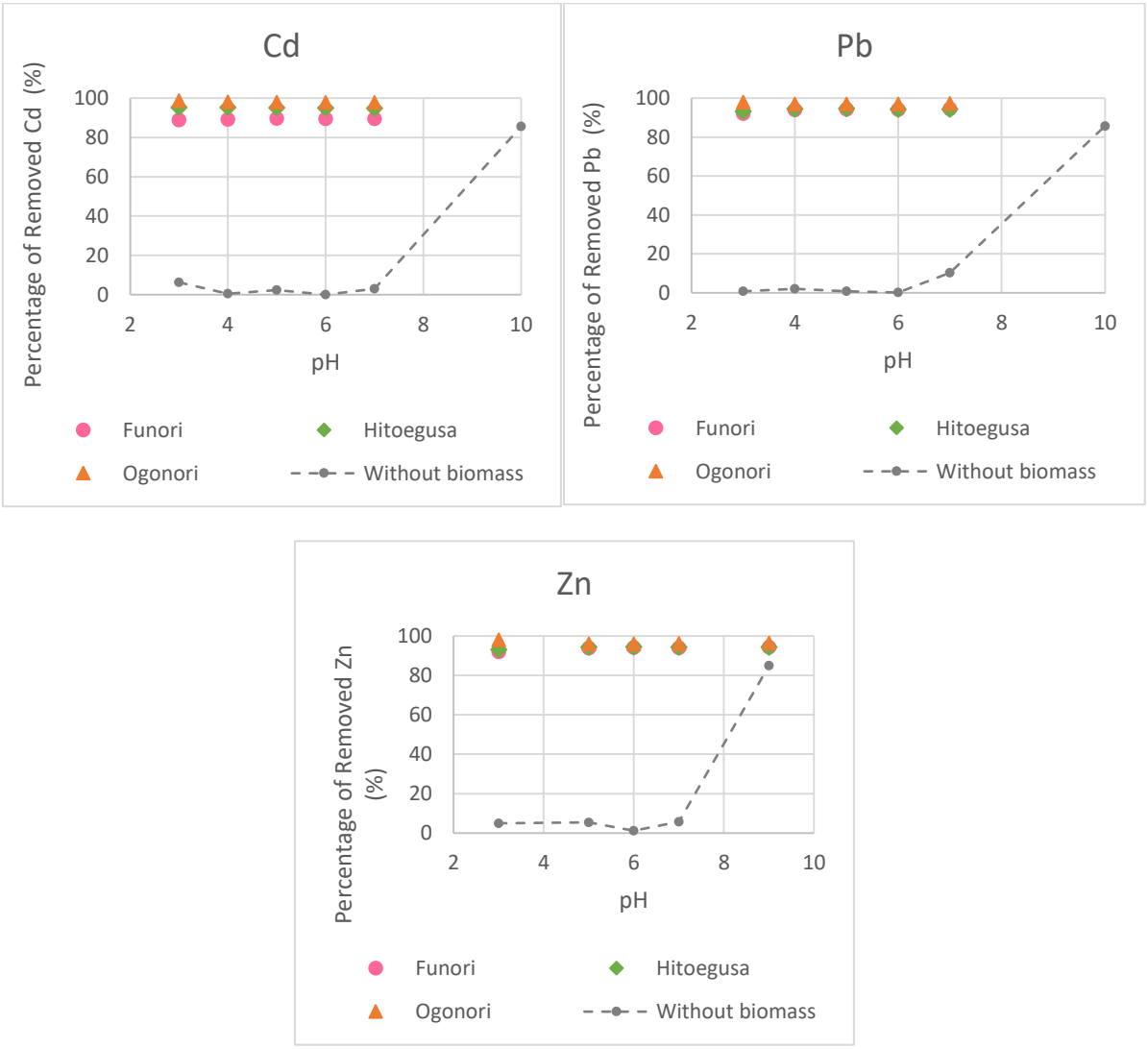


Figure 4.16 Effect of the biomass on the pH.
Co: 2mg/L, Contact time: 1h, Temp: 25°C, Dosage: 4g/L

The solution used for all three biosorbents initially had a pH of 5.5. After 1 hour of contact with funori the pH of the zinc solution shifted from 5.5 to 6.1 even in the first 15 minutes, this final pH was the same for the rest of all time intervals. Hitoegusa final pH was of 5.4 barely affecting the solution. Conversely, Ogonori greatly changed the solution all the way up to a pH of 10. Because, the behavior of the final pH for cadmium

and lead was exactly the same as for zinc, including its graphic description was considered unnecessary.

Generally, when the pH is increased, the amount of hydroxide ions is also increased in the solution. Metal ions react with these OH- ions and are precipitated as metal hydroxide. Under highly alkaline conditions (pH>8), the contribution of biosorption may become small. When the pH is 10, we can see that even without biomass the removal percentage (due to precipitation) of cadmium/lead and zinc can reach the 85.7 and 93.9% correspondingly **Figure 4.16**.

The increase in the pH is **due to the presence of the amine group in ogonori**. The lone pair of electrons on the nitrogen atom of amines makes these compounds basic. With the FTIR analysis of the ogonori biomass we could confirm the presence of the amine group due to its vibrations at 1639 and 1041cm^{-1}. Also we observed that after performing a chemical modification of Ogonori, in which the amine group was treated until it became a methyl group (in other words it was eliminated), the pH of the solution did not increase anymore all the way to 10 (change of pH: pH_i: 5 → pH_f: 4). This will be discuss in further detail with the investigation of the biosorption mechanism in Chapter 5.

Therefore, it is possible to think that a great percentage of the removal of metals when using ogonori is due to its alkalinity. By increasing the pH of the solution substantially, metal hydroxide is formed and precipitate to the bottom, allowing a physical separation. The high alkalinity caused by the addition of ogonori is directly related to the functional groups contained in its cell wall.

4.4.3. Isotherms

The capacity of an adsorbent can be described by its equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the adsorbent (Vinod K. Gupta and Rastogi, 2008). The equilibrium isotherms are illustrated in the Figures

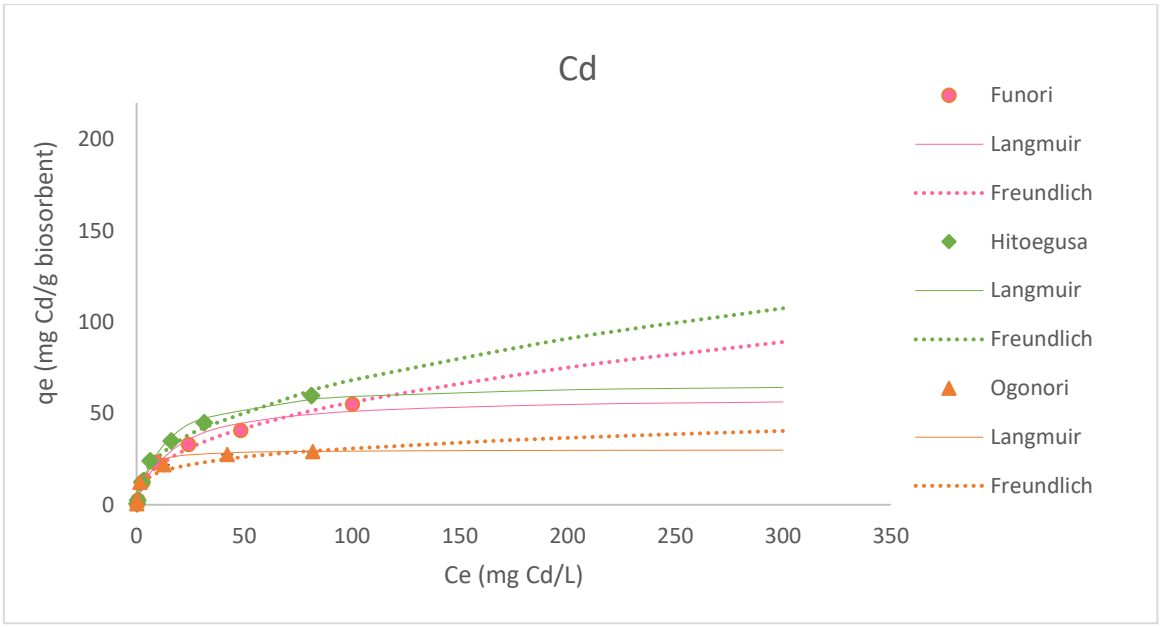


Figure 4.17 Langmuir and Freundlich isotherm plots for biosorption of **Cd(II)** onto funori, hitoegusa and ogonori. (Conc. range: 2-300 mg/L; biomass dosage: 4 g/L; contact time: 1h; pH: 5; temperature: 25 ◦C)

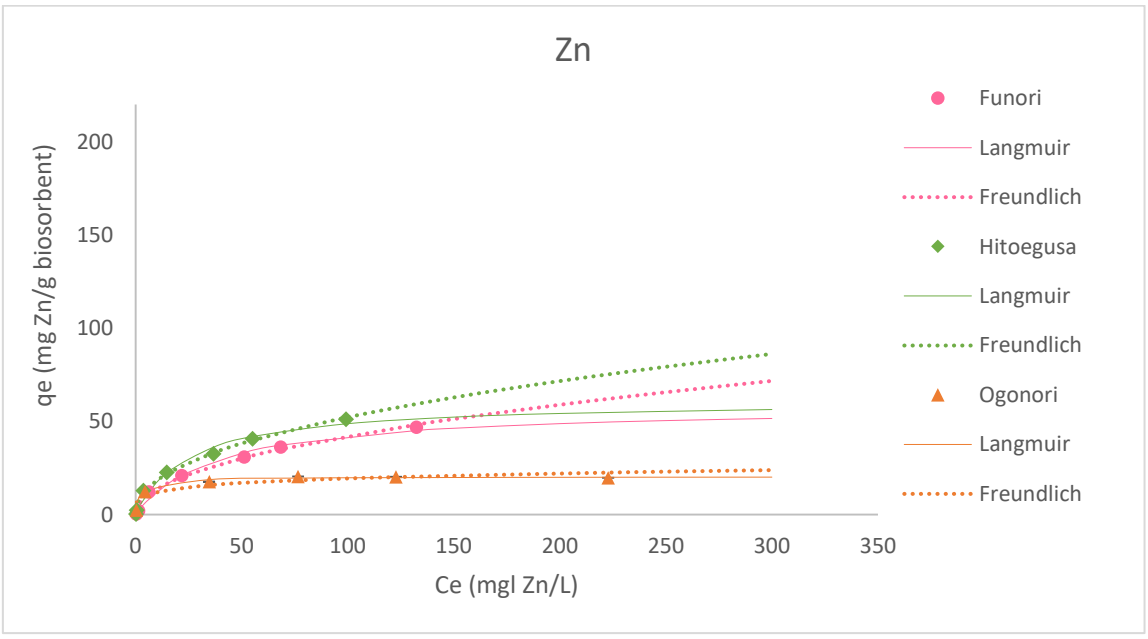


Figure 4.18 Langmuir and Freundlich isotherm plots for biosorption of **Zn(II)** onto funori, hitoegusa and ogonori. (Conc. range: 2-300 mg/L; biomass dosage: 4 g/L; contact time: 1h; pH: 5; temperature: 25 ◦C)

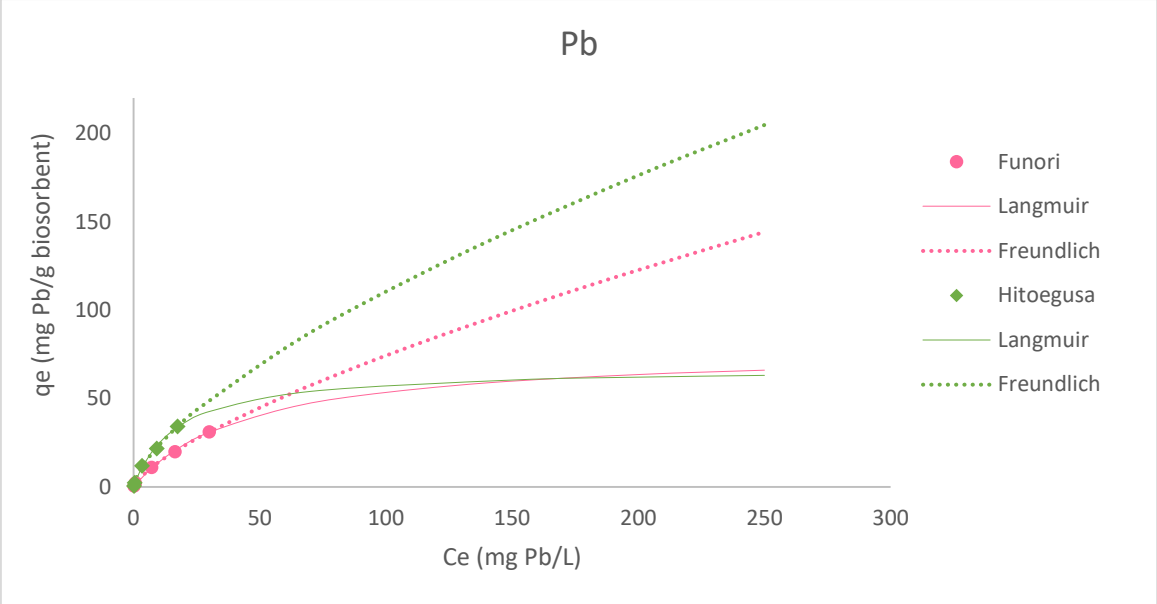


Figure 4.19 Langmuir and Freundlich isotherm plots for biosorption of **Pb(II)** onto funori and hitoegusa biomass. (Conc. range: 2-150 mg/L; biomass dosage: 4 g/L; contact time: 1h; pH: 5; temperature: 25 ◦C)

The obtained Langmuir and Freundlich parameters q_m (maximum sorption capacity,), K_L (Langmuir intensity constant), K_F (affinity parameter) and n (dimensionless heterogeneity parameter constant) for Cd, Pb and Zn are presented in Table 4.4.

Table 4.4 Langmuir and Freundlich estimated parameters for biosorption of Cd(II), Pb(II) and Zn(II)

			Langmuir parameters					**Freundlich parameters**		
Metal	pH	Biomass	q_m (mg/g)	q_m (mmol/g)	K_L (L/mg)	K_L (L/mmol)	R^2	K_F (L/mg)	1/n	R^2
Cd(II)	5	Hitoegusa	67.1	0.596	0.08	8.60	0.992	10.15	0.41	0.977
		Funori	59.3	0.527	0.06	7.09	0.978	8.06	0.42	0.982
		Ogonori	30.2	0.269	0.37	41.92	0.979	10.08	0.22	0.948
Zn(II)	5	Hitoegusa	61.2	0.936	0.04	2.57	0.979	6.40	0.46	0.993
		Funori	58.2	0.891	0.03	1.70	0.985	4.53	0.48	0.989
		Ogonori	20.3	0.311	0.35	23.01	0.990	8.05	0.19	0.865
Pb(II)	5	Hitoegusa	67.4	0.325	0.06	11.84	0.995	4.99	0.67	0.998
		Funori	78.0	0.376	0.02	4.52	0.997	2.63	0.72	1.000

In Figure 4.17 to Figure 4.19, we can see that individual isotherm of each biomass didn't follow a steadily rising pattern from the beginning to the end. In other words, their biosorption capacity changed between low concentrations and high concentrations. That is why when asking "Which alga is a *better* biosorbent??" There is no direct answer

to that until we describe under what conditions: Better at low concentrations? At high concentrations? (This assuming all the environmental parameters of the system are the same). A "better" biosorbent at low concentrations may be "inferior" at higher ones and vice versa.

For the same low concentrations the biosorption capacities of cadmium and zinc followed the order of ogonori >hitoegusa >funori.

Ogonori is a better sorbent than hitoegusa which in turn is superior to funori in that concentration range **Figure 4.21 (a)** and **(b)**.

Hitoegusa exhibited a higher lead removal capacity than funori among the lower equilibrium concentration values **Figure 4.21(c)**.

This is important because surface waters are expected to have relatively low concentrations, which may still be harmful and need to be decreased to even lower ones inside the limits of environmental guidelines.

A curve with a steep initial slope indicates a biosorbent which has a high capacity for the metal ions in the low residual concentration range. That means that the biosorbent has a high affinity for the adsorbed species (Volesky, 2004).

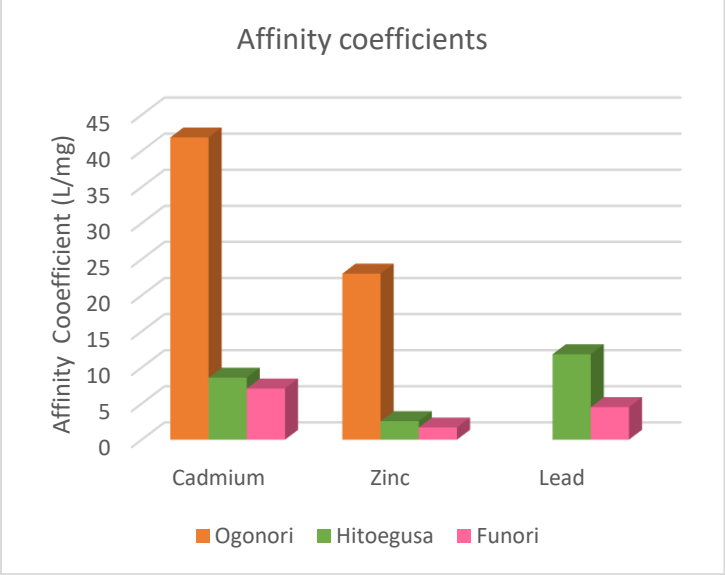


Figure 4.20 Langmuir model affinity coefficients of Cd, Zn and Pb towards Ogonori, Hitoegusa and Funori

This affinity is indicated by the coefficient K_L in eq. (2). The higher the values of K_L imply a greater affinity of the metal ions towards the biosorbent (Romera et al., 2007).

The calculated values of the affinity between the biomass and cadmium ions were of 0.37, 0.08 and 0.06 L/mg and zinc values were 0.35, 0.04 and 0.03 L/mg for ogonori, hitoegusa and funori. Regarding lead they were of 0.06 and 0.02 L/mg for hitoegusa and funori. Summarizing, the **tendency of the affinity** towards cadmium and zinc is of ogonori >hitoegusa >funori, and for lead of hitoegusa> funori. The affinity between the metals and the algae is in correspondence with the observed pattern of adsorption in low concentrations showed in **Figure 4.21**.

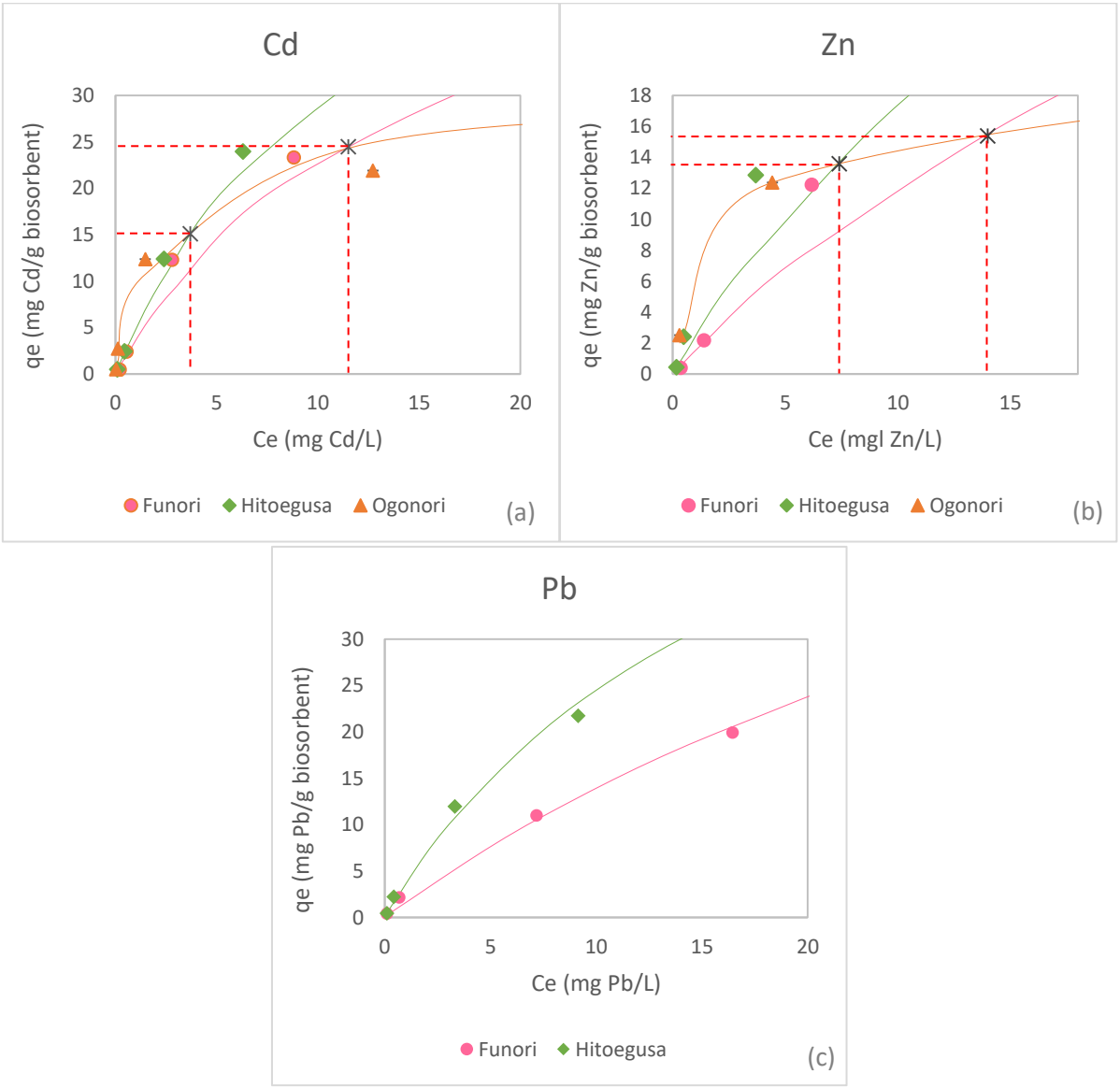


Figure 4.21 Magnified images of Figures 4.16, 4.17 and 4.18.
Removal of (a) cadmium, (b) zinc and (c) lead with algal biomass at low concentrations range.

The performance of two biosorbents is the same (in terms of q) at the point where their curves intersect. The intersection points of ogonori-hitoegusa and ogonori-funori are graphically depicted by an asterisk in **Figure 4.21 (a)** and **(b)**. At cadmium concentrations of 3.7 and 11.5mg/L, ogonori performance was equal to the hitoegusa and funori. Similarly, ogonori's efficiency for zinc removal was the equivalent as hitoegusa and funori at concentrations of 7.4 and 14mg/L.

The removal effectiveness of cadmium and zinc by hitoegusa was higher than funori's no matter the concentration range since both curves never intercept. The biosorption of lead by funori seem to be equal around concentrations of 170mg/L, being slightly higher in the range of high concentrations. Both curves are almost overlapping, meaning there is not substantial difference between their performances.

When the limitation of the maximum residual sorbate concentration is not of a concern and the purpose is to saturate the sorbent as much as possible (no matter how much of the sorbate may still be 'left over' in the solution), hitoegusa is a better sorbent for cadmium and zinc than funori and ogonori because it accumulates more metals at higher residual sorbate concentrations. The saturation of a biosorbent may be useful in the recovery of high concentrations of precious metals, or if the biosorbent will be used at the first stages of the treatment of wastewaters. In these cases a biosorbent with the highest q_{max} is preferable.

If individually each isotherm had followed a similar rising pattern we would have expected ogonori to be the biosorbent with the highest biosorption capacity. However, hitoegusa was the seaweed with the highest adsorption capacity, around the double and triple of the capacity of ogonori for cadmium and zinc. The performance of algae is no longer the same as when metals were removed at low concentrations.

A possible explanation for ogonori's sudden decrease of biosorption at higher concentrations is its influence on the solution pH. At a concentration of 2 mg/L (relatively low), after ogonori was suspended in the solution for one hour, **the pH changed from 5.5 to 10**. Which means ognori is acting like a weak base affecting the solution pH. However, at higher concentrations, since the solution is saturated with metal, even when it's in contact with ogonori the change between the initial and final

pH is smaller (Figure 4.22). At a concentration of 10 mg/L, the solutions tended to reach a pH of 9.4 and as the metal concentration increased, the pH of the solution decreased until it stabilized in 7.2 and 6.3 for cadmium and zinc.

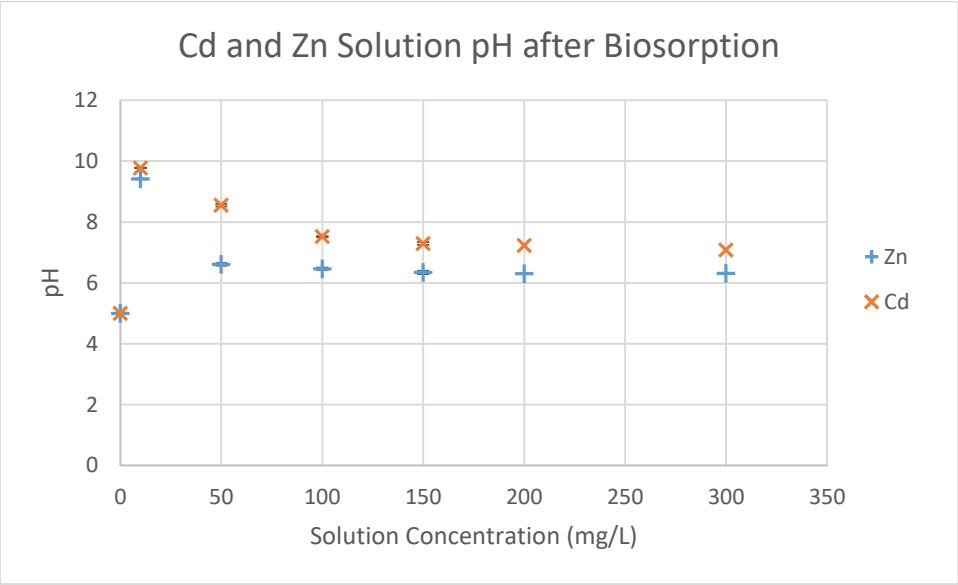


Figure 4.22 Final pH of Cd and Zn solutions after biosorption with ogonori. (Conc. range: 2-300 mg/L; ogonori dosage: 4 g/L; contact time: 1h; pH: 5; temperature: 25 ◦C)

With regard to the characterization of the biomass. We determined that the average particle size increases in the order of hitoegusa, ogonori and funori. Results indicate size is 240µm, 483µm and 549µm for each algae respectively. The specific surface area (SSA) of hitoegusa, ogonori and funori was observed to be 0.16, 0.42 and 0.14 m2/g.

If we assumed a monolayer adsorption (the data fits Langmuir model). The amount of algal surface covered by metal is given in Table 4.5 .

If we considered the SSA as main characteristic influencing the biosorption process, ogonori is expected to have the highest adsorption capacity, however hitoegusa showed a higher removal efficiency despite having a smaller contact surface.

From this we can see that the biosorption capacity not only depends on the surface area itself but also on the amount of active sites contained in this area.

Table 4.5 Amount of Cd, Zn and Pb per unit of area of Hitoegusa, Funori and Ogonori

Metal	Biomass	Max. Adsorption Capacity (mg/m²)
Cd(II)	Hitoegusa	419.38
	Funori	423.57
	Ogonori	71.90
Zn(II)	Hitoegusa	382.50
	Funori	415.714
	Ogonori	48.33
Pb(II)	Hitoegusa	421.25
	Funori	557.14

Also, from the plotted curves we can see that funori and hitoegusa data for all metals was adjusted better by the Freundlich model. Conversely, ogonori fitted better the Langmuir model. This is confirmed by the obtained values of R^2 cofficients. Despite this, since the values for Cd(II), Pb(II) and Zn(II) by hitoegusa and funori still fitted well the Langmuir model, a comparative study using maximum adsorption capacity as reference is still possible.

The maximum adsorption capacities of Cd(II), Pb(II) and Zn(II) for hitoegusa were of 67.1, 61.2, and 67.4 mg/g respectively. On the other hand, the funori maximum adsorptions for Cd(II), Pb(II) and Zn(II) were of 59.3, 58.2, and 78.0 mg/g respectively. Finally, the highest amounts of Cd(II) and Zn(II) that can be removed with ogonori were of 30.2, and 20.3 mmol/g.

Both hitoegusa and funori showed a relatively higher removal capacity of Zn when compared with similar biosorbents from data recorded in the literature. We can see that our algae behaves similarly to previously studied biomass, showing an adsorption tendency of Pb>Cd>Zn (**Figure 4.23** and **Table 4.6**). One possible explanation is the influence of the ionic characteristics of each metal in the reaction with the functional groups of the algae during the biosorption process.

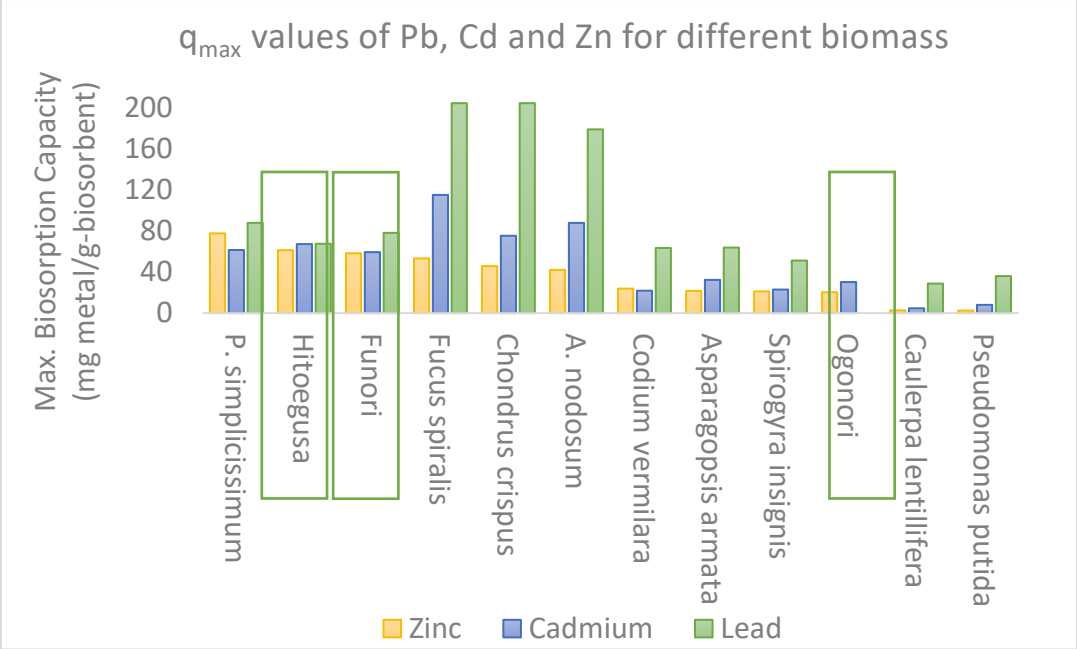


Figure 4.23 Comparison of the estimated values of the maximum adsorption of Cd(II), Zn(II) and Pb(II) on Funori, Hitoegusa and Ogonori, against the reviewed data of previous studies performed under same parameters.

Table 4.6 Order of the adsorption affinity of Cd, Zn and Pb by different biosorbents

Biomass	Type	Affinity order	References
Penicillium simplicissimum	Fungi	Pb>Zn>Cd	(Fan et al., 2008)
Fucus spiralis	Brown algae	Pb>Cd>Zn	(Romera et al., 2007)
Chondrus crispus	Red algae	Pb>Cd>Zn	(Romera et al., 2007)
Ascophyllum. nodosum	Brown algae	Pb>Cd>Zn	(Romera et al., 2007)
Codium vermilara	Green algae	Pb>Cd>Zn	(Romera et al., 2007)
Asparagopsis armata	Red algae	Pb>Cd>Zn	(Romera et al., 2007)
Spirogyra insignis	Green alage	Pb>Cd>Zn	(Romera et al., 2007)
Caulerpa lentillifera	Green algae	Pb>Cd>Zn	(Pavasant et al., 2006)
Pseudomonas putida	Bacteria	Pb>Cd>Zn	(Pardo et al., 2003)
Hitoegusa	Green algae	Pb>Cd>Zn	This study
Funori	Red algae	Pb>Cd>Zn	This study

The relationship between some of the ionic characteristics of Cd, Pb and Zn (Table 4.7) and the maximum adsorption capacity of Funori and Hitoegusa was determined with a linear regression. Based on the study done by (Chen and Wang, 2007) of the yeast *Saccharomyces cerevisiae*.

Table 4.7 Ionic characteristics of Cd, Pb and Zn (source: (Can and Jianlong, 2007))

Properties	Pb	Zn	Cd
Electronegativity (Xm)	2.33	1.65	1.69
Covalent index (X_m^2r)	6.41	2.04	2.71
Atomic radius (AR)	1.54	1.31	1.48
Ionization Potential (IP)	15.032	17.964	16.908
Polarizing power (Z/r^2)	1.44	3.56	2.22

In the case of Hitoegusa the affinity of the metals correlated the best with the atomic radius. Contrary, the polarizing power seems to have a negative effect in the biosorption.

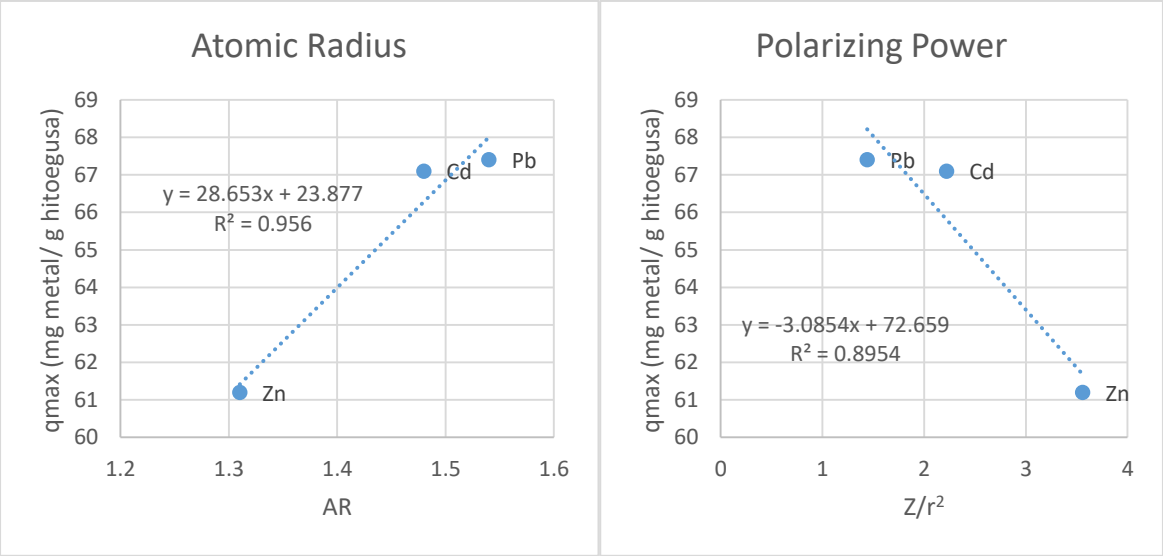


Figure 4.24 Correlation between max. biosorption capacities of hitoegusa and the atomic radius and the polarizing power of Cd, Pb and Zn

The negative correlation between the polarizing power and the biosorption capacity indicates that the metals had a more covalent character, seeking for functional groups containing sulfur and nitrogen.

As for funori the adsorption seem to be favored with the increase of the covalent index.

The covalent index is an indicator for a metal ion of the importance of covalent interactions relative to ionic interactions. The greater the values of the covalent index, the greater it's potential to form covalent bonds with functional group in the following order: S > N > O.

Ionization potential is the energy necessary to remove an electron from an isolated atom or molecule. The higher the ionization energy, the more difficult it is to remove an electron. Therefore, ionization energy is in indicator of reactivity. Despite Pb having the highest ionization potential the reactivity with Funori is not affected. Probably the contribution of ionic bonding was less.

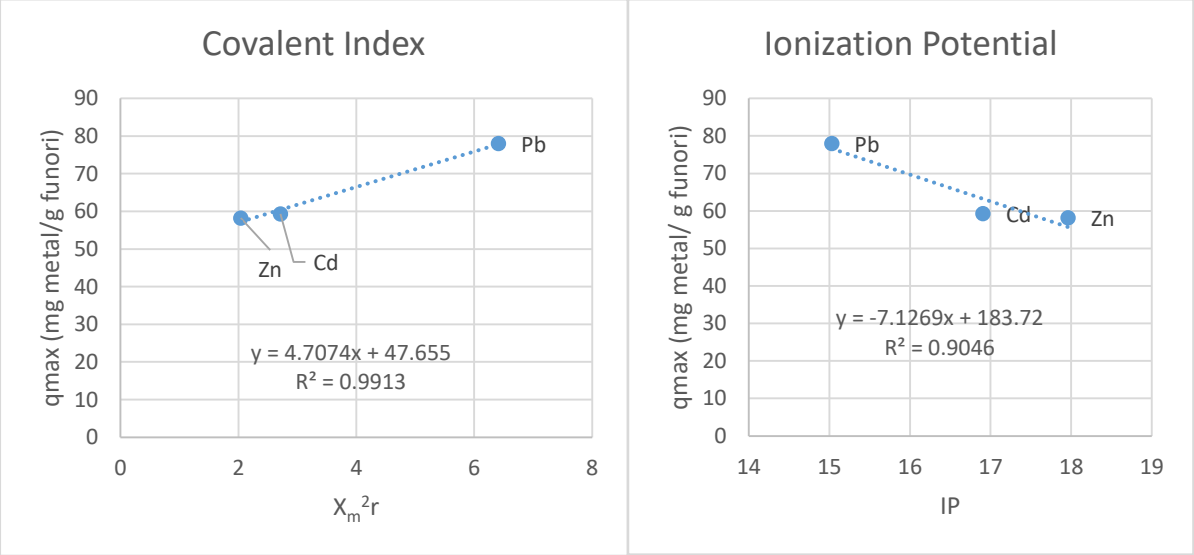


Figure 4.25 Correlation between max. biosorption capacities of funori and the covalent index and the ionization potential of Cd, Pb and Zn

4.5. Conclusions

This study focused on the biosorption of As(III and V), Se(IV), Cd(II), Pb(II) and Zn(II) ions onto algal biomass (hitoegusa, funori and ogonori) from aqueous solution. Neither hitoegusa nor funori were capable of removing the anionic metals (As and Se) in any degree. This is suspected to be related to the predominant biosorption mechanism of these algae. The operating parameters, pH of solution, contact time, and temperature, were effective on the biosorption efficiency of the cationic metals. The metals reached the equilibrium rapidly at about 15 mins. Their kinetics followed the pseudo-second order model. Biosorption equilibrium of hitoegusa and funori was better described by the Freundlich isotherm model. Biosorption onto ogonori, on the other hand, was better described by the Langmuir model. The biosorption capacity of hitoegusa for Cd(II), Pb(II), and Zn(II) estimated by the Langmuir fit was found to be 67.1, 67.4 and 61.2 mg/g,

and of funori was 59.3, 78.0, and 58.2 mg/g, respectively. The maximum adsorption capacity of Cd(II) and Zn(II) by ogonori were of 30.2, and 20.3 mg/g.

4.6. References

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Chapter 5

Biosorption Mechanism

Abstract

Biosorption have been proven as an effective wastewater treatment. In the recent years one of the main challenges in regards this technology still is the understanding of the removal mechanism. Understanding the mechanism of biosorption will lead us to its commercial application under the most optimum conditions. Since more reliable mathematical models based on the actual mechanisms could be employed to predict the influence of the parameters affecting it. In this study, the biosorption mechanisms of funori, hitoegusa and ogonori were confirmed by the functional group blocking, potentiometric titrations, FTIR, SEM-EDX and desorption results.

Results shows that the removal of cationic metals by hitoegusa, funori and ogonori biomass were due to (i) ion exchange and chemisorption (ii) ion exchange (iii) cation exchange and precipitation. Since cation exchange played a key role in the uptake of metal the removal of As and Se was not favored when using these algae.

Our results revealed that all three algae could be employed as an effective and low-cost biosorbent for removal of Pb^{2+}, Zn^{2}+ and Cd^{2+} from contaminated water sources.

Keywords:

Metal speciation, ion exchange, chemisorption, functional groups, algae biosorption mechanism

5.1. Introduction

The metal binding properties of different biosorbents have been widely investigated, but the mechanisms responsible are still poorly understood. The main objective of studying biosorption is obviously to optimize its application. Rather than establishing optimal conditions by a lengthy and expensive trial and error process, one should aim for conceptual understanding that allows predictions to be made. For example, knowing that the mechanism of biosorption is largely based on ion exchange implies that changes in the ionic strength of the solution will affect metal uptake (Naja and Volesky, 2011).

Algae mechanism studies to date is limited to brown seaweeds. The mechanism of green and red seaweed species have not been evaluated to any extent (**Table 3.3**). Considering the big differences in the cell wall structures between the different types of algae and that the biosorption processes essentially take place in the cell wall, it is expected that the mechanisms responsible for the metal binding will differ according to its cell walls too. Therefore in the present study the biosorption mechanism of metals by green algae and red algae was investigated with hitoegusa, funori and ogonori as representative species.

5.2. Metal speciation

5.2.1. Arsenic

The most common oxidation states of arsenic found in water are As(III) and As(V). The speciation of arsenic is mainly dependent on its tendency to acquire or lose electrons (reduction potential) and the pH conditions of the solution (Smedley and Kinniburgh, 2002)(Vaclavikova et al., 2008). **Figure 5.1** represents the relation between arsenic reduction-oxidation potential and pH through a Pourbaix Diagram. As(V) most likely occurs under oxidizing conditions, in both acidic or alkaline mediums. When the pH is below 7, most of As(V) is dissociated as its monovalent form ($H_2AsO_4^-$) and at alkaline conditions is predominantly found as divalent arsenic ($HAsO_4^{2-}$). On the contrary, the reducing states favors the occurrence of As(III), along the pH scale is mainly found as arsenous acid (H_3AsO_3) which is the more stable specie and starts dissociating only at highly alkaline conditions (pH: 9-14).

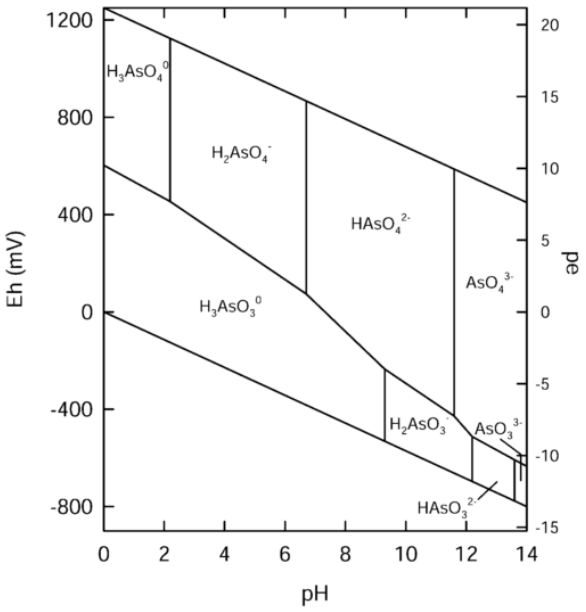

Figure 5.1 Potential/pH diagram of arsenic species in water

The redox and the pH conditions contribute to making As(V) removal easier when compared to As(III) elimination.

5.2.2. Selenium

In nature selenium exists in four oxidation states: Se(-II), Se(0), Se(IV) and Se(VI) from this only Se(VI) and Se(VI) can be found in water as it was previously mentioned. Se(IV) is considered more toxic than Se(VI) (Barceloux, 1999)(Tuzen and Sari, 2010).

The **Figure 5.2** is a graphic representation of the speciation of selenium according to the pH and the oxygen and organic matter amounts (oxidizing-reducing environments). In strongly acidic conditions, the hydrogen selenate ion, $HSeO_4^-$ is formed. However as for Se(VI) the most stable form (divalent SeO_4^{-2}) happens under oxidizing conditions and in an alkaline medium. Under milder redox conditions, selenite exists, as monovalent $HSeO_3^-$ in the neutral spectrum and divalent SeO_3^{2-} the more alkaline the conditions become. Selenite reduces to elemental selenium at low pH and reducing environments.

While H_2Se is a relatively strong acid, the hydrogen selenide (HSe^-) is a strong reducing agent (Barceloux, 1999). The higher or lower the pH, the more soluble the compounds become, therefore water under this pH conditions show higher selenium concentrations (WHO, 2011a).

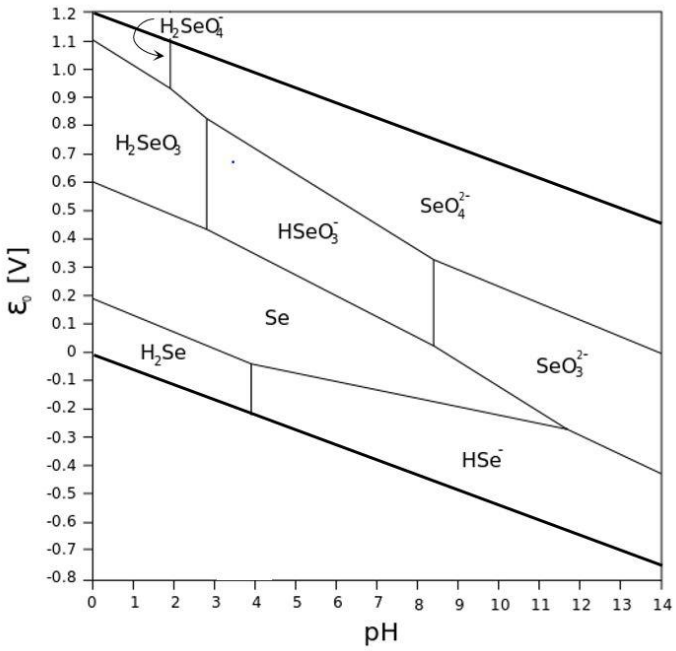

Figure 5.2 Potential/pH diagram of selenium species in water

5.2.3. Cadmium

Figure 5.3 shows the different cadmium species present in aqueous solutions depending on its pH. According to the graph cadmium in water can be found under 4 possible stable phases: divalent cadmium (Cd^{2+}), cadmium hydroxide ($Cd(OH)_2$) and other ionic species such as $Cd(OH)_3^-$ and $Cd(OH)^+$.

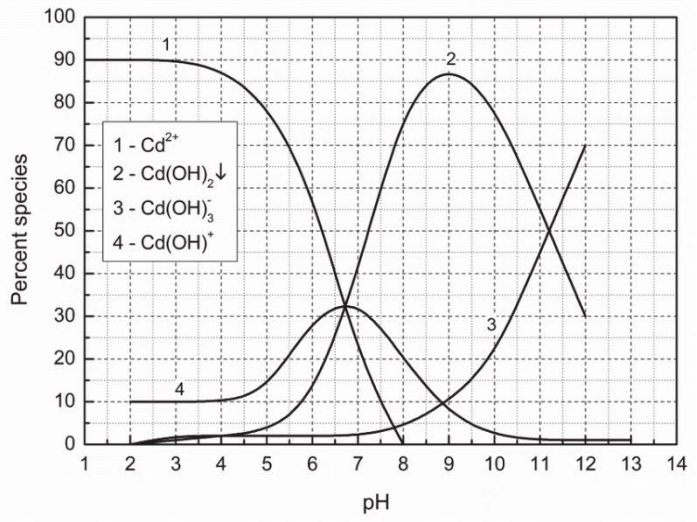

Figure 5.3 Speciation diagram for aqueous cadmium (Soǒ and Kalembkiewicz, 2016)

Along the acid range of the pH (and in oxygenated conditions) cadmium exists as free divalent form. And in alkaline pH (above the 7.5) cadmium stops being available for biosorption as it starts to precipitate in the low soluble form of $Cd(OH)_2$(Farooq et al., 2010).

5.2.4. Lead

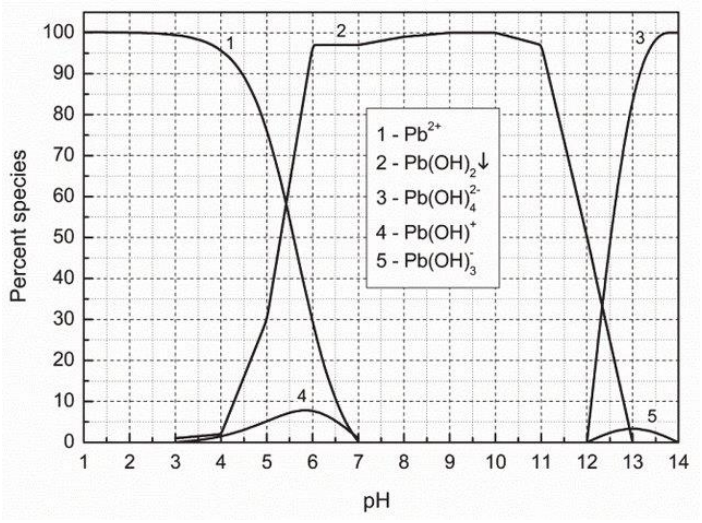

Figure 5.4 Speciation diagram for aqueous lead (Soćo and Kalembkiewicz, 2016)

From **Figure 5.4** it can be understand, that like cadmium, lead is found in its divalent form (Pb^{2+}) at low alkaline (pH<5.5) and oxygenated conditions. At a pH of 6, less predominant $Pb(OH)^+$ soluble specie and solid $Pb(OH)_2$ begin to form. Lead hydroxide becomes the dominant specie until a pH of 12. In extreme alkaline (pH>12.5) solutions is mostly found as $Pb(OH)_4^{2-}$ and $Pb(OH)_3^-$. After pH 6, biosorption of lead may not be the most suitable removal method, since a big portion of the metal will start to precipitate.

5.2.5. Zinc

The distribution of the ionic species of zinc according to the pH are shown in **Figure 5.5**. Zinc in water can be found predominantly in its divalent form (Zn2+). At pH 8 the monovalent form starts to form in a less amount. At very basic mediums (pH>9) zinc will start to precipitate in the form of hydroxide.

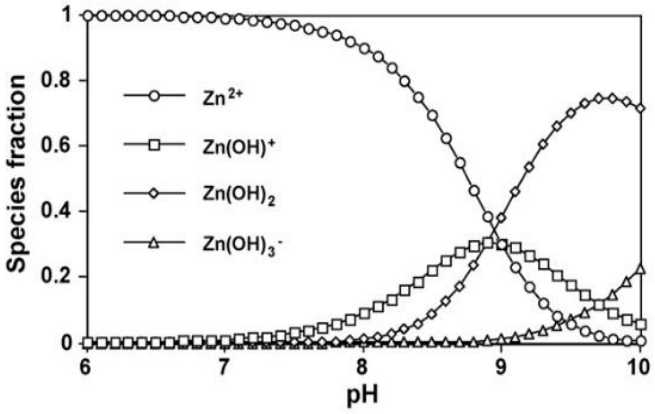

Figure 5.5 Speciation diagram for aqueous zinc (Lu et al., 2007)

5.3. Algae

The term algae refer to a large and diverse assemblage of eukaryotic organisms that contain chlorophyll and carry out oxygenic photosynthesis. Algae abound in nature in aquatic habitats, freshwater, marine and moist soil. It shows considerable diversity in the structure and chemistry of their cell walls. In many cases the cell wall is composed of a network of cellulose fibrils, but it is usually modified by the addition of other polysaccharides (Wang and Chen, 2009). The cell walls of brown algae (Phaeophyta) generally contain three components: cellulose, the structural support; alginic acid (a polymer of mannuronic and guluronic acids (M and G) and the corresponding salts of sodium, potassium, magnesium and calcium) and sulfated polysaccharides (fucoidan matrix). Red algae (Rhodophyta) also contain cellulose, but their interest in connection with biosorption lies in the presence of sulfated polysaccharides made of galactanes (agar and carragenates). Green algae (Chlorophyta) are mainly cellulose, it can also contain xylan and mannan (Romera et al., 2006b).

Figure 5.6 and Figure 5.7 show the structures of the main components of the cell walls of hitoegusa and funori respectively. Hitoegusa specifically has rhamnan sulfate which is a soluble polyrhamnose saccharide that is composed by rhamnose and sulfated rhamnose.

Table 5.1 Summary table of the cell walls characteristics of Green, Red and Brown algae. Source: (Domozych, 2011)

Algae taxon	General wall characteristics	Biochemical features
Green algae *Chlorophyta*	Scales, theca and fibrillar / matrix composite	Cellulose, pectins, xyloglucans, xylans, AGP, extension and lignin
Red algae *Rhodophyta*	Fibrillar /matrix composite, mucilages	Cellulose, mannans, xylans; agar and carageenans (sulfated galactans), lignin
Brown algae *Phaeophyta*	Fibrillar /matrix composite	Cellulose, acidic polysaccharides (alginates)

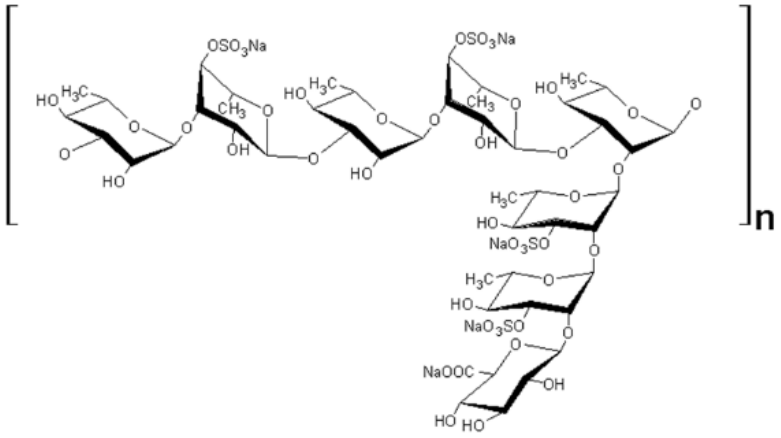

Figure 5.6 Chemical structure of rhamnan sulfate isolated from hitoegusa (*Monostroma nitidum*). Source: (Tako, 2017)

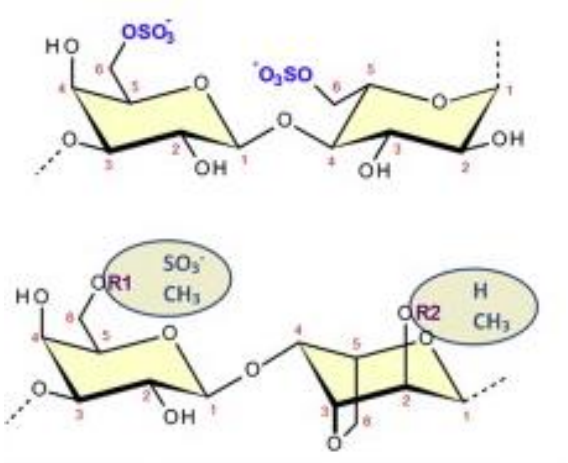

Figure 5.7 Chemical structure of the polysaccharide repeating unit of Funori (*Gloiopeltis furcata*). Source: (Tuvikene et al., 2015)

The basic components of the polysaccharides of the red algal genus *Gloiopeltis* are 3,6-anhydro-a-L-galactose (3.0 e34.4%) and b-D-galactose-6-sulfate.

5.4. Biosorption mechanisms

Biological material is complex and a variety of mechanisms may be operative under given conditions. The variety of structural components present in biomass means that many functional groups are able to interact with metal species, e.g. carboxyl, phosphate, hydroxyl, amino, thiol, etc., to varying degrees and influenced by physicochemical factors. For biosorption, defined as a physicochemical process independent of metabolism, such mechanisms as physisorption, ion exchange, complexation/coordination and micro-precipitation may be important (Gadd, 2009).

Since biosorption processes essentially take place in the cell wall, the mechanisms responsible for the metal binding differ according to the biomass type (Vijayaraghavan and Balasubramanian, 2015).

5.4.1. Analytical techniques used in the study of the biosorption mechanism

With the application of different analytical techniques, valuable information to a better understanding of the biosorption process can be obtained (**Figure 5.8**). Many of these analytical techniques require costly equipment and are very expensive to carry out as routine measurements.

Some interesting applications of these analytical techniques in biosorption studies are condensed in **Table 5.2**..

Table 5.2 Examples of researches reporting the application of certain analytical techniques to study biosorption process

Technique	References
SEM-EDX	(Ariff et al., 1999)(Han et al., 2006)
FTIR /IR	(Raize et al., 2004) (Pavasant et al., 2006)(Elangovan et al., 2008)
ICP/AAS	(Chojnacka et al., 2005)(Verma et al., 2008)
XPS	(Park et al., 2005)

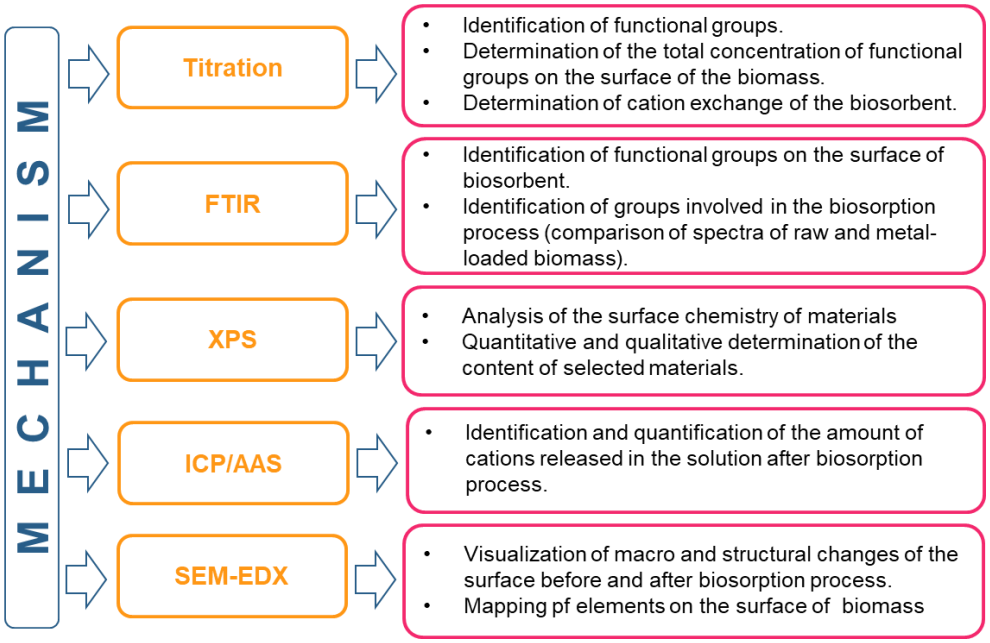

Figure 5.8 Techniques used in the identification of the mechanism of biosorption. Source: Adapted from (Michalak et al., 2013)

5.4.1.1. Scanning Electron Microscope, Energy-dispersive X-ray spectroscopy (SEM-EDX)

EDX make use of X-rays emitted from the lower part of a sample's interaction volume during electron beam bombardment that carries a specific energy according to their molecular weight. This method is routinely coupled with SEM analysis to achieve more complete results.

5.4.1.2. Fourier Transform Infrared spectroscopy (FTIR)

One important characteristic of a biosorbent is the surface functional groups present, which are largely characterized by the IR spectroscopy method. Infrared light is irradiated onto a sample of an unknown compound. Different bond types (functional groups) in the unknown molecule absorb different frequencies of the infrared light. For example, an O-H bond absorbs infrared light of a different frequency than a C-H bond. The IR spectrometer feeds this data into a computer that then plots the frequencies of the light that isn't absorbed by the sample (the transmittance of light) versus the amount of transmittance to give an IR spectrum. This technique is only capable of providing a qualitative description. Specifically, most biosorption studies utilize FTIR

just to determine the availability of certain surface functional groups as part of the structure of biosorbents, although further probing the influence of these groups towards the metal binding process is also possible (Arief et al., 2008)(Michalak et al., 2013). Although IR is not able to provide enough information to find the exact structure of a 'new' molecule, in conjunction with other spectroscopic tools, such as NMR and mass spectrometry, IR can help provide valuable information to help piece together the overall structure.

5.4.1.3. Inductively Coupled Plasma (ICP)

ICP or other techniques such as Absorption Atomic Spectrophotometry (AAS) are useful to measure the metal elemental concentrations in solution. In biosorption these techniques can provided useful information when the contents of the solution before and after biosorption are analyzed.

5.4.1.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a special chemical analysis technique used to resolve the elemental composition, empirical formulae, chemical and electronic states of the elements that exist within the surface region of a sample. XPS is employed to determine the valence state of the absorbate bound on the biomass.

5.4.2. Parameters affecting the mechanism

5.4.2.1. pH

Solution pH is one of the most important regulator of biosorption affecting the solution chemistry of the pollutants themselves, the activity of functional groups in the biosorbents, and competition with coexisting ions in solution (Vijayaraghavan and Yun, 2008).

5.4.2.2. Temperature

Increases in the temperature usually enhances biosorptive removal of adsorptive pollutants when increased by increasing surface activity and kinetic energy of the adsorbate, but which may also damage the physical structure of the biosorbent (Park et al., 2010). The effect of temperature on biosorption depends on the adsorption heat (enthalpy change).

5.4.2.3. Ionic strength

Ionic strength of solution which when increased, reduces biosorptive removal of adsorptive pollutants by competing with the adsorbate for binding sites on the biosorbent (Fomina and Gadd, 2014).

5.4.3. Previously proposed biosorption mechanisms

The mechanism of biosorption by green algae; hitoegusa and red algae; funori might be adsorption, ion exchange, complexation, micro-precipitation or a combination of them. These mechanism are illustrated in **Figure 5.9**.

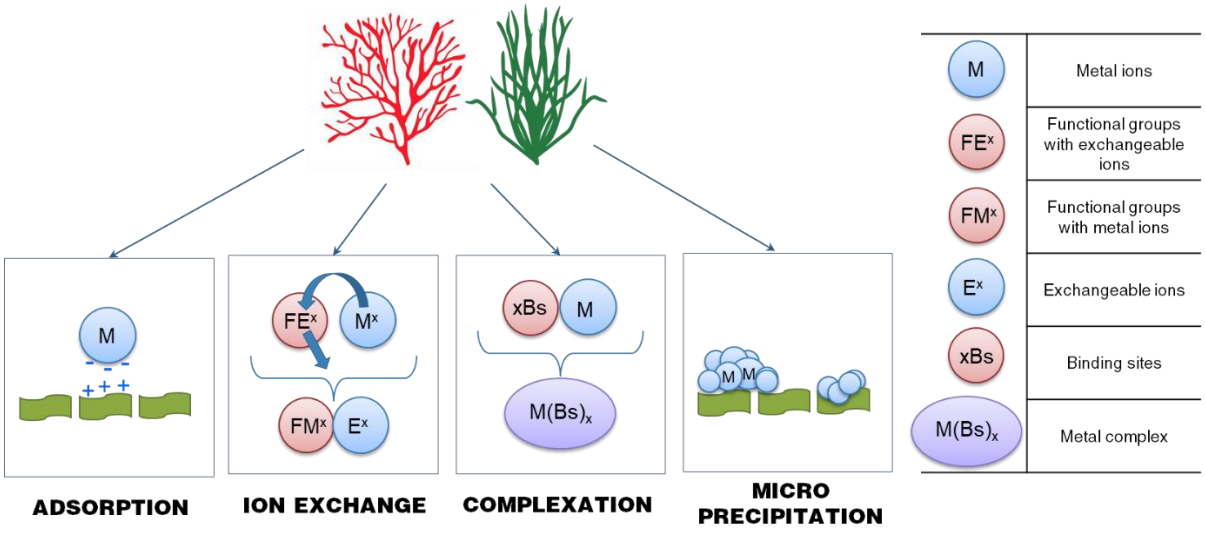

Figure 5.9 Potential biosorption mechanisms of red and green algae.
Source:Adapted from (Mahajan and Sud, 2012).

5.5. Objectives

a) Characterize the functional groups on cell wall structures of Hitoegusa and Funori
b) Investigate the influence and binding mechanisms of those functional groups.

5.6. Materials and methods

5.6.1. Chemicals

All used chemicals were analytical grade from Kanto Chemical unless stated otherwise. For The used metals solutions were prepared from 100 mg/L standards. Adjustment of pH was done with solutions 0.1 to 3 M of NaOH and HCl.

5.6.2. Equipment

The glassware was properly cleaned before use with a hydrochloric acid solution and then washed several times with deionized water. All the solutions were prepared with deionized water obtained from a Milli-Q reference purification system. The pH measurements were made using a pH Meter HM-30R. Samples were agitated in a TAITEC SR-2DS shaker. In preparation for the filtration process, samples were centrifuged in a tabletop centrifuge Kubota 4000. Samples for FTIR analysis were lyophilized with an Eyela FDU-1200 dryer. Dry samples, before and after biosorption, were examined with the Thermo Scientific Nicolet 6700 spectrophotometer. Before their observation with the electron microscope samples were coated with gold using a JEOL FINE COAT Ion Sputter JFC 1100. The morphology of the algae was analyzed with a FE-SEM-EDX JEOL, JXA-8530F. The addition of the volumes during the potentiometric titrations was done using an automatic Hirschmann Opus titration unit. The residual metal solutions were analyzed by inductively coupled plasma mass spectrometry (8800 Triple Quadrupole ICP-MS, Agilent Technologies).

5.6.3. Biosorbents preparation

All biosorbents were commercially acquired. They were pulverized using an Osaka pulverizer to a particle size of 0.5mm. 1 mg of each algae was stored in a 50mL centrifuge tube for its further analysis.

5.6.4. Ion Exchange Experiments

The concentrations of Na^{+}, K^{+}, Mg^{2+} and Ca^{2+} ions were analyzed by Inductively Coupled Plasma Mass Spectrometry from the obtained solutions after the biosorption process ocurred under the conditions explained in the section 4.3.4.2. The results presented below belong to samples prepared at pH 5. The detailed process is represented in **Figure 5.11**.

5.6.5. Titration of the Algae

The titration process is depicted in **Figure 5.10**. The dried and pulverized biomass (2.5 g) were protonated by soaking in 500mL of 0.2M HCl. The suspension was shaken for 4 hours at 250 rpm. This hydrolysis under acidic conditions ensured that any remaining ions e.g. Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} were removed from the seaweed surface. Leaving all sites activated available for quantification. After this, the biomass were centrifuged at 3000 rpm for 3 minutes. The supernatant was discarded if its pH was still acidic. Instead, the biomass was suspended in milli-Q water, shaken for 5 minutes, then centrifuged and the pH was measured again. This washing procedure was repeated for about 6 or 7 times until the pH of the supernatant was between 4.40 and 4.7. The treated biomass was dried in an oven at 60C until dryness (48-72 hours) and stored in polyethylene bottles until required.

For each titration, 0.2 g of the protonated biomass were dispersed in 50mL of a 1mM NaCl solution (for keeping a constant ionic strength). Titration was carried out by stepwise addition of 0.15mL of 0.1M NaOH to the beaker while the suspension was stirred. After each addition of titrant, the system was allowed to equilibrate until a stable pH reading was obtained.

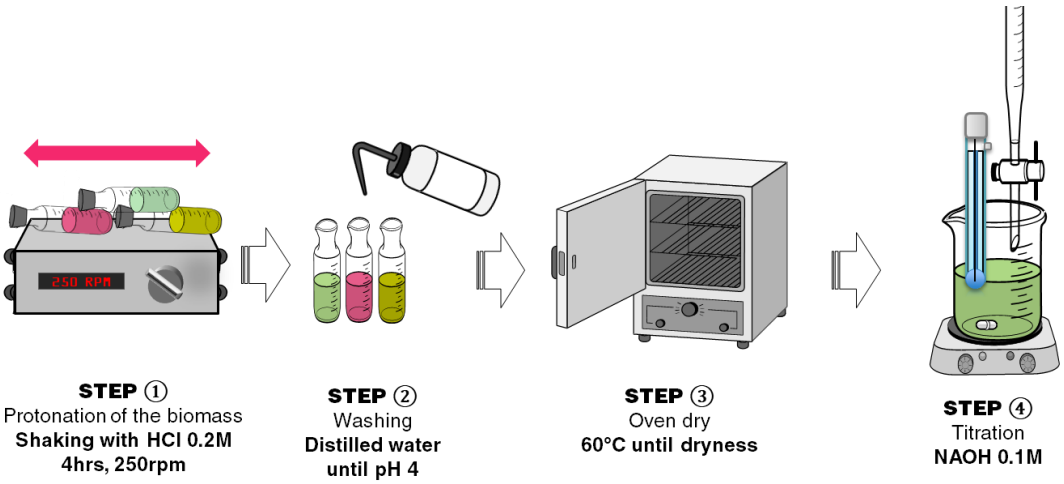

Figure 5.10 Diagram of the potentiometric titration process

5.6.6. FT-IR

Exhausted algae samples (loaded with the targeted metals) were obtained from the performed kinetic experiments (see section 4.3.6.1. for more details). After their filtration, the samples taken at 24 hours, were centrifuge again. Their aqueous content was thrown away. And the tubes containing the biomass were store in a freezer for at least 24 hours. The frozen samples were processed by vacuum freeze-drying for another 24 hours.

The FT-IR spectra of biomass samples (before and after metal loading) in the wave number range of 700–4000 cm^{-1} were recorded in a FTIR spectrometer.

Data were corrected by running a background spectrum between each sample measurement. A background spectrum is a spectrum which is exclusively induced by the instrument and its environment (it is obtained when measuring without sample).

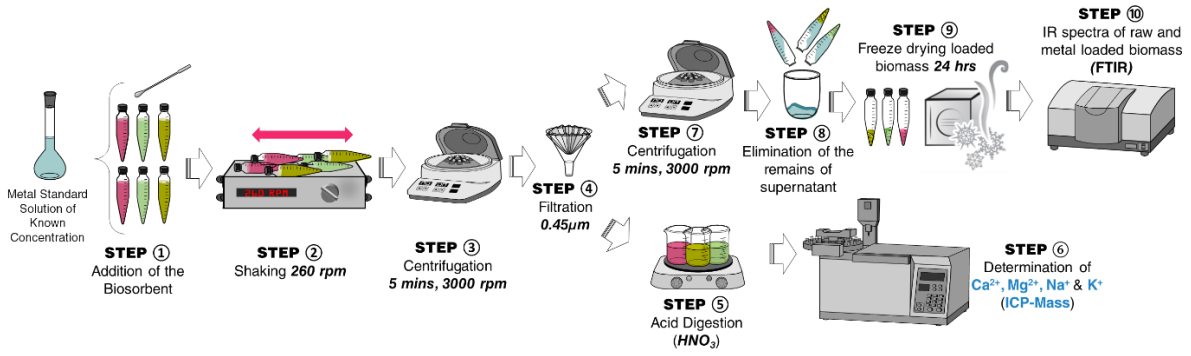

Figure 5.11 Scheme of the general process of the cation exchange experiments and FTIR analysis

5.6.7. SEM-EDX

Figure 5.12 shows the preparation process of the samples before the SEM-EDX analysis.

Natural and metal-loaded biomass were also examined by Scanning Electron Microscopy (SEM). The biomass (0.16 g) were exposed to a 100mg/L metal solution over a 1 hour period. Immediately after centrifugation and the elimination of the supernatant the algae were fixed in 2.5% of glutaraldehyde for 24 hours to prevent alterations in their structure through decomposition. Fixation is the first and most important step for optimum preservation of biological samples. A fixation process stops cellular processes and aims to preserve the specimen as close as possible to its natural state. Through fixation, the structure of the sample is stabilized so that it can withstand both subsequent processing steps and examination under the SEM (Kashi et al., 2014).

Glutaraldehyde was dissolved in a phosphate buffer solution. For preparing the phosphate buffer, initially, two solutions were made. Solution A (0.2M monobasic sodium phosphate solution): 31.21g of $NaH_2PO_4.2H_2O$ were dissolved in 1L of water. And solution B (0.2M dibasic sodium phosphate solution): 71.64g of $Na_2HPO_4.12H_2O$ were dissolved 1L with distilled water.

500 mL of 0.2M phosphate buffer stock solution were prepared by mixing 115 ml of solution "A" and adding 385 ml of the solution "B". After, the pH of the solution was adjusted to 7.4 using either solution "A" or "B". Finally, 10 mL of 50% glutaraldehyde solution for Electron Microscopy (FUJIFILM Wako Pure Chemical) were added to 100 mL of the phosphate stock solution. This was brought to a final volume of 200 mL with water.

SEM demands that water and organic fluids must be removed from samples. The term “dehydration” is used to describe the removal of water. It involves slow substitution of the water in the tissue with an organic solvent. Because biological materials are predominately composed of water, dehydration is potentially a very disruptive. The most commonly used dehydrating agents are methanol, ethanol and acetone. The dehydration process is accomplished by passing the tissue through a series of increasing alcohol concentrations (Mogana and Patchamuthu, 2015). After fixated, samples were rinsed with 5 mL of fresh phosphate buffer solution (no fixative added) in the fume hood for three times. Then the buffer was replaced with 5 mL of 50% ethanol solution and samples were left in it for 1 hour and 30 minutes at 4°C. This was repeated with a solution of 60% ethanol. Subsequently, samples were soaked sequentially in 5mL of 70%, 80%, 90% and 100% ethanol solutions for 1 hour at 4°C. The 100% ethanol step was repeated once more. After this, samples were considered dehydrated and ready for drying. Dehydration must be conducted relatively rapidly in order to prevent excessive extraction of alcohol and acetone-soluble compounds, but slow enough to prevent plasmolysis (a contraction of the protoplast of a plant cell).

Proper preparation does not end after the dehydration. Before using the SEM, specimens need to be thoroughly dried. Most biological specimens require drying with a critical point dryer (CPD) to avoid collapse. If a CPD is unavailable, it may be practical

in some instances to use a less expensive alternative like a chemical drying agent. (Fischer et al., 2012).

We dried our samples using special grade 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) reagent from FUJIFILM Wako Pure Chemicals.

The 100% ethanol solution containing the samples was exchanged with 5mL of a 1:2 solution of HMDS: 100% ethanol and left for 20 minutes.

Followed by a replacement with 5 mL of a fresh solution of 2:1 HMDS: ethanol for 20 minutes. Lastly with 5mL of 100% HMDS for 20 minutes (two times). When the samples were submerged in the final 100% HMDS solution they were left covered loosely in a fume hood overnight (or the necessary time until dryness). The HMDS evaporated, leaving the samples ready for sputter coating and imaging in the SEM.

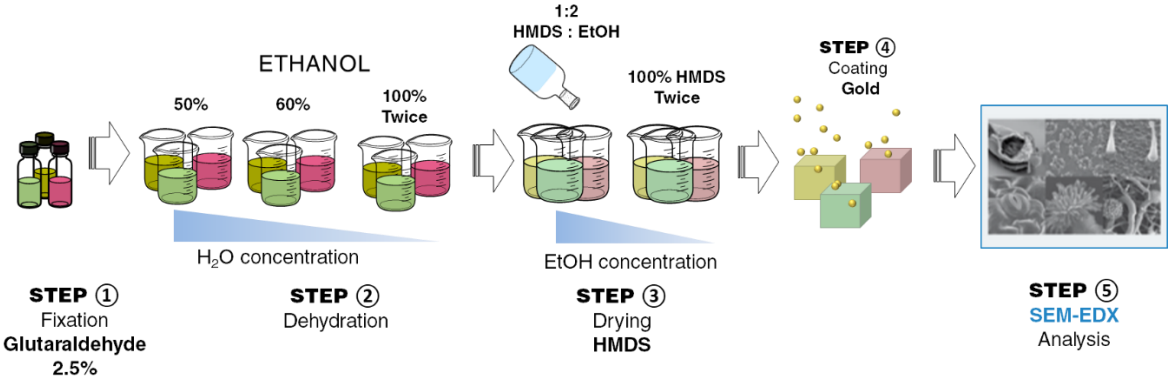

Figure 5.12 Experimental set-up for SEM-EDX analysis.

On a note of safety, HMDS vapor should not be breathed in, all steps involving HMDS chemical agent need to be carried out in the fume hood wearing the necessary personal protective gear as it is highly toxic. Any solution mixed with ethanol should not be stored in a closed bottle as vapor pressure can build up and cause an explosion (Kashi et al., 2014).

Due to the non-conductive nature of biological samples, their surface acts as an electron trap. This accumulation of electrons on the surface is called "charging" and creates extra-white regions on the sample's image. This can be avoided by applying an ultra-thin coating of electrically-conducting metal (gold, platinum, silver, etc) onto its surface. The sputter coating preparation technique can be used to improve image quality and

resolution. The algal samples were placed on carbon tape and pasted to the appropriate mount, and were gold-sputtered at 1kV and 10mA for about 3 minutes.

Samples were observed and photographed with a Scanning Electron Microscope, operating at 15 kV. The microscope was equipped with an energy dispersive X-ray system in order to obtain information on elemental composition of the surface of the algae.

5.6.8. Chemical Modification of the Biomass

Chemical modification techniques are also of value in characterizing the functional groups responsible for metal binding (Gardea-Torresdey et al., 1990)(Tobin et al., 1990).

The dried and powdered biomass was subjected to the chemical treatments for modifications as described below. The modified biomass was lyophilized before use.

After modification, 0.16g of the biomass were shaken for 1 hour in a 2mg/L solution (pH 5) of the three target metals. Samples were centrifuged, filtered and digested. Their residual concentration was quantified with the ICP.

5.6.8.1. Esterification of the Carboxylic Acids

Two grams of raw biomass were suspended in 130 mL of anhydrous methanol and 1.2 mL of concentrated hydrochloric acid (HCl) were added to suspension. The mixture was agitated on a rotary shaker for 6 h at 125 rpm (Yan and Viraraghavan, 2008). The resulting reaction takes place as follows:

$$\overline{\mathrm{R}}\mathrm{COOH} + \mathrm{CH_3OH} \overset{\mathrm{H^+}}{\rightarrow} \overline{\mathrm{R}}\mathrm{COOCH_3} + \mathrm{H_2O}$$

Where $\overline{\mathrm{R}}$ denotes the organic network of the biomass molecules. Although it is well known that metal ions can coordinate to esters, the binding ability should be greatly reduced and a marked decrease in metal uptake should occur.

5.6.8.2. Methylation of Amines

The Eschweiler–Clarke reaction (also called the Eschweiler–Clarke methylation) is a chemical reaction whereby a primary (or secondary) amine is methylated using excess formic acid and formaldehyde.

Two grams of biomass were heated under reflux with 40 mL of formaldehyde (HCHO) and 80 mL of formic acid (HCOOH) (Panda et al., 2006). The resulting reaction occurs as follows:

$$\overline{R}CH_2NH_2 + \xrightarrow{HCHO,HCOOH} \overline{R}CH_2N(CH_3)_2 + CO_2 + H_2O$$

Because of the methylation of the amino groups, their participation in metal biosorption is expected to be inhibited, resulting in a reduction in the metal biosorption capacity on the residual biomass.

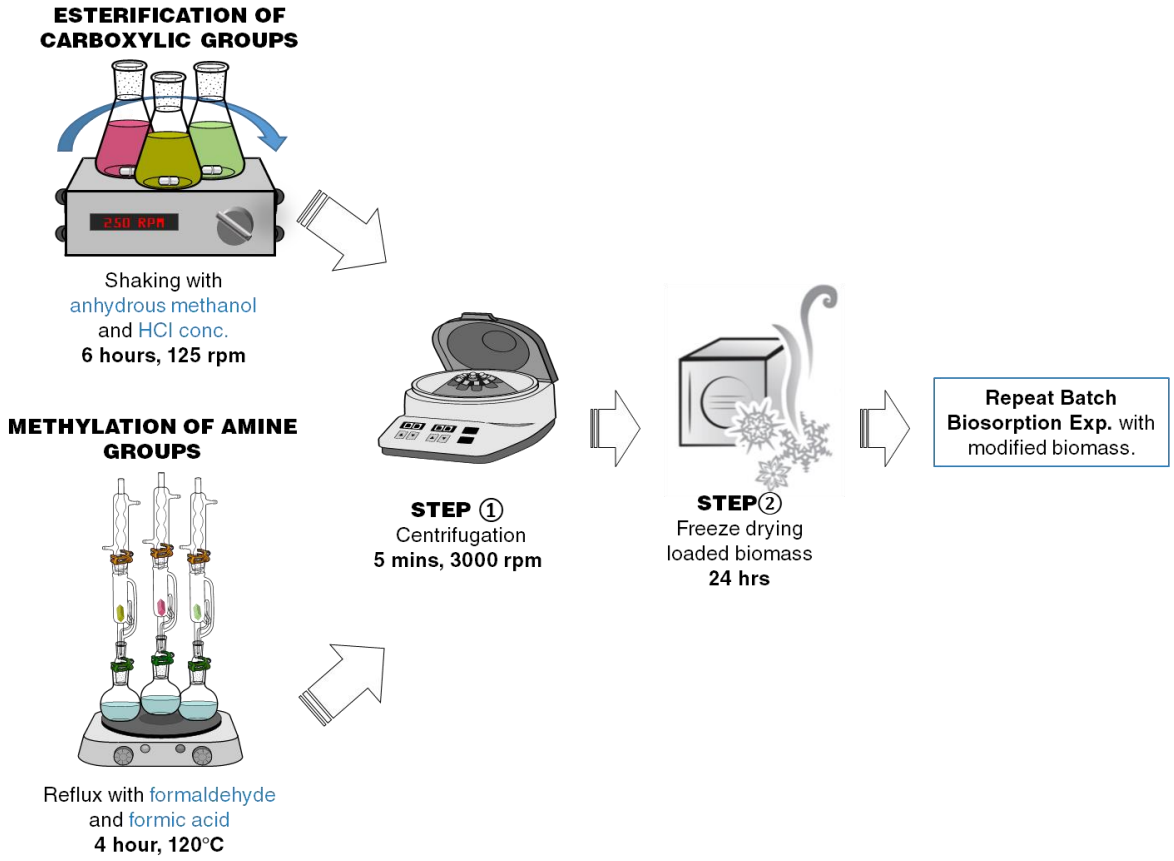

Figure 5.13 Experimental arrangement for the chemical modification of functional groups.

5.6.9. Desorption Experiments

For the desorption study, 0.50 g biomass was contacted for 1 hour with a 50 ml metal solution (25 mg/L) at pH 5 and 25°C temperature. After adsorption experiment, the biomass was collected by filtration and washed with distilled water for three times, to remove residual metal on the surface. Then it was transferred to 50 ml of 0.2M HCl the desorbent solutions. The mixture was shaken for 1 h, then the filtrates were analyzed to

determine the metal concentration after desorption. Desorption ratio was calculated from the amount of metal ions adsorbed on the biomass and the final metal ion concentration in desorption medium, as the following equation:

$$\text{Desorption ratio} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions absorbed}} \times 100$$

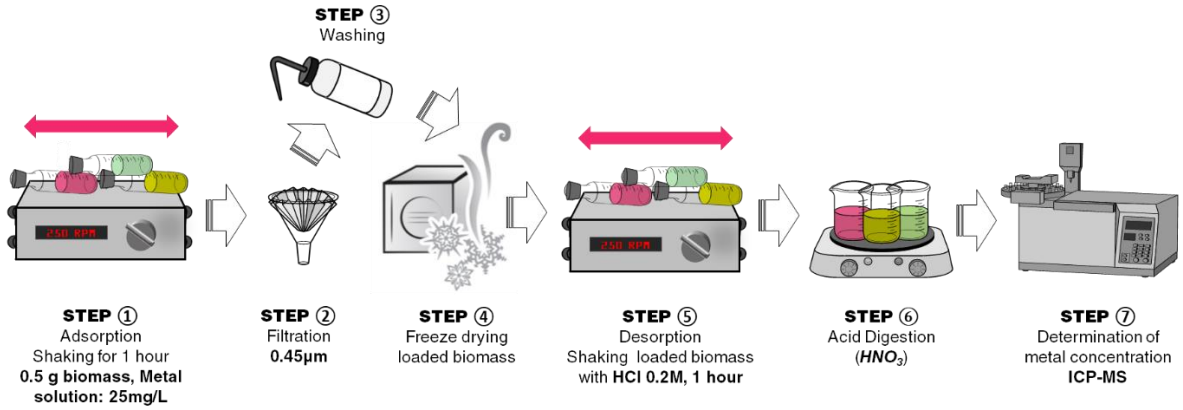

Figure 5.14 Experimental scheme of the desorption process.

5.7. Results and Discussion

5.7.1. Ion Exchange Experiments

The multi-elemental analysis of the solution after biosorption revealed the presence of cations (that were not present in the solution before the process). When heavy metal ions appeared in the solution, cations of other metals and protons were exchanged from the binding places with the heavy metal ions

The detected ions in the remaining aqueous solutions after the sorption processes were Na^+, K^+, Mg^{2+} and Ca^{2+}. It was attempted to establish a relation between the removed metals with the cations found in the aqueous solution after the equilibriums were reached. Figure 5.15 shows the sum of meq of the cations in the aqueous solutions vs. meq of cadmium removed by the different biomass. Initially, the released ions' concentration was higher than the removed cadmium (funori and ogonori), after the (a)
released ions and cadmium removed were similar. This correlation was kept between funori cations and cadmium.

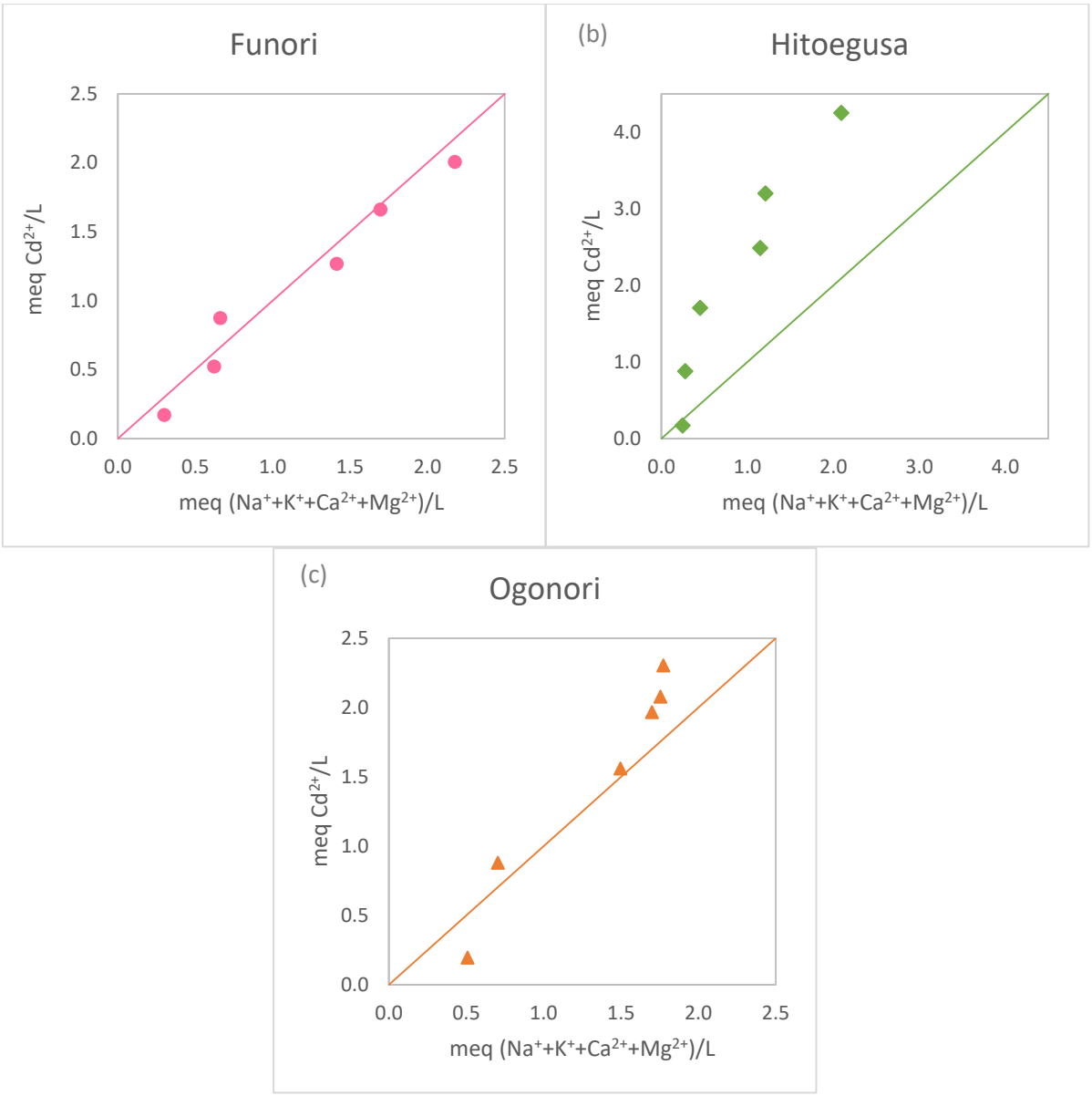

Figure 5.15 Correlation between the cadmium removed from the aqueous solution by (a) funori (b) hitoegusa (c) ogonori and the cations released from the biomass after 1 hour biosorption. Conc. range: 2-300 mg/L; biomass dosage: 4 g/L; contact time: 1h; pH: 5; temperature: 25 ◦C

However, for ogonori at the cadmium removed concentration was higher than released ions. The diagonal line indicates the ideal proportional relation 1:1 between metal uptake and sum of ions released. On the other hand it seems like the amount of removed cadmium by ion exchange with hitoegusa is lower than funori and ogonori; **Figure 5.15(b)** shows that the cadmium removal was higher than the sum of ions released by hitoegusa. This quantity of released ions indicates that approximately 50.7% of the initial Cd^{2+} in a 300 mg/L (5.34 meq/L) solution was exchanged with the ions released from the hitoegusa. The cadmium must be removed by other mechanism since the

removal was higher than the ions released; for this reason the data do not adjust to the diagonal line.

The process can be visualized as follows: the alkali and alkaline earth metal ions (especially K^+, Ca^{2+}, and Mg^{2+}) are initially bound onto the organic functional groups in the algae. When the heavy metal ions (Cd^{2+}, Pb^{2+} and Zn^{2+}) are introduced into the solution, they compete with the alkali and alkaline earth metal ions for the adsorption sites (i.e., organic functional groups). As the binding strength (affinity) between alkali and alkaline earth metal ions for the adsorption sites (i.e., organic functional groups). As the binding strength (affinity) between the heavy metal ions and functional groups is greater than that be-tween the alkali and alkaline earth metal ions and functional groups, the heavy metal ions are adsorbed onto the biosorbent. The alkali and alkaline earth metal ions are meanwhile stripped from the biosorbent and released to the solution phase.

5.7.2. Potentiometric Titration

Figure 5.16 to **Figure 5.*18*** show the respective potentiometric curves of funori, hitoegusa and ogonori resulting from the addition of NaOH. The various amounts of acidic groups in the biomass and their corresponding pKa values were evaluated by identifying the inflection points of the titration curves. However, this can be quite difficult and a better indication of the position of these inflections was obtained from first derivative plots of average pH titration data (Figures 5.10, 5.11, 5.12(a)).

The first derivative plots consist of the midpoint of successive amounts of NaOH added (x-axis) versus dpH/dV (y-axis). The number of strong acidic groups was determined from the first peak in the first derivative plots (0.367, 3.671 and 0.112 mmol/g for funori, hitoegusa and ogonori, respectively) while the total number of acidic groups was determined from the final peak (1.374 for funori, 4.173 for hitoegusa and 1.217 mmol/g for ogonori)(Murphy et al., 2007). The number of weak acidic groups was then calculated by difference. Once these values were established, the corresponding pKa values were then identified from the original titration curve.

(a)

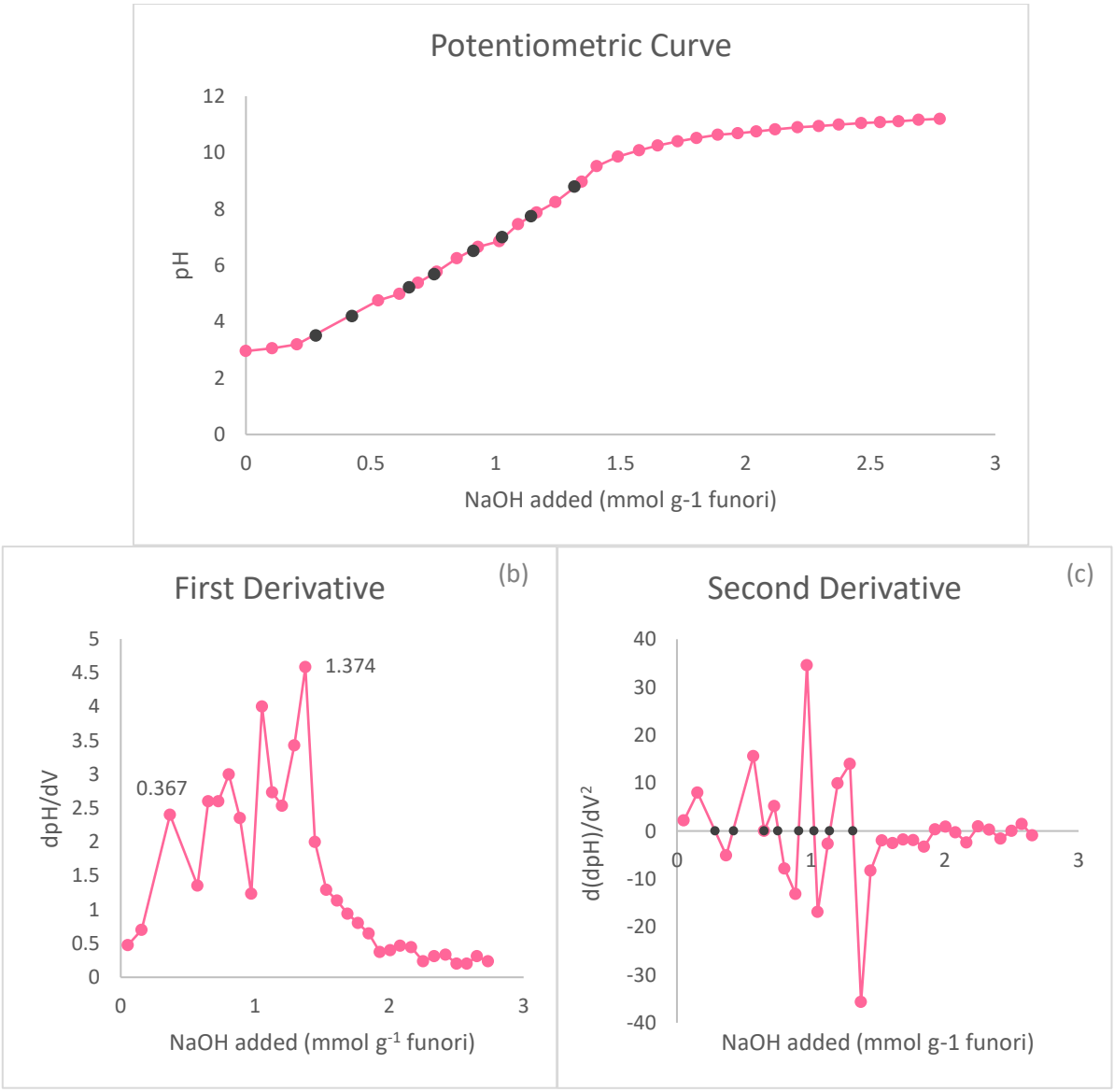

Figure 5.16 (a) Potentiometric curve (b) first derivative and (c) second derivative plots of titration data for funori.

Since the observed inflection points are also the maximum values of the first derivative of the titration curves (Herrero et al., 2005). The way to calculate a maximum point is to find the point at which the derivative of its equation equals zero.

Hence, all crossing points on the x-axis from the 2nd derivative curve, were chosen from the population of the added values. Each of those points represents an inflection in the first derivative. These points are probable functional groups for all measured pH at a pKa position.

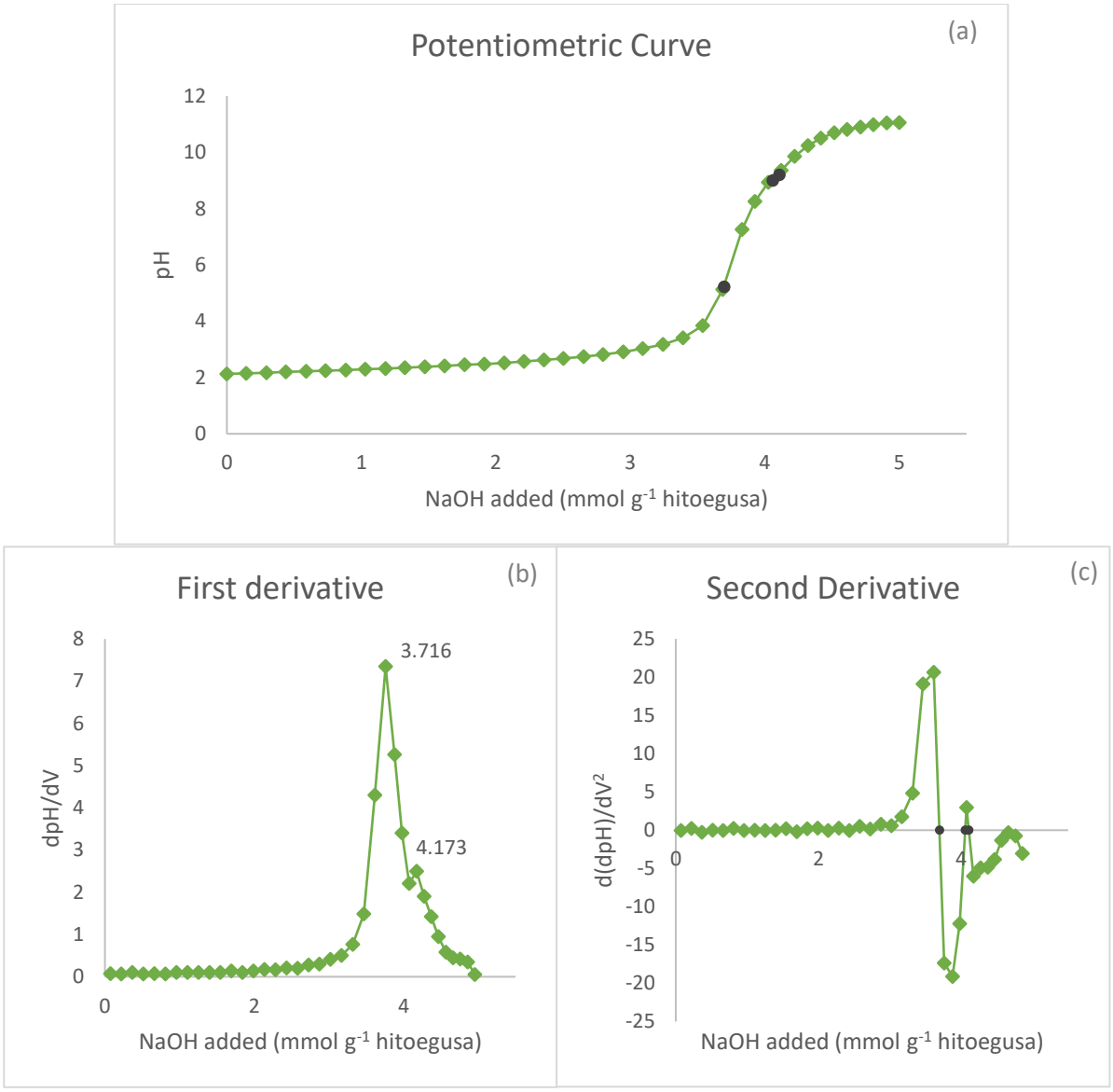

Figure 5.17 (a) Potentiometric curve (b) first derivative and (c) second derivative plots of titration data for hitoegusa.

Reading the location of each inflection point on the y-axis gave a potential pKa to each functional group respectively. The pKa value can directly give the approximate charged state of that functional group at a specific solution pH (Samoraj et al., 2015). The amount of functional groups contained on the cell surface and their pKa values determined by potentiometric titration are presented in

Table 5.3 and

Sulphate groups usually only contribute to metal binding at low pH and their typical pKa values are in the range 2–4 (Sheng et al., 2004). Apparent pK_a values in this range

were not detected by titration for funori and ogonori, but the presence of sulphonate groups on the surface of funori was later confirmed by FTIR analysis.

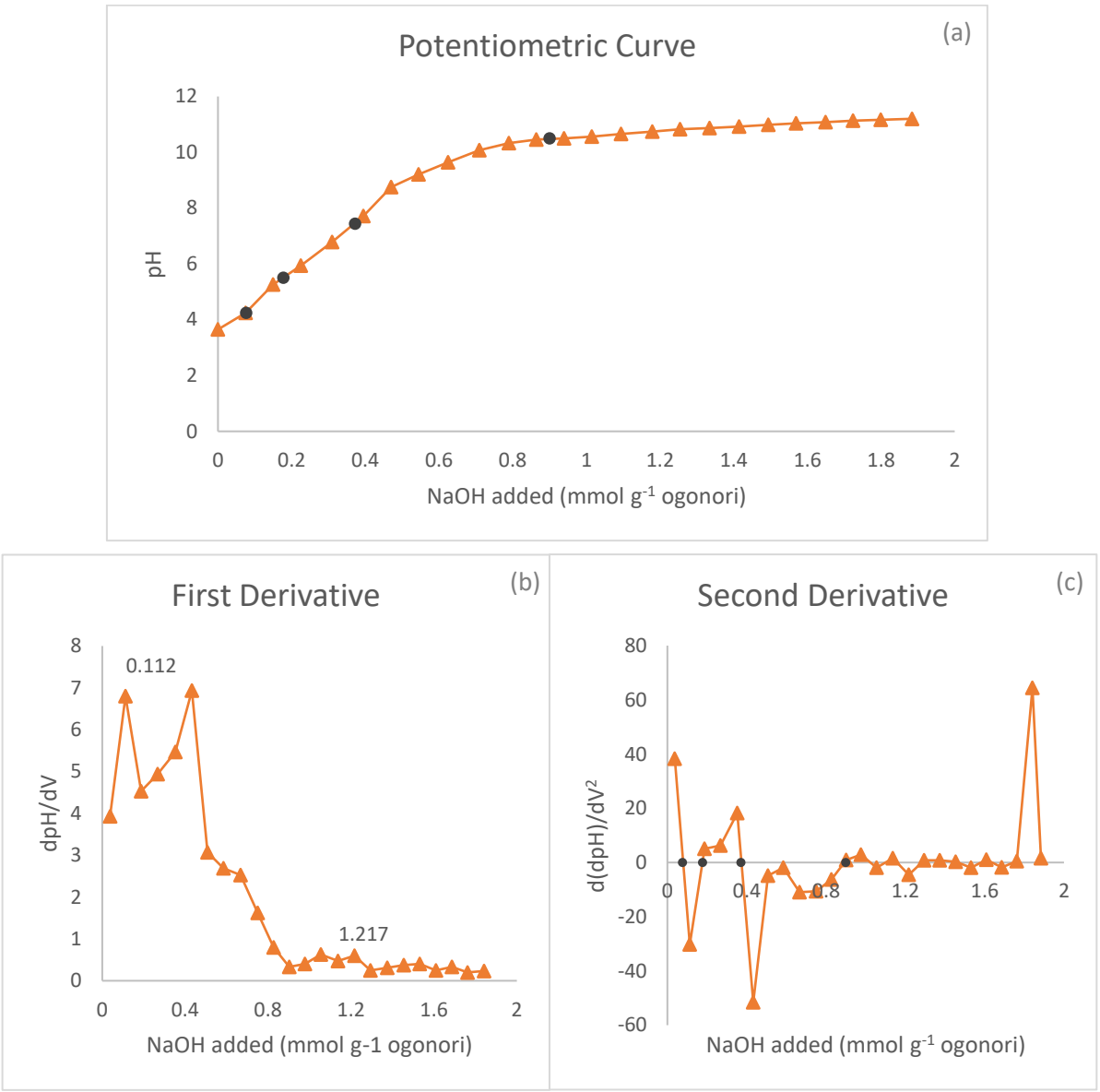

Figure 5.18 (a) Potentiometric curve (b) first derivative and (c) second derivative plots of titration data for ogonori.

Table 5.3 Quantity of funori, hitoegusa and ogonori acidic groups determined by titration

Algae	Quantity of acidic groups (mmol g⁻¹ biomass)		
	Total	Strong	Weak
Funori	1.374	0.367	1.007
Hitoegusa	4.173	3.761	0.412
Gracilaria	1.217	0.112	1.105

Table 5.4 Functional groups assigned to assumed pKa

Possible pKa			Binding Group	pKa	References
Funori	Hitoegusa	Gracilaria			
3.51	---	---	Sulphate, nitrate	2-4	1
4.20 5.22	4.8	4.24	Carboxyl	4-5	1
5.69 6.52	6.3	5.50	Thiol and phosphate	6-7	2
7.01	--	7.44	Phosphoryl	7	1
7.75 8.8	7.9 10.7	10.51	Amine and hydroxyl	8-13	2

1 (Samoraj et al., 2015), 2 (Naja and Volesky, 2011)

5.7.3. FT-IR

The infrared spectrum of a molecule is the result of the vibrations of the atoms within the molecule; the symmetry and bond strengths of the molecule as a whole determine the number and frequency of vibrations. When a metal molecule is adsorbed, it causes a change (even small), in the symmetry of the molecule, and any quantitative measure of this change can be directly related to the nature of adsorption. **If the molecule is physically adsorbed**, it is exposed mainly to weak intermolecular forces of the van der Waals and hence its symmetry is only slightly perturbed. Accordingly, **the infrared spectrum is altered only slightly, and small frequency shifts, usually less than 1%, are observed**. **During chemisorption process, however**, the symmetry of the molecules in the surface becomes completely different, the surface bond is very strong and the adsorption maybe dissociative in nature. In this case, **a completely new infrared spectrum is observed and band shifts** and intensities are far removed from those of the adsorbate and adsorbent (Hair, 1967).

When using FTIR in the past to investigate the mechanism of gold and cobalt biosorption by the biomass of brown algae *S. natans* and *A. nodosum* (Kuyucak and Volesky, 1989). No significant conclusions could be drawn at that time. However, the

samples used, referred to as "free biosorbent", were the untreated raw biomass actually loaded with the alkali and alkaline earth ions (Na^+, K^+, Mg^{2+}, and Ca^{2+}) initially present in seawater. For this reason, no obvious variation could be detected between the "raw" biomass and cadmium-loaded biosorbent. Consequently, in the present work, the protonated algal biomass was chosen as a free biosorbent control (rather than untreated biomass), for the comparison with the spectra of metal loaded algae. The wavenumber positions where functional groups adsorb are consistent, despite the effect of temperature, pressure, sampling, or change in the molecule structure in other parts of the molecules.

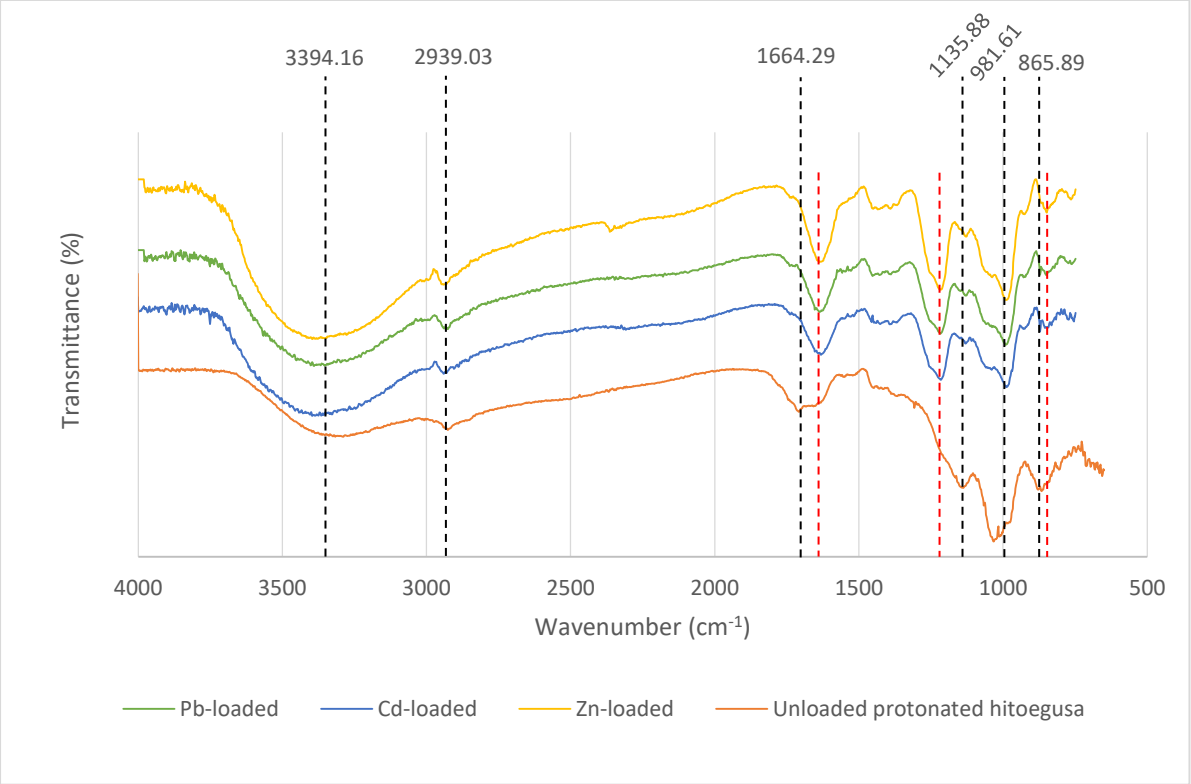

Figure 5.19 FTIR spectrum of raw and metal loaded Hitoegusa

The IR spectrum of the protonated hitoegusa (Figure 5.19) showed a signal at 3394.16 cm^{-1} from the stretching vibration of O–H and at 2939cm^{-1} due to stretch vibration of C–H. In addition, signals at 1664.29 cm^{-1}, belongs to the asymmetric stretch vibration of COO- of uronic acids; and 1135.88 cm^{-1}, to symmetric stretch vibration of C–O within COOH (Segneanu et al., 2012). 981.61 cm^{-1} peak is from the stretching vibration of C–O. The spectrum also showed a band corresponding to sulfate ester: the peaks at 865.89

cm^{-1} derived from the bending vibration of C–O–S of sulfate in axial position (Mao et al., 2008).

From the spectra of the loaded biomass three absorbance peak shifts were observed. These changes were exactly the same for all three metals. The shifts of the peaks indicate that biosorption of cadmium, lead and zinc by hitoegusa also happens through chemisorption process. This is agreement with the results obtained from the ion exchange experiments. Bands at 1664.29 cm^{-1} and at 1135.88 cm^{-1} changed to 1623.80 cm^{-1} and 1214.95 cm^{-1} respectively, both signals belong to the carboxylic groups. The signal of the sulfate group was also affected by the attachment of the metal onto the surface of hitoegusa.

The FTIR spectrum of the protonated funori (**Figure 5.20**) revealed bands corresponding to stretching vibrations of O–H and C-H at 3280.37 cm^{-1} and 2939cm^{-1}.

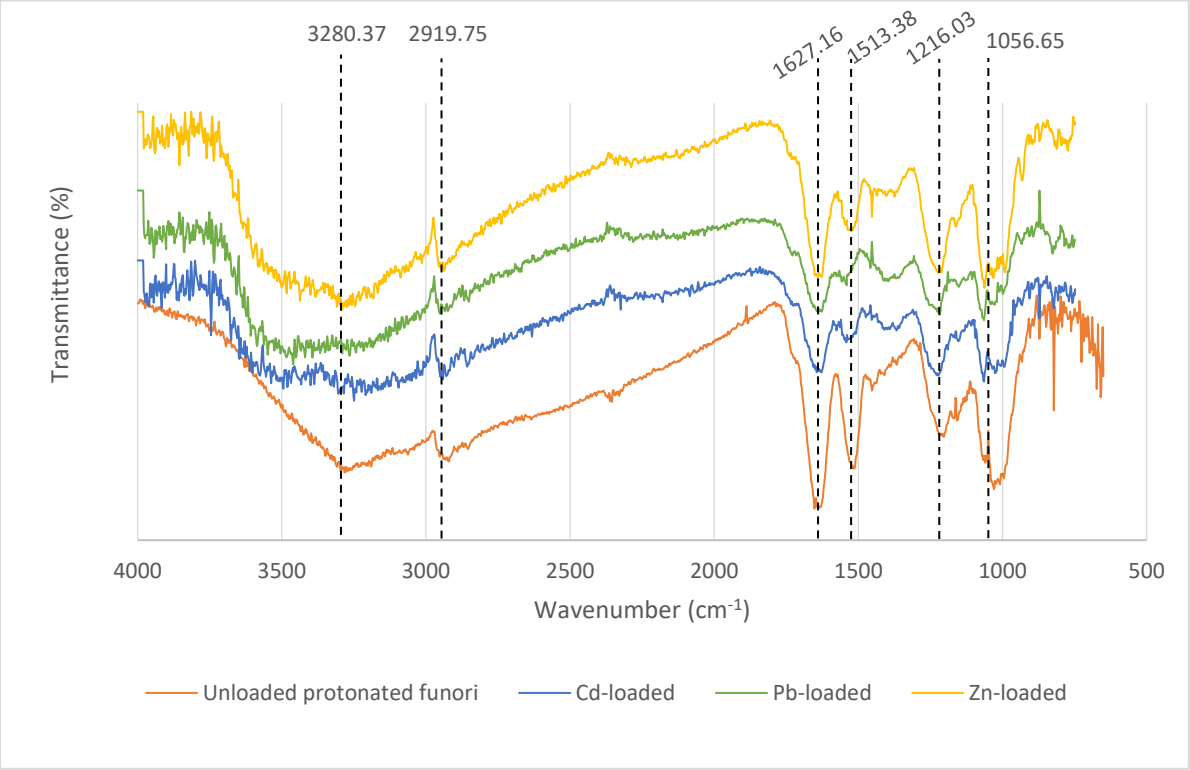

Figure 5.20 FTIR spectra of raw and metal loaded Funori

The signal at 1627.16 cm^{-1} is indicates the presence of carboxylic group (Segneanu et al., 2012). Also a band at around 1220 cm^{-1}, was identified which is indicative of the sulfate

ester substitution (Yu et al., 2010)(Gómez-Ordóñez and Rupérez, 2011). The signal at 1056 is attributable to C-O-C bridge of 3,6-AG residues (Tuvikene et al., 2015).

In a substitution process from one cationic salt by a cationic metal, the nature of the bond does not change, hence the frequency of its vibration should not either. And because the vibration is the same we cannot perceive any change between the spectrum from the raw and the loaded biomass. When a ligand coordinates to a metal atom M, new modes of vibration, not present in the free ligand, may become infrared active. In other words, metal complexation did not occur on the surface of funori since no changes were perceived between the unloaded and metal-loaded spectra **Figure 5.20**.

Most of the signals emitted in ogonori spectra are in the fingerprint region (500-1500 cm-1) (**Figure 5.21**). The spectrum of the unloaded ogonori showed peaks at 1639.11, 1149.96 and 1041.37 cm-1 which are due to amine (Rajan et al., 2015), carboxylic (Segneanu et al., 2012) and aliphatic amine (Radhika and Mohaideen, 2015) groups respectively. The spectra obtained after biosorption with ogonori similarly like the ones obtained for funori, do not showed shifts between the raw control and the metal loaded.

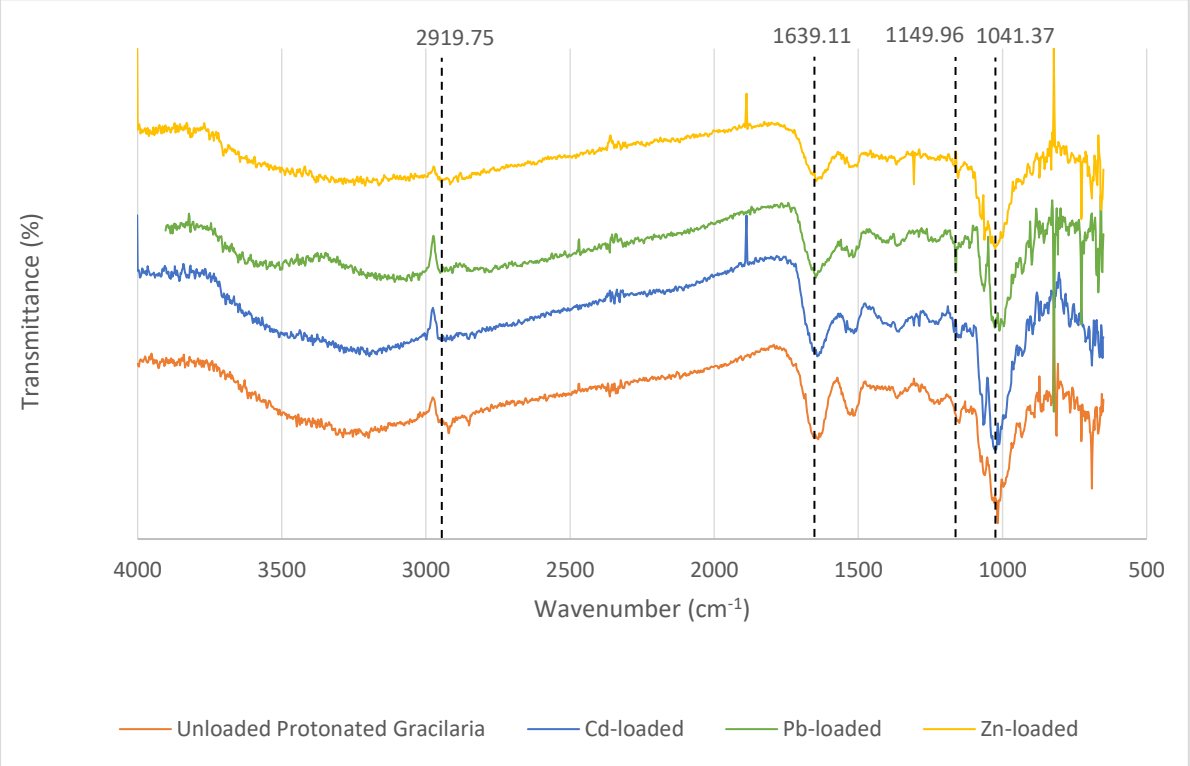

Figure 5.21 FTIR spectra of raw and metal loaded Ogonori

However, from the ion exchange experiments, we understood that despite there was a released of cations after the biosorption of metals with ogonori, the amount of the absorbed metals was higher than the released ions. For this reason we considered, even chemisorption did not occur there must be another mechanism beside cation exchange that causes the removal of metals when using ogonori.

5.7.4. SEM-EDX

Figure 5.22 shows the SEM image of the surface of the untreated and metal-loaded algae. Before the biosorption, the cell surface was smooth and even after the biosorption the surface became rough. General morphological changes of the shape were observed when comparing the metal loaded images with the image of the raw algae.

When a particle of a given volume is divided in parts, the total volume does not change. However, the specific surface area does change. It increases multiply by the amount of divisions. Hence, the smaller the particle size the larger the surface area is expected to be.

Table 5.5 Particle sizes and specific surface areas of funori, hitoegusa, ogonori

Algae	Particle size (μm)	Specific surface area (m^2/g)
Funori	549	0.14
Gracilaria	483	0.42
Hitoegusa	240	0.16

Among our data, the alga with the smallest particle size is hitoegusa, however the alga with the largest SSA is Ogonori (Table 5.5). When observing the SEM images of unloaded ogonori and hitoegusa a clear difference in their surface can be seem (Figure 5.22 IB, IC). Hitoegusa has a very smooth surface while ogonori has along and thin shape full of voids. The roughness of ogonori's surface, which is a sign of high porosity, explains its high surface area despite its particle size is bigger than the particles of hitoegusa and funori.

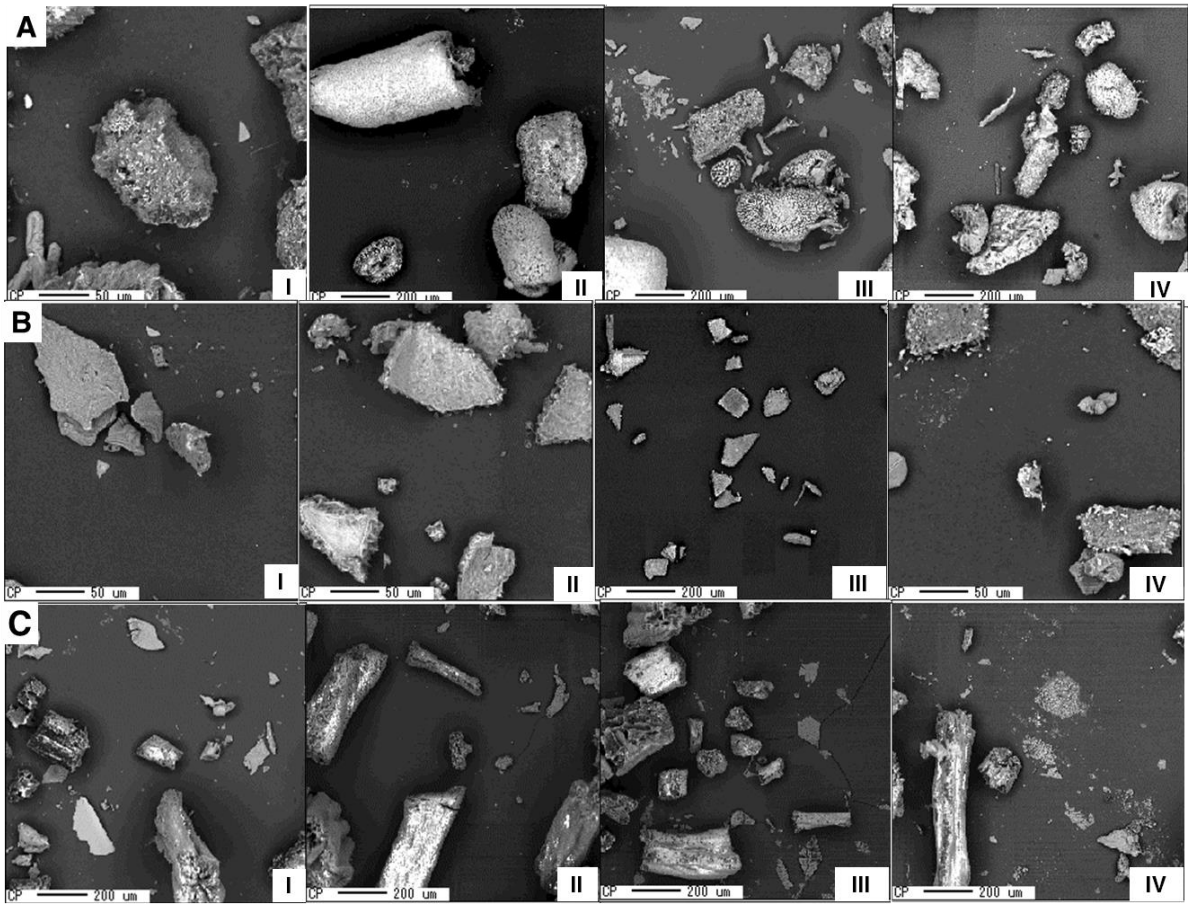

Figure 5.22 SEM images of the raw and metal loaded algae (A) Funori before biosorption (I) and loaded with Cd(II), Pb(II) and Zn(II) ions (II, III, IV), (B) Hitoegusa before biosorption (I) and loaded with Cd(II), Pb(II) and Zn(II) ions (II, III, IV), (C) Ogonori before biosorption (I) and loaded with Cd(II), Pb(II) and Zn(II) ions (II, III, IV).

The X-ray mapping (**Figure 5.23**) gave a visible evidence of metal ions on the cell wall of the seaweeds. Mapping images clearly showed that cadmium, lead and zinc ions were adsorbed on the surface of all three algae after biosorption. Specific localization of the metal ions on the surface of the algae was observed. All the tested algae showed qualitative and quantitative changes in the metals binding to the surface. The different concentration and localization of ions were indicated by appropriate colors

Before the biosorption, the EDX spectra of biomass revealed the presence of C, N, O, P, K, Na, Mg and Ca. The changes in the biomass of hitoegusa and funori observed after metal uptake included generally increases in carbon concentrations and decreases in sulfur, oxygen, calcium and magnesium. Ogonori on the other hand displayed increases of sulfur.

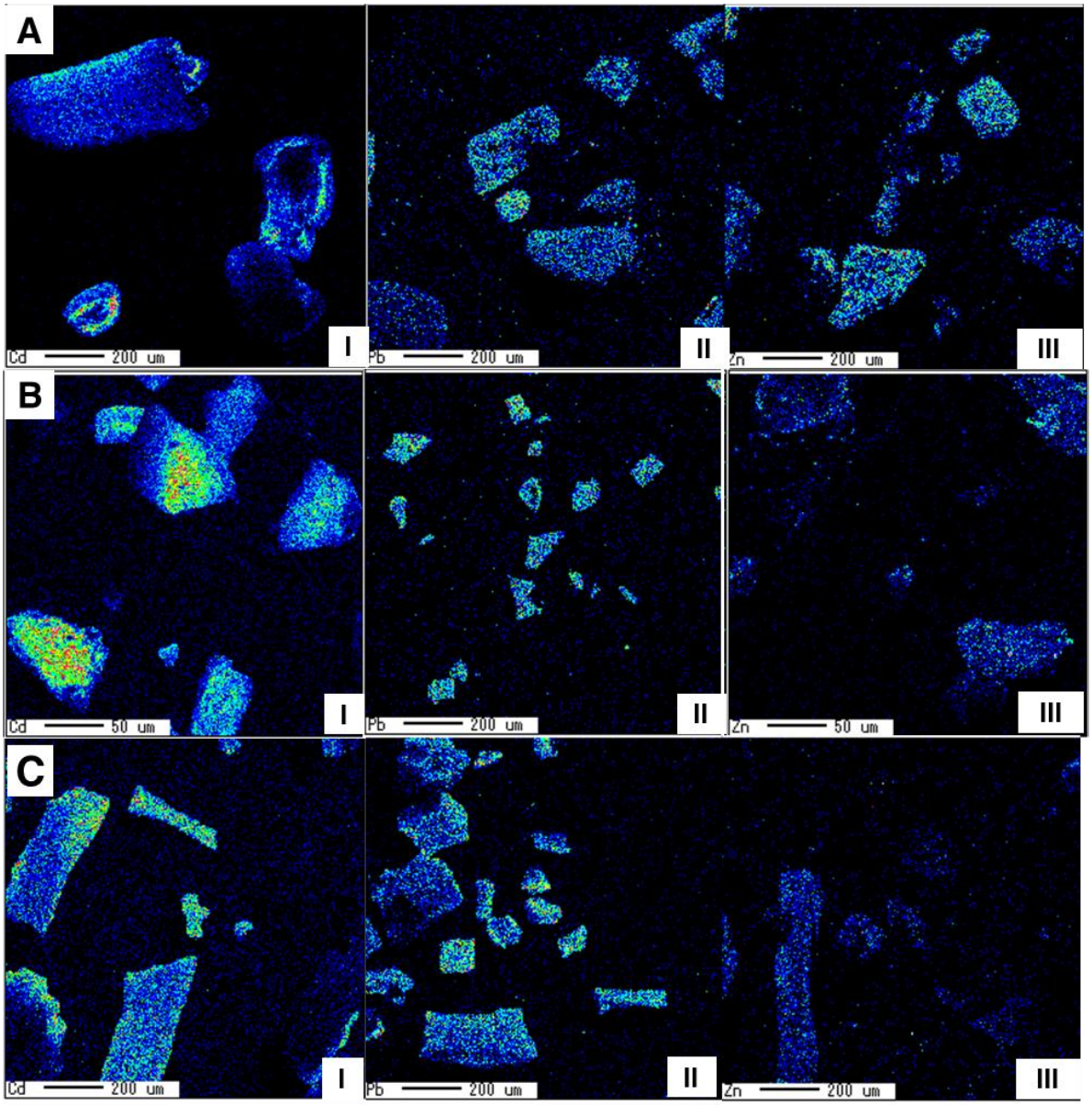

Figure 5.23 X-ray mapping of SEM images of the metal loaded algae (A)Funori (I) Cd-loaded, (II) Pb-loaded and (III) Zn-loaded, (B)Hitoegusa (I) Cd-loaded, (II) Pb-loaded and (III) Zn-loaded, (C)Ogonori (I) Cd-loaded, (II) Pb-loaded and (III) Zn-loaded.

While adsorbing cadmium, the peak of potassium disappeared from Hitoegusa biomass (Figure 5.24 and Figure 5.25). This further indicated that K was released in the process of the metal adsorption. Moreover, the distinctive peaks of cadmium, lead, and zinc on the cell surface of all three algae (Figure 5.26), indicates that the metals were absorbed onto the cells surface

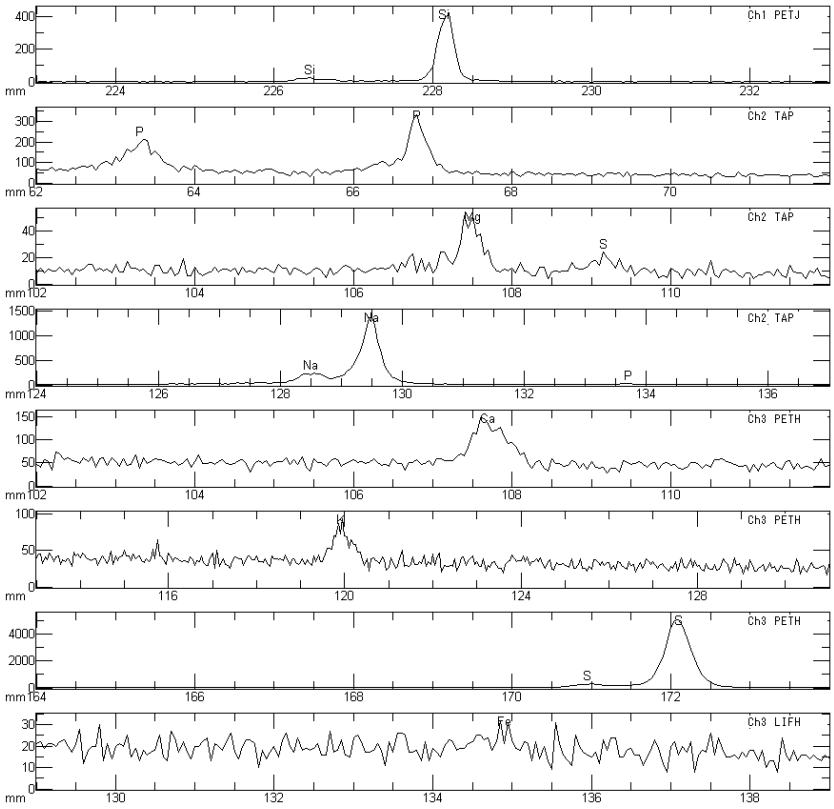

Figure 5.24 EDX spectra of Hitoegusa before biosorption. Identified peaks: Si, P, Mg, Na, Ca, K, and S

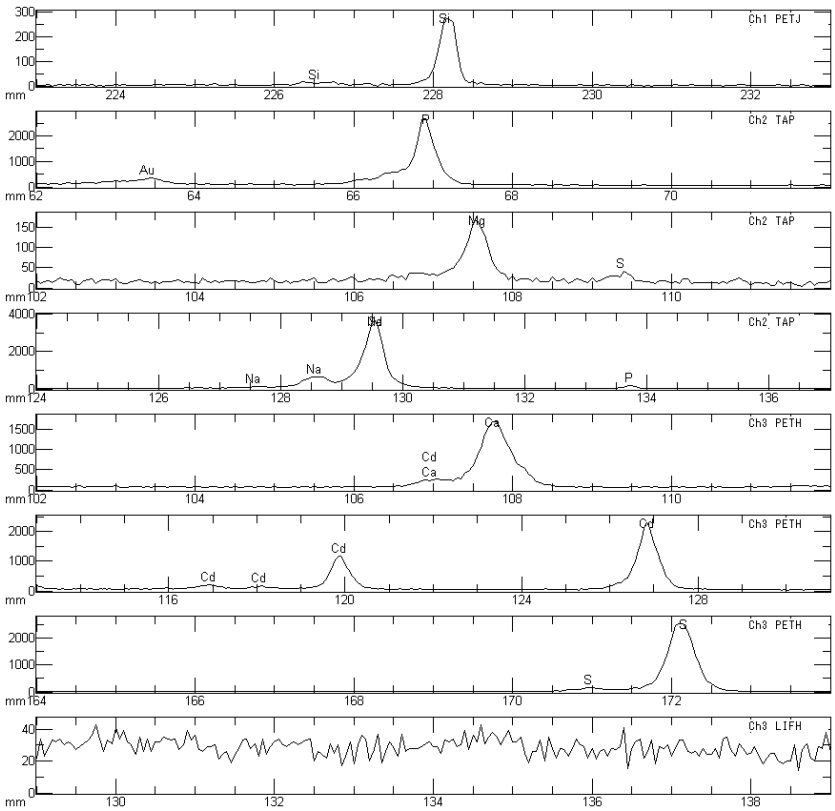

Figure 5.25 EDX spectra of Hitoegusa after cadmium biosorption. Identified peaks: Si, P, Mg, Na, Ca, Cd and S

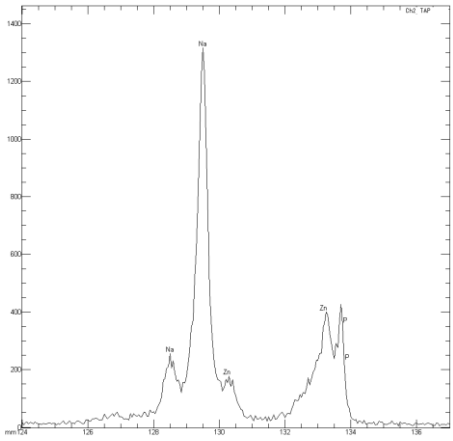

Figure 5.26 EDX spectra of Hitoegusa after zinc biosorption.

5.7.5. Chemical Modification

The results of experiments on chemically modified surface of the cell wall are shown in Table 5.6. In the case of metal biosorption by hitoegusa and funori we found that the process was hindered when carboxyl groups were esterified, showing their important role in the biosorption process, however blockage of the amine group had no effect in the biosorption by these two algae. When removing metals with ogonori, esterification of carboxylic groups and methylation of amines reduced its adsorption capacity for all the studied metals.

Table 5.6 Heavy metal adsorption capacity of untreated and chemically modified algal biomass.

Biomass	Metal	Untreated	Esterification of Carboxyl	Methylation of Amine
Funori	Cd	0.0042	0.0005	0.0042
	Pb	0.0022	0.001	0.0021
	Zn	0.006	0.0007	0.006
Hitoegusa	Cd	0.0045	0.001	0.0044
	Pb	0.002	0.001	0.002
	Zn	0.007	0.002	0.006
Ogonori	Cd	0.005	0.001	0.002
	Pb	0.0023	0.0013	0.0017
	Zn	0.007	0.002	0.003

When the carboxyl groups were esterified, the biosorption of Pb, Cd and Zn was significantly reduced. The reductions in Cd, Pb and Zn removals were 88.7 %, 66.0 %, and 89.5% for funori, of 97.8%, 72.2%, and 74.6% for hitoegusa and of 80.4%, 48.4%, and 75.7% for ogonori, respectively. The algae most affected by this modification was hitoegusa.

The diminution of the metal uptake after esterification carboxylic acids of can be compared to the contribution of carboxyl functional groups to the overall biosorption phenomenon. Analysis of the contribution of the carboxyl to the metal biosorption by the different algae revealed that the metal binding efficiency of carboxyl functional groups varies widely from a biomass to another. This variation certainly depends on the carrier polymer, the surroundings of the function, and the presence of other important complexing groups in the biosorbent material. The carboxyl groups are thus enclosed in various sites with different binding constants.

Reduction in metal biosorption was also observed for ogonori with methylated amino groups. The reductions reached 60.2%, 34.2%, and 57.9% for Cd, Pb, and Zn respectively, in the case of a methylation of the amino groups.

Carboxylic groups played a more important role than amine in the removal of metals by ogonori (**Figure 5.27**).

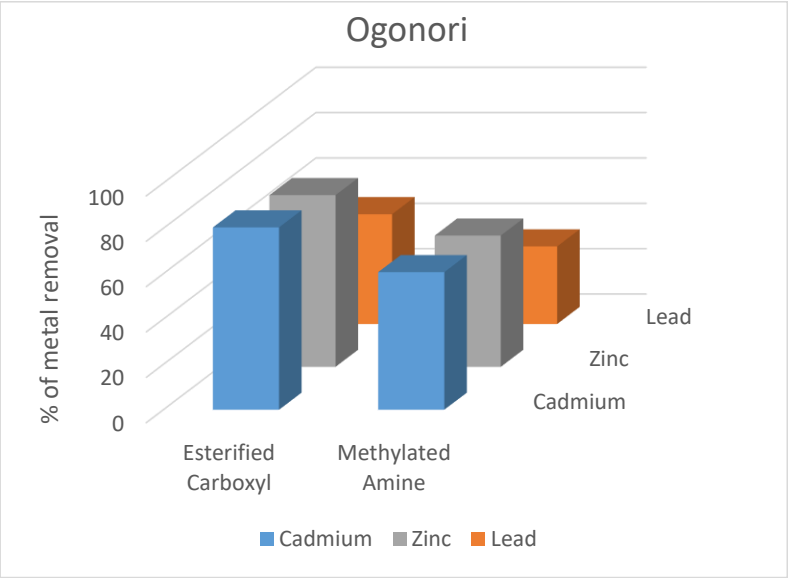

Figure 5.27 Reduction percentage of Cd(II), Zn(II) and Pb(II) adsorption capacities after biomass modification

The both modified biomass of ogonori did not increase the alkalinity of the solution as the untreated ogonori did. Initial pH was of 5 for both carboxyl and amine modificated biomass, after one hour contact, the final pH was in average of 3.39 and 3.59 for all metal solutions respectively. Since amines, like ammonia, are strong enough bases that they are completely protonated in dilute acid solutions. Blocking the amine group, made ogonori incapable of increasing the pH of the solution and hence the removal of the metals was also affected. This may possible to think that beside cation exchange mechanism ogonori can removed metals through precipitation because of the high alkalinity of its amines.

5.7.6. Desorption Experiments

Desorption is not only a useful tool to estimate the potential reusability of a biosorbent but also can provide important information regarding the mechanism of biosorption.

In adsorption through physisorption process the molecules of the substance are held by the surface of the adsorbent by weak forces of attraction (Van dar Waals forces) & there is no chemical reaction taking place between the adsorbent and adsorbate (substance to be adsorbed). On the other hand in chemisorption there is a chemical reaction between the adsorbate and adsorbent. The regeneration of physical adsorbed adsorbates is easy, but regeneration of chemisorbed molecules is difficult. Hence, a low percentage of recovery indicates chemisorption process. Ion exchange mechanism is thought to be reversible, and usually more than 90% of the adsorbed metal could be recovered through acid washing (Han et al., 2006).

When considering the choice of the eluent it is necessary to evaluate both efficiency of desorption and preservation of biosorption capacity of the biomass. If desorbent fulfills the assigned criteria it is possible to recover metal ions in the form of concentrated solution and to regenerate the biosorbent that can be used in another biosorption cycle (Chojnacka et al., 2005). After comparing different elution agents, several researchers have demonstrated that HCl is not only efficient in desorbing metal ions but is inexpensive as well (Aldor et al., 1995)(Vinok K. Gupta and Rastogi, 2008).

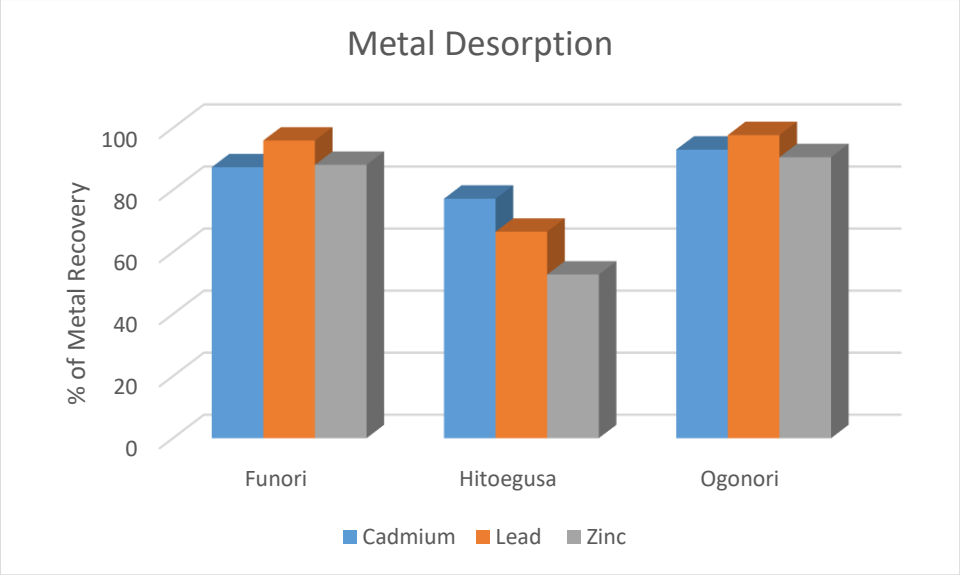

Figure 5.28 Effectiveness of metal desorption from funori, hitoegusa and ogonori using HCl 0.2M as eluent after 1 hour with a solid-to-liquid ratio of 10 g/L.

The metal release efficiencies from the biomass are shown in **Figure 5.28.**

The percentage of metal recovery followed the order of Pb>Cd>Zn. And the desorption efficiency of the biomass followed the tendency of ogonori> funori> hitoegusa for all three metals. The low percentage of metal recovery from the hitoegusa alga confirmed the result obtained from the FTIR analysis, metals were adsorbed into the surface by chemisorption at some degree. These results also supported the information obtained of the adsorption of metals by funori and ogonori through ion exchange mechanism.

Figure 5.29 summarizes the proposed mechanism based on the obtained results.

(Raize et al., 2004) reported that nickel biosorption mechanism on *Sargassum vulgaris* (brown alga), was mainly ion exchange. However, cadmium was mainly removed by chelation, and lead through the combination of ion exchange, chelation, and precipitation. Unlike Sargassum, the removal mechanisms of cadmium, lead and zinc was the same for each of our three algae. Probably because of the differences in the binding sites nature between algae species and their reaction with the metals. As for brown algae, *Sargassum vulgaris,* alginic acid and sulfated polysaccharides, acted as the main biding sites.

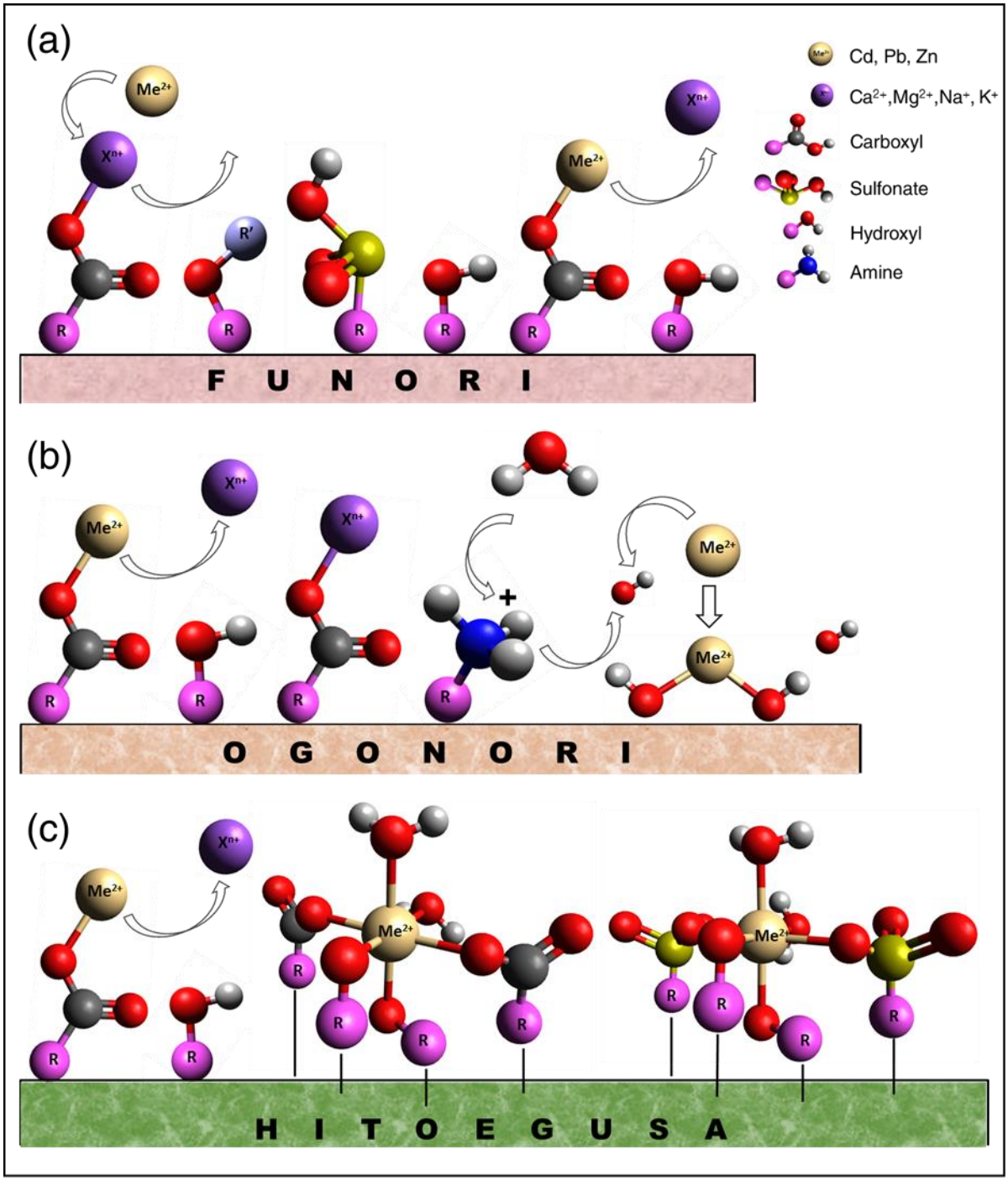

Figure 5.29 Proposed removal mechanism of (a) funori: ion exchange (b) Ogonori: ion exchange and precipitation and (c) Hitoegusa: ion exchange and chemisorption

Funori removed cadmium, lead and zinc in a similar way as Spirulina sp removed cadmium and copper (Chojnacka et al., 2005). The biomass has characteristics similar to weakly acidic ion-exchangers.

The most important characteristic of ogonori it is high alkalinity due to amine group.

Metal biosorption with hitoegusa was partly through a chemical bind and through

cation exchange. Cadmium on rice straw (Ding et al., 2012),manganese adsorbed by tomato husk (García-Mendieta et al., 2012) and cadmium, lead and zinc on agave bagasse (Velazquez-Jimenez et al., 2013) were removed by ion exchange and complexation too.

Table 5.7 Comparison of the predominant biosorption mechanisms of several metals from different types of biosorbents and the mechanism of Funori, Ogonori and Hitoegusa

Biosorbent	Type	Target metal	Mechanism	Functional Groups	References
Rhizopus oligosporus	Fungus	Pb(II)	Ion exchange, micro precipitation	nd	(Ariff et al., 1999)
Sargassum vulgaris	Brown macroalgae	Cd(II) Ni(II) Pb(II)	Cd: chelation, Ni: ion Exchange, Pb: ion exchange, chelation, micro precipitation	carboxyl, amino, sulfhydryl, and sulfonate	(Raize et al., 2004)
***Spirulina* sp.**	Blue-green algae	Cr(III),Cd (II),Cu(II)	Ion exchange, physisorption	Carboxyl, phosphate and hydroxyl	(Chojnacka et al., 2005)
Chlorella miniata	Green microalgae	Cr(III)	Complexation	Carboxyl, phosphate and amine	(Han et al., 2006)
Mucor rouxii	Fungus	Pb(II), Cd(II), Ni(II), Zn(II)	Ion exchange	Carboxylate, phosphate and amine	(Yan and Viraraghavan, 2008)
Microcystis	Blue-green algae	Sb(II)	Physisorption, complexation	Carboxyl, hydroxyl and amino	(Sun et al., 2011)
Auricularia polytricha	Fungus	Cd(II), Cu(II), Pb(II)	Ion exchange, complexation	Carboxyl, amine/hydroxyl, amino, phosphoryl	(Huang et al., 2012)
Rice Straw	Agricultural waste	Cd(II)	Ion exchange and complexation	Carboxyl and Hydroxyl	(Ding et al., 2012)
Green Tomato Husk	Agricultural waste	Fe(III), Mn(II)	Ion exchange and complexation	Carboxyl, hydroxyl, amides	(García-Mendieta et al., 2012)
Soybean Meal Waste	Agricultural waste	Cr(III), Cu(II)	Ion exchange, coordination and precipitation	Carboxyl and hydroxyl	(Witek-Krowiak and Harikishore Kumar Reddy, 2013)

Agave Bagasse	Agricultural waste	Cd(II), Pb(II) and Zn(II)	Ion exchange and complexation	Carboxyl, hydroxyl, sulfur and nitrogen	(Velazquez -Jimenez et al., 2013)
Hitoegusa	Green algae	Cd(II), Pb(II) and Zn(II)	Ion exchange and complexation	Carboxyl, hydroxyl, and sulfonate	This study
Ogonori	Red algae	Cd(II), Pb(II) and Zn(II)	Ion exchange and precipitation	Carboxyl and amine	This study
Funori	Red algae	Cd(II), Pb(II) and Zn(II)	Ion exchange	Carboxyl and hydroxyl	This study

5.8. Conclusions

Results showed that the biosorption of Cd(II), Pb(II) and Zn(II) by hitoegusa, funori and ogonori biomass differed between each alga.

SEM-EDX result confirmed visually and quantitatively the attachment of cadmium, lead, and zinc into the algal surface.

Metals were removed with funori predominantly by an ion exchange process through the release of Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} into the solution phase. The exchanging of cations from the biomass to the solution was also observed when using both, hitoegusa and ogonori. The FTIR spectrum of hitoegusa showed that the peaks of carboxylic and sulfate groups suffered shifts. Indicating metals complexes formed with these functional groups. Metal complexation did not occur when the ions were uptaken by funori and ogonori, since the FTIR results showed no change in the frequencies of the spectra between the raw biomass and the ones of the metal-loaded biomass. The carboxylic groups of hitoegusa and funori played a major role in the removal of all three metals.

The presence of amine in the surface of ogonori was confirmed through the potentiometric titrations and FTIR studies. Because of it, ogonori is highly alkaline favoring the removal of metal through precipitation too.

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Chapter 6

Final Remarks

1.1. General Conclusions

This study focused on the biosorption of As(III and V), Se(IV), Cd(II), Pb(II) and Zn(II) ions onto algal biomass (funori, hitoegusa and ogonori) from aqueous solution. Neither one of the algae was capable of removing the anionic metals (As and Se) in any degree. This is suspected to be related to the predominant biosorption mechanism of these algae. The operating parameters, pH of solution, contact time, and temperature, affected the biosorption efficiency of the cationic metals. The cationic metals (cadmium, lead, and zinc) reached the equilibrium rapidly within about 15 mins. Their kinetics followed the pseudo-second order model. Biosorption equilibrium of hitoegusa and funori was better described by the Freundlich isotherm model. Biosorption onto ogonori, on the other hand, was better described by the Langmuir model. The biosorption capacity of hitoegusa for Cd(II), Pb(II), and Zn(II) estimated by the Langmuir fit was found to be 67.1, 67.4 and 61.2 mg/g, and of funori was 59.3, 78.0, and 58.2 mg/g, respectively. The maximum adsorption capacity of Cd(II) and Zn(II) by ogonori were of 30.2, and 20.3 mg/g.

SEM-EDX results confirmed visually the attachment of cadmium, lead, and zinc into the algal surface. The biosorption of Cd(II), Pb(II) and Zn(II) by funori was predominantly based on an ion exchange mechanism through the release of Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} into the solution phase. We also observed that complexation of the metals ions with funori did not occur, since the FTIR results showed no change in the frequencies of the spectrums between the raw funori and the ones of the funori loaded with metal. The blockage of the carboxyl group in the funori biomass reduced its uptake capacity even up to 66%. Thus one of the main groups responsible for the uptake of Cd(II), Pb(II) and Zn(II) by funori is the carboxylic group.

The exchanging of cations from the biomass to the solution was also observed when using both, hitoegusa and ogonori. However, ion exchange was not the only mechanism involved in the removal of Cd(II), Pb(II), and Zn(II) by these two algae,.

The FTIR results of Hitoegusa showed shifts in the peaks of carboxylic and sulfate groups when adsorbing all three metals. An indication that chemical adsorption happened between them and the metals. That is why the esterification of its carboxylic groups resulted in a decreased of biosorption. The higher reduction in its adsorption after modification when compared with the other two algae was due to metals having a higher affinity to hitoegusa it was capable of bind ligands by chemical binding, and ionic interactions, while funori and ogonori bound the metals mostly by ionic interactions.

As with funori, metal ions did not form complexes with the functional groups present in the surface of ogonori either. The presence of amine in the surface of ogonori was confirmed through the potentiometric titrations and FTIR studies. Since amines are basic in water (under certain conditions), ogonori behaved as a strong base increasing the pH of the metal solutions to a point where not only cation exchange happened but metals were also eliminated by their precipitation in the form of hydroxides. Because of this, the methylation of the amine group of ogonori, reduced its removal efficiency significantly.

Since the prevailing mechanism of all algae was through a cation exchange phenomenon, the removal of anionic species as arsenic and selenium is not favored which explains why both algae biosorbents were unable to remove these metals from water.

1.2. General Recommendations

- When comparing the capacity of two or more metals by one same biosorbent, molar terms should be preferred (e.g. μmol/g, nmol/mg, etc).
- For an efficient removal of anionic metals with biosorption a pretreatment of the biomass is recommended (any physicochemical upgrade of the biomass). Further studies are necessary to evaluate the cost effectiveness of pretreatment at large scale.

- When using potentiometric tritations and FTIR to investigate the mechanism of a biomass it is recommended to use a protonated sample as control. When the untreated raw biomass, this it is already loaded with the naturally contained alkali and alkaline earth ions (Na^+, K^+, Mg^{2+}, and Ca^{2+}) uptake as nutrients from the seawater. This makes the quantification of acidic groups to be lower when titrating the biomass and also difficult to conclude about the actual mechanism when comparing the spectra since no changes will be observed.
- Considering the limitations detected in regards to the application of biosorption technique, future studies should aim to:
    - Investigate efficient immobilization methods for biomass that have already been proved as effective biosorbents. An evaluation of how the techniques may affect the biosorption rate and capacity of these sorbents and how much the implementation costs change the total costs are necessary. Instead of investigating the physicochemical characteristics of a non-yet-studied biomass.
    - Explore complex scenarios (multi-metal solutions). Since the final goal of any water treatment study is its application at an industrial level. Studies need to adjust to more realistic conditions like i.e. the co-existence of different pollutants.

A-1.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF CADMIUM

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
	Spirulina sp	Blue-green algae	—	The live biomass was sun dried for 48 h	Dirt particles were removed from algae by washing with water several times.	—	0.3	25		6	35-38	16	(Doshi et al., 2007)
Green coconut shell	*Cocos nucifera*	Agricultural waste	0.2-0.297	—	—	20-1000	0.5	100		7	27		(Pino et al., 2006)
	Ascophyllum nodosum	Macro algae (Brown)				10-200				4.9			(Holan et al., 1993)
Lemon peels		Agricultural waste	0.17-0.11	Oven dried at 38◦C-40◦C to constant weight (12h)		10-702	0.1			5.0	—		(Schiewer and Patil, 2008)
Orange peels		Agricultural waste	0.17-0.9	Oven dried at 38◦C-40◦C to constant weight (12h)	The fruit materials were washed three times with nano-pure water to remove extraneous materials.F ollowed by treatment with 0.1 N HNO3 for 6 h.	10-700	0.1			5.0	—		(Schiewer and Patil, 2008)
	Sargassum natans	Macro algae (Brown)								3.5			(Holan et al., 1993)
Spiral wrack / Flat wrack	*Fucus spiralis*	Macro algae (Brown)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	6	—	2	(Romera et al., 2007)
—	*Cystoseira barbata*	Macro algae (Brown)	0.6-1	Dried at 80 °C for 12 h	Algae was rinsed several times with deionize water. Then dried under sunlight, and then sieved to a size range 600–1000µm. A sample of biomass was soaked in 0.2M CaCl2 solution for 24h under slow stirring. The solution pH was fixed at pH 5.0. The calcium-treated biomass was washed several times using deionized water.	0-500	0.1	50	2	4.5	20	1	(Yalçin et al., 2012)
—	*Anabaena sphae rica*	Blue-green algae	0.2	Oven dry at 40°C, to constant weight	The algae was recultivated in BG11 medium containing the following macroelements: K2HPO4, MgSO4, CaCl2, citric acid, Na2CO3,Na2EDTA, and ferric ammonium citrate. he algal cultures were incubated at 24±2°C, under continuous illumination (2500 lux). The biomass was collected by centrifugation at 5000 rpm for 10 min. The algal biomass was washed with distilled water for five times.	50-300	0.2	100	2	5.5	25	1	(Abdel -Aty et al., 2013)
	Chlorella vulgaris	Micro algae (Green)	—	Dried at 60◦C	After 4–5 days of growth, the algal cells were centrifuged at 4000 rpm at laboratory tempera- ture for 5–6 min and then washed twice with double-distilled water and then was dried.	25-200	7.5	100		4.0	20	2	(Aksu, 2001)
Grapefruit peels		Agricultural waste	0.17-0.10	Oven dried at 38◦C-40◦C to constant weight (12h)	The fruit materials were washed three times with nano-pure water to remove extraneous materials.F ollowed by treatment with 0.1 N HNO3 for 6 h.	10-701	0.1			5.0	—		(Schiewer and Patil, 2008)

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Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
	Fucus vesiculosus	Macro algae (Brown)	<0.5	dried in an oven at 60 ◦C	The algae was collected by Algamar in the northern Atlantic coasts of Spain. The alga was washed and pulverized.	10-150	—	—	0.5	6.0	23	2	(Mata et al., 2008)
Usaba-aonori	*Enteromorpha linza*	Macro algae (Green)	0.6-1	Oven 60°C, 24h	The raw alga was rinsed several times with deionize water, dried under sunlight, and then sieved to a size range 600–1000μm. A sample of biomass was soaked in 0.2M CaCl2 solution for 24h under slow stirring. The solution pH was fixed at pH 5.0. The calcium-treated biomass was washed several times using deionized water.	10-1000	0.1	50	2	5	25	0.33	(Yalçin, 2014)
Makombu (DW)	Laminaria japonica	Macro algae (brown)	0.30-0.45	Before treatment: it was oven dried at 40°C, to constant weight	The powered biomass was washed with distilled water and dried in an oven at 60°C. To avoid the effect of salt, 10 g of powdered alga was suspended in 500 ml distilled water, stirred for 10 min. Then the biomass was separated by centrifugation. The process was repeated five times till the effluents became almost transparent. The washed biomass was then dried in an oven at 60°C until a constant weight was reached.	0 -725	0.02	15	1	5.2	20	2	(Liu et al., 2009)
Bushy Berry Wrack	*Cystoseira baccata*	Macro algae (Brown)	0.5-1	Oven dried at 60◦C overnight	The alga was washed with tap and deionized water to eliminate impurities.	10-350	0.1	40	2.5	4.5	25	4	(Lodeiro et al., 2006)
	Oedogonium sp.	Macro algae (Green)	0.063-0.105	Sun dried for 4 days followed by oven dry at 70 ◦C, 24h	Before use, it was washed with distilled water to remove dirt and was kept on a filter paper to reduce the water content.	20-200	0.1	100		5.0	25	0.92	(Gupta and Rastogi, 2008)
Knotted wrack / Norwegian kelp	*Ascophyllum nodosum*	Macro algae (Brown)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	6	—	2	(Romera et al., 2007)
	Galaxaura oblongata	Macro algae (Red)	500-850	dried at 60 ◦C for 24 h	Samples of the biomass were collected from the Mediterranean Sea at Abu Quir beach, Alexandria, Egypt, during summer season (July, 2009). The collected algae were rinsed thoroughly with distilled water in order to remove any adhering debris.				10	5	25	1	(Ibrahim, 2011)
	Chondracanthus chamissoi	Macro algae (Red)											(Yipmantin et al., 2011)
Gulfweed	*Sargassum sp.*	Macro algae (Brown)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.1	100	1	5.5	23	1	(Sheng et al., 2004)
	Padina sp.	Macro algae (Brown)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.1	100	1	5.5	23	1	(Sheng et al., 2004)

A-1.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF CADMIUM

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
Carrageen / Irish Moss	*Chondrus crispus*	Macro algae (Red)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	6	—	2	(Romera et al., 2007)
	Ulva sp.	Macro algae (Green)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.1	100	1	5.5	23	1	(Sheng et al., 2004)
	Ulva onoi	Macro algae (Green)											(Suzuki et al., 2005)
	Penicillium simplicissimum	Fungi	0.250	dried at 60 ◦C for 24 h	The strain was maintained on potato-dextrose agar slants and stored at 4 ◦C. The fungus was cultivated on a rotary shaker (120rpm) at 28 ◦C for 72h in 250ml conical Erlenmeyer flask containing 100ml of growth medium. The growth medium consisted of(g l−1): dextrose, 20;peptone,10;NaCl, 0.2; CaCl2, 0.1; KCl, 0.1;K2HPO4, 0.5;NaHCO3, 0.05; MgSO4, 0.25; FeSO4·7H2O, 0.005. The harvested biomass was washed with distilled water, dried, and powdered in a mortar, then was stored in a desiccator and used for the following experiments.	50-300	0.10	—	—	5.0	28	12.0	(Fan et al., 2008)
Rice husk (wet sorbent)	—	Agricultural waste	Between two sieves of 16 and 60 mesh	Before acid treatment: air-dried to constant weight	Wash, then air dried. 13Msulfuric acid were added to the rice husk and the mixture was heated to 175–180 ◦C for 20 min with occasional stirring. Filter and store in a diluted solution of H2SO4	25-250	0.1	100		6.0	45	2	(El-Shafey, 2007)
Rice husk (dry sorbent)	—	Agricultural waste	Between two sieves of 16 and 60 mesh	Before acid treatment: air-dried to constant weight. After	Wash, then air dried. 13Msulfuric acid were added to the rice husk and the mixture was heated to 175–180 ◦C for 20 min with occasional stirring. Filter and store in a diluted solution of H2SO4	25-250	0.1	100		6.0	45	2	(El-Shafey, 2007)
	Ulva lactuca (waste from oil extraction industry)	Macro algae (Green)	1-1.5	Oven 85°C, 24h	The green algae waste biomass, used in this study as biosorbent, was obtained after the solvent extraction of oil. The collected biomass was washed several times with double distilled water to remove impurities.	23-382	0.2	25	8	5	20	1	Bulgariu and Bulgariu, 2012)
—	*Gracilaria sp.*	Macro algae (Red)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.1	100	1	5.0	23	1	(Sheng et al., 2004)
	Pterocladia capillacea	Macro algae (Red)	500-850	dried at 60 ◦C for 24 h	Samples of the biomass were collected from the Mediterranean Sea at Abu Quir beach, Alexandria, Egypt, during summer season (July, 2009). The collected algae were rinsed thoroughly with distilled water in order to remove any adhering debris.				10	5	25	1	(Ibrahim, 2011)
Harpoon weed	*Asparagopsis armata*	Macro algae (Red)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the Mediterranean coast of Malaga, in southern Spain. The biomass was washed with distilled water several times. The overflow containing small particles was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.5	6	—	2	(Romera et al., 2007)

A-1.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF CADMIUM

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
	Jania rubens	Macro algae (Red)	500-850	dried at 60 ◦C for 24 h	Samples of the biomass were collected from the Mediterranean Sea at Abu Quir beach, Alexandria, Egypt, during summer season (July, 2009). The collected algae were rinsed thoroughly with distilled water in order to remove any adhering debris.				10	5	25	1	(Ibrahim, 2011)
Sea lettuce	*Ulva lactuca.*	Macro algae (Green)	0.5	Oven 60°C, 48h	The alga was washed with deionized water.	10-400	2	100	20	5	20	1	(Sari and Tuzen, 2008)
Grape stalks	—	Agricultural waste	1-1.5	Oven dried at 110◦C to constant weight	Grape stalk waste generated in wine production	4.4-505.1	0.1	15.0	6.7	5.5	20.0	2.0	(Martínez et al., 2006)
—	*Spirogyra insignis*	Macro algae (Green)	<0.5	Oven dry at 60°C, to constant weight	*S. insignis* , harvested from fresh water. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.1	100	1	6	—	2	(Romera et al., 2007)
—	*Codium vermilara*	Macro algae (Green)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	6	—	2	(Romera et al., 2007)
—	*Chaetomorpha sp*	Macro algae (Green)	2.0	First air dried for 24h, then oven dried at 80°C, to constant weight	The algae were washed twice with tap water and thereafter with double distilled water	20-80	0.1	—	—	—	—	2	(Nirmal Kumar et al., 2009)
—	*Valoniopsis pachynema*	Macro algae (Green)	2.0	First air dried for 24h, then oven dried at 80°C, to constant weight	The algae were washed twice with tap water and thereafter with double distilled water	20-80	0.1	—	—	—	—	2	(Nirmal Kumar et al., 2009)
—	*Gelidium sesquipedale*	Macro algae (Red)	0.25-1	Oven dried at 60◦C	Algae was air-dried to remove odours and most water for 2 days, next it was dried and sieved.	10-300	0.20	100	2	5.3	20	0.17-0.33	(Vilar et al., 2006)
Rice straw		Agricultural waste	<0.5	The powder was dried in an electrically heated blast dry	It was washed with distilled water, crushed with grinder, sieved with a standard sieve to obtain powder.	25-350	1	100		5	25	3	(Ding et al., 2012)
—	*Mucor rouxii*	Fungi	0.15	Dried at 60◦C for 24 h	The fungi was cultured in YPG medium (i.e., yeast extract (3 g/l), peptone (10 g/l), and glucose (dextrose) (20 g/l)). The pH of the growth media was adjusted to 4.5. Biomass was harvested by filtering the mixture of culture through a 150-mm sieve. The biomass collected was washed with distilled water. The cells were soaked in 0.2M NaOH solution for 30 min. Then, it was washed with deionized water until the pH of the wash attains the neutral range, i.e. The biomass was then autoclaved for 30min at 121C and 124 kPa and dried	10	0.01-.2	75	—	5.0	—	6	Yan and Viraraghavan, 2003)

A-1.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF CADMIUM

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
Sea lettuce	*Ulva lactuca*	Macro algae (Green)	2.0	First air dried for 24h, then oven dried at 80°C, to constant weight	The algae were washed twice with tap water and thereafter with double distilled water	20-80	0.1	—	—	—	—	—	(Nirmal Kumar et al., 2009)
—	*Pseudomonas putida*	Bacteria	—	Freeze-drying –40°C to –50°C and a pressure of 10mbar. Store at –3 °C in the darkness until use.	Cells were grown in flasks at 30 °C with shaking at 200 rpm for 24 h. The growth media for the experiments were Tryptic Soy Agar (TSA) from Merck, prepared by dissolving 40 g in 1L deionized water (pH 7.3 at 37 °C), and Tryptic Soy Broth (TSB) from Biolife prepared by dissolving 30 g in deionized water to total dissolution (pH 7.3 at 37 °C). These growing media were sterilized in an autoclave at 121°C for 20min before inoculation.	0-1000	0.1	100	1	6	30	0.17	(Pardo et al., 2003)
—	*Caulerpa lentillifera*	Macro algae (Green)	0.841-2	Dried at 80 °C for 12 h	The alga was washed.	10-350	0.5	30	16.7	5.0	23	1	(Pavasant et al., 2006)
—	*Cladophora fascicularis*	Macro algae (Green)	2.0	First air dried for 24h, then oven dried at 80°C, to constant weight	The algae were washed twice with tap water and thereafter with double distilled water	20-80	0.1	—	—	—	—	2	(Nirmal Kumar et al., 2009)
—	*Caulerpa sertularioides*	Macro algae (Green)	2.0	First air dried for 24h, then oven dried at 80°C, to constant weight	The algae were washed twice with tap water and thereafter with double distilled water	20-80	0.1	—		—	—	—	(Nirmal Kumar et al., 2009)
Sugar beet pulp		Agricultural waste	0.15-0.2	Oven dried at 100◦C to constant weight	It was extensively washed with tap water to remove soil and dust.	—	0.4	50		5.3	25	1.17	(Pehlivan et al., 2008)

A-1.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF CADMIUM

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
	Spirulina sp	Blue-green algae	355	—	—	—	1.2	—		sulphonic, carboxylic (fatty acid and amino acids), phosphate, amide, hydroxyl (polysaccharide)	?	(Doshi et al., 2007)
Green coconut shell	*Cocos nucifera*	Agricultural waste	286	0.019	0.981					?	?	(Pino et al., 2006)
	Ascophyllum nodosum	Macro algae (Brown)	215		0.990						?	(Holan et al., 1993)
Lemon peels		Agricultural waste	209.08	0.002	0.88						?	(Schiewer and Patil, 2008)
Orange peels		Agricultural waste	150.63	0.001	0.35						?	(Schiewer and Patil, 2008)
	Sargassum natans	Macro algae (Brown)	132		0.99							(Holan et al., 1993)
Spiral wrack / Flat wrack	*Fucus spiralis*	Macro algae (Brown)	114.9	0.11	0.99	—	—	—	—	?	?	(Romera et al., 2007)
—	*Cystoseira barbata*	Macro algae (Brown)	114.4	0.033	0.992	—	—	—	pseudo second order k2:0.34 g/mgmin, qe:0.70 mg/g, r2:0.999	Amide, Carbonyl	*BD	(Yalçin et al., 2012)
—	*Anabaena sph aerica*	Blue-green algae	111.1	18.88	0.980	15.31	0.39	0.991	—	Amino, Carboxyl and Hydroxyl	?	(Abdel -Aty et al., 2013)
	Chlorella vulgaris	Micro algae (Green)	111.1	0.025	0.993	8.23	0.49	0.983	pseudo second order k2:3410 g/mgmin, qe:62.5 mg/g, r2:0.999	?	?	(Aksu, 2001)
Grapefruit peels		Agricultural waste	110.16	0.005	0.93						?	(Schiewer and Patil, 2008)
	Fucus vesiculosus	Macro algae (Brown)	108.21	0.113	0.9972	—	—	—	—	?	?	(Mata et al., 2008)

A-1.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF CADMIUM

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
Usaba-aonori	*Enteromorpha linza*	Macro algae (Green)	107.1	0.031	0.996	10.97	0.39	0.964	—	carboxyl groups of alginic acid	*BD	(Yalçin, 2014)
Makombu (DW)	Laminaria japonica	Macro algae (brown)	104.5	0.014	0.972				—			(Liu et al., 2009)
Bushy Berry Wrack	*Cystoseira baccata*	Macro algae (Brown)	101	0.04	0.995	5.96	0.32	0.97	pseudo second order k2:0.008 g/mgmin, qe:56.21 mg/g, r2:0.9998	Carboxyl	*BD	(Lodeiro et al., 2006)
	Oedogonium sp.	Macro algae (Green)	88.2	0.019	0.995	4.894	0.6	0.934	pseudo second order k2:0.643 g/mgmin, qe:117.6 mg/g, r2:0.998	Amino, Carboxyl, Hydroxyl and Carbonyl	*BD	(Gupta and Rastogi, 2008)
Knotted wrack / Norwegian kelp	*Ascophyllum nodosum*	Macro algae (Brown)	87.7	0.15	0.99	—	—	—	—	?	?	(Romera et al., 2007)
	Galaxaura oblongata	Macro algae (Red)	85.5	0.0984	0.998							(Ibrahim, 2011)
	Chondracanthus chamissoi	Macro algae (Red)	85.4	0.19	0.987							(Yipmantin et al., 2011)
Gulfweed	*Sargassum sp.*	Macro algae (Brown)	85.4	0.101	0.94	—	—	—	—	Carboxyl, Ether, Amino	*BD	(Sheng et al., 2004)
	Padina sp.	Macro algae (Brown)	84.3	0.050	1.00	—	—	—	—	Carboxyl, Ether, Amino	*BD	(Sheng et al., 2004)
Carrageen / Irish Moss	*Chondrus crispus*	Macro algae (Red)	75.2	0.06	0.99	—	—	—	—	?	?	(Romera et al., 2007)
	Ulva sp.	Macro algae (Green)	65.2	0.013	0.98	—	—	—	—	?	*BD	(Sheng et al., 2004)
	Ulva onoi	Macro algae (Green)	61.9	0.021	0.984							(Suzuki et al., 2005)
	Penicillium simplicissimum	Fungi	61.4	0.02	0.981	9.032	0.37	0.90	—	?	?	(Fan et al., 2008)

A-1.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF CADMIUM

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
Rice husk (wet sorbent)	—	Agricultural waste	41.2	0.093	0.999	12.2	0.238	0.889	pseudo second order K2:0.00239 g/mgmin qe:28.249 mg/g, R^2:0.998	Carboxyl and Hydroxyl	ü	(El-Shafey, 2007)
Rice husk (dry sorbent)	—	Agricultural waste	38.8	0.087	0.998	11.7	0.233	0.916	pseudo second order K2:0.00139 g/mgmin, qe:26.171 mg/g, R^2:0.997	Carboxyl and Hydroxyl	ü	(El-Shafey, 2007)
	Ulva lactuca (waste from oil extraction industry)	Macro algae (Green)	34.61	0.014	0.987	—	0.82	0.942	pseudo second order k2:0.057 g/mgmin, qe:5.89 mg/g, r2:0.999	?	?	(Bulgariu and Bulgariu, 2012)
—	*Gracilaria sp.*	Macro algae (Red)	33.7	0.188	0.81	—	—	—	—	?	*BD	(Sheng et al., 2004)
	Pterocladia capillacea	Macro algae (Red)	33.5	0.0444	0.984							(Ibrahim, 2011)
Harpoon weed	*Asparagopsis armata*	Macro algae (Red)	32.3	0.09	0.96	—	—	—	—	?	?	(Romera et al., 2007)
	Jania rubens	Macro algae (Red)	30.5	0.0422	0.977							(Ibrahim, 2011)
Sea lettuce	*Ulva lactuca.*	Macro algae (Green)	29.2	0.07	0.997	7.8	0.9	0.981	pseudo second order k2:0.25 g/mgmin, qe:0.99 mg/g, r2:0.999	?	?	(Sari and Tuzen, 2008)
Grape stalks	—	Agricultural waste	27.9	0.062	0.983	0.212	0.457	0.91	pseudo second order k2:0.391 g/mgmin, qe:1.41 mg/g, r2:0.999	O H groups bound to methyl and methylene radicals; these groups are present on the lignin structure	?	(Martínez et al., 2006)
—	*Spirogyra insignis*	Macro algae (Green)	22.9	0.12	0.99	—	—	—	—	?	?	(Romera et al., 2007)
—	*Codium vermilara*	Macro algae (Green)	21.80	0.10	0.99	—	—	—	—	?	?	(Romera et al., 2007)
—	*Chaetomorpha sp*	Macro algae (Green)	20.4	0.371	0.690	—	0.38	0.482	—	?	?	(Nirmal Kumar et al., 2009)
—	*Valoniopsis pachynema*	Macro algae (Green)	18.9	0.358	0.97	—	0.30	0.811	—	?	?	(Nirmal Kumar et al., 2009)

A-1.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF CADMIUM

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
—	*Gelidium sesquipedale*	Macro algae (Red)	18.0	0.19	0.998	—	—	—	pseudo second order k2:0.9 g/mgmin, qe:42.4 mg/g, r2:0.989	?	?	(Vilar et al., 2006)
Rice straw		Agricultural waste	13.9	0.66	0.998	2.38	0.34	0.875		Hydroxyl, alkene, carboxylic acids	ü	(Ding et al., 2012)
—	*Mucor rouxii*	Fungi	8.4	2.67	0.72	6.81	0.08	0.57	pseudo second order k2:0.004 g/mgmin, qe:6.62 mg/g, r2:0.96	?	?	(Yan and Viraraghavan, 2003)
Sea lettuce	*Ulva lactuca*	Macro algae (Green)	8.3	0.121	0.725	—	0.30	0.583	—	?	?	(Nirmal Kumar et al., 2009)
—	*Pseudomonas putida*	Bacteria	8.0	6.85	0.999	—	—	—	—	?	?	(Pardo et al., 2003)
—	*Caulerpa lentillifera*	Macro algae (Green)	4.7	0.074	0.995	—	0.45	0.96	—	Carboxylic, Amine and Sulfonate	?	(Pavasant et al., 2006)
—	*Cladophora fascicularis*	Macro algae (Green)	4.6	0.321	0.733	—	0.11	0.03	—	?	?	(Nirmal Kumar et al., 2009)
—	*Caulerpa sertularioides*	Macro algae (Green)	2.7	0.264	0.203	—	0.31	0.042	—	?	?	(Nirmal Kumar et al., 2009)
Sugar beet pulp		Agricultural waste	0.13	0.124	0.740	7.16	0.98	0.99		Carboxyl	*BD	(Pehlivan et al., 2008)

A-2.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF LEAD

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
—	*Mucor rouxii*	Fungi	—	The biomass was freeze-dried at 0◦C and at reduce pressure for 2 days.	After 24 h cultivation, 10 mL of the seed culture was then transferred to inoculate 100 mL PYG broth. The cultures were grown at pH 4.5 and temperature 25 o C on orbital shaker at 200 rpm for one week. The fungi biomass was then harvested by filtration, washed with water, resuspended and washed again	200.0		200	0.05-1.5	6.0	25	0.2	(Lo et al., 1999)
—	*Corynebacterium glutamicum*	Bacteria	—	Oven 60°C, 24h	The dried raw biomass was treated with a 1 M HNO3 solution for 24 h, thereby replacing the natural mix of ionic species with protons. The acid-treated biomass, designated as protonated biomass, was washed with deionized distilled water several times and thereafter dried at 60 ◦C in an oven for 24 h.	0-3936	0.25	50	5	5.0	20	—	(Choi and Yun, 2004)
—	*Turbinaria conoides*	Macro algae (brown)	0.7–1	60°C, at overnight	It was protonated using 0.1MHCl for 3 h. The samples were then washed in distilled water and dried at 60◦C overnight.	0-1000	0.20	100	2	4.5	30	—	(Senthilkumar et al., 2007)
Makombu (EC1)	*Laminaria japonica*	Macro algae (brown)	0.30-0.45	Before treatment: it was oven dried at 40°C, to constant weight	10g of powdered biomass was taken into a flask together with 150 ml of dimethyl sulphoxide (DMSO) and stirred for 24 h at room temperature. Then 20 ml of epichlorohydrin was added to the mixture to undergo the crosslinking reaction at 20 °C for 2 h. Twenty milliliters of 5M NaOH solution was added and stirred for 5 h at 50 °C. After cooling down to room temperature, it was filtered and washed with 70% aqueous 2-propanol followed by 0.5M HCl and finally with 70% aqueous 2-propanol to neutral pH. The sample was kept for dry in an oven at 60 °C overnight	0 -725	0.02	15	1	5.2	20	2	(Luo et al., 2006)

A-2.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF LEAD

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
Makombu (EC2)	*Laminaria japonica*	Macro algae (brown)	0.30-0.45	Before treatment: it was oven dried at 40°C, to constant weight	10g of powdered biomass was taken into a flask together with 150 ml of dimethyl sulphoxide (DMSO) and stirred for 24 h at room temperature. Then 20 ml of epichlorohydrin was added to the mixture to undergo the crosslinking reaction at 20 °C for 2 h. Twenty milliliters of 5M NaOH solution was added and stirred for 5 h at 50 °C. After cooling down to room temperature, it was filtered and washed with 20% aqueous 2-propanol followed by 0.5M HCl and finally with 20% aqueous 2-propanol to neutral pH. The sample was kept for dry in an oven at 60 °C overnight	0 -725	0.02	15	1	5.2	20	2	(Luo et al., 2006)
Bull Kelp (DP95Ca)	*Durvillaea potatorum*	Macro algae (brown)	0.30-060	Oven 100°C, 24h	A simple of 20g of native biomass (300-600 um) was treated with 400ml of 0.2M CaCl2 solution for 24h under slow stirring. The solution pH was kept constant at pH 5.0 using 0.1M HNO3. The calcium treated biomass was washed several times with deionized water.	83 -932	0.20	100	2	5.0	20	24	(Matheickal and Yu, 1999)
Makombu (PC)	*Laminaria japonica*	Macro algae (brown)	0.30-0.45	Before treatment: it was oven dried at 40°C, to constant weight	10g of powdered biomass was oxidized in 10mM solution of potassium permanganate at 30 °C for 30 min. Reacted mixture was separated by centrifugation and washed thoroughly with distilled water and dried in an oven at 60 °C	0 -725	0.02	15	1	5.2	20	2	(Luo et al., 2006)
—	*Ulva sp.*	Macro algae (Green)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.10	100	1	5.0	23	1	(Sheng et al., 2004)
—	*Sargassum hystrix*	Macro algae (brown)	0.2-0.5	After beach dried: Oven 50°C, at overnight	The biomass of algae was extensively washed with distilled water and sun-dried on the beach.	0-640	0.10	50	2	4.5	30	3	(Jalali et al., 2002)
	Chondracanthus chamissoi	Macro algae (Red)											(Yipmantin et al., 2011)
Gulfweed	*Sargassum sp.*	Macro algae (brown)	0.3-0.7	Oven 70°C, 24h	It was washed with distilled water to remove particulate material from their surface.	40-1000	0.10	25	4	5.0	40	2	(Martins et al., 2006)

A-2.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF LEAD

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
(ER95Ca)	*Ecklonia radiata*	Macro algae (brown)	0.30-0.60	Oven 100°C, 24h	A simple of 20g of native biomass (300-600 um) was treated with 400ml of 0.2M CaCl2 solution for 24h under slow stirring. The solution pH was kept constant at pH 5.0 using 0.1M HNO3. The calcium treated biomass was washed several times with deionized water.	83 -932	0.20	100	2	5.0	20	24	(Matheickal and Yu, 1999)
—	*Padina sp.*	Macro algae (brown)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.10	100	1	5.0	23	1	(Sheng et al., 2004)
—	*Cladophora cri spata*	Macro algae (Green)	—	Oven dried at 100°C for 6 hours	The cells were rinsed with tap water, washed twice with distilled water and then dried.	25-250	0.25	100	2.5	5.0	25	0.5	(Özer et al., 1994)
Makombu (DW)	Laminaria japonica	Macro algae (brown)	0.30-0.45	Before treatment: it was oven dried at 40°C, to constant weight	The powered biomass was washed with distilled water and dried in an oven at 60°C. To avoid the effect of salt, 10 g of powdered alga was suspended in 500 ml distilled water, stirred for 10 min. Then the biomass was separated by centrifugation. The process was repeated five times till the effluents became almost transparent. The washed biomass was then dried in an oven at 60°C until a constant weight was reached.	0 -725	0.02	15	1	5.2	20	2	(Luo et al., 2006)
Gulfweed	*Sargassum sp.*	Macro algae (brown)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.10	100	1	5.0	23	1	(Sheng et al., 2004)
Phosphorylated Orange Juice	—	Agricultural waste	?	The solid product (obtained after treatment) was dried in a convection oven for 24 h at 60◦C.	10 g of dried orange waste were soaked in 200 mL of dimethyl formamide (DMF) overnight in a 500 mL three-necked flask equipped with a magnetic stirrer and then 30 g of urea was added into the reactor followed by 18 g of phosphoric acid drop wisely. The suspension was stirred at 150◦C. After cooling, it was washed with 70% methanol followed by water washing till neutrality.	—	0.03	15	1.7	4.4	30	24	(Ghimire et al., 2008)
—	*Sargassum natans*	Macro algae (brown)	0.2-0.5	After beach dried: Oven 50°C, at overnight	The biomass of algae was extensively washed with distilled water and sun-dried on the beach.	0-640	0.10	50	2	4.5	30	3	(Jalali et al., 2002)

A-2.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF LEAD

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
—	*Cystoseira barbata*	Macro algae (brown)	0.6-1	Dried at 80 °C for 12 h	Algae was rinsed several times with deionize water. Then dried under sunlight, and then sieved to a size range 600–1000µm. A sample of biomass was soaked in 0.2M CaCl2 solution for 24h under slow stirring. The solution pH was fixed at pH 5.0. The calcium-treated biomass was washed several times using deionized water.	0-500	0.10	50	2	4.5	20	1	(Yalçin et al., 2012)
Peacock's Tail	*Padina pavonia*	Macro algae (brown)	0.2-0.5	After beach dried: Oven 50°C, at overnight	The biomass of algae was extensively washed with distilled water and sun-dried on the beach.	0-640	0.10	50	2	4.5	30	3	(Jalali et al., 2002)
	Fucus vesiculosus	Macro algae (brown)	<0.5	dried in an oven at 60 ◦C	The algae was collected by Algamar in the northern Atlantic coasts of Spain. The alga was washed and pulverized.	10-150	—	—	0.5	5.0	23	2	(Mata et al., 2008)
—	*Scenedesmus obliquus*	Micro algae (Green)	1.2	Oven dried at 100◦C to constant weight	Algal culture was incubated at 24 ± 2°C under continuous illumination (2,500 lux) without aeration. After 8 days of cultivation period, exponentially grown algal cells were harvested by centrifugation. A sample of 5 g of dry S. obliquus biomass (0.2 mm) was treated with 250 mL of 0.2 M CaCl2 solution for 24 h under slow stirring. The solution was kept at constant pH 4 (optimum pH value for calcium activation). Then was washed	—	0.050	100	0.50	4.0	25	—	(Abdel Ghafar et al., 2014)
Carrageen / Irish Moss	*Chondrus crispus*	Macro algae (Red)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.5	4.0	—	2	(Romera et al., 2007)
Spiral wrack / Flat wrack	*Fucus spiralis*	Macro algae (brown)	<0.5	Oven dried at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.5	3.0	—	2	(Romera et al., 2007)

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Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
—	*Cladophora fascicularis*	Macro algae (Green)	4-5	Oven 60°C, 24h	It was washed several times with distilled water.	45-901.6	0.20	100	2	5.0	25	—	(Deng et al., 2007)
Usaba-aonori	*Enteromorpha linza*	Macro algae (Green)	0.6-1	Oven 60°C, 24h	The raw alga was rinsed several times with deionize water, dried under sunlight, and then sieved to a size range 600–1000µm. A sample of biomass was soaked in 0.2M CaCl2 solution for 24h under slow stirring. The solution pH was fixed at pH 5.0. The calcium-treated biomass was washed several times using deionized water.	10-1000	0.10	50	2	5.0	25	0.33	(Yalçin, 2014)
Bushy Berry Wrack	*Cystoseira baccata*	Macro algae (brown)	0.5-1	Oven dried at 60◦C overnight	The alga was washed with tap and deionized water to eliminate impurities.	10-2000	0.10	40	2.5	4.5	25	4	(Lodeiro et al., 2006)
Knotted wrack / Norwegian kelp	*Ascophyllum nodosum*	Macro algae (brown)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	3.0	—	2	(Romera et al., 2007)
Rose waste biomass	—	Agricultural waste	0.1-0.25	Sun dried for seven days to constant weight. Dried	—	10-640	0.05	100	0.5	5.0	30	0.66	(Javed et al., 2007)
—	*Oedogonium* sp.	Macro algae (Green)	0.063-0.105	Sun dried for 4 days followed by oven dry at 70 ◦C, 24h	Before use, it was washed with distilled water to remove dirt and was kept on a filter paper to reduce the water content.	20-200	0.01	10	0.5	5.0	25	1.5	(V. K. Gupta & Rastogi, 2008)
Water silk	*Spirogyra sp.*	Macro algae (Green)	0.063-0.105	Sun dried for 4 days followed by oven dry at	Before use, it was washed with distilled water to remove dirt and was kept on a filter paper to reduce the water content.	200	0.05	100	0.5	5.0	25	1.67	(Gupta and Rastogi, 2008)
—	Sphaerotilus natans	Bacteria	—	Freeze-dryed					1.0	5.0	30		(Pagnanelli et al., 2003)
Sea lettuce	Ulva lactuca	Macro algae (Green)	0.2-0.6	After beach dried: Oven 50°C, at overnight	The biomass of algae was extensively washed with distilled water and sun-dried on the beach.	0-640	0.10	50	2	4.5	30	3	(Jalali et al., 2002)

A-2.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF LEAD

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
—	Rhizopus oligosporus	Fungi	0.3-0.6	Oven dry at 55◦C for 18h	A 5 ml spore suspension obtained from potato dextrose agar slant was inoculated into a 500 ml shake flask containing 200 ml of liquid medium. This medium consisted of; glucose, 40 g/l; yeast extract, 10 g/l; MgSO4 á 7H2O, 1 g/l; NaNO3, 1 g/l; H2KPO4, 1 g/l. The initial pH of the culture was adjusted to 5.5. The flasks were incubated at 30 °C in an orbital shaker agitated at 250 rev/min for 5 days. During the cultivation the fungus grew in the form of mycelium. The mycelia were separated from the liquid by filltration. The mycelia were resuspended and rewashed for three times. The wet mycelium biomass was dried.	10-700	0.05	100	0.5	5.0	30	14.0	(Ariff et al., 1999)
—	*Pseudomonas aeruginosa* ASU 6a	Bacteria	—	—	It was isolated on Acetamide broth. Acetamide media was inoculated at 37 1C for 48 h.	0-160	0.10	100	1	6.0	30	0.5	(Gabr et al., 2008)
—	*Anabaena sph aerica*	Blue Green Algae	0.2	Oven dry at 40°C, to constant weight	The algae was recultivated in BG11 medium containing the following macroelements: K2HPO4, MgSO4, CaCl2, citric acid, Na2CO3,Na2EDTA, and ferric ammonium citrate. he algal cultures were incubated at 24±2°C, under continuous illumination (2500 lux). The biomass was collected by centrifugation at 5000 rpm for 10 min. The algal biomass was washed with distilled water for five times.	50-300	0.10	100	1	3.0	25	1.5	(Abdel -Aty et al., 2013)
Raw orange peels		Agricultural waste	0.5	Dried at 60°C	It was cut into small pieces, washed several times with double distilled wate								(Feng and Guo, 2012)
—	*Scenedesmus obliquus*	Micro algae (Green)	0.2	Oven dried at 100◦C to constant weight	Algal culture was incubated at 24 ± 2˚C under continuous illumination (2,500 lux) without aeration. After 8 days of cultivation period, exponentially grown algal cells were harvested by centrifugation. The algal biomass was washed with distilled water five times to avoid any effect of salt and then dried.	—	0.075	100	0.75	4.0	25	—	(Abdel Ghafar et al., 2014)
—	*Polysiphonia violacea*	Macro algae (Red)	0.2-0.8	After beach dried: Oven 50°C, at overnight	The biomass of algae was extensively washed with distilled water and sun-dried on the beach.	0-640	0.10	50	2	4.5	30	3	(Jalali et al., 2002)

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Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
—	*Nostoc* sp.	Blue Green Algae	0.063-0.105	Sun dried for 4 days followed by oven dry at 70 ◦C, 24h	Before use, it was washed with distilled water to remove dirt and was kept on a filter paper to reduce the water content.	20-200	0.01	10	0.5	5.0	25	1.2	(V. K. Gupta & Rastogi, 2008)
—	*Gracilaria sp.*	Macro algae (Red)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.10	100	1	5.0	23	1	(Sheng et al., 2004)
	Spirogyra neglecta	Macro algae (Green)				100.0			0.1	5.0		0.2	(Singh et al., 2007)
	Spirogyra sp.	Macro algae (Green)	50-250 mes	70 °C for 24 h	Before use, it was washed with distilled water to remove dirt and kept on filter paper to reduce water content. The biomass was then sun-dried for 4 days	100.0				5.0	25	1.0	(Lee and Chang, 2011)
	Galaxaura oblongata	Macro algae (Red)	500-850	dried at 60 ◦C for 24 h	Samples of the biomass were collected from the Mediterranean Sea at Abu Quir beach, Alexandria, Egypt, during summer season (July, 2009). The collected algae were rinsed thoroughly with distilled water in order to remove any adhering debris.				10	5	25	1	(Ibrahim, 2011)
	Penicillium simplicissimum	Fungi	0.250	dried at 60 ◦C for 24 h	The strain was maintained on potato-dextrose agar slants and stored at 4 ◦C. The fungus was cultivated on a rotary shaker (120rpm) at 28 ◦C for 72h in 250ml conical Erlenmeyer flask containing 100ml of growth medium. The growth medium consisted of(g l–1): dextrose, 20;peptone,10;NaCl, 0.2; CaCl2, 0.1; KCl, 0.1;K2HPO4, 0.5;NaHCO3, 0.05; MgSO4, 0.25; FeSO4·7H2O, 0.005. The harvested biomass was washed with distilled water, dried, and powdered in a mortar, then was stored in a desiccator and used for the following experiments.	50-300	0.10	—	—	5.0	28	12.0	(Fan et al., 2008)
—	*Valoniopsis pachynema*	Macro algae (Green)	2.0	First air dried for 24h, then oven dried at	The algae were washed twice with tap water and thereafter with double distilled water	20-80	0.10	—	—	—	—	2	(Nirmal Kumar et al., 2009)
—	*Cladophora glomerata*	Macro algae (Green)	0.2-0.5	After beach dried: Oven 50°C, at overnight	The biomass of algae was extensively washed with distilled water and sun-dried on the beach.	0-640	0.10	50	2	4.5	30	3	(Jalali et al., 2002)

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Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
Sea lettuce	*Ulva lactuca* . (waste from oil extraction industry)	Macro algae (Green)	1-1.5	Oven 85°C, 24h	The green algae waste biomass, used in this study as biosorbent, was obtained after the solvent extraction of oil. The collected biomass was washed several times with double distilled water to remove impurities.	23-382	0.20	25	8	5.0	20	1	(Bulgariu and Bulgariu, 2012)
	Corallina mediterranea	Macro algae (Red)	500-850	dried at 60 ◦C for 24 h	Samples of the biomass were collected from the Mediterranean Sea at Abu Quir beach, Alexandria, Egypt, during summer season (July, 2009). The collected algae were rinsed thoroughly with distilled water in order to remove any adhering debris.				10	5	25	1	(Ibrahim, 2011)
—	*Gelidium sesq uipedale*	Macro algae (Red)	0.25-1	Oven dried at 60◦C	Algae was air-dried to remove odours and most water for 2 days, next it was dried and sieved.	10-300	0.20	100	2	5.3	20	0.17-0.33	(Vilar et al., 2005)
Harpoon weed	*Asparagopsis armata*	Macro algae (Red)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the Mediterranean coast of Malaga, in southern Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	4.0	—	2	(Romera et al., 2007)
—	*Codium vermilara*	Macro algae (Green)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	5.0	—	2	(Romera et al., 2007)
—	*Gracilaria corticata*	Macro algae (Red)	0.2-0.5	After beach dried: Oven 50°C, at overnight	The biomass of algae was extensively washed with distilled water and sun-dried on the beach.	0-640	0.10	50	2	4.5	30	3	(Jalali et al., 2002)

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Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
—	*Spirogyra insignis*	Macro algae (Green)	<0.5	Oven dry at 60°C, to constant weight	*S. insignis* , harvested from fresh water. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	5.0	—	2	(Romera et al., 2007)
Grape stalks	—	Agricultural waste	1-1.5	Oven dried at 110◦C to constant weight	Grape stalk waste generated in wine production	31-394	0.10	15	6.7	5.5	20	2.0	(Martínez et al., 2006)
	Cladophora sp.	Macro algae (Green)	50-250 mes	70 °C for 24 h	Before use, it was washed with distilled water to remove dirt and kept on filter paper to reduce water content. The biomass was then sun-dried for 4 days	100.0				5.0	25	1.0	(Lee and Chang, 2011)
Rice straw	—	Agricultural waste	0.075-0.15	Oven dry at 80◦C for 24h	The rice straw was cut into small pieces. Later it was washed on a piece of cloth and later dry for 24h re-sieved then it was dried again in the oven for 1h at 80◦C.	—	0.40	100	4	5.5	25	30	(Amer et al., 2017)
Taiwan-ogonori	*Gracilaria can aliculata*	Macro algae (Red)	0.2-0.7	After beach dried: Oven 50°C, at overnight	The biomass of algae was extensively washed with distilled water and sun-dried on the beach.	0-640	0.10	50	2	4.5	30	3	(Jalali et al., 2002)
—	*Chaetomorpha sp*	Macro algae (Green)	2.0	First air dried for 24h, then oven dried at 80°C, to constant weight	The algae were washed twice with tap water and thereafter with double distilled water	20-80	0.10	—	—	—	—	2	(Nirmal Kumar et al., 2009)
—	*Pseudomonas putida*	Bacteria	—	Freeze-drying –40°C to –50°C and a pressure of 10mbar. Store at –3 °C in the darkness until use.	Cells were grown in flasks at 30 °C with shaking at 200 rpm for 24 h. The growth media for the experiments were Tryptic Soy Agar (TSA) from Merck, prepared by dissolving 40 g in 1L deionized water (pH 7.3 at 37 °C), and Tryptic Soy Broth (TSB) from Biolife prepared by dissolving 30 g in deionized water to total dissolution (pH 7.3 at 37 °C). These growing media were sterilized in an autoclave at 121°C for 20min before inoculation.	0-1000	0.10	100	1	4.5	30	0.17	(Pardo et al., 2003)

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Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
Sea lettuce	*Ulva lactuca.*	Macro algae (Green)	0.5	Oven 60°C, 48h	The alga was washed with deionized water.	10-400	2.00	100	20	5.0	20	1	(Sari and Tuzen, 2008)
	Pterocladia capillacea	Macro algae (Red)	500-850	dried at 60 ◦C for 24 h	Samples of the biomass were collected from the Mediterranean Sea at Abu Quir beach, Alexandria, Egypt, during summer season (July, 2009). The collected algae were rinsed thoroughly with distilled water in order to remove any adhering debris.				10	5.0	25	1	(Ibrahim, 2011)
—	*Cladophora fascicularis*	Macro algae (Green)	2.0	First air dried for 24h, then oven dried at 80°C, to constant weight	The algae were washed twice with tap water and thereafter with double distilled water	20-80	0.10	—	—	—	—	—	(Nirmal Kumar et al., 2009)
	Jania rubens	Macro algae (Red)	500-850	dried at 60 ◦C for 24 h	Samples of the biomass were collected from the Mediterranean Sea at Abu Quir beach, Alexandria, Egypt, during summer season (July, 2009). The collected algae were rinsed thoroughly with distilled water in order to remove any adhering debris.				10	5	25	1	(Ibrahim, 2011)
Sea lettuce	*Ulva lactuca*	Macro algae (Green)	2.0	First air dried for 24h, then oven dried at 80°C, to constant weight	The algae were washed twice with tap water and thereafter with double distilled water	20-80	0.10	—	—	—	—	—	(Nirmal Kumar et al., 2009)
—	*Caulerpa lentillifera*	Macro algae (Green)	0.841-2	Dried at 80 °C for 12 h	The alga was washed.	0-330	0.50	30	16.7	5.0	23	1	(Pavasant et al., 2006)

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Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
—	*Mucor rouxii*	Fungi	0.15	Dried at 60◦C for 24 h	The fungi was cultured in YPG medium (i.e., yeast extract (3 g/l), peptone (10 g/l), and glucose (dextrose) (20 g/l)). The pH of the growth media was adjusted to 4.5. Biomass was harvested by filtering the mixture of culture through a 150-mm sieve. The biomass collected was washed with distilled water. The cells were soaked in 0.2M NaOH solution for 30 min. Then, it was washed with deionized water until the pH of the wash attains the neutral range, i.e. The biomass was then autoclaved for 30min at 121C and 124 kPa and dried	10	0.01-.2	75	—	5.0	—	5	(Yan and Viraraghavan, 2003)
—	*Caulerpa sertularioides*	Macro algae (Green)	2.0	First air dried for 24h, then oven dried at 80°C, to constant weight	The algae were washed twice with tap water and thereafter with double distilled water	20-80	0.10	—	—	—	—	—	(Nirmal Kumar et al., 2009)
Sugar beet pulp		Agricultural waste	0.15-0.2	Oven dried at 100◦C to constant	It was extensively washed with tap water to remove soil and dust.	—	0.40	50		5.0	25	1.17	(Pehlivan et al., 2008)

A-2.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF LEAD

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
—	*Mucor rouxii*	Fungi	769.2	0.038	0.95	—	—	—	—	?	?	(Lo et al., 1999)
—	*Corynebacterium glutamicum*	Bacteria	567.7	—	—	—	—	—	—	?	?	(Choi and Yun, 2004)
—	*Turbinaria conoides*	Macro algae	439.4	0.05	0.84	—	—	—	—	Carboxyl	BD	(Senthilkumar et al., 2007)
Makombu (EC1)	*Laminaria japonica*	Macro algae (brown)	346	0.31	0.97	1.54	0.149	0.789	—	Carboxylate groups of alginate	?	(Luo et al., 2006)
Makombu (EC2)	*Laminaria japonica*	Macro algae (brown)	335.7	0.01	1.00	1.47	0.172	0.831	—	Carboxylate groups of alginate	?	(Luo et al., 2006)
Bull Kelp (DP95Ca)	*Durvillaea potatorum*	Macro algae (brown)	321.2	2.4	—	—	—	—	—	?	?	(Matheickal and Yu, 1999)
Makombu (PC)	*Laminaria japonica*	Macro algae (brown)	319.1	0.31	0.97	1.19	0.317	0.683	—	Carboxylate groups of alginate	?	(Luo et al., 2006)
—	*Ulva sp.*	Macro algae (Green)	302.5	0.01	0.91	—	—	—	—	?	*BD	(Sheng et al., 2004)
—	*Sargassum hystrix*	Macro algae (brown)	285.0	430	1.00	39.5	0.357	0.968	—	Carboxyl and sulfate groups	?	(Jalali et al., 2002)
	Chondracanthus chamissoi	Macro algae (Red)	283.5	0.089	0.99							(Yipmantin et al., 2011)
Gulfweed	*Sargassum sp.*	Macro algae (brown)	266.0	0.153	1.00	96	0.227	0.963	pseudo second order k2:0.032 g/mgmin, qe:13.4mg/g, r2:1.000	?	?	(Martins et al., 2006)

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			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
(ER95Ca)	*Ecklonia radiata*	Macro algae (brown)	261.1	0.19	—	—	—	—	—	?	?	(Matheickal and Yu, 1999)
—	*Padina sp.*	Macro algae (brown)	259.0	0.045	0.97	—	—	—	—	Carboxyl, Ether, Amino	*BD	(Sheng et al., 2004)
—	*Cladophora cri spata*	Macro algae (Green)	251.3	0.015	—	15.49	0.49	—	—	?	?	(Özer et al., 1994)
Makombu (DW)	Laminaria japonica	Macro algae (brown)	250.7	0.1	0.93	1.03	0.204	0.916	—	Carboxylate groups of alginate	?	(Luo et al., 2006)
Gulfweed	*Sargassum sp.*	Macro algae (brown)	240.4	0.069	0.95	—	—	—	—	Carboxyl, Ether, Amino	*BD	(Sheng et al., 2004)
Phosphorylated Orange Juice	—	Agricultural waste	238.3	0.037	0.99	—	—	—	—	Phosphoric acid groups	*BD	(Ghimire et al., 2008)
—	*Sargassum natans*	Macro algae (brown)	238.0	560	1.00	47.4	0.29	0.935	—	Carboxyl and sulfate groups	?	(Jalali et al., 2002)
—	*Cystoseira barbata*	Macro algae (brown)	228.6	0.176	1.00	—	—	—	pseudo second order k2:0.44 g/mgmin, qe:0.95 mg/g, r2:0.999	Amide, Carbonyl	*BD	(Yalçin et al., 2012)
Peacock's Tail	*Padina pavonia*	Macro algae (brown)	217.4	720	0.99	46.3	0.27	0.98	—	Carboxyl and sulfate groups	?	(Jalali et al., 2002)
	Fucus vesiculosus	Macro algae (brown)	211.34	0.076	0.97	—	—	—	—	?	?	(Mata et al., 2008)
—	*Scenedesmus obliquus*	Micro algae (Green)	207.2	19.1	0.66	78.1	0.602	0.963	—	amino, carboxyl, hydroxyl, and carbonyl groups	?	(Abdel Ghafar et al., 2014)
Carrageen / Irish Moss	*Chondrus crispus*	Macro algae (Red)	204.1	0.01	0.98	—	—	—	—	?	?	(Romera et al., 2007)

A-2.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF LEAD

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
Spiral wrack / Flat wrack	*Fucus spiralis*	Macro algae (brown)	204.1	0.13	0.99	—	—	—	—	?	?	(Romera et al., 2007)
—	*Cladophora fascicularis*	Macro algae (Green)	198.5	0.04	1.00	37.46	0.28	0.997	—	Amino and hydroxyl	*BD	(Deng et al., 2007)
Usaba-aonori	*Enteromorpha linza*	Macro algae (Green)	197.8	0.04	1.00	21.262	0.37	0.954	—	carboxyl groups of alginic acid	*BD	(Yalçin, 2014)
Bushy Berry Wrack	*Cystoseira baccata*	Macro algae (brown)	186.0	0.34	0.99	3.57	0.167	0.84	pseudo second order k2:0.001 g/mgmin, qe:142.97 mg/g, r2:0.9998	Carboxyl	*BD	(Lodeiro et al., 2006)
Knotted wrack / Norwegian kelp	*Ascophyllum nodosum*	Macro algae (brown)	178.6	0.09	0.99	—	—	—	—	?	?	(Romera et al., 2007)
Rose waste biomass	—	Agricultural waste	151.1	0.03	0.99	6.75	0.32	0.8423	pseudo second order k2:0.010 g/mgmin, qe: mg/g, r2:0.999	?	?	(Javed et al., 2007)
—	*Oedogonium* sp.	Macro algae (Green)	144.9	0.022	1.00	8,069	0.57	0.925	pseudo second order k2:0.797 g/mgmin, qe:63.29 mg/g, r2:0.996	Amino and carboxyl	?	(V. K. Gupta & Rastogi, 2008)
Water silk	*Spirogyra sp.*	Macro algae (Green)	140.8	0.02	0.99	8.01	0.53	0.916	pseudo second order k2:0.0031 g/mgmin, qe:111.11 mg/g, r2:0.998	amino, carboxyl, hydroxyl and carbonyl groups,	*BD	(Gupta and Rastogi, 2008)
—	Sphaerotilus natans	Bacteria	134.7	0.198	0.99							(Pagnanelli et al., 2003)
Sea lettuce	Ulva lactuca	Macro algae (Green)	126.5	990	0.93	42.5	0.19	0.974	—	?	?	(Jalali et al., 2002)
—	Rhizopus oligosporus	Fungi	126.0	0.0351	0.95	—	—	—		Mg2+, P+, S2+, and K+ were noticed as the elements present on the surface of the native cells.	*BD	(Ariff et al., 1999)

A-2.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF LEAD

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
—	*Pseudomonas aeruginosa* ASU 6a	Bacteria	123.0	0.21	0.99	40.04	0.38	0.99			*BD	(Gabr et al., 2008)
—	*Anabaena sph aerica*	Blue Green Algae	122.0	19.19	0.97	28.28	0.26	0.980	—	Amino, Carboxyl and Hydroxyl	?	(Abdel -Aty et al., 2013)
Raw orange peels		Agricultural waste	113.5									(Feng and Guo, 2012)
—	*Scenedesmus obliquus*	Micro algae (Green)	112.0	56.91	0.86	22.35	0.768	0.994	—	amino, carboxyl, hydroxyl, and carbonyl groups	?	(Abdel Ghafar et al., 2014)
—	*Polysiphonia violacea*	Macro algae (Red)	102	13200	0.75	89.8	0.02	0.920	—	?	?	(Jalali et al., 2002)
—	*Nostoc* sp.	Blue Green Algae	93.5	0.023	0.99	8.338	0.44	0.949	pseudo second order k2:0.864 g/mgmin, qe:44.05 mg/g, r2:0.993	Amino and carboxyl	?	(V. K. Gupta & Rastogi, 2008)
—	*Gracilaria sp.*	Macro algae (Red)	93.2	0.034	0.90	—	—	—	—	?	*BD	(Sheng et al., 2004)
	Spirogyra neglecta	Macro algae (Green)	91.9	0.014	0.96							(Singh et al., 2007)
	Spirogyra sp.	Macro algae (Green)	90.9	0.024	0.99	9.22	0.41	0.981				(Lee and Chang, 2011)
	Galaxaura oblongata	Macro algae (Red)	88.6	0.0951	1.00							(Ibrahim, 2011)
	Penicillium simplicissimum	Fungi	87.7	0.04	0.99	11.6	0.41	0.88	—	?	?	(Fan et al., 2008)
—	*Valoniopsis pachynema*	Macro algae (Green)	83.3	0.191	0.25	—	0.77	0.759	—	?	?	(Nirmal Kumar et al., 2009)
—	*Cladophora glomerata*	Macro algae (Green)	73.5	2160	0.69	37.5	0.12	0.892	—	?	?	(Jalali et al., 2002)

A-2.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF LEAD

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
Sea lettuce	*Ulva lactuca* . (waste from oil extraction industry)	Macro algae (Green)	66.40	0.014	1.00	—	0.75	0.891	pseudo second order k2:0.057 g/mgmin, qe:5.89 mg/g, r2:0.999	?	?	(Bulgariu and Bulgariu, 2012)
	Corallina mediterranea	Macro algae (Red)	64.3	0.0671	1.00							(Ibrahim, 2011)
—	*Gelidium sesquipedale*	Macro algae (Red)	64.0	360	0.97	—	—	—	pseudo second order k2:0.9 g/mgmin, qe:42.4 mg/g, r2:0.989	?	?	(Vilar et al., 2005)
Harpoon weed	*Asparagopsis armata*	Macro algae (Red)	63.7	0.04	0.99	—	—	—	—	?	?	(Romera et al., 2007)
—	*Codium vermilara*	Macro algae (Green)	63.3	0.11	0.99	—	—	—	—	?	?	(Romera et al., 2007)
—	*Gracilaria corticata*	Macro algae (Red)	54	1580	0.86	24.8	0.13	0.987	—	?	?	(Jalali et al., 2002)
—	*Spirogyra insignis*	Macro algae (Green)	51.1	0.57	0.99	—	—	—	—	?	?	(Romera et al., 2007)
Grape stalks	—	Agricultural waste	49.9	0.4	0.96	0.296	0.161	0.729	pseudo second order k2:0.391 g/mgmin, qe:1.41 mg/g, r2:0.999	O H groups bound to methyl and methylene radicals; these groups are present on the lignin structure	?	(Martínez et al., 2006)
	Cladophora sp.	Macro algae (Green)	46.5	0.025	1.00	6.63	0.33	0.98				(Lee and Chang, 2011)
Rice straw	—	Agricultural waste	42.6	0.09	0.99	3.7	0.70	0.959	—	Carboxylic acids	ü	(Amer et al., 2017)
Taiwan-ogonori	*Gracilaria canaliculata*	Macro algae (Red)	41.8	2320	0.72	21.3	0.11	0.827	—	?	?	(Jalali et al., 2002)

A-2.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF LEAD

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
—	*Chaetomorpha sp*	Macro algae (Green)	37.0	2.079	0.98	—	0.37	0.952	—	?	?	(Nirmal Kumar et al., 2009)
—	*Pseudomonas putida*	Bacteria	36.0	18.48	1.00	—	—	—	—	?	?	(Pardo et al., 2003)
Sea lettuce	*Ulva lactuca.*	Macro algae (Green)	34.7	0.05	0.99	10.5	0.9	0.98	pseudo second order k2:0.29 g/mgmin, qe:1.01 mg/g, r2:0.999	?	?	(Sari and Tuzen, 2008)
	Pterocladia capillacea	Macro algae (Red)	34.1	0.04	0.95							(Ibrahim, 2011)
—	*Cladophora fascicularis*	Macro algae (Green)	31.3	0.242	0.53	—	0.58	0.599	—	?	?	(Nirmal Kumar et al., 2009)
	Jania rubens	Macro algae (Red)	30.6	0.0422	0.99							(Ibrahim, 2011)
Sea lettuce	*Ulva lactuca*	Macro algae (Green)	29.4	0.296	0.93	—	0.48	0.913	—	?	?	(Nirmal Kumar et al., 2009)
—	*Caulerpa lentillifera*	Macro algae (Green)	28.7	0.072	0.98	—	0.68	0.95	—	Carboxylic, Amine and Sulfonate	?	(Pavasant et al., 2006)
—	*Mucor rouxii*	Fungi	25.22	0.87	0.86	10.73	0.4	0.8	pseudo second order k2:0.011 g/mgmin, qe:12.89 mg/g, r2:0.95	?	?	(Yan and Viraraghavan, 2003)
—	*Caulerpa sertularioides*	Macro algae (Green)	21.3	0.416	0.94	—	0.38	0.906	—	?	?	(Nirmal Kumar et al., 2009)
Sugar beet pulp		Agricultural waste	0.37	0.476	0.60	5.6	1.0	0.99		Carboxyl	*BD	(Pehlivan et al., 2008)

A-3.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ZINC

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
	Scenedesmus obliquus	Micro algae (Green)	—	dried at 100◦C for 24 h	Cells of the freshwater green microalga S. obliquus (L) were isolated from a heavy metal-polluted site in northern Portugal. Algae was cultivated in PHM medium, containing 1 g/L Tris–HCl buffer but without EDTA. Cultures were maintained at 25°C, under continuous light, at an irradiance of 29.18 lE/(s.m2), provided by cool light fluorescent lamps. In all experiments, the microalgal cells were harvested at the exponential phase (after 2–3 days of growth), and then used as inoculum.	10-75			0.02	6-7	25	1.5	(Monteiro et al., 2011)
Eucalyptus bark	*Eucalyptus sheathiana*	Agricultural waste	0.106	dried at 105 ◦C for 24 h	Eucalyptus barks were collected from Eucalyptus sheathiana trees at Perth, Western Australia between February and March 2013. The barks were washed repeatedly with distilled water to remove impurities such as sand and leaves	20-70	0.02	50	0.4	5.1	30	2	(Afroze et al., 2016)
	Penicillium simplicissimum	Fungi	0.250	dried at 60 ◦C for 24 h	The strain was maintained on potato-dextrose agar slants and stored at 4 ◦C. The fungus was cultivated on a rotary shaker (120rpm) at 28 ◦C for 72h in 250ml conical Erlenmeyer flask containing 100ml of growth medium. The growth medium consisted of(g l–1): dextrose, 20;peptone,10;NaCl, 0.2; CaCl2, 0.1; KCl, 0.1;K2HPO4, 0.5;NaHCO3, 0.05; MgSO4, 0.25; FeSO4·7H2O, 0.005. The harvested biomass was washed with distilled water, dried, and powdered in a mortar, then was stored in a desiccator and used for the following experiments.	50-300	0.10	—	—	5.0	28	12.0	(Fan et al., 2008)
—	*Mucor rouxii*	Fungi	—	The biomass was freeze-dried at 0◦C and at reduce pressure for 2 days.	After 24 h cultivation, 10 mL of the seed culture was then transferred to inoculate 100 mL PYG broth. The cultures were grown at pH 4.5 and temperature 25 o C on orbital shaker at 200 rpm for one week. The fungi biomass was then harvested by filtration, washed with water, resuspended and washed again	200.0		200.0	0.05-1.5	6.0	25.0	0.2	(Lo et al., 1999)

A-3.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ZINC

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
Makombu (DW)	Laminaria japonica	Macro algae (brown)	0.30-0.45	Before treatment: it was oven dried at 40°C, to constant weight	The powered biomass was washed with distilled water and dried in an oven at 60°C. To avoid the effect of salt, 10 g of powdered alga was suspended in 500 ml distilled water, stirred for 10 min. Then the biomass was separated by centrifugation. The process was repeated five times till the effluents became almost transparent. The washed biomass was then dried in an oven at 60°C until a constant weight was reached.	0 -725	0.02	15	1	5.2	20	2	(Liu et al., 2009)
Spiral wrack / Flat wrack	*Fucus spiralis*	Macro algae (Brown)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	6	—	2	(Romera et al., 2007)
—	*Padina sp.*	Macro algae (Brown)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.1	100	1	5.5	23	1	(Sheng et al., 2004)
horseradish tree	*Moringa oleifera* Lam.	Agricultural waste	<0.255	Oven dried at 60 8C for 72 h	Biomass was extensively washed with distilled water to remove particulate material from their surface.Dried biomass was cut, ground using food processor and then sieved to obtain adsorbent with homogenous known particle size.	50-200	—	—	0.5	7.0	30	24.0	(Bhatti et al., 2007)
Carrageen / Irish Moss	*Chondrus crispus*	Macro algae (Red)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	6	—	2	(Romera et al., 2007)

A-3.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ZINC

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
Knotted wrack / Norwegian kelp	*Ascophyllum nodosum*	Macro algae (Brown)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	6	—	2	(Romera et al., 2007)
—	*Ulva sp.*	Macro algae (Green)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.1	100	1	5.5	23	1	(Sheng et al., 2004)
Gulfweed	*Sargassum sp.*	Macro algae (Brown)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.1	100	1	5.5	23	1	(Sheng et al., 2004)
—	Sphaerotilus natans	Bacteria	—	Freeze-dryed					1.0	5.0	30		(Pagnanelli et al., 2003)
—	*Gracillaria sp.*	Macro algae (Red)	0.5-0.8	Dried at 60◦C overnight	It was washed with copious quantities of deionized water.	207-373	0.1	100	1	5.0	23	1	(Sheng et al., 2004)
—	*Codium vermilara*	Macro algae (Green)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the northern Atlantic coast of Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	6	—	2	(Romera et al., 2007)
Harpoon weed	*Asparagopsis armata*	Macro algae (Red)	<0.5	Oven dry at 60°C, to constant weight	The algae was collected on the Mediterranean coast of Malaga, in southern Spain. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.05	100	0.50	6	—	2	(Romera et al., 2007)
Raw orange peels		Agricultural waste	0.5	Dried at 60°C	It was cut into small pieces, washed several times with double distilled wate								(Feng and Guo, 2012)

A-3.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ZINC

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
—	*Spirogyra insignis*	Macro algae (Green)	<0.5	Oven dry at 60°C, to constant weight	*S. insignis* , harvested from fresh water. The biomass was washed with distilled water several times. The overflow containing small particles was was centrifuged at 5000 rpm for 10–15 min. Then, after removal of the clear liquid, the pellet was mixed with previously-washed biomass to avoid large losses of it. Finally it was dried.	10-150	0.1	100	1	6	—	2	(Romera et al., 2007)
—	*Mucor rouxii*	Fungi	0.15	Dried at 60◦C for 24 h	The fungi was cultured in YPG medium (i.e., yeast extract (3 g/l), peptone (10 g/l), and glucose (dextrose) (20 g/l)). The pH of the growth media was adjusted to 4.5. Biomass was harvested by filtering the mixture of culture through a 150-mm sieve. The biomass collected was washed with distilled water. The cells were soaked in 0.2M NaOH solution for 30 min. Then, it was washed with deionized water until the pH of the wash attains the neutral range, i.e. The biomass was then autoclaved for 30min at 121C and 124 kPa and dried	10	0.01-.2	75	—	5.0	—	7	(Yan and Viraraghavan, 2003)
Palm tree leaves		Agricultural waste	—	—	The leaves were thoroughly washed by distilled water to remove any impurities, dried, ground, and sieved and then stored in bottles.	20-300	0.10	50	2	5.5	25	—	(Al-Rub, 2006)
	Ulva fasciata	Macro algae (Green)	0.075	dried in sunlight for 10 days	The collected algae was washed with deionized water several times to remove impurities. Then was dried, and the resulting product was directly used as adsorbent.	20-100	0.10	30	3	5	30.0	24	(Kumar et al., 2006)
—	*Caulerpa lentillifera*	Macro algae (Green)	0.841-2	Dried at 80 °C for 12 h	The alga was washed.	0-330	0.5	30	16.7	5	23	1	(Pavasant et al., 2006)

A-3.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ZINC

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	Dosage (g/L)	pH	Temp. (°C)	Equilibrium time (h)	References
—	*Pseudomonas putida*	Bacteria	—	Freeze-drying –40°C to –50°C and a pressure of 10mbar. Store at –3 °C in the darkness until use.	Cells were grown in flasks at 30 °C with shaking at 200 rpm for 24 h. The growth media for the experiments were Tryptic Soy Agar (TSA) from Merck, prepared by dissolving 40 g in 1L deionized water (pH 7.3 at 37 °C), and Tryptic Soy Broth (TSB) from Biolife prepared by dissolving 30 g in deionized water to total dissolution (pH 7.3 at 37 °C). These growing media were sterilized in an autoclave at 121°C for 20min before inoculation.	0-1000	0.1	100	1	4.5	30	0.17	(Pardo et al., 2003)

A-3.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ZINC

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
	Scenedesmus obliquus	Micro algae (Green)	330	0.03	?	—	—	—	—	?	?	(Monteiro et al., 2011)
Eucalyptus bark	*Eucalyptus sheathiana*	Agricultural waste	128.21	0.06	0.94							(Afroze et al., 2016)
	Penicillium simplicissimum	Fungi	77.5	0.03	0.99	8.248	0.40	0.89	—	?	?	(Fan et al., 2008)
—	*Mucor rouxii*	Fungi	65.7	0.032	0.96	—	—	—	—	?	?	(Lo et al., 1999)
Makombu (DW)	*Laminaria japonica*	Macro algae (brown)	54.3	0.011	0.98				—			(Liu et al., 2009)
Spiral wrack / Flat wrack	*Fucus spiralis*	Macro algae (Brown)	53.2	0.11	0.99	—	—	—	—	?	?	(Romera et al., 2007)
—	*Padina sp.*	Macro algae (Brown)	53.0	0.04	0.99	—	—	—	—	Carboxyl, Ether, Amino	*BD	(Sheng et al., 2004)
horseradish tree	*Moringa oleifera* Lam.	Agricultural waste	52.1	0.15	1.00		0.12	0.99	—	?	?	(Bhatti et al., 2007)
Carrageen / Irish Moss	*Chondrus crispus*	Macro algae (Red)	45.7	0.07	0.99	—	—	—	—	?	?	(Romera et al., 2007)
Knotted wrack / Norwegian kelp	*Ascophyllum nodosum*	Macro algae (Brown)	42.0	0.22	0.99	—	—	—	—	?	?	(Romera et al., 2007)
—	*Ulva sp.*	Macro algae (Green)	35.3	0.018	0.97	—	—	—	—	Carboxyl, Ether, Amino	*BD	(Sheng et al., 2004)
Gulfweed	*Sargassum sp.*	Macro algae (Brown)	32.7	0.208	0.95	—	—	—	—	Carboxyl, Ether, Amino	*BD	(Sheng et al., 2004)
—	Sphaerotilus natans	Bacteria	32.7	0.459	0.97							(Pagnanelli et al., 2003)
—	*Gracillaria sp.*	Macro algae (Red)	26.2	0.194	0.83	—	—	—	—	?	*BD	(Sheng et al., 2004)

A-3.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ZINC

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
—	*Codium vermilara*	Macro algae (Green)	23.8	0.03	0.96	—	—	—	—	?	?	(Romera et al., 2007)
Harpoon weed	*Asparagopsis armata*	Macro algae (Red)	21.6	0.07	0.99	—	—	—	—	?	?	(Romera et al., 2007)
Raw orange peels		Agricultural waste	21.3									(Feng and Guo, 2012)
—	*Spirogyra insignis*	Macro algae (Green)	21.1	0.04	0.95	—	—	—	—	?	?	(Romera et al., 2007)
—	*Mucor rouxii*	Fungi	16.6	0.10	0.71	2.07	0.61	0.75	pseudo second order k2:0.067 g/mgmin, qe:2.43 mg/g, r2:0.96	?	?	(Yan and Viraraghavan, 2003)
Palm tree leaves		Agricultural waste	14.6	0.06	0.99	3.01	0.31	—	—	hydroxyl, carboxylic, and phenolic on	?	(Al-Rub, 2006)
	Ulva fasciata	Macro algae (Green)	13.5	0.0936	1.00	1.4	0.4	0.983	—	?	?	(Kumar et al., 2006)
—	*Caulerpa lentillifera*	Macro algae (Green)	2.66	0.067	0.99		0.65	0.97	—	Carboxylic, Amine and Sulfonate	?	(Pavasant et al., 2006)
—	*Pseudomonas putida*	Bacteria	2.5	1.06	0.99	—	—	—	—	?	?	(Pardo et al., 2003)

A-4.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ARSENIC III

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	pH	Temp. (°C)	Equilibrium time (h)	References
Rinds of the fruit malabar tamarind	*Garcinia gummi-gutta*	Agricultural waste			Immobilization procedure	500 - 2500			6.0	30	0.5	(Kamala et al., 2005)
Coconut Husk Carbon		Agricultural waste			Synthesized with HSO4 (18M) and impregnated with copper	50-600			12	30	4	(Manju, Raji, & Anirudhan, 1998)
Rinds of the fruit malabar tamarind	*Garcinia gummi-gutta*	Agricultural waste	<0.2	Oven dried, 60◦C, 24h	Washed with distilled water	50-1000	0.5	100	6.0	30	0.5	(Kamala et al., 2005)
Orange Juice Residue		Agricultural waste			modification of phosphorylation followed by loading with Iron III	—			7 to 11	30	24	(Ghimire et al., 2002)
-	*Ulothrix cylindricum*	Macro algae (Green)	0.5	After washed, Oven dried, 60◦C, 48h	Sampleswerewashed several times using deionized water to remove extraneous and salts. The driedalgaebiomass was chopped, and sieved	10 - 400	0.1	25	6.0	20	1	(Tuzen et al., 2009)
	Xanthoria parietina	Fungi										(Sari and Tuzen, 2010)
-	*Mougeotia genuflexa*	Macro algae (Green)	0.063-0.105				0.4	100	6.0	20	1	(Sari et al., 2011)
-	*Inonotus hispidus*	Fungi										(Sari and Tuzen, 2009)
-	*Penicillium purpurogenum*	Fungi			None	10 - 750			5.0	20	4	(Say, Yılmaz, & Denizli, 2003)
Sugarcane Bagasse		Agricultural waste			None	75			9.0	24	2	(Tajernia, Ebadi, & Nasernejad, 2014)
Waste tea fungal biomass (Iron		Fungi			Autoclaved at 15 psi for 15 min and then inmersed in FeCl4	As III: 1.3 / As V:0.09			7.2	30	1	(Murugesan et al., 2006)
Sweet lime peel	*Citrus Limetta*	Agricultural waste			None	50 - 200			6.0	40	4	(Kamsonlian, Suresh, Majumder, & Chand, 2013)
Drumstick tree (seed powder)	*Moringa olefeira*	Agricultural waste			None	1 - 100			7.5	—	—	(Kumari et al., 2006)
Waste tea fungal biomass		Fungi			None	1.3			7.2	30	0.75	(Murugesan et al., 2006)
Banana peel	na	Agricultural waste			None	10 - 150			7.0	35	1.5	(Kamsonlian, Balomajumder, & Chand, 2012)

A-4.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ARSENIC III

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	pH	Temp. (°C)	Equilibrium time (h)	References
Parsley (PCTTFe)	*Petroselinum crispum*	Agricultural waste			PCFe was Pyrolyzed and then retreated with FeCl3	0.05 - 2			6.5	18	24	(Jiménez-Cedillo et al., 2013)
Crab shells		Agricultural waste			Washed with HCl	<1			7.0	40	—	(Zhang et al., 2014)
Rice Polish	*Oryza sativa*	Agricultural waste			None	100 - 1000			7.0	20	1	(Ranjan, Talat, & Hasan, 2009)
Parsley (PCFe)	*Petroselinum crispum*	Agricultural waste			Iron modified, 500 mL FeCl3 for 5 hrs	0.05 - 2			6.5	18	24	(Jiménez-Cedillo et al., 2013)
Atlantic Cod fish scales	na	Agricultural waste			None	0.2 - 1			4.0	---	130	(Rahaman, Basu, & Islam, 2008)

A-4.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ARSENIC III

			Langmuir constants			Freundlich constants					
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	References
Rinds of the fruit malabar tamarind	*Garcinia gummi-gutta*	Agricultural waste	704.11	0.008	0.965	—	—	—	—	Ester, Carboxyl	(Kamala et al., 2005)
Coconut Husk Carbon		Agricultural waste	146.3	0.02	—	—	—	—	—	---	(Manju, Raji, & Anirudhan, 1998)
Rinds of the fruit malabar tamarind	*Garcinia gummi-gutta*	Agricultural waste	128.1	0.011	0.971	—	—	—	—	Ester, Carboxyl	(Kamala et al., 2005)
	Rhodococcus sp	Bacteria	77.3	0.018	0.993						(Prasad et al., 2011)
Orange Juice Residue		Agricultural waste	70.43						—	Carboxylic	(Ghimire et al., 2002)
-	*Ulothrix cylindricum*	Macro algae (Green)	67.2	0.01	0.997	2.85	0.53	0.98	pseudo second order k2:0.179 g/mgmin, qe:4.4 mg/g, r2:0.997	Hydroxyl, Amine, Carbonyl, Carboxyl	(Tuzen et al., 2009)
	Xanthoria parietina	Fungi	63.8	0.0094	0.9976						(Sari and Tuzen, 2010)
-	*Mougeotia genuflexa*	Macro algae (Green)	57.48	0.025	0.998						(Sari et al., 2011)
-	*Inonotus hispidus*	Fungi	51.9	0.016	0.997						(Sari and Tuzen, 2009)
-	*Penicillium purpurogenum*	Fungi	35.6	0.00165	0.99				—	Carboxyl, Phosphate	(Say, Yılmaz, & Denizli, 2003)
Sugarcane Bagasse		Agricultural waste	11.900	0.590	0.985	4.4	0.45	0.985	pseudo second order K2:0.07720 g/mgmin, r2:0.998	Carbonyl and Hydroxyl	(Tajernia, Ebadi, & Nasernejad, 2014)
Waste tea fungal biomass (Iron		Fungi	5.4	—	—	—	0.58	—	pseudo first order AsIII (K1:-0.078x10-3/min), AsV (K1:-0.039x10-4/min)		(Murugesan et al., 2006)

A-4.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ARSENIC III

			Langmuir constants			Freundlich constants					
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	References
Sweet lime peel	*Citrus Limetta*	Agricultural waste	3.11	0.29	0.942	1.199	0.21	0.999	pseudo second order AsIII (k2: 0.23 g/mgmin, qe:2.25 mg/g, r2:0.999), AsV (k2: 0.61 g/mgmin, qe:3.47 mg/g, r2:0.999	Hydroxyl, Amide, Amine, carboxyl, ketonic, Aromatic and Aliphatic	(Kamsonlian, Suresh, Majumder, & Chand, 2013)
Drumstick tree (seed powder)	*Moringa olefeira*	Agricultural waste	1.59	0.04	0.96	—	—	—	pseudo first order AsIII (K1:0.049/min), AsV (0.065/min)		(Kumari et al., 2006)
Waste tea fungal biomass (Autoclaved)		Fungi	1.11	—	—	—	0.86	—	pseudo first order AsIII (K1:-0.580x10-3/min), AsV (K1:-0.043x10-3/min)		(Murugesan et al., 2006)
Banana peel	na	Agricultural waste	1.03	0.29	0.928	0.78	0.74	0.993	pseudo second order k2:0.382 g/mgh, qe:0.683 mg/g, r2:0.998	Hydroxyl, Amine	(Kamsonlian, Balomajumder, & Chand, 2012)
Parsley (PCTTFe)	*Petroselinum crispum*	Agricultural waste	0.31	1.78	0.97	0.23	0.66	0.96	pseudo second order AsIII (k2:34.69 g/mgmin, r2:0.94), AsV (k2:13.62 g/mgmin, r2:0.99)	Hydroxyl,	(Jiménez-Cedillo et al., 2013)
Crab shells		Agricultural waste	0.166	—	—	—	—	—	pseudo second order k2:0.576 g/mgmin, qe:0.016 mg/g, r2:1.00	Amide (Niu, Volesky, & Cleiman, 2007)	(Zhang et al., 2014)
Rice Polish	*Oryza sativa*	Agricultural waste	0.139	5	0.996	0.0014	0.73	0.998	pseudo second order As III (K2:3.21x10-13 g/mgmin, qe:0.0588mg/g, r2:0.997), AsV(K2:3.72x10-13 g/mgmin, qe:0.073mg/g, r2:0.991)		(Ranjan, Talat, & Hasan, 2009)
Parsley (PCFe)	*Petroselinum crispum*	Agricultural waste	0.06	0.34	0.91	0.016	0.82	0.9	pseudo second order AsIII (k2:34.69 g/mgmin, r2:0.94), AsV (k2:5.05 g/mgmin, r2:0.99)	Hydroxyl, Carboxyl	(Jiménez-Cedillo et al., 2013)
Atlantic Cod fish scales	na	Agricultural waste	0.0248	5.2	0.985	0.68	0.61	0.964	—	Carboxyl, Amide, Nitryl, Alkyl (Basu et al., 2006)	(Rahaman, Basu, & Islam, 2008)

A-5.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ARSENIC V

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	pH	Temp. (°C)	Equilibrium time (h)	References
	Rhazya stricta	Agricultural waste			None	25,50,75,100,125			5.0	---		(Badr & Al-Qahtani, 2013)
Orange Juice Residue		Agricultural waste			modification of phosphorylation followed by loading with Iron III	---			As III:7-11, AsV:2-6	30		(Ghimire et al., 2002)
	Xanthoria parietina	Fungi										(Sari and Tuzen, 2010)
-	*Inonotus hispidus*	Fungi			Samples were washed several times using deionisedwater to remove extraneous and salts					20		(Sari and Tuzen, 2009)
	Lessonia nigrescens	Macro algae (brown)			None	50-600			2.5	20		(Hansen, Ribeiro, & Mateus, 2006)
	Crab shells				None	9 - 100			4.0	---		(Jeon, 2011)
Parsley (PCTTFe)		Agricultural waste			PCFe was Pyrolyzed and then retreated with FeCl3	0.05 - 2			6.5	18		(Jiménez-Cedillo et al., 2013)
Coconut Coir Pith		Agricultural waste			Synthesized with epichlorohydrin and dimethylamine + HCl treatment	5 - 100			7.0	20		(Anirudhan & Unnithan, 2007)
	Waste tea fungal biomass (Iron	Fungi			Autoclaved at 15 psi for 15 min and then inmersed in FeCl4	As III: 1.3 / As V:0.09			7.2	30		(Murugesan et al., 2006)
	Crab shells (Acid Washed)				Washed with HCl	---			2.5	20 - 25		(Niu, Volesky, & Cleiman, 2007)
	Waste tea fungal biomass	Agricultural waste			Autoclaved at 15 psi for 15 min	As III: 1.3 / As V:0.9			7.2	30		(Murugesan et al., 2006)
Pine leaves	*P. roxburghii*	Agricultural waste			None	5 - 30			4.0	25		(Shafique et al., 2012)
Sweet lime peel	*Citrus Limetta*	Agricultural waste			None	50 - 200			As III:6.0/ AsV:4.0	40		(Kamsonlian, Suresh, Majumder, & Chand, 2013)
	Moringa Seed Powder	Agricultural waste			None	1 - 100			As III:7.5/ AsV:2.5	---		(Kumari et al., 2006)
Parsley (PCFe)		Agricultural waste			Iron modified, 500 mL FeCl3 for 5 hrs	0.05 - 2			6.5	18		(Jiménez-Cedillo et al., 2013)
Rice Polish		Agricultural waste			None	100 - 1000			As III:7.0/ AsV:4.0	20		(Ranjan, Talat, & Hasan, 2009)

A-5.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ARSENIC V

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	pH	Temp. (°C)	Equilibrium time (h)	References
	Atlantic Cod fish scales	Agricultural waste			None	0.2 - 1			4.0	---		(Rahaman, Basu, & Islam, 2008)

A-5.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ARSENIC V

			Langmuir constants			Freundlich constants					
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	References
	Rhazya stricta	Agricultural waste	162	56720	0.995	17.62	0.57	0.971			(Badr & Al-Qahtani, 2013)
Orange Juice Residue		Agricultural waste	67.43		.				---	Carboxylic	(Ghimire et al., 2002)
	Xanthoria parietina	Fungi	60.3	0.012	0.997						(Sari and Tuzen, 2010)
-	*Inonotus hispidus*	Fungi	59.6	0.012	0.997						(Sari and Tuzen, 2009)
	Lessonia nigrescens	Macro algae (brown)	45.2	KL:0.013	—	KF:3.41, 1/n:0.4			pseudo first order K1:0.00107/min	Carboxylic, Amino	(Hansen, Ribeiro, & Mateus, 2006)
	Crab shells		35.92	KL:0.054	—	—			---	Hydroxyl, Amide, Nitro	(Jeon, 2011)
Parsley (PCTTFe)		Agricultural waste	18.17	0.005	0.99	KF:0.09, 1/n:1.02, r2:0.99			pseudo second order AsIII (k2:34.69 g/mgmin, r2:0.94), AsV (k2:13.62 g/mgmin, r2:0.99)	Hydroxyl,	(Jiménez-Cedillo et al., 2013)
Coconut Coir Pith		Agricultural waste	13.57	0.371	0.99	—			pseudo second order	Amine	(Anirudhan & Unnithan, 2007)
	Waste tea fungal biomass (Iron treatment)	Fungi	10.26	—		0.91			pseudo first order AsIII (K1:-0.078x10-3/min), AsV (K1:-0.039x10-4/min)		(Murugesan et al., 2006)
	Crab shells (Acid Washed)		8.3	—		—			---	Amide	(Niu, Volesky, & Cleiman, 2007)
	Waste tea fungal biomass (Autoclaved)	Agricultural waste	4.95	—		3.8			pseudo first order AsIII (K1:-0.580x10-3/min), AsV (K1:-0.043x10-3/min)		(Murugesan et al., 2006)
Pine leaves	*P. roxburghii*	Agricultural waste	3.27	0.12	0.989	0.04	0.94	0.986	pseudo second order K2: 21.145g/mgmin, qe:0.0232mg/g, r2:0.999	Carboxyl, Amine, Hydroxyl	(Shafique et al., 2012)

A-5.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF ARSENIC V

			Langmuir constants			Freundlich constants					
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	References
Sweet lime peel	*Citrus Limetta*	Agricultural waste	3.11	0.8119	0.92	1.722	0.13	0.994	pseudo second order AsIII (k2: 0.23 g/mgmin, qe:2.25 mg/g, r2:0.999), AsV (k2: 0.61 g/mgmin, qe:3.47 mg/g, r2:0.999	Hydroxyl, Amide, Amine, carboxyl, ketonic, Aromatic and Aliphatic	(Kamsonlian, Suresh, Majumder, & Chand, 2013)
	Moringa Seed Powder	Agricultural waste	2.16	0.09	0.98	—			pseudo first order AsIII (K1:0.049/min), AsV (0.065/min)		(Kumari et al., 2006)
Parsley (PCFe)		Agricultural waste	0.19	2.3	0.98	0.15	0.61	0.94	pseudo second order AsIII (k2:34.69 g/mgmin, r2:0.94), AsV (k2:5.05 g/mgmin, r2:0.99)	Hydroxyl, Carboxyl	(Jiménez-Cedillo et al., 2013)
Rice Polish		Agricultural waste	0.147	15.6	0.998	0.0033	0.77	0.997	pseudo second order As III (K2:3.21x10-13 g/mgmin, qe:0.0588mg/g, r2:0.997), AsV(K2:3.72x10-13 g/mgmin, qe:0.073mg/g, r2:0.991)		(Ranjan, Talat, & Hasan, 2009)
	Atlantic Cod fish scales	Agricultural waste	0.03	8.8	0.988	0.4	0.65	0.984	---	Carboxyl, Amide, Nitryl, Alkyl (Basu et al., 2006)	(Rahaman, Basu, & Islam, 2008)

A-6.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF SELENIUM IV

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	pH	Temp. (°C)	Equilibrium time (h)	References
Red mushroom	*Ganoderma Lucidum*	Fungi	<200 µm	Oven 60°C, 24h	Wash with distilled water.	20-140	0.7	100	5	20	90	(Nettem & Almusallam, 2013)
---	*Cladophora hutchinsiae*	Macro algae (Green)	0.5 mm	Oven 60°C, 48h	Wash with distilled water.	10-400	0.80	100	5	20.0	60	(Tuzen & Sari, 2010)
Tree barks	*Eucalyptus camaldulensis barks*	Agricultural waste	0.85–1.70 mm	Sun dried (3 days) and oven 60 °C, 48 h.	The powdered tree bark (after oven drying) was immersed in 1.0 L of 4N C4H6O6 (tartaric acid) and placed in a mechanical shaker at 300 rpm for 24 h. The samples were filtered and rinsed with distilled water, until the pH was neutral.	100.0	?	?	5	30.0	90	(Rajamohan & Rajasimman, 2015)
Rice husk (wet sorbent)	---	Agricultural waste	Between two sieves of 16 and 60 mesh	Before acid treatment: air-dried to constant weight.	Wash, then air dried. 13Msulfuric acid were added to the rice husk and the mixture was heated to 175–180 ◦C for 20 min with occasional stirring. Filter and store in a diluted solution of H2SO4	25-250	0.1	100	1.5	45	200	(El-Shafey, 2007b)
Rice husk (dry sorbent)	---	Agricultural waste	Between two sieves of 16 and 60 mesh	Before acid treatment: air-dried to constant weight. After acid treatment: oven drying at 120 ◦C to constant weight.	Wash, then air dried. 13Msulfuric acid were added to the rice husk and the mixture was heated to 175–180 ◦C for 20 min with occasional stirring. Filter and store in a diluted solution of H2SO4	25-250	0.1	100	1.5	45	200	(El-Shafey, 2007b)
Peanut shell (wet)	---	Agricultural waste	Between 1 to 0.3mm	Before acid treatment: air-dried to constant weight.	Wash, then air dried. 13Msulfuric acid were added to the rice husk and the mixture was heated to 170 ◦C for 25 min with occasional stirring. Filter and store in a diluted solution of H2SO4.	25-250	0.10	100	2	25	260	(El-Shafey, 2007a)

A-6.1 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF SELENIUM IV

Common name	Scientific name	Type	Particle size (mm)	Drying conditions	Treatment	Concentration range (mg/L)	Biomass addition (g)	Solution (mL)	pH	Temp. (°C)	Equilibrium time (h)	References
Peanut shell (dry)	---	Agricultural waste	Between 1 to 0.3mm	Before acid treatment: air-dried to constant weight. After acid treatment: oven drying at 120 ◦C to	Wash, then air dried. 13Msulfuric acid were added to the rice husk and the mixture was heated to 170 ◦C for 25 min with occasional stirring. Filter and store in a diluted solution of H2SO4.	25-250	0.10	100	2	25	330	(El-Shafey, 2007a)
Haiiro-shiwogusa	*Cladophora sericea*	Macro algae (Green)	5 mm	Oven 55°C, 24h	Wash with distilled water.	2-50	0.25	25	2	20	—	(Filote et al., 2017)
Bagasse fly ash	---	Agricultural waste	?	Oven 105°C, 72h	The adsorbent was washed with 0.1 M FeCl3 solution.	0.1-0.5	0.2	50	2-3	20	—	(Wasewar, Prasad, & Gulipalli, 2009)
Wheat bran	---	Agricultural waste	<178 µm	Oven 60°C, 24h	Wash with double-distilled	0.1-1	1.00	50	2	20.0	—	(Hasan & Ranjan, 2010)

A-6.2 SUMMARY CHART OF DIFFERENT BIOSORBENTS IN THE REMOVAL OF SELENIUM IV

			Langmuir constants			Freundlich constants						
Common name	Scientific name	Type	qmax (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2	kinetics	Functional Groups	Mechanism	References
Red mushroom	*Ganoderma Lucidum*	Fungi	127.0	0.04	0.993	8.50	0.599	0.993	pseudo first order K1: 0.0212 min^{-1} R^2:0.9942	Amino, Carboxyl and Hydroxyl	?	(Nettem & Almusallam, 2013)
---	*Cladophora hutchinsiae*	Macro algae (Green)	74.9	0.01	0.996	2.8	0.530	0.960	pseudo second order K2:0.249 g/mgmin, qe:3.02 mg/g, R^2:0.999	Amide, Carboxyl and Hydroxyl	?	(Tuzen & Sari, 2010)
Tree barks	*Eucalyptus camaldulensis barks*	Agricultural waste	41.0	0.04	0.960	1.7	0.398	0.993		?	?	(Rajamohan & Rajasimman, 2015)
Rice husk (wet sorbent)	---	Agricultural waste	40.9	0.03	0.998	3.8	0.442	0.962	pseudo second order K2:0.00366 g/mgh, qe:12.594 mg/g, R^2:0.999	Carboxyl and Hydroxyl	x	(El-Shafey, 2007b)
Rice husk (dry sorbent)	---	Agricultural waste	34.1	0.02	0.997	2.7	0.464	0.985	pseudo second order K2:0.00271 g/mgh, qe:11.637mg/g, R^2:0.999	Carboxyl and Hydroxyl	x	(El-Shafey, 2007b)
Peanut shell (wet)	---	Agricultural waste	32.3	0.03	0.995	—	—	—	—	Carboxyl and Hydroxyl	BD	(El-Shafey, 2007a)
Peanut shell (dry)	---	Agricultural waste	23.8	0.03	1.000	—	—	—	—	Carboxyl and Hydroxyl	BD	(El-Shafey, 2007a)
Haiiro-shiwogusa	*Cladophora sericea*	Macro algae (Green)	4.00	0.01	0.980	0.03	0.880	0.980	—	Amino, Carboxyl and Hydroxyl	?	(Filote et al., 2017)
Bagasse fly ash	---	Agricultural waste	0.21	22.8	0.992	—	0.710	0.993		Hydroxyl, Silanol groups (Si-OH),	BD	(Wasewar, Prasad, & Gulipalli, 2009)
Wheat bran	---	Agricultural waste	0.09	20.3	0.993	2.3	0.769	0.996	pseudo second order K2:0.001375 g/mgh, qe:55.55mg/g, R^2:0.998		?	(Hasan & Ranjan, 2010)

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