Masterthesis

Optimization of aquatic Cu(II) removal within a competitive metal ion sorption against Cd(II) and Pb(II) on low-cost biomass of artichoke

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Scriptie ingediend tot het behalen van de graad van master in de industriële wetenschappen: chemie

▶▶ UHASSELT   KU LEUVEN

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Faculteit Industriële ingenieurswetenschappen
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Acknowledgments

After 1.5 years of document arranging and organizing, the set off of my foreign exchange to Cartagena (SE Spain) had finally become a fact in February earlier this year. In this period I have been investigating the aquatic competitive Cu(II) sorption on raw biomass of artichokes and attempted to optimize it by finding the most favourable conditions. This subject was assigned on the 18th of March, which implies that the entire project had to be completed in less than 3 months. Now that we have passed this period, I am finally able to present my master's thesis, which would not have been the result as it is now without the help of a significant group of people.

First and foremost, a heartfelt thank you to my internal supervisors *Dr. Marta Doval Miñarro* and *Dr. Maria Isabel Saavedra* for guiding me throughout the entire project. Their support, continuous optimism and enthusiasm have been a key in order to success my thesis within the limited time frame. In addition, I sincerely want to thank my external supervisor, *Prof. Dr. Ir. Leen Braeken*, for all the help she offered from across the border. Thanks to her effort and attention to detail, she provided important feedback during the research in order to systematically enhance its quality. Furthermore, my gratitude goes out to *Mr. Jeroen Lievens* for his linguistic advice and structural adjustments during the Master thesis's seminar.

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Nomenclature

Term	Definition
Bioaccumulation	Phenomenon in which toxic substances, heavy metals in this case, accumulate in living organisms, which endangers health, environment and life
Biota	An open physio-chemical system, which is capable to maintain, to reproduce, to grow and to adapt to changes in short and long-term due to matter and energy exchange with the environment on the one hand, and to an internal metabolism on the other hand
Design of Experiments (DoE)	Systematic methodology which traces the interactive relationships between the process output and its causative factors
Hypercalciuria	Condition in which the kidneys produce elevated levels of Calcium
Oedema	Condition in which abnormal levels of fluid accumulate in the interstitium (subcutaneous cavities in the body), causing severe pain
Osteoporosis	Condition which decreases the bone density and disturbs the bone matrix whereby the bone is more likely to break
Performance characteristic	Output parameter whose responses are used to assess the tested parameters in the DoE
Renal disfunction	Inability of a kidney to maintain its normal function, causing metabolites and waste products to accumulate in the blood
Robust design	Design in which the quality and reliability of a certain process is adjusted to the desired requirements in order to preserve customer satisfaction

Abstract in English

Cu(II), Pb(II) and Cd(II) are the most abundant heavy metal ions found in industrial wastewaters. Through water streams, they are capable of migrating into ecosystems and accumulate in the human body where their carcinogenic and toxic properties may express. This research on the removal of metal ions from water streams is commissioned by *QUIMYTEC* and focusses on the optimization of the competitive aquatic Cu(II) sorption against Cd(II) and Pb(II) on low-cost biomass of artichokes.

Based on *Taguchi's Orthogonal Array (OA) design* methodology, the influence of pH, initial metal concentration and biomass dosage on the sorption mechanism was evaluated. These parameters were selected from the *system* and *parameter* design after preliminary study and subsequently tested at 3 different levels in a 25 °C isothermally performed batch experiment for 24 h. Furthermore, the sorption capacity was introduced as the performance characteristic to be maximized in the Taguchi analysis. Subsequently, the process capacities were calculated from Inductively *Coupled Plasma - Atomic Emission Spectroscopy (ICP-OES)* responses of the analysed batch sequence and lastly evaluated by the *MiniTab* software.

From the analysis, it appears that the initial Cu(II) and Pb(II) concentration exert the most import main effects, whilst two-factor interactions between Cu-Cd and Cu-Pb appear to be non-existing. A maximum Cu(II) sorption capacity of 6.77 mg/g was obtained by adding 0.5 g/L biomass and adjusting the pH to 5 in an ionic solution which contained 50 mg/L of Cu(II) and 10 mg/L of Cd(II) and Pb(II). Based on these settings, a kinetic experiment was conducted in order to modulate the evolution towards equilibrium. The evolution of this pseudo-second-order sorption process was described by *Langmuir, Freundlich and Temkin* model, of which the *Langmuir* isotherm fits the most precisely.

Abstract in Dutch

Cu(II), Pb(II) en Cd(II) zijn de meest voorkomende zware metaalionen in industriële afvalwaters. Doorheen water kunnen ze migreren naar ecosystemen en accumuleren in het menselijke lichaam waarin hun kankerverwekkende en toxische eigenschappen mogelijk tot uiting kunnen komen. Dit onderzoek naar de verwijdering van zware metalen uit water stromen is toegewezen door *QUIMYTEC* en focust op de optimalisatie van de competitieve aquatische Cu(II) sorptie op profijtige biomassa van artisjokken.

Aan de hand van *Taguchi* zijn *Orthogonale Array (OA)* ontwerpmethodologie werd de invloed van pH, initiële metaalconcentratie en biomassadosering op het sorptiemechanisme geëvalueerd. Deze parameters werden na de voorstudie in *system* en *parameter design* geselecteerd en vervolgens isotherm getest op 3 verschillende levels in een batch reeks op 25 ° C gedurende 24 uur. Verder werd de sorptiecapaciteit geïntroduceerd als de te maximaliseren prestatiekarakteristiek in de *Taguchi* analyse. Deze procescapaciteiten werden berekend aan de hand van *Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-OES)* responsies na analyse van de batchexperimenten en tenslotte geëvalueerd door de *MiniTab* software.

Uit de analyse blijkt dat de initiële Cu(II) en Pb(II) concentratie de belangrijkste hoofdeffecten teweeg brengen, terwijl twee-factor interacties tussen Cu-Cd en Cu-Pb onbestaande lijkt. Een maximale Cu(II) sorptiecapaciteit van 6.77 mg/g werd verkregen door 0.5 g/L biomassa toe te voegen aan een ionische oplossing die 50 mg/L Cu(II) bevat en 10 mg/L aan Cd(II) en Pb(II), en bijgevolg de pH op 5 in te stellen. Op basis van deze instellingen werd een kinetisch experiment uitgevoerd om de evolutie van het proces naar evenwicht te moduleren. De evolutie van dit pseudo-tweede-orde sorptieproces werd beschreven door het *Langmuir*, *Freundlich en Temkin* model, waarvan de *Langmuir* isotherm de meest precieze benadering weergeeft.

CHAPTER 1 - Introduction

1.1 Placement of the research

This research into the optimization of aquatic Cu(II) biosorption on lignocellulosic biomass is commissioned by research group QUIMYTEC of the *Universidad Politécnica de Cartagena* (UPCT). QUIMYTEC is located in the *Escuela Técnica Superior de Ingeniería Industrial* (ETSII) on *campus Alfonso XIII* in Cartagena, adjacent to the former *Cartagena-La Unión* mining district. This district has been a very important factor for the establishment and development of QUIMYTEC and its research on environmental purification.

1.1.1 *Cartagena-La Unión* mining district

The *Cartagena-La Unión* mining district has been the centre for heavy metal extraction within the Region of Murcia for over 2000 years. This geological area of approximately 50 km² near the Mediterranean sea in [SE] Spain (**Figure 1** - Geographical location of the Cartagena-La Unión mining district *[3]*) has a soil rich with Cu, Pb, Zn, Ag, Sn, Fe and Mn which are mainly present as oxides and sulphides [1]. In the 20th century, the area gradually evolved into a major metal producing and processing industrial site and became a very important economic centre within its region. The economic growth in the early 50's resulted in an increasing demand for metal, which entailed a large-scale heavy metal pollution of the surrounding ecosystem. Eventually the *Cartagena-La Unión* mining district closed its doors in 1992 [2].

Figure 1 - Geographical location of the Cartagena-La Unión mining district *[3]*

To this day, increased concentrations of heavy metals are measured in aqueous streams, soils and biota in and around the former mining site [2]. This large-scale environmental problem is one of the main topics QUIMYTEC is involved with. With its focus on chemical and environmental technology, QUIMYTEC conducts research into the biological removal of these toxic metallic impurities out of contaminated aquatic effluents [4].

1.1.2 Importance of water purification

Water is a finite resource that is predominant for the existence and development of various ecosystems and all life forms within them. Subsequently, it is a key element for the maintenance and development of human kind and its economy. With a rising world population and consequently an increasing demand for water in order to maintain it, water is becoming more scarce every day [5]. Furthermore, the contamination of water with organic and inorganic pollutants compromises the availability of fresh water use. In order to make this contaminated water available again, numerous of wastewater purification techniques must be used. This makes the presence of good waste water management of great importance as is apparent from the UNESCO quote below [6].

"In a world where demands for freshwater are ever growing, and where limited water resources are increasingly stressed by over-abstraction, pollution and climate change, neglecting the opportunities arising from improved wastewater management is nothing less than unthinkable" [7, p. V]*.*

The most common inorganic contaminants that are found in wastewater streams appear to be heavy metals. Nowadays, the following separation techniques are mainly used as a treatment for this kind of contaminated effluents; Chemical precipitation, ion exchange, membrane filtration, coagulation, flocculation, flotation and electrochemical separation. These techniques are expensive, energy intensive and often initiate other side problems such as toxic sludges [6]. In response to this, an increasing demand of new and more profitable separation techniques arouses. This research goes even one step further and investigates low-cost biological sorption techniques in order to separate the most common heavy metals in industrial wastewater systems, namely Cu(II), Pb(II) and Cd(II) [8].

1.1.3 Biosorption

In its attempt to purify contaminated water streams, QUIMYTEC applies the principles of biosorption. This recent green technology aims to decrease elevated levels of polluting substances in the environment by applying biomass or micro-organisms as a separation mechanism [9]. In this research, biosorption refers to the removal of toxic inorganic metals as it can also be used to reduce the concentration of organic pollutants. In general, this study applies biomass from agro-industrial waste of globe artichokes (*Cynara scolymus L.)* to accumulate metallic pollutants within its lignocellulosic structure in order to purify contaminated water streams.

Biosorption has developed a major importance in numerous pieces of research due to its high efficiency, low cost, versatility and applicability in comparison to the other separation techniques as described in *1.1.2 Importance of water purification* [10]. Within the environment, biosorption is responsible for a significant proportion of the natural matter exchange. The key in elaborating this natural phenomenon into an industrial regime consists of understanding the mechanisms which entail sorption properties on the first hand, and to study the influence of physicochemical parameters on both equilibrium and kinetics on the other hand [11]. Furthermore, this principle enables a low-cost alternative to water treatment and also provides the opportunity to valorise this agro-industrial waste stream. An overall diagram regarding the placement of the research is shown in **Fout! Verwijzingsbron niet gevonden.**.
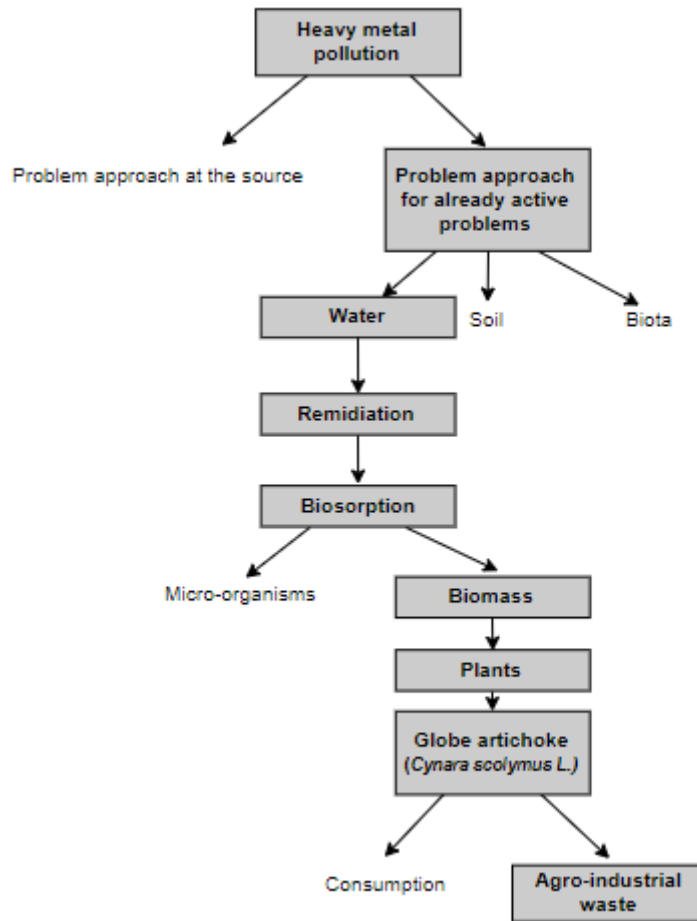
Figure 2 - Schematic representation of the principle applied in this research

1.2   Problem statement

The origin of this research is directly attributable to the already mentioned contamination of heavy metals in water streams of the surrounding ecosystem of the *Cartagena-la Unión* mining district. However, a solution to this problem also affects the enormous agro-industrial waste production within the local artichoke food industry. Therefore, it is cited as a secondary problem as this study may lead to the valorisation of these waste streams.

1.2.1   Main problem

The *Cartagena-La Unión mining district* has been the centre for heavy metal extraction for thousands of years. This exploitation of mainly Cu, Pb, Zn, Ag, Sn, Fe and Mn was unfortunately accompanied by a large-scale dispersion of them in the surrounding ecosystem. Even after 1992, when all the exploitation and metal industrial operations came to a standstill, heavy metal dispersion still occurred. This is because in addition to industrial pollution, natural elements such as weather conditions also play an important role within this metal mobilization. This main problem is therefore caused by both natural and industrial factors [1].

1.2.1.1 Industrial factors

The industrial factors in this problem statement are directly attributable to industrial waste disposals. It is due to human actions that large amounts of industrial waste waters were discharged into natural water streams within the mining district. These waste waters, which came from melt and metallurgical processes, still contained very high concentrations of heavy metals in which mainly Cd(II), Pb(II) and Cu(II) carry a significant share [8]. Until the middle of the last century, the discharge of waste water was a standard procedure within the industrial site [3].

After meters of thick sediments in river beds and elevated concentrations of heavy metals in bivalve shells were found in the *Portman Bay* around the district in 1955, a law finally prohibited the disposal of metal-containing industrial waste into water streams. Around the same period, the exploitation industry was on the rise thanks to the development of new extraction techniques. The old underground extraction techniques were surface inefficient and only yielded a limited amount of ores whilst the new surface extraction techniques where more efficient in every way [3]. This evolution in heavy metal exploitation led to a strong increase in production which, in turn, resulted in a massive increase of mine tailings. These tailings are remnants of ores in which the largest amount of valuable metals has already been extracted by metallurgic processes. The problem of these tailings is that they are continuously exposed to weather elements such as wind and rain that will eventually initiate the establishment of the natural factors within this case [12].

1.2.1.2 Natural factors

The natural factors in this problem statement are mainly erosion of heavy metals via wind and water. Previous research has shown that this erosion is predominant compared to former industrial discharges in terms of metal dispersion across the region [3]. The degree of erosion by wind in this region is considered very high due to its maritime location near the Mediterranean Sea. Especially in spring, when an elevated activity of the eastern wind takes place, this wind erosion reaches a peak [13]. As mentioned above, the dispersion of heavy metals by wind erosion has to do with the surface discharge of mining tailings which at that time still contained a high level of metal residues caused by less efficient metallurgic processes. Due to this industrial surface pollution, the tailings were exposed to the weather elements which in turn spread the pollutants over the surrounding area as a fine contaminated dust. Of the 50 km² area of the mining district, approximately 160 ha are covered by heavy metal tailings and 820 ha are former exploitation areas which are continuously exposed to the elements of nature [3].

Water erosion on the other hand is proven to be the dominant natural factor. This bigger concern has to do with the short but intense rainfalls which are characteristic of the local Mediterranean climate. Just like wind erosion, contaminants derived from mining tailings are transported through the environment. Due to the presence of 7 small creeks within the mining area, the contaminants that are dragged along by rain can spread over a much larger area than by wind erosion [2],[3] .

1.2.1.3 Potential risk

These metallic pollutants eventually end up in agricultural soils and both in sweet and salty water streams that are rich with living organisms. During a later stage, they migrate into fruits and vegetables on the first hand, and into aquatic organisms such as shells and fishes on the other hand. In this way, they end up in the human food chain and eventually build up in human bodies due to an improperly metabolization of it [14]. In order to clarify the impact of this main problem, it is important to define the size of the population that are directly affected by the effects of this pollution. The exposed area has over 200,000 inhabitants of which the majority is located in the city of Cartagena. Furthermore, it

is also important to realize that a larger population is affected due to exports of local goods such as vegetables, fruits and fish [2][3].

The reason why heavy metal spreading is such a dangerous phenomenon is related to the toxic properties against plants and animals, which are carried by most of the heavy metals. Unlike organic structures, heavy metals are not degraded properly into the human body, which entails that its amount will only increase due to bioaccumulation. These rising levels of metals in the body consequently create an increasing risk for the toxic effects that are related to them. When these effects are expressed, one speaks of metal poisoning [14]. Only the toxic effects of Cd, Pb and Cu will be further discussed here as the research exclusively focuses on these heavy metals.

Both Pb and Cd are considered as carcinogenic substances, which means that they have a high tendency in the human body to develop cancer cells. Pb can be considered as highly toxic. Excessive bioaccumulation of it due to long-term exposure may result in paralysis caused by impairment of the central nervous system, oedema, muscular weakness, kidney damage, brain damage, psychosis, autism, hyperactivity, muscular weakness, birth defects and even death. On a long term basis, elevated bioaccumulation of Cd could cause osteoporosis, renal disfunction, hypercalciuria, kidney damage and disturbance of our calcium metabolism [15]. Finally, Cu is considered to be the least toxic of the elements considered in the investigation. Nevertheless, it still causes serious consequences when it is present in the body at elevated levels. Possible disorders that copper poisoning entails are kidney damage, brain damage, chronic anaemia and liver cirrhosis [14].

1.2.2 Secondary problem

Spain is known as one of the largest food exporters in Europe. Its massive agro-industry accounts for approximately 9% of the total economy within the country thanks to goods such as wine, olive oil, vegetables and fruits. As a result, this industry has been one of the key players for the export growth in Spain. Such a huge demand for Spanish goods goes hand in hand with a large-scale production which in turn entails in massive agro-waste generation [16].

The main principle in agro-industry is the conversion of raw goods into goods that are ready for consumption. In this process, the product in question will only lose weight as it is stripped of non-edible parts. This removed mass should end up somewhere else to be in balance and that is exactly what maintains the waste problem. This problem only gets more extensive when looking at artichoke canning manufacturers. The immature flower heads and the inner bed are the only edible parts of the whole artichoke crop, which implies that stems, outer leaves and flower ends are all released as waste. The mass of agro-waste amounts to approximately 70% of the entire plant [17]. This problem only becomes more extensive when looking at the high water requirements within the 7 months growth period of the artichokes [5],[17]. It takes approximately 790 L to obtain 1 kg of artichokes that is for consumption [18]. This high demand for water is an increasing problem as fresh water sources are becoming more scarce worldwide, certainly when it is known that the agro-waste of the artichoke has been responsible for approximately 2/3 of the total water consumption [7]. This increases the importance of valorising this agro-waste stream [19].

As already mentioned, the focus of the research is not situated on this problem and therefore it has not been analysed as thoroughly as the main problem. Nevertheless, it is important to identify this problem as it offers the opportunity for low-cost research as this agro-waste is available in extensive quantities while the demand for it is limited due to its little particle commissioning [5]. Despite the fact that the artichoke remains are generally used as cattle feed, they do carry an important chemical composition that is increasingly gaining importance in contemporary research. The plant exhibits for example good antioxidant properties thanks to the presence of polyphenols. Further, the most

important application is situated in the sorbing ability of the artichoke due to a high content of cellulose, and to a lesser extent lignin, in its fibres [14]. This makes the use of agro-waste from artichokes interesting for metal sorption purposes. In this way, artichoke waste streams can be valorised which entails the principles of a circular economy.

1.3   Objectives

The main goal in this research is to optimize the aquatic Cu(II) removal within a competitive metal ion sorption against Cd(II) and Pb(II) on low-cost biomass of artichoke. As a consequence of the large scale of this research, a series of secondary objectives is listed alongside this main objective. In order to achieve this main objective and thus this research, the following additional sub-objectives need to be clarified:

- Which physicochemical parameters have the most favourable influence on Cu(II) sorption on lignocellulosic biomass?
- What are the most suitable levels to test these parameters of interest within a Taguchi Orthogonal Array [OA] design?
- Which Loss function is most suitable in order to approach the quality requirements for this sorption process?
- Which of the selected parameters have the greatest effect on the Cu(II) removal during competitive ion sorption against Pb(II) and Cd(II)? Which parameters constitute the most influential two-factor interactions?
- Which isothermic pseudo-second order model describes the Cu(II) sorption the most accurately?
- What is the influence of the presence of Cd(II) and Pb(II) on the kinetics of Cu(II) during the competitive sorption process?
- What are the most favourable settings for the most influential parameters in order to optimize the Cu(II) removal whilst taking the influence of the competitive ions into account?

1.4   Approach

The overall approach of this research will make it possible to define and clarify the sub-objectives in order to achieve the main goal. Before an experimental plan can be drawn up, the principle of lignocellulosic ion sorption must be studied in detail first. On the basis of a preliminary study, promising parameters which carry an important influence within this sorption process are listed. Further advanced research will then statistically determine which 5 parameters are the most interesting to test within this *Design of Experiments* (DoE). According to the Taguchi methodology, this corresponds to the first phase of the research which he called *system design*. Subsequently, preliminary study will also provide the opportunity to define the boundaries of the selected parameters and as a result values can be assigned to the parameter levels. This parameter setting can then be tested experimentally according to a modified orthogonal array (OA) with the aim of obtaining design responses of the performance characteristic. Taguchi describes this second phase as the *parameter design* [20].

A $[3^5]$-matrix is obtained by testing these 5 selected parameters at 3 different levels in an experimental batch sequence. This classifies the DoE into a full fractional 3^5 experiment, which corresponds to 243 experiments. Taking into account that this research has to be fully executed in 3 months, it is important that the size of this experimental sequence is minimized into a reasonably practical one. In order to reduce this large sequence of experiments into an acceptable quantity, Taguchi's OA methodology is applied. According to this methodology it is not about the execution of the entire matrix but rather about getting the most important information out of a specific and compact selection within it [21]. In order to achieve this reduction, the principle only focuses on two-factor interactions and main effects

whilst higher-order interactions are considered non-existent [22]. In addition, this methodology will also provide the opportunity to determine the most influential main effects and two-factor interactions among the tested parameters. Subsequently, the kinetics of the sorption process are described by applying isotherm equilibrium models of both Langmuir and Freundlich, as well as Temkin, in order to see which one fits best. Eventually, the kinetics of the process are thoroughly studied and combined with the knowledge from the Taguchi OA design to set-up an optimizing experimental sequence. This series of experiments will ultimately provide the most favourable conditions for optimizing the Cu(II) removal in the sorption process.

CHAPTER 2 – Preliminary study

2.1   Principles of lignocellulosic metal sorption

Extensive research reveals that lignocellulosic-based biomass has a high metal sorption capacity [14],[23],[24],[25] which, in many cases, is comparable to the ones of commercial resins for ion exchange [24]. Biomass of this nature has a versatile applicability within wastewater treatment for two important reasons. The first reason is the non-selective sorption property of lignocellulosic structures which entails the ability to remove a wide variety of metals instead of just one specific metal [25]. The second reason has to do with the operational flexibility of the biomass. In commercial wastewater treatment, the sorbents must be regenerated at certain times when they have reached their maximum uptake capacity. The regeneration of lignocellulosic biomass is found to be very efficient in comparison with those of other sorbents that are often expensive and time-consuming within water purification processes [24]. These two factors in combination with the low cost and abundant availability of lignocellulosic agro-waste make a large-scale commissioning of it in wastewater treatment feasible. Additionally, the production, application and regeneration of lignocellulosic materials can take place without potentially adverse effects on the environment [23],[25].

2.1.1   Biomass

Lignocellulosic biomass can be obtained from numerous different sources such as wood species, stems, crops, fruit stones, hulls, straws, shells, leaves, seeds, grasses, by-products and agro-wastes [25],[26]. Although biomass of this nature has an extensive applicability in water purification, this research only focuses on the metal removal. In fact, it is the application of raw lignocellulosic biomass that is the most popular among the large variety of renewable sorbents [24]. Raw biomass is biomass obtained by merely applying physical operations on the initial agro-waste, e.g. cutting and grinding. This research focusses on the use of raw biomass, which implies that chemical modification will not be executed. Nevertheless, it is important to note that several studies have revealed that these modifications favourably influence the sorption capacity q_e in comparison to raw biomass [24],[25],[27],[28]. **Table 1** – Influence of chemical modifying techniques on the sorption capacities of different lignocellulosic biomass shows the enhancement in sorption capacities of several lignocellulosic biomasses after chemical modifications compared to the initial capacity of the corresponding raw biomass.

Table 1 – Influence of chemical modifying techniques on the sorption capacities of different lignocellulosic biomass *[23]*

Biomass type	Modifying agent	Metal ion	Increase in q_e (%)	Reference
T. aestivum	Urea	Cd(II)	822.8	*Farooq et al. [29]*
S. bengalense	Urea	Pb(II)	167.4	*Farooq et al. [29]*
O. sativa	Urea	Cu(II)	55.2	*Athar et al. [30]*
Sorghum bicolor L.	Thiourea	Pb(II)	183.4	*Salman et al. [31]*
Orange peels	Grafted polymerization	Cd(II)	362.9	*Feng et al. [28]*
Orange peels	Grafted polymerization	Pb(II)	319.5	*Feng et al. [28]*

Lignocellulose structures mainly consists of cellulose, lignin and hemicellulose polymers that are held together in a complex matrix due to intramolecular interactions [32]. This complex structure can be found in the cell wall of different woody plants in which the three construction components are present in varying proportions depending on the nature of the lignocellulosic source. As shown in **Figure 3** - Lignocellulosic structure *[33]*, cellulose appears as an unbranched polysaccharide that is built up from glucose dimer blocks by glycosidic ($\beta - 1,4$) bonds. As a result of the parallel configuration of these cellulose chains, they are able to interact intramolecularly as well as intermolecularly by hydrogen bonds. This enables them to form a tight network, which entails that cellulose occurs in most cases in a crystalline structure. Hemicellulose, unlike cellulose, is completely amorphous due to the branching and the short chain lengths of its polysaccharides. This hemicellulose structure is formed by repetitions of pentoses and hexoses as well as acetyl and uronic acid groups. Finally, lignin is present as a non-linear complex of macromolecules, which is formed by essentially C-C covalent and ethereal bonds [32],[33].
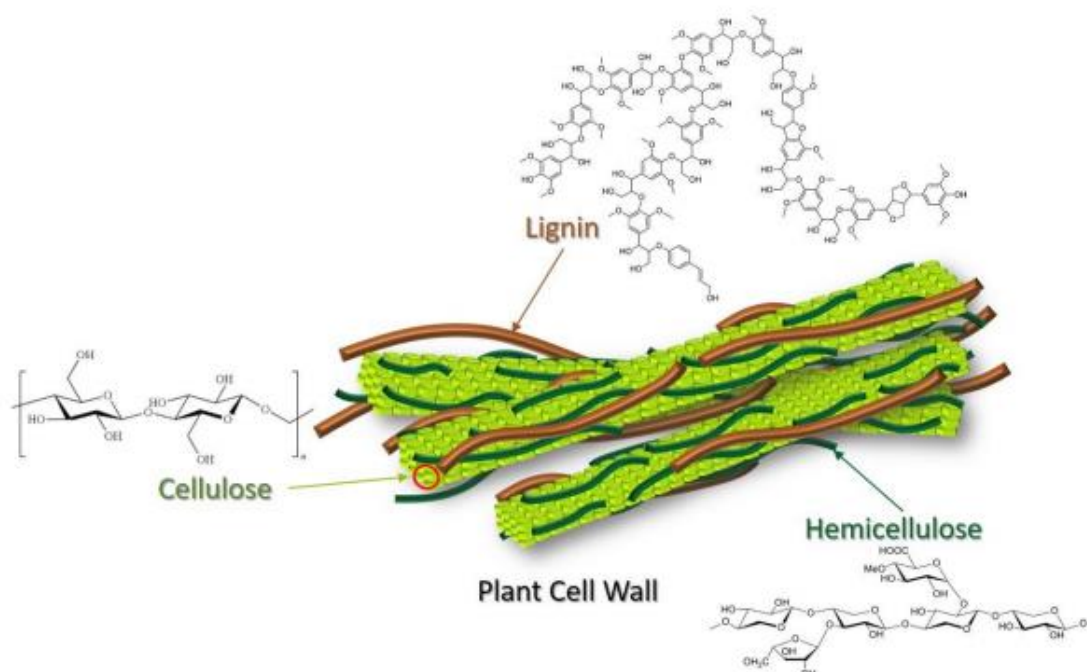
Figure 3 - Lignocellulosic structure *[33]*

The interpolymer interactions between the building blocks of the lignocellulose structures include ester and ethereal linkages on the first hand, and hydrogen bonds on the other hand. Lignin is connected with cellulose and hemicellulose as a Lignin-polysaccharide complex formed by ester and ethereal linkages. There are no intra-molecular interactions within lignin and cellulose polymers, but an intra-ester linkage is expected to occur between the hemicellulose polymers. Furthermore, the connection between hemicellulose and cellulose is obtained by hydrogen bonds that are presumably formed due to the parallel orientation of the polymers. However, these hydrogen bonds are weak due to a lack of primary alcohol functions on the external part of the pyranoside rings within hemicellulose polymers. This series of intermolecular interactions between the main components is decisive for the complex structure of lignocellulose biomass [32]. Moreover, these main biomolecules contain numerous functional groups that can provide interactions with metal ions [25]. The nature of these functional groups and their interaction mechanism are further described in *2.1.2 Biosorption mechanism*.

Extensive research has shown that complex compact structures such as lignocellulose compounds have an adverse effect on the metal ion diffusion [25]. In fact, these compact structures causes an hindrance

for metal ion migration to the interior parts of the matrix on the first hand, and causes a reduction of metal complexation due to the limited availability of reactive sites in the matrix on the other hand. When the biomass is physically modified, a larger active surface is created so that metal ions are more likely to find reactive functional groups and subsequently interact with them. Therefore, lignocellulosic-based biomass commonly occurs in the form of powder or flakes in experimental research [24],[25].

2.1.2 Sorption mechanism

The biosorption process of metals takes place through two different phases. The solvated metal ions must initially migrate through the liquid before they can penetrate into the solid porous biomass, which implies that diffusion is involved in the mechanism [34]. The progress of this diffusion is considered to be gradual due to several concentration gradients within membranes and cell walls of the biomass. This gradient stimulates the entrapment of metal ions in both intra- and interfibrillar cavities within the complex polysaccharide network [9]. Furthermore, the actual interaction mechanism on lignocellulosic structures has a high complexity because it relies on both physical and chemical principles. This physicochemical metal separation is mainly based on complexation, ion exchange, precipitation and adsorption properties of the functional groups on lignocellulosic biomass [25]. Moreover, various factors such as physical environmental conditions, origin of lignocellulosic material and chemical conditions of the ionic solution have their influence on the efficiency of the sorption process [23],[24].
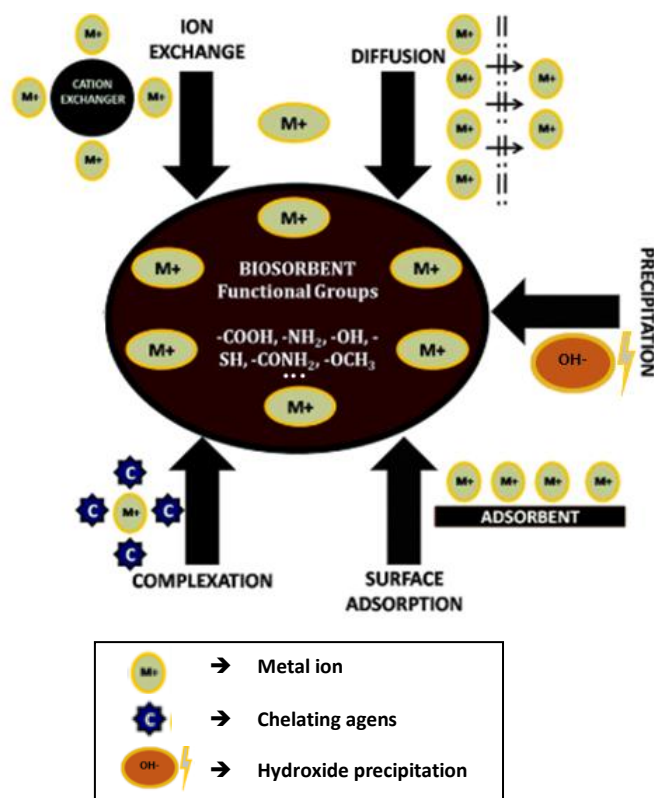
Figure 4 - Biosorption mechanism [63]

Figure 4 is a representation of the main physicochemical processes within the biosorption mechanism of lignocellulosic biomass. This implies that each of these five factors are responsible for a certain part of the total metal removal. A first important factor is precipitation on the surface of the biomass due to the presence of hydroxyl groups within lignin, cellulose and hemicellulose [26]. The interactions of the metal ions with the alcoholic groups results in its removal out of the solution due to the formation of solid hydroxide precipitates. Furthermore, lignocellulosic structures contain carboxyl, ester, phenolic, acetamido, amino, amido and sulphydryl groups which have a certain affinity for heavy metal

complexation [25]. The cause of this phenomenon is the property of electron pair donation to positively charged metal ions carried by this series of functional groups [24]. Simultaneously with these other processes, also ion exchange occurs between metal ions and cations such as K^+, Na^+, Ca^{2+} and Mg^{2+} that are present in the biomass. In addition, these metal ions are also bound to the sorbent as a result of substitution with the initially present hydrogens. Adsorption occurs in surface pores of the biomass and as a result of *Van Der Waals* attraction forces. Finally, the importance of gradual diffusion manifests itself by entrapment of the ions in intra- and interfibrillar cavities in the polysaccharide matrix as already described [26].

However, the affinity of the lignocellulose biomass for the metallic species is also highly dependent on the nature of its ions. In fact, properties such as the hydrated ionic radius, the electronegativity and the covalent index of the metal ion contribute to the selectivity of the biomass [25]. The corresponding values of these properties for the examined ions Cd(II), Pb(II) and Cu(II) are shown in **Table 2** – Ionic properties of Cd(II), Pb(II) and Cu(II) concerning the sorption process.

Table 2 – Ionic properties of Cd(II), Pb(II) and Cu(II) concerning the sorption process

Ionic properties	Metal ion		
	Cd(II)	Pb(II)	Cu(II)
Hydrated ionic radius (Å)	4.26	4.01	4.19
Electronegativity	1.70	1.90	1.90

Since the covalent index is the same for all three ions, the difference in affinity for each ion can be explained by the different values for the hydrated ionic radius and electronegativity. First of all, the hydrated ionic radius plays an important role in the mass transfer of the ions from the ionic solution to the biomass. The greater the hydrated radius, the more resistance it entails during transport towards the biomass in comparison with ions which have smaller radii. Based on this property, the following sequence can be drawn from high to low affinity: Pb(II) (4.01) > Cu(II) > Cd(II). The second aspect has to do with a difference in electrostatic interactions. These interactions are stronger as the difference in electronegativity between metallic cation and 'counter ion on the surface of the biomass[1] is larger. The greater this difference, the more favoured they are within the ion exchange mechanism. Based on this property, the following sequence can be drawn from high to low affinity; Cd(II) (1.70) > Pb(II) (1.90) ≥ Cu(II) (1.90). However, not only the ionic properties are decisive for the progression of the biosorption process since the chemical composition of the biomass also plays an important role. Overall, one can conclude that the sorption process of metals on lignocellulosic biomass is a complex mechanism in which several intense non-linear interactions occur [25].

2.1.3 Equilibrium modelling

Studying equilibrium conditions between sorbent and sorbate is fundamental in understanding, designing and optimizing sorption processes as they provide important information concerning the physicochemical sorption behaviour. This information is necessary to evaluate any sorption process on its industrial feasibility and applicability [35],[36],[37]. Moreover, sorption equilibrium studies provide the opportunity to describe the mobility of a sorbate from the liquid towards the solid phase. In general, sorption equilibrium is reached when a dynamic balance is established between the interface sorbate concentration on the one hand, and the sorbate concentration in the bulk of the liquid phase on the other hand. It eventually occurs within sorption processes when the solid sorbent and the sorbate-containing liquid phase have been contacted for sufficient time [38].

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[1] The counter ions on the surface of the artichoke biomass are mainly O (EN 3.5), as well as N(EN 3.0) and S(EN 2.5) to a lesser extent. These counter ions are uniformly distributed over the entire biomass, which implies that the overall affinity is dependent on the electronegativity of the ion binding to these sites.

In order to modulate the equilibrium relationship between metal ions and lignocellulosic biomass in this research, sorption isotherms are applied. These isotherms provide an approximation of the actual state of equilibrium as they specify the relationship between equilibrium concentrations C_e of metal ions in both, the bulk of the liquid phase and the solid surface of the biomass [37]. Because of this concentration relationship, isotherm models are mostly expressed as sorption capacities q_e. However, the actual state of equilibrium is complex to approach since there is variation on the structural occurrence, and thus on the energetic binding power, of active surfaces within biomass [38]. Nevertheless, there are numerous empirical isotherm models which describe the sorption-based equilibrium well [36]. **Table 3 -** Isotherm models of Langmuir, Freundlich and Temkin [26]is a representation of the applied isotherms in this study.

Table 3 - Isotherm models of Langmuir, Freundlich and Temkin [26]

Isotherm model	Equation		Linear expression	
Langmuir	$q_e = \dfrac{Q_m . K_L . C_e}{1 + K_L . C_e}$	(1)	$\dfrac{C_e}{q_e} = \dfrac{1}{K_L . Q_m} + \dfrac{C_e}{Q_m}$	(2)
Freundlich	$q_e = k_F . C_e^{\frac{1}{n}}$	(3)	$ln(q_e) = ln(k_F) + \dfrac{1}{n} . ln(C_e)$	(4)
Temkin	$q_e = \dfrac{R.T}{b_T} . ln(K_T . C_e)$	(5)	$q_e = \dfrac{R.T}{b_T} . ln(K_T) + \dfrac{R.T}{b_T} . ln(C_e)$	(6)

Langmuir and *Freundlich* are amongst the most applied isotherm models in equilibrium studies [26],[35],[36],[37],[38]. In both models, as well as in *Temkin* model, characterization constants such as K_L, k_F, n, b_T and K_T can be found. These constants were introduced to describe the surface properties and the affinity of the sorbent [36].

2.1.3.1   *Langmuir isotherm*

Langmuir isotherm is by far the most widely applied equilibrium model in specifying liquid-solid sorption processes [35]. In his methodology, *Langmuir* assumed that a monolayer of sorbate is formed on the outer surface of the sorbent during the sorption process. A monolayer is defined as an uniformly covered film of sorbate around the sorbent, which entails that *Langmuir* isotherm is only valid for sorbents whose surface represent structural, and therefore energetic, uniformity [35]. After all, structural and energetic surface heterogeneity of biomass would lead to the formation of an uneven layer instead of a monolayer as it entails variation in ion-sorbent interaction strength across the entire biomass.

The monolayer in this model is considered to impede further transmigration of the sorbate through the outer surface of the sorbent. Moreover, the sorbing ability is considered to be independent of sorbate surface coverage. This implies that sorbate binding on a specific site is independent of the occupancy conditions of adjacent sites on the one hand, and that no interactions between adjoining sorbates occur on the other hand. In addition, it is noted that this model also corresponds to the dominant mechanism of ion exchange [38]. Equation (1) in **Table 3 -** Isotherm models of Langmuir, Freundlich and Temkin [26] represents the non-linear expression of *Langmuir* isotherm in which q_m refers

to maximum sorbate uptake, whilst the *Langmuir* constant b refers to the maximum sorption capacity of the monolayer [35].

2.1.3.2   Freundlich isotherm

Unlike *Langmuir, Freundlich* assumed that sorbent surfaces were rather heterogenous instead of uniform [35],[36],[37],[38]. This implies that several binding sites on the sorbent surface are carrying different sorption capacities due to structural, and consequently energetic, variation. As a result, the monolayer principle can no longer be assumed to define the sorption equilibrium, but instead, *Freundlich* introduced the application of a multilayer model. Using this model, he established an empirical relationship in which the total sorbate uptake is determined as the sum, of all individually sorbate uptakes on each site at the sorbent surface, as long as the sorption energy decreases experimentally over time [38]. The model can be applied for multilayer sorption processes, as well as for nonideal sorption processes [39]. As represented in equation (2) in **Table 3**, *Freundlich* introduces two constants, namely K_F and n. K_F is the *Freundlich* constant and is a measure of the sorbent surface heterogeneity. High values of this constant correspond to a high degrees of heterogeneity of the considered active sites. Furthermore, the *Freundlich* exponent n is present in the inverse form $(1/n)$ and takes the energy diversity, as well as the relative magnitude, into account. When $(1/n) > 1$, the *Freundlich* isotherm is concave as increasing surface concentrations results in an increasing sorption energy. When $(1/n) < 1$, the opposite tendency occurs whereby sorption energy decreases whilst surface concentration is increasing, resulting in a convex isotherm [37]. However, the isotherm model is thermodynamically limited as Henry's law is no longer approached at vanishing concentrations [39].

2.1.3.3   Temkin isotherm

Temkin's methodology is, unlike *Langmuir* and *Freundlich*, not based on the introduction of monolayer or multilayer models to describe the sorption equilibrium, but focusses on indirect interactions between sorbent and sorbate. This isotherm model assumes that the sorption heat, which is released whilst covering the sorbent surface with sorbate, decreases rather linearly instead of logarithmic as the process proceeds towards equilibrium [37],[40]. As represented in equation (3) in **Table 3**, *Temkin* introduced constants in order to implement sorbent-sorbate interactions into his isotherm [40]. K_T is the *Temkin* isotherm and refers to the mentioned interactions, whilst the *Temkin* constant b_T is a measure for sorption heat related with these interactions. The terms *R* and *T* refer respectively to the gas constant and the absolute temperature [37].

2.2   System and parameter design

S*ystem design* is the first procedure to be performed within the Taguchi optimization methodology. In this primary stage, the main parameters with a noticeable influence on the sorption process are listed and discussed. The parameters within this process are of a physio-chemical nature. The chemical parameters exert their influence in the ionic solution whilst the physical parameters are responsible for the environmental conditions of the process. The parameters that will be discussed in this study are pH, biomass dosage, temperature, contact time, initial concentration of the metal ions and the nature of the metal ion species. Furthermore, *parameter design* will provide the opportunity to define the boundaries of the selected parameters, which entails that values can be assigned to the parameter levels. Eventually, these parameter settings are tested, according to a modified orthogonal array (OA), in a series of batch experiments as will be explained in section *3.2 Batch sequence*.

2.2.1   pH

The pH of aqueous solutions is proven to be a dominant factor within heavy metal biosorption [24],[25],[32],[41],[42]. It is known to affect the underlying mechanisms within the sorption process what makes the metal ion uptake capacity of the biomass strongly dependent on it [43]. The pH setting has a significant influence on the dissociation rate of the functional groups on the surface of the biomass, the competition between metallic ions in order to bind on active sites and the chemical

metallic properties within the ionic solution [42]. Overall, an improvement of the metal ion removal behaviour is found with an increasing pH. This relationship maintains until the pH exceeds a certain limit so that the hydroxides present in the solution start to precipitate the metal ions [41].

Zhong et al. investigated the biosorption of lignocellulosic bamboo and found a remarkably increase in the sorption capacity of Pb(II) when the pH was elevated from 2 to 5. Also an enhancement in Cd(II) removal was noted when the pH in the solution was increased to 6 [24]. The same trend for Cd(II) removal can be found in the research about metal ion biosorption on olive cake by *Al-Anber et al.* [44]. Also *Pino et al.* show in their research that the biosorption of metals on green shells of coconuts appears to be highly pH dependent. A strong increase in Cd(II) removal was observed during a transition from pH 4 to 7. For the pH range between 7 and 9, a weakened efficiency was encountered for the metal removal due to the formation of hydroxide precipitates [45].

This tendency can be explained on the basis of protonation and deprotonation as a result of the pH adjustment. At low pH, there is an excess of protons in the solution which causes protonation of the functional groups of the lignocellulosic sorbent. In this way, the negatively charged active sites on the surface of the biomass are neutralized which implies that electrostatic interactions with positively charged metallic ions does not longer occur due to repulsion forces [24],[25],[32]. Moreover, a low pH adjustment leads to competition between protons and metal ions in their way to find binding sites which results in less uptake of it by the biomass. Similar behaviour was also recognized by metal sorption on algae [41]. When the pH increases, the functional groups will have a lower degree of protonation, which causes them to become more negatively. In this way, the electrostatic interactions between the negatively charged functional groups and the positively charged metal ions are stimulated [25]. Overall, it can be stated that the pH is a parameter of interest as it has an important influence on both the metallic binding to the biomass by electrostatic attraction and the ionic exchange [24].

2.2.2 Dosage of biomass

The amount of biomass is a crucial parameter for evaluation of the biosorption performance [25],[32],[42],[46]. Overall, the efficiency of the process enhances when the dosage of biomass increases. This can be explained by the increase of active binding sites, which are capable of binding the metal ions, when more biomass is added. However, from a certain excess of biomass this tendency will reverse as a result of interference between the active binding sites [42].

Rajesh et al. noted that the efficiency of the sorption process indeed increases when the dosage of milled biomass is elevated to a certain limit due to the presence of more active sites. However at higher dosages of the biomass, the sorption trend appeared to be decremental caused by overlapping and aggregation of the active sites [32]. *Rosales et al.* stated from their study that the increasing efficiency of the sorption process was present up to a dosage of 1 g/L of grapefruit peeling biomass. At 1 g/L the biomass uptake was maximal whilst at higher doses they also experienced a decrease of the metal diffusion rate into the matrix. *Rosales et al.* also explained that this tendency has to do with the overlap of active sites when a biomass dosage above 1 g/L is applied [46].

2.2.3 Temperature

The influence of temperature on the sorption process is highly dependent on its endothermic or exothermic nature. Depending on the structure and the present functional groups of the biomass in combination with the thermodynamics of the process, the temperature is capable to alter the sorption equilibrium to a certain extend. However, the temperature appears to cause contrasting effects in several researches [42]. An elevated temperature can be beneficial for the kinetics and the surface activity on the first hand, but it can cause permanent damage to the structural integrity of the biomass on the other hand [47]. However, sorption processes are often studied isothermally in order to prevent fluctuating effects of the temperature [25],[26],[32],[47].

2.2.4 Contact time

The time of contact between the biomass and the ionic solution is most apparent during the first hours of the process as it tries to reach equilibrium. Once this balance is reached, the full capacity of the biomass is used [25],[32],[48],[46]. *El messaoudi et al.* noted that the sorption of metals on modified lignocellulosic biomass in their study occurs in three phases. The first stage is considered to have a rather fast sorption due to many available active sites. In the next stage, the sorbing capacity gradually decreases as the active binding sites are becoming more occupied by metal ions. Finally, the system achieves equilibrium in the third phase when the functional groups are fully saturated and consequently the maximum capacity of the biomass is utilized [48]. *Also Rosales et al.* encountered in their research into the biosorption capacities of grapefruit peelings that the metal ion removal was the most intense in the first few minutes of the trial. Furthermore, they observed the same tendency as *El messaoudi et al.* which discloses that the remaining time towards equilibrium is accompanied by gradual decrease of the sorption intensity [46].

2.2.5 Initial metal concentration

Another parameter that influences the metal sorption on lignocellulosic biomass is the initial concentration of the metallic species in the solution. Extensive studies observed an alternating progression of the metal sorption when varying the initial concentration [32]. The reason for this is that the initial metal concentration appears to have an influence on the availability of active sites in the biomass. Furthermore, it functions as a driving force for the ion transfer from the solution to the biomass. [41].

In their research into the biosorption of Pb(II) and Cd(II) on biomass of *Pinus sylvestris*, *Taty-Cortodes et al.* found that the initial concentration exhibits interesting effects on the process. They noted that a high initial concentration of Pb (II) and Cd (II) had a beneficial effect on its sorption. According to them, the increased sorption performance has to do with a more favourable transport of the metal ions under these conditions. Due to this improved transport, the ions in the solution can migrate more easily to the active sites on the biomass. However when the initial concentration becomes too high, the active sites on the biomass are saturated more quickly which results in preventing further ion uptake [49]. Generally, it is noted that the impact on the sorption process, as a result of the initial metal concentration, is of a high degree [24],[32].

2.2.6 Interference of other metal ions

The presence of other ions in the solution can affect the degree of inclusion for a specific ion, that is present in the same ionic solution, on the biomass. The reason for this is the difference in affinity of the biomass for various metal ions. The nature of the ions varies depending on its electro-negativity, polarizability, hydrated ionic radius and its tendency to bind active sites due to cation-π interactions. Negatively charged sites on the biomass surface are more likely to bind metal ions which have a smaller hydrated ionic radius and a larger positive charge [32],[50],[51].

Mendoza-Castillo et al. found that the Pb(II) sorption rates were higher than the ones of Zn(II), Ni(II) and Cd(II). According to them, this has to do with the fact that Pb(II) exhibits the smallest hydrated ion radius in combination with the highest electronegativity [25].

2.3 Taguchi's methodology

The Japanese engineer *Genichi Taguchi* developed a design philosophy in the 50's with the purpose to bring quality within systems and processes. His principle is based on a robust design approach in which the improvement of the fundamental function of a process is the main focus [52]. This fundamental function is discussed on the basis of a well-defined quality or performance characteristic by applying loss functions. The operation of a process is globally dependent by the verifiable characteristics or adjustable parameters on the one hand, and by the influence of the uncontrollable characteristics or

side effects on the other hand. The controllable parameters can be practically executed according to an OA sequence, after *system* and *parameter design* as mentioned in *1.4 Approach* and executed in *2.2 System and parameter design*, in order to obtain responses from the chosen performance characteristic within the design. The responses are then converted into a signal-to-noise ratio (S/N) in order to evaluate them according to the assigned loss function. Taguchi therefore makes the statement that a system or process is qualitatively when the controllable parameters are set so that the S/N ratio is maximized whilst the standard deviation of the response characteristic is minimized. This is what he described as *tolerance design* and in which he particularly paid attention to the variation around the target value of a quality characteristic due to noise effects. A robust design is thus obtained when a suitable setting of the controllable characteristics is found so that its fundamental function can be performed optimally and that simultaneously the influence of the noise factors can be regarded as insensitive to the quality of the process [20]. This method enhances engineering productivity as it provides a flexible and practically acceptable way to design and to experiment in a research. Furthermore it also ensures that significant amounts of money, time and effort can be spared which in other cases would normally be lost during the design stage [53].

2.3.1 Loss functions

Generally, a process is considered qualitatively when its performance characteristic meets the imposed specifications at all times. These specifications include a small interval around the target value in which the performance characteristic may take on a response such that the fundamental function of the process still can proceed. The boundaries of this interval are defined by a lower and upper specification limit as shown in **Figure 5**. A loss of quality is only assumed when the performance characteristic generates a response that is located outside this well-specified interval. In this general way of thinking, the loss changes instantaneously from non-existing to existing when passing the boundaries of the specifications. It can therefore clearly be defined outside the limits of the interval on the basis of a step-function such as L_0 in the graph [20].
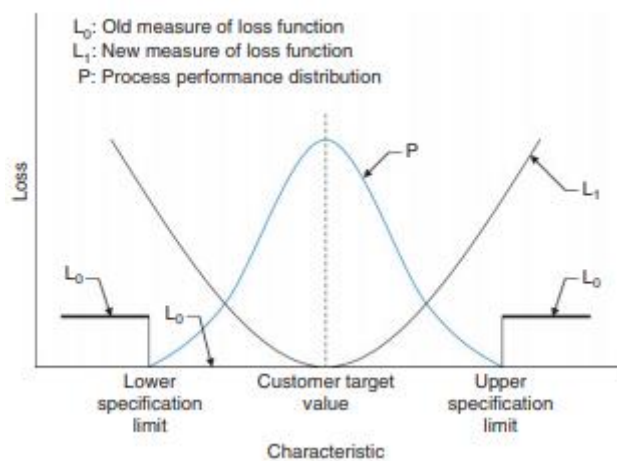
Figure 5 - Graphical representation of the general (L_0) and Taguchi's (L_1) loss function *[20]*

However, Taguchi had a different philosophy about describing the quality of a process. He thought that a process can only be qualitatively when the response of the output characteristic accurately describes the target value. Consequently, any deviation from this target value is detrimental to the quality and must therefore be regarded as a loss. Furthermore, contrary to the general way of thinking, he finds that quality loss does not build up instantaneously but rather gradually as the deviation around the target increases. For this reason, Taguchi stepped down from the step-function thought and established a new quadratic relationship to visualize the gradual loss of quality of a process such as L1 in the graph [20],[53].

Loss functions are inherently linked to the Taguchi methodology as they visualize the deviations in relation to the requested quality of systems and processes. He further substantiates that this process quality is of great importance for both economical and customer satisfaction aspects. Any variation from the target performance will result in a rising dissatisfaction of the customers [54]. Both, level and variation control is thus a necessity to ensure the quality requirements in a design stage [52]. Because the requirements regarding the quality characteristics are often different for many processes, the loss function is also described in several ways by Taguchi. There are mainly 3 categories in which the requirements regarding the quality of the performance characteristic can be grouped: Smaller-Is-Better, Larger-Is-Better and Target-Is-Best [55]. These categories are of great importance for the evaluation of the responses of the performance parameter as will be apparent from the next sub-section.

2.3.2   Signal to Noise Ratio

The effectiveness of a design can be evaluated based on an unambiguous response which brings both, the desired average and the undesired deviation around it, into account. Such a response is called a Signal to Noise ratio in which '*Signal*' stands for the average response of the output characteristic whilst '*Noise*' refers to the standard deviation around this mean according to non-controllable side effects. The values of these ratios are determined by filling in the data from the analysis results of an experimental sequence into the formula of the desired quality function. This function is dependent on the requirements imposed on the operation of a process. The different loss functions are applied based on the set requirements for the performance characteristic (Smaller-Is-Better/Larger-Is-Better/Target-Is-Best) and should have the possibility to maximize the S/N ratio whilst minimizing the loss [20],[56].
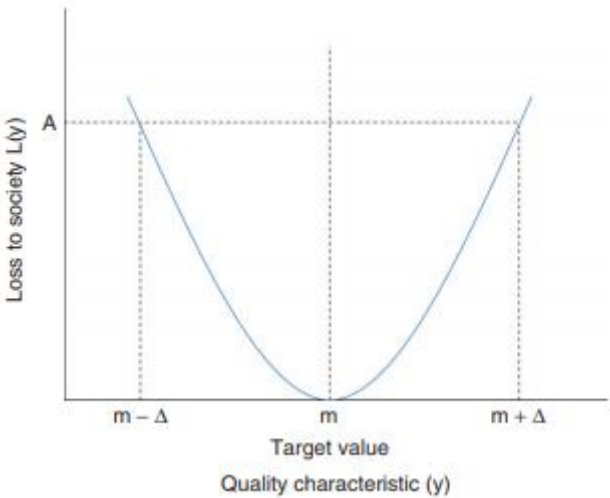
Figure 6 - The loss in function of the target value of the quality characteristic

Figure 6 shows a representation of the graph of the loss *L(y)* as a function of the target value of the quality characteristic *y*. In this graph, *m* is defined as the target value and Δ represents the upper and lower tolerance limit for the deviation on the response. Furthermore, *A* stands for the average loss of quality. Depending on the assigned quality criteria, the associated loss function will be defined differently because it needs to entail a different focus to the design in any of the 3 quality cases. These different formulas for the loss functions will consequently provide a difference in the S/N ratio determination as will be apparent from the following sub-sections [20].

2.3.2.1   Smaller-Is-Better

This quality criterion aims for the smallest possible response of the output characteristic. A response value of zero is in this case considered to be the optimal situation which generates the highest degree

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of quality for the process whilst any variation around this target causes an increase in loss. The performance characteristic can be defined in this case by the following formula for the loss function:

$$L(y) = \frac{A}{\Delta^2} y^2 \qquad (7)$$

Subsequently, a relation for the performance characteristic must be drawn up on the basis of this loss function in order to evaluate its response properly. In this way one obtains an S/N ratio that needs to be maximized in order to ensure the quality requirements. The conversion of the response to a S/N ratio according to the loss function is obtained by the next formula:

$$\frac{S}{N} = -10 \log \left[\frac{\left(\sum_{i=1}^{n} y_i^2 \right)}{n} \right] \qquad (8)$$

In this S/N ratio, the mean and variance are both implemented and are considered to be proportional to each other. The number of observations is represented by n whilst y_i stands for the response of the performance characteristic for observation i [20],[54],[56].

2.3.2.2   Larger-Is-Better

This quality criterion aims for the largest possible response of the output characteristic. In this case the desired requirements are inverse to the ones of the case Smaller-Is-Better. Only large values of the output characteristic are desirable for the process quality. The performance characteristic can be described by the following loss function:

$$L(y) = \frac{A\Delta^2}{y^2} \qquad (9)$$

Subsequently, a relation for the performance characteristic must be drawn up on the basis of this loss function in order to evaluate its response properly. In this way one obtains an S/N ratio that needs to be maximized in order to ensure the quality requirements set by the costumer. The conversion of the response to a S/N ratio according to the loss function is obtained by the next formula:

$$\frac{S}{N} = -10 \, log \left[\frac{\sum_{i=1}^{n} \left(\frac{1}{y_i^2} \right)}{n} \right] \qquad (10)$$

It is noted that this formula of the S/N ratio is exactly the opposite of the one in the case for Smaller-Is-Better. Also in this definition of the ratio both the mean and the variance are implemented together and the aim is again to maximize it in order to meet the requirements as much as possible. The number of observations is represented by n whilst y_i stands for the response of the performance characteristic for observation i [20],[54],[56].

2.3.2.3   Target-Is-Best

This quality criterion aims for a target response which is a finite value different from zero. Any variation around this desired value detracts from the quality requirements. The following loss function is then introduced to interpret the target value depending on the accuracy and deviation of output characteristic:

$$L(y) = \frac{A}{\Delta^2} (y - m)^2 \qquad (11)$$

Since the target value is a finite value different from zero, an adjustment term has to be defined in order to move the mean of the response towards the target value in the case it deviates from it.

Because in most processes the mean and the standard deviation are proportional to each other, the response of the performance characteristic can be converted to a S/N ratio the next formula:

$$\frac{S}{N} = 10 \, log \frac{\bar{y}^2}{s^2} \tag{12}$$

which *y* stands for the mean and s respectively represents the standard deviation. When the mean and variance are considered proportional, the S/N ratio strives to achieve the best possible connection with the target value while deviations due to noise are as low as possible. In this way the ratio can be maximized just like in the other cases [20],[54],[56].

2.3.3 OA design

In order to be able to assess a process on the basis of its quality, values must be assigned to the S/N ratios of the desired quality requirement. This evaluation process forms the *tolerance design* within Taguchi's methodology as mentioned before [52]. To make this ratio determination possible, an experimental sequence must be performed in order to obtain responses from the factor settings. It is in this phase of the design where Taguchi introduces orthogonal arrays to ensure that all tested levels of the factors of interest are balanced and thus can be considered as equivalent. As a result of this balancing, these parameters can be evaluated separately from each other regarding their functionality in the process, irrespective of the design its fractionality [22]. These factors of interest arise from the preliminary parameter research during the *system design* step as executed in section *2.2*. Based on the same study, values can subsequently be attributed to the various levels of the selected parameters of interest in the *parameter design* in order to test them in an experimental sequence. If this DoE was performed as a full fractional experiment, the $[3^5]$-matrix would yield a series of 243 experiments. To avoid such a large sequence, Taguchi uses the same OA design to extract the most important process knowledge from the entire matrix through only a modest number of experimental runs. So Taguchi globally reduces the experimental execution to a practically feasible one whilst making it possible to evaluate each selected parameter separately within the process [20],[55],[56].

In an orthogonal array, each factor setting for each parameter is repeated the same number of times in order to create a balanced pattern. In this way each column of the matrix, which is represented by one of the selected parameters of interest, can independently be assessed regarding its influence in the process. The rows of the matrix in turn determine the levels at which the characteristic should be tested during the experiments. All levels occur the same number of times in different rows of the orthogonal array. This equal distributing property that arises from this type of arrays is described by Taguchi as pair-wise balancing [20][22]. The structure of the orthogonal array for this research will be discussed in *Chapter 3 - Materials and methods*.

CHAPTER 3 – Materials and Methods

3.1 Artichoke biomass

The biomass applied in this research is obtained from agro-waste of globe artichokes (*Cynara scolymus L.*), which are perennial plants originating from the Mediterranean and belonging to the sunflower family (*Asteraceae*) [57]. The person in charge of research group QUIMYTEC cultivated artichokes in his garden (Murcia, Spain)[4] with the aim of applying them in research into Cu (II), Cd(II) and Pb(II) sorption behaviour.

3.1.1 Pre-treatment

Fresh artichokes, obtained from the head of QUIMYTEC, were stored in a refrigerator at 4 ° C before being pre-treated. Stems and outer bracts were removed from the artichoke crops by knife and further cut into smaller parts of approximately 2 cm. Subsequently, these chopped pieces were blanched for 15 min in water at 85 °C in order to inactivate present enzymes by denaturation. This stage of the pre-treatment is necessary as enzymes are capable of oxidizing present polyphenols, which causes to lower the amount of active sites and thus reduces the overall sorption capacity [57]. After blanching, the sodden mass was dried for approximately 3 days in a *J.P Selecta DIGIHEAT SERIES* drying chamber at 65 °C and eventually milled in a *Tristar KM-2270* electrical grinder. This mechanical comminution is applied in order to reduce particle size, crystallinity and the polymerization degree of present polysaccharides in lignocellulosic structures [32]. This structural surface evolution of artichoke material through milling is monitored by *Scanning Electron Microscopy* (SEM) as shown in **Figure 7** – SEM picture of the artichoke surface structure before milling (A) and after milling (B)

In addition, the SEM images provide information on the surface structure of the applied biomass on a microscopic scale. . Since the research focusses on the sorption capacity of raw biomass, no further chemical modification is applied. The resulting biomass was stored dry and dark until used in the experimental procedures.
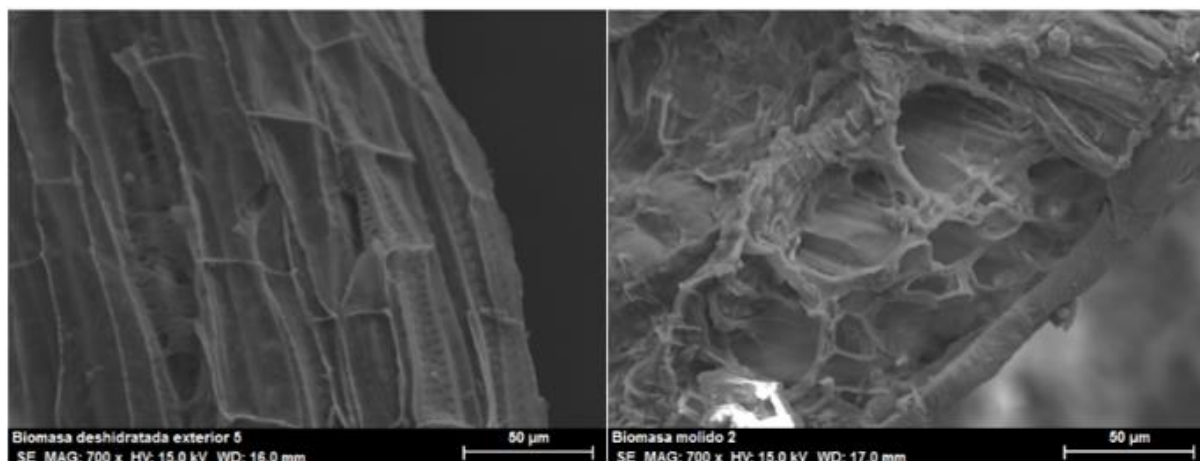
Figure 7 – SEM picture of the artichoke surface structure before milling (A) and after milling (B)

In addition, the SEM images provide information on the surface structure of the applied biomass on a microscopic scale. This makes it possible to observe the predominant longitudinal orientation of the filamentous structures. This channel-shaped micro structure provides a low resistance against liquid transfer throughout its fibres, which increases the chance of metal ion retention within it. Furthermore, it can be seen that the biomass surface has a certain roughness due to the presence of cavities with a variation in size and shape. This surface roughness appears to stimulate the metal ion fixation during the sorption process.

3.1.2 Characterization

QUIMYTEC applied *Fourier Transform Infrared* (FTIR) spectroscopy in previous studies to determine the specific nature of the biomass. This technique makes it possible to provoke molecular vibrations within the biomass by exposing it with IR radiation. The radiation interacts in a specific way with the different present organic compounds at different wavenumbers, causing them to generate an unique combination of peaks within the spectral region as shown in

Figure **8** - FTIR spectrum of the applied artichoke biomass. This FTIR spectrum is obtained from the QUIMYTEC database and is only used to characterize the applied biomass in this research. The FTIR procedure to acquire this spectrum was not disclosed by QUIMYTEC, and therefore not further discussed. Based on the *IR spectroscopy interaction table* [58], the most intense peaks were identified and linked to molecules that normally occur in lignocellulosic structures. The characterization of the spectral region, and thus the biomass, is represented in **Table 4** - FTIR peak identification.
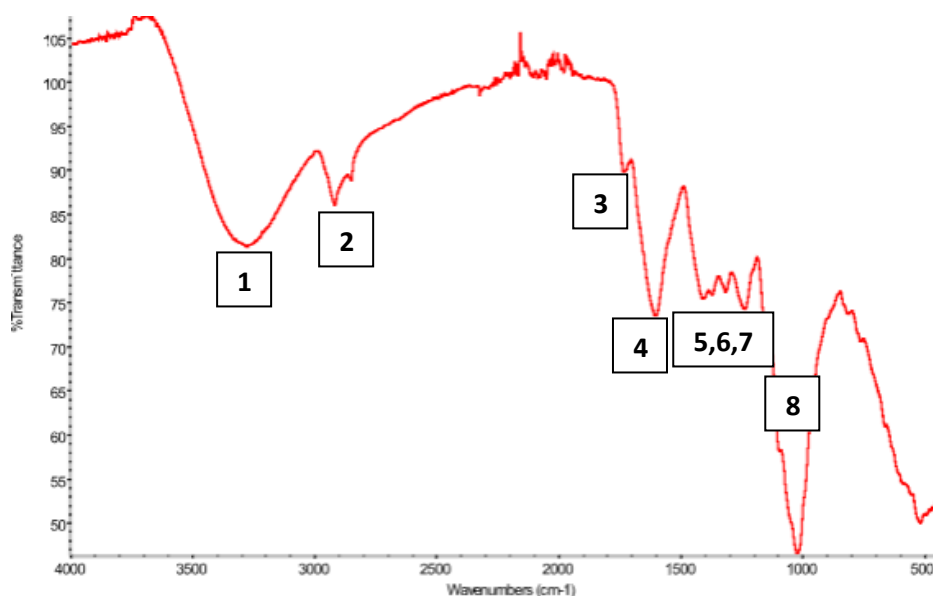
Figure 8 - FTIR spectrum of the applied artichoke biomass

Table **4** - FTIR peak identification

Peak	Intensity	Wavenumber (cm^{-1})	Functional group	Molecular vibration	Wavenumber range (cm^{-1})	Occurrence in lignocellulose
1	strong-broad	3273.09	O-H	stretching	3550-3200	intermolecular bonded alcohols
2	strong-broad	2918.45	N-H	stretching	3000-2800	amino groups
	weak-broad	2918.45	O-H	stretching	3200-2700	intramolecular bonded alcohols
3	weak	1728.66	C=0	stretching	1730-1715	ester linkages
4	medium	1603.76	C=C	stretching	1650-1566	cyclic alkenes
	medium	1603.76	N-H	bending	1650-1580	amino groups

5	medium	1408.46	O-H	bending	1440-1395	carboxylic acids
	medium	1408.46	O-H	bending	1420-1330	alcohol groups
6	medium	1315.70	O-H	bending	1390-1310	phenols
7	medium	1236.59	C-S	stretching	1250-1020	sulphonic acids
8	strong	1021.43	C-O	stretching	1075-1020	alkyl ethers
	strong	1021.43	C-O	stretching	1210-1163	ester linkages
	strong	1021.43	C-O	stretching	1205-1124	tertiary alcohols
	strong	1021.43	C-O	stretching	1150-1085	aliphatic ethers
	strong	1021.43	C-O	stretching	1124-1087	secondary alcohols
	strong	1021.43	C-O	stretching	1085-1050	primary alcohols

3.2 Batch sequence

The *system design* was the first procedure to be performed within the Taguchi optimization methodology. In this primary stage, the main parameters with a noticeable influence on the sorption process were listed and discussed. Furthermore, the boundaries of the selected parameters were defined in the *parameter design*, which entails that values can be assigned to the different parameter levels. These parameter setting can then be experimentally tested within a batch sequence, according to a modified OA, with the aim of obtaining design responses of the performance characteristic.

3.2.1 OA design

First and foremost, the parameter selection is performed before a batch sequence can be established. This selection forms the outcome of the *system* and *parameter design* and makes it possible to implement the factors of interest in an appropriate OA.

3.2.1.1 Parameter selection

pH, biomass dosage, temperature, contact time, initial concentration and interference of metal ions are the physio-chemical parameters discussed in *section 2.2 System and parameter design*. From this series, only 5 factors can be implemented in the DoE, which entails that a parameter selection must be performed. The outcome of the selection can be found in **Table 5** - Selected factors and their corresponding levels and is explained below.

Table 5 - Selected factors and their corresponding levels

Level	$C_{0,Cu}\ (mg.L^{-1})$	$C_{0,Cd}\ (mg.L^{-1})$	$C_{0,Pb}\ (mg.L^{-1})$	pH[2]	$D\ (g.L^{-1})$
1	10	10	10	3	0.5
2	20	20	20	4	1.0
3	50	50	50	5	2.0

The biosorption process is irrevocably linked to the presence of sorbate and sorbent. An amount of ions and biomass is thus always required within the system. In order to adjust these quantities in a controlled manner throughout the process, it is necessary to implement the initial metal ion concentration $C_{o,i}$ and biomass dosage *D* in this DoE. As mentioned before, Cu(II), Pb(II) and Cd(II) are among the most abundant heavy metal ions found in industrial wastewaters [8]. The research therefore focuses on the presence of all three, which implies that 3 factors for the initial concentration are introduced in this DoE, namely *$C_{0,Cu}$, $C_{0,Cd}$* and *$C_{0,Pb}$,* which will be tested at respectively 10-20-50

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[2] Initially, pH was tested at levels 4-5-6. However, pH 6 resulted in premature hydroxide precipitation of present metal ions, causing them to be removed out of the solution before even being exposed to the biomass. This implied that outcoming data of the experiments at pH 6 were no longer reliable, and therefore the pH settings were subsequently adjusted to 3-4-5.

mg/L. These factors are of interest as the initial metal concentration appears to have an influence on the availability of active sites in the biomass. Furthermore, it functions as a driving force for the ion transfer from the solution to the biomass [41]. Moreover, they provide a multicomponent system in which interference between the present ions is reflected, and thus can be discussed afterwards. Besides the initial concentration, biomass dosage D is implemented to control amount of sorbent within the process. It is a crucial parameter for the evaluation of the biosorption performance as it is directly responsible for the sorption capacity [25],[32],[42],[46]. The influence of this factor will be tested in the batch experiments by dosing respectively 0.5-1.0-2.0 mg/L of biomass.

The pH of aqueous solutions is proven to be a dominant factor within heavy metal biosorption [24],[25],[32],[41],[42]. It is known to affect the underlying mechanisms within the sorption process what makes the metal ion uptake capacity of the biomass strongly dependent on it [43]. The pH setting has a significant influence on the dissociation rate of the functional groups on the surface of the biomass, the competition between metallic ions in order to bind on active sites and the chemical metallic properties within the ionic solution [42]. As a result, pH is selected as the final factor of interest and will be tested at settings 3-4-5 within this DoE.

The influence of temperature on the sorption process is highly dependent on its endothermic or exothermic nature. Depending on the structure and the present functional groups of the biomass in combination with the thermodynamics of the process, the temperature is capable to alter the sorption equilibrium to a certain extend. However, the temperature appears to cause contrasting effects in several researches [42]. In previous research by QUIMYTEC, an attempt was made to determine the thermodynamic nature of this sorption process based on sorption enthalpy calculations by using the *Boltzmann* equation. It was found that this sorption process is slightly endothermic, which implies that a negligible influence of the temperature can be presumed. However, sorption processes are often studied isothermally in order to prevent fluctuating effects of the temperature [25],[26],[32],[47]. Therefore, the batch experiments in this research are performed isothermally at 25 °C.

At last, time of contact between biomass and the ionic solution is discussed. The contact time has the most influence during the first hours of the sorption process. This has to do with the fact that the amount of active sites in the biomass gradually decreases over time as they interact with present metal ions. Sites that undergo interactions do no longer carry metal-binding properties, what generally results in a lower neat ion uptake. This ion uptake decreases gradually as the sorption process tries to reach equilibrium. Once this balance is reached, the full capacity of the biomass is used and thus no more active sites are present [25],[32],[48],[46]. In order to ensure that the system in this research achieves equilibrium, and thus the full capacity of the biomass is utilized, the batch experiments will be carried out for 24 h.

3.2.1.2   Modified OA

If this DoE was performed as a full fractional experiment, the $[3^5]$-matrix would yield a series of 243 experiments. To avoid such a large sequence, Taguchi's OA design is applied to extract the most important process knowledge from the entire matrix through only a modest number of experimental runs. Since 5 different factors are tested at 3 different levels, the only OA model that fits is one of type L27-$[3^{13}]$. This matrix, as represented in **Table 6** - L27-$[3^{13}]$ orthogonal array, is suitable for designs at 3 levels and up to 13 factors.

Table 6 - L27-$[3^{13}]$ orthogonal array

L27-$[3^{13}]$	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2	2	2	2	2	2

3	1	1	1	1	3	3	3	3	3	3	3	3	3
4	1	2	2	2	1	1	1	2	2	2	3	3	3
5	1	2	2	2	2	2	2	3	3	3	1	1	1
6	1	2	2	2	3	3	3	1	1	1	2	2	2
7	1	3	3	3	1	1	1	3	3	3	2	2	2
8	1	3	3	3	2	2	2	1	1	1	3	3	3
9	1	3	3	3	3	3	3	2	2	2	1	1	1
10	2	1	2	3	1	2	3	1	2	3	1	2	3
11	2	1	2	3	2	3	1	2	3	1	2	3	1
12	2	1	2	3	3	1	2	3	1	2	3	1	2
13	2	2	3	1	1	2	3	2	3	1	3	1	2
14	2	2	3	1	2	3	1	3	1	2	1	2	3
15	2	2	3	1	3	1	2	1	2	3	2	3	1
16	2	3	1	2	1	2	3	3	1	2	2	3	1
17	2	3	1	2	2	3	1	1	2	3	3	1	2
18	2	3	1	2	3	1	2	2	3	1	1	2	3
19	3	1	3	2	1	3	2	1	3	2	1	3	2
20	3	1	3	2	2	1	3	2	1	3	2	1	3
21	3	1	3	2	3	2	1	3	2	1	3	2	1
22	3	2	1	3	1	3	2	2	1	3	3	2	1
23	3	2	1	3	2	1	3	3	2	1	1	3	2
24	3	2	1	3	3	2	1	1	3	2	2	1	3
25	3	3	2	1	1	3	2	3	2	1	2	1	3
26	3	3	2	1	2	1	3	1	3	2	3	2	1
27	3	3	2	1	3	2	1	2	1	3	1	3	2

In this OA, each factor setting for each parameter is repeated the same number of times in order to create a balanced pattern. This equal distributing property that arises from this type of arrays is described by Taguchi as pair-wise balancing [20],[22]. In this way each column of the matrix, which is represented by one of the selected parameters of interest, can independently be assessed regarding its influence in the process. The rows of the matrix, in turn, determine the levels at which the characteristic should be tested during the experiments. Based on this, a batch sequence is drawn up as shown in **Table 7** - Batch sequence.

Table 7 - Batch sequence

Experimental order	Design order	Coding	Cu (mg/L)	Cd mg/L	Pb mg/L	Ph	D (g/L)
1	15	Cd1-F	20	50	50	3	0.5
2	26	Cd2-F	50	20	20	5	0.5
3	11	Cd3-F	10	20	50	4	0.5
4	14	Cd4- F	20	20	10	3	0.5
5	23	Cd5-F	20	20	10	3	0.5
6	17	Cd6-F	50	20	20	5	0.5
7	18	Cd7-F	50	50	10	5	0.5
8	13	Cd8-F	20	10	20	3	0.5
9	22	Cd9-F	20	10	20	3	0.5
10	25	Cd10-F	50	10	50	5	0.5
11	24	Cd11-F	20	50	50	3	0.5

12	20	Cd12-F	10	20	50	4	0.5
13	3	Cd13-F	10	50	20	4	0.5
14	21	Cd14-F	10	50	20	4	0.5
15	4	Cd15-F	20	10	20	3	0.5
16	19	Cd16-F	10	10	10	4	0.5
17	16	Cd17-F	50	10	50	5	0.5
18	5	Cd18-F	20	20	10	3	0.5
19	12	Cd19-F	10	50	20	4	0.5
20	1	Cd20-F	10	10	10	4	0.5
21	7	Cd21-F	50	10	50	5	0.5
22	8	Cd22-F	50	20	20	5	0.5
23	9	Cd23-F	50	50	10	5	0.5
24	2	Cd24-F	10	20	50	4	0.5
25	6	Cd25-F	20	50	50	3	0.5
26	27	Cd26-F	50	50	10	5	0.5
27	10	Cd27-F	10	10	10	4	0.5
1	6	Cu1-F	20	50	20	5	2
2	14	Cu2-F	20	20	50	5	2
3	17	Cu3-F	50	20	10	4	2
4	2	Cu4-F	10	20	20	3	2
5	9	Cu5-F	50	50	50	4	2
6	16	Cu6-F	50	10	20	4	2
7	23	Cu7-F	20	20	50	5	2
8	24	Cu8-F	20	50	20	5	2
9	8	Cu9-F	50	20	10	4	2
10	5	Cu10-F	20	20	50	5	2
11	11	Cu11-F	10	20	20	3	2
12	13	Cu12-F	20	10	10	5	2
13	7	Cu13-F	50	10	20	4	2
14	1	Cu14-F	10	10	50	3	2
15	21	Cu15-F	10	50	10	3	2
16	15	Cu16-F	20	50	20	5	2
17	25	Cu17-F	50	10	20	4	2
18	12	Cu18-F	10	50	10	3	2
19	10	Cu19-F	10	10	50	3	2
20	27	Cu20-F	50	50	50	4	2
21	18	Cu21-F	50	50	50	4	2
22	20	Cu22-F	10	20	20	3	2
23	4	Cu23-F	20	10	10	5	2
24	3	Cu24-F	10	50	10	3	2
25	19	Cu25-F	10	10	50	3	2
26	22	Cu26-F	20	10	10	5	2
27	26	Cu27-F	50	20	10	4	2
1	22	Pb1-F	20	10	50	4	1
2	23	Pb2-F	20	20	20	4	1
3	8	Pb3-F	50	20	50	3	1
4	5	Pb4-F	20	20	20	4	1
5	20	Pb5-F	10	20	10	5	1

6	4	Pb6-F	20	10	50	4	1
7	24	Pb7-F	20	50	10	4	1
8	27	Pb8-F	50	50	20	3	1
9	2	Pb9-F	10	20	10	5	1
10	10	Pb10-F	10	10	20	5	1
11	1	Pb11-F	10	10	20	5	1
12	25	Pb12-F	50	10	10	3	1
13	11	Pb13-F	10	20	10	5	1
14	7	Pb14-F	50	10	10	3	1
15	26	Pb15-F	50	20	50	3	1
16	6	Pb16-F	20	50	10	4	1
17	18	Pb17-F	50	50	20	3	1
18	21	Pb18-F	10	50	50	5	1
19	14	Pb19-F	20	20	20	4	1
20	19	Pb20-F	10	10	20	5	1
21	9	Pb21-F	50	50	20	3	1
22	15	Pb22-F	20	50	10	4	1
23	17	Pb23-F	50	20	50	3	1
24	16	Pb24-F	50	10	10	3	1
25	13	Pb25-F	20	10	50	4	1
26	12	Pb26-F	10	50	50	5	1
27	3	Pb27-F	10	50	50	5	1

This batch sequence consists of 3 different series, with each containing 27 experiments. They are coded as Cd-F, Cu-F and Pb-F and each performed by one of the 3 Master students in order to make the experimental execution achievable within 3 months. The coding is related to the kind of ion whose sorption is attempted to be optimized. Since this research focusses on the Cu(II) removal, the Cu-F series are performed and discussed in the following sections. Furthermore, it appears that the batch sequence consists of 81 rows instead of 27 as in the corresponding OA. This can be explained by the principle of repetition that is applied in Taguchi designs [55]. In fact, the batch sequence would normally consist of 27 different experiments, which implies that the Cd-F, Cu-F and Pb-F series each contain 9 different experiments. However, each individual experiment is repeated 3 times during the batch procedure in order to introduce an average and a standard deviation among the performance responses of experiments with the same parameter settings. This also declares the randomized order for the experimental implementation as can be seen in **Table 7** - Batch sequence. Randomization, in combination with repetition, provides the opportunity to trace uncontrollable side effects over time by comparing the 3 performance responses of one and the same experiment. The output values of these repetitions, which are obtained from experiments at equal parameter settings, are expected to be equivalent, which entails that mutual deviations in output are caused by uncontrollable by noise factors over time. In order to obtain these responses from the batch sequence, ionic solutions have to be prepared according to the different factor settings and dosed with the corresponding amount of biomass. The initial concentrations of the 3 examined ions, together with the pH, are controlled during the preparation of the ionic solutions.

3.2.2 Ionic solutions

The different ions in the solutions are obtained by dissolving the corresponding nitrate hydrate salts. Cadmium Nitrate 4-hydrate $(Cd(NO_3)_2.4H_2O)$, Lead Nitrate 3-hydrate $(Pb(NO_3)_2.3H_2O)$ and

Cupper Nitrate 3-hydrate ($Cu(NO_3)_2.3H_2O$), produced by PanReac®, were used to prepare the 1000 ppm Cd(II), Pb(II) and Cu(II) stock solutions.

3.2.2.1 Preparation of 1000 ppm stock solutions

Since work is done at aquatic conditions, the concentration in ppm corresponds to the concentration in mg/L. This implies that stock solutions with a volume of 1L need to contain 1000 mg of ions in this case. Only a certain fraction of the total molecular weight of the nitrate-hydrate salts is produced by the cation. Therefore, the ratio of the atomic weight of the cation to the molecular weight of the whole salt can be used to determine the amount of salt that needs to be added in order obtain the desired 1000 ppm stock solution. The values for these amounts are represented by m_{salt} in **Table 8** - Mass data of the applied chemicals.

Table 8 - Mass data of the applied chemicals

Ion	$A_r(g.mol^{-1})$	$M_{salt}(g.mol^{-1})$	$m_{salt}(g.L^{-1})$
Cu(II)	63.55	241.60	3.8017
Cd(II)	112.41	308.49	2.7443
Pb(II)	207.21	331.20	1.5985

3.2.2.2 Preparation of dilutions

These 1000 ppm stock solutions function as ionic source during the preparation of the 9 ionic solutions within the Cu-F series. Based on dilutions, the parameter settings of the initial concentrations can be controlled such as in the established series. Since each of the 9 ionic solutions is applied 3 times at 100 ml within the experimental procedure, a total amount of 500 ml was prepared of every single solution. **Table 9** shows the volumes of the added 1000 ppm stock solutions in the dilution series.

Table 9 - Dilution series

Dilution	Experiments	Cu (ml)	Cd (ml)	Pb (ml)	pH
Cu-1	1,8,16	10	25	10	5
Cu-2	2,7,10	10	10	25	5
Cu-3	3,9,27	25	10	5	4
Cu-4	4,11,22	5	10	10	6
Cu-5	5,20,21	25	25	25	4
Cu-6	6,13,17	25	5	10	4
Cu-7	12,23,26	10	5	5	5
Cu-8	14,19,25	5	5	25	6
Cu-9	15,18,24	5	25	5	6

When the solution was prepared according to the desired concentrations, only the corresponding pH needed to be adjusted left according to the values of the dilution series. The pH of the dilutions was measured with a *CRISON MicropH 2000*. Furthermore, the pH of the dilutions were artificially decreased by adding 0.1M HCl or increased by adding 0.1M NaOH. During this pH control, the solution was magnetically stirred with a *JP Selecta AGIMATIC-N* to ensure sufficient mixing between solution and pH regulators. Eventually, when the pH was adjusted, a 10 ml sampling was made from each solution in order to determine the precise initial concentrations by ICP-OES analysis afterwards. This analysis was performed by employees of the *I + D + I* analysis team of the UPCT whilst using a *Perkin Elmer Optima 8300* as represented in **Figure 9** .

Figure 9 – Perkin Elmer Optima 8300 applied by I + D + I

3.3 Experimental procedure

The experimental implementation is based on contacting ionic solutions with corresponding amounts of prepared biomass as defined in the batch sequence. This method is primarily based on weighing the desired amount of biomass in a Erlenmeyer flask on a SARTORIUS AX224 analytical balance and subsequently adding 100 ml of the corresponding ionic solution. From the moment that sorbent and sorbate are in contact with each other, the contact time starts to run. Each sorption process is carried out for 24 h to ensure that equilibrium is reached, and thus the full capacity of the biomass is utilized. During this 24 h process, the Erlenmeyer is placed in a *VELP FOC cooled incubator* at 25 ° C to create isothermal conditions. Furthermore, the Erlenmeyer's were placed on an *IKA KS 130 Basic shaker* in order to provide agitation and to prevent accumulation of biomass on the bottom.

After the procedure, samples of 10 ml were taken in order to determine the equilibrium concentrations of the ions. The samples were taken with the aid of a syringe through a nylon MILLIPORE MILLEX-HN micro-filter in order to prevent the presence of biomass particles since the subsequent ICP-OES analysis is very sensitive to impurities after all.

3.4 Taguchi OA analysis

As described in the previous section, samples of all ionic solutions were taken before and after 24 h of contact with the biomass. The initial ($C_{o,Cu}$) and equilibrium ($C_{e,Cu}$) concentrations were determined by the mentioned *ICP-OES* sample analysis and used to assess the overall sorption behaviour of Cu(II) within the process. This assessment was based on Taguchi OA analysis of a performance parameter. In this research, the equilibrium sorption capacity $q_{e,Cu}$ was introduced as the performance characteristic to be maximized. $q_{e,Cu}$ is a measure of the total Cu(II) ion uptake at equilibrium, calculated from the difference of $C_{o,Cu}$ and $C_{e,Cu}$, that is generated by a certain metered biomass m in a specified volume V [29]. The equation of this sorption capacity is shown in the formula below:

$$q_e\left(\frac{mg}{g}\right) = \frac{\left[C_{o,Cu}\left(\frac{mg}{L}\right) - C_{e,Cu}\left(\frac{mg}{L}\right)\right]}{m(g)} . V(L) \tag{13}$$

Equation (13) was applied to calculate the sorption capacities of the Cu-F series within the batch sequence as represented in **Table 10**. The batch volume V was kept constant at a value of 0.100 L throughout the entire batch sequence.

Table 10 - Equilibrium sorption capacity determination of the Cu-F series

Coding	$C_{o,Cu}(mg.L^{-1})$	$C_{e,Cu}(mg.L^{-1})$	$\Delta C_{Cu}(mg.L^{-1})$	$m(g)$	$q_{e,Cu}(mg.g^{-1})$
Cu1-F	20.714	12.939	7.775	0.2012	3.864
Cu2-F	21.596	13.764	7.832	0.2017	3.883
Cu3-F	52.200	34.203	17.997	0.2020	8.909
Cu4-F	9.883	6.088	3.795	0.1997	1.900
Cu5-F	51.544	37.920	13.625	0.1991	6.843
Cu6-F	49.882	37.130	12.753	0.2013	6.335
Cu7-F	21.596	13.924	7.672	0.1999	3.838
Cu8-F	20.714	11.966	8.748	0.2005	4.363
Cu9-F	52.200	34.356	17.844	0.2008	8.887
Cu10-F	21.596	13.753	7.843	0.2016	3.890
Cu11-F	9.883	5.912	3.971	0.2016	1.970
Cu12-F	20.343	9.361	10.982	0.2020	5.437
Cu13-F	49.882	35.992	13.890	0.1968	7.058
Cu14-F	9.604	6.538	3.066	0.2026	1.513
Cu15-F	9.536	6.014	3.522	0.2012	1.751
Cu16-F	20.714	12.721	7.993	0.2010	3.976
Cu17-F	49.882	35.563	14.319	0.2006	7.138
Cu18-F	9.536	6.051	3.485	0.2003	1.740
Cu19-F	9.604	6.616	2.988	0.2006	1.490
Cu20-F	51.544	39.397	12.147	0.1996	6.086
Cu21-F	51.544	39.353	12.192	0.1997	6.105
Cu22-F	9.883	5.837	4.046	0.2018	2.005
Cu23-F	20.343	9.505	10.838	0.2009	5.395
Cu24-F	9.536	6.129	3.407	0.2018	1.688
Cu25-F	9.604	6.559	3.045	0.2015	1.511
Cu26-F	20.343	9.753	10.590	0.2000	5.295
Cu27-F	52.200	34.483	17.717	0.2044	8.668

A total of 27 Cu(II) sorption capacities were calculated from the completed batch series. Analogously, the Cu(II) sorption capacities of the Cd-F and Pb-F series were determined alongside this Cu-F series in order to obtain response information of the entire matrix. This implied that a total of 81 sorption capacities could be introduced as performance characteristics in the existing L27 OA. The surplus of performance responses, obtained from the batch sequence, has to do with the previously mentioned repetitions during the design. Since 3 replicates were performed for every single parameter setting, each row in the L27 OA could be evaluated based on its 3 associated responses. Output values of replicates are expected to be equivalent, which entails that mutual deviations in output are caused by uncontrollable noise factors over time [59]. These responses were inserted in column 6, 7 and 8 of the L27 OA in order to establish the outer array whilst the inner array was represented by the controllable parameters in the 5 first columns. In order to examine the influences and the effects of the inner array on this outer array, a static Taguchi OA analysis was performed by applying the *MiniTab* software. In such a static design, the controllable factors are defined at fixed levels in order to make the process robust to noise factor changes. Its purpose is to determine which parameter settings are the most

favourable in order to generate a response that approaches the target value very closely whilst encountering the least possible variation due to uncontrollable noise factors [59]. The interpretation of the overall Taguchi OA analysis in this research is represented in **Figure 10** - Taguchi OA analysis interpretation.

Before the OA could be analysed, the desired system quality requirements had to be entered first in the software according to one of the mentioned loss functions as described in section *2.3.1 Loss functions*. As mentioned in section *2.3.2 Signal to Noise Ratio*, the effectiveness of a design can be evaluated based on an unambiguous S/N response which brings both, the desired average and the undesired deviation around it, into account. In this case, the goal was to maximize the performance parameter as the purpose of this research is to optimize the overall Cu(II) sorption. This implies that the greater the sorption capacity, the better the quality requirements are satisfied. This principle is in line with the quality criterion of *Larger-Is-Better* and was therefore selected as the applied loss function, represented by equation (9), in the software analysis. Because of this setting, *MiniTab* considered that only large values of the output characteristic are desirable for the process quality because they trigger a high S/N ratio. The ratios were determined in the software by means of equation (10) which was defined in the larger-is-better quality criterion section.

Finally, the effects and interactions to be investigated were selected in the *MiniTab* software. As mentioned before, Taguchi OA designs only focuses on two-factor interactions and main effects whilst higher-order interactions are considered non-existent [22]. In addition, this methodology will also provide the opportunity to determine the most influential main effects and two-factor interactions among the parameters of interest. Since this research focusses on the Cu(II) removal, only two-factor interactions, in which the initial Cu(II) concentration is always present as the first factor, were selected in the software. Alongside these two-factor-interactions, also the main effects of the controllable parameters were selected and analysed.
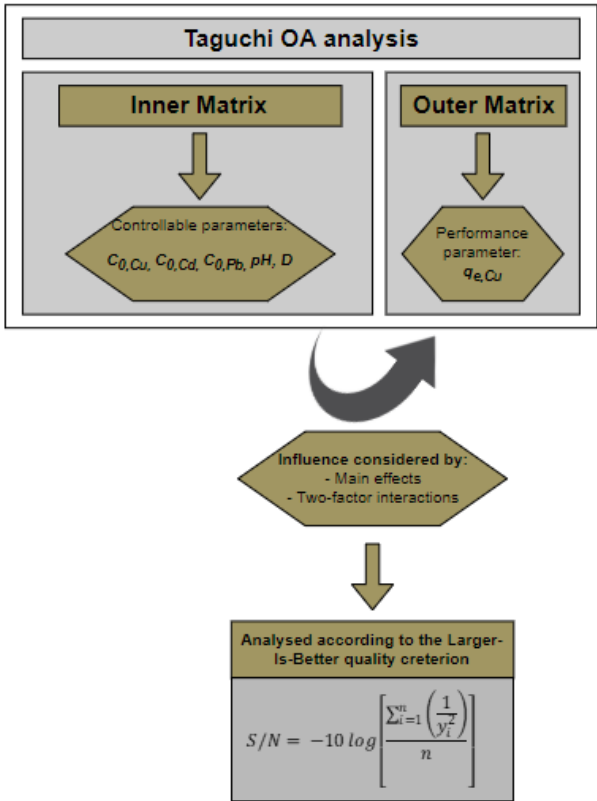

Figure 10 - Taguchi OA analysis interpretation

Chapter 4 – Results and discussion

4.1 Taguchi optimization

The first 8 columns in Table 11 represent the input of the Taguchi OA analysis whilst column 9 refers to its calculated output. $q_{e,Cu,1}$, $q_{e,Cu,2}$ and $q_{e,Cu,3}$ refer to the equilibrium Cu(II) sorption capacity of the 3 replicates, which were selected as performance characteristics throughout the analysis. The S/N ratios which are present in the 9the column were calculated by the software, based on the Larger-Is-Better requirements for quality loss. The highest sorption capacity obtained for the Cu(II) ions throughout the experimental sequence is 11.9 mg/g.

Table 11 – The applied L27 OA and the corresponding (S/N) ratios

Run	$C_{0,Cu}$ $(mg.L^{-1})$	$C_{0,Cd}$ $(mg.L^{-1})$	$C_{0,Pb}$ $(mg.L^{-1})$	pH	D $(g.L^{-1})$	$q_{e,Cu,1}$ $(mg.g^{-1})$	$q_{e,Cu,2}$ $(mg.g^{-1})$	$q_{e,Cu,3}$ $(mg.g^{-1})$	S/N
Cd-1	20	50	50	3	0.5	3.3	3.2	1.7	7.6
Cd-2	50	20	20	5	0.5	11.9	11.4	11.6	21.3
Cd-3	10	20	50	4	0.5	1.7	1.5	1.6	4.1
Cd-4	20	20	10	3	0.5	7.6	6.0	7.7	16.8
Cd-5	50	50	10	5	0.5	9.7	8.5	11.4	19.7
Cd-6	20	10	20	3	0.5	7.4	6.5	7.3	17.0
Cd-7	50	10	50	5	0.5	5.3	6.1	5.6	15.1
Cd-8	10	50	20	4	0.5	4.3	3.4	3.6	11.4
Cd-9	10	10	10	4	0.5	6.5	6.3	5.9	15.9
Cu-1	20	50	20	5	2.0	3.9	4.4	4.0	12.2
Cu-2	20	20	50	5	2.0	3.9	3.8	3.9	11.8
Cu-3	50	20	10	4	2.0	9.0	8.9	8.9	19.0
Cu-4	10	20	20	3	2.0	1.9	2.0	2.0	5.9
Cu-5	50	50	50	4	2.0	6.8	6.1	6.1	16.0
Cu-6	50	10	20	4	2.0	6.4	6.9	7.2	16.7
Cu-7	20	10	10	5	2.0	5.5	5.4	5.3	14.6
Cu-8	10	10	50	3	2.0	1.5	1.5	1.5	3.6
Cu-9	10	50	10	3	2.0	1.8	1.7	1.7	4.8
Pb-1	20	10	50	4	1.0	3.7	3.1	3.4	10.5
Pb-2	20	20	20	4	1.0	5.3	4.6	4.5	13.5
Pb-3	50	20	50	3	1.0	4.9	5.0	4.8	13.8
Pb-4	10	20	10	5	1.0	4.6	4.8	4.5	13.3
Pb-5	20	50	10	4	1.0	5.8	5.9	5.8	15.3
Pb-6	50	50	20	3	1.0	5.9	6.0	5.8	15.4
Pb-7	10	10	20	5	1.0	4.3	4.4	4.3	12.8
Pb-8	50	10	10	3	1.0	7.5	6.6	6.5	16.7
Pb-9	10	50	50	5	1.0	2.5	2.3	2.1	7.2

In addition, an overall ranking of the controllable parameters was obtained from the software program. This ranking is based on the variance in contribution to the process output for one and the same parameter at different levels and is assessed by Delta values. These values were calculated as the difference between highest and lowest S/N ratio of every parameter column. The first 3 rows in these columns represent the average S/N ratios of the 3 conducted replicates at the applicable

parameter level as can be seen in Table 12. At last, *Minitab* generated a S/N variance analysis which is used to evaluate the significance of the main effects on the process based on the P-values. The variance analysis of the S/N ratios is shown Table 13 and the main effects are plotted in **Figure 11** – Main effects plot for SN ratios (Larger-Is-Better). These represented tables and plots are used in order to discuss the main effects in the following sections.

Table 12 - Response Table for Signal to Noise Ratios (Larger-Is-Better)

Level	Cu	Cd	Pb	pH	D
1	8.8	13.6	15.1	11.3	14.3
2	13.3	13.3	14.0	13.6	13.2
3	17.1	12.2	10.0	14.2	11.6
Delta	8.3	1.5	5.2	2.9	2.7
Rank	1	5	2	3	4

Table 13 - Analysis of variance for SN ratios (Larger-Is-Better)

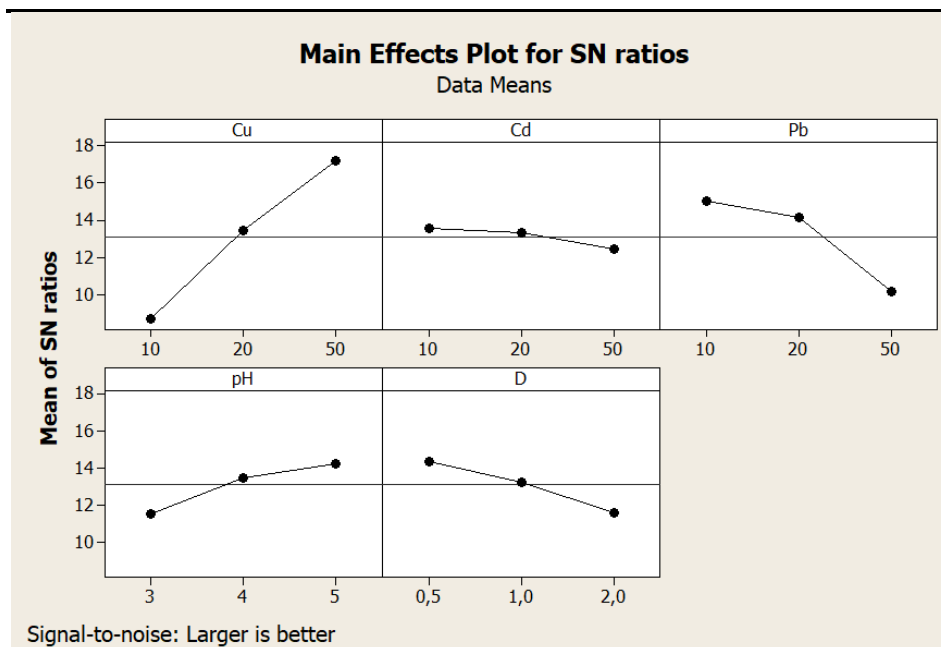| Source	DF	Seq SS	Adj SS	Adj MS	F	P
Cu	2	310.37	310.37	155.19	29.62	0.00(0)
Cd	2	10.75	10.75	5.38	1.03	0.40(1)
Pb	2	133.34	133.34	66.67	12.73	0.00(3)
pH	2	43.16	43.16	21.58	4.12	0.05(9)
D	2	33.00	33.00	16.50	3.15	0.09(8)
Cu*Cd	4	23.71	23.71	5.93	1.13	0.40(7)
Cu*Pb	4	7.09	7.09	1.77	0.34	0.84(5)
Resid. Error	8	41.91	41.91	5.24		
Total	26	603.33				

Figure 11 – Main effects plot for SN ratios (Larger-Is-Better)

4.1.1 Effect of initial metal concentration

The initial concentration of Cu(II) is ranked first in the response table of the Taguchi analysis. This implies that it exerts the greatest effect on the sorption process, which is also reflected in the variance

analysis. A P-value of 0.00(0) is linked to the influence of the copper concentration, which entails that its effect can be considered as significant (P < 0.05(0)) within the sorption process. A maximal S/N value of 17.1 is noted at level 3, which corresponds to 50 mg/L. Next in rank is the initial Pb(II) concentration. With a P-value of 0.00(3), this factor appears to exert a significant effect, which is the most intense at level 1. A maximal S/N ratio of 15.1 is obtained for this concentration setting of 10 mg/L. The last in rank, at position 5, is the initial concentration of Cd(II) that apparently has a limited effect on the output of the process. The corresponding P-value of 0.40(1) points to the existence of a non-significant effect (P > 0.05(0)), which indicates just a slight influence on the process. At level 1, at an initial Cd(II) concentration of 10 mg / L, a maximum S/N ratio of 13.6 is obtained.

A rising trend of the S/N ratio is noted when increasing the initial Cu(II) concentration, whilst decreasing the initial Cd(II) and Pb(II) concentration. This tendency seems logical when looking at the statistical shares of the ions within the solution. When Cu(II) is present in larger quantities than its competitive ions, it is more likely that a Cu(II) ion meets the active sites of the biomass instead of a Cd(II) or Pb(II) ion. As a result, the active sites are more occupied by Cu(II) ions, so that a larger part of the sorption capacity is carried by these ions. The sorption capacity is limited due to a finite number of active sites on the biomass, which implies that the active sites need to interact with Cu(II) ions in order to maximize the S/N ratio. Furthermore, the initial metal concentration is the driving force for mass transfer during the sorption process. The greater the concentration difference between the metal ions in the solution and at the biomass, the greater the driving force and consequently improved mass transfer. Due to this improved transport, the ions in the solution can migrate more easily to the active sites on the biomass. A high Cu(II) concentration of 50 mg/L and low Pb(II) and Cd(II) concentration of 10 mg/L therefore ensure a mass transfer advantage for Cu(II) ions, which makes it easier for them to reach and bind the biomass.
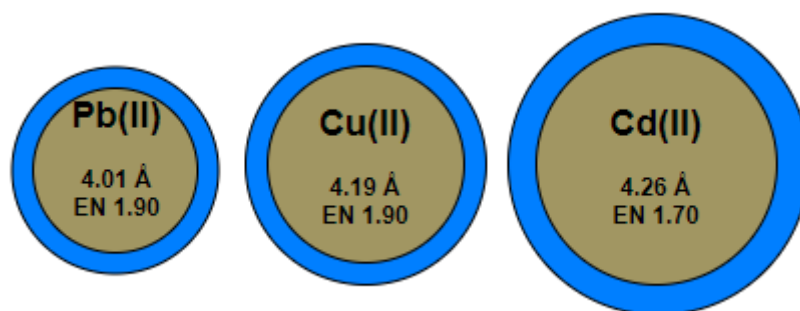

Figure 12 - Ionic properties of Pb(II), Cu(II) and Cd(II)

As mentioned in section *2.1.2 Sorption mechanism*, the ionic nature has an important influence on the sorption process as well. This influence has to do with the different ionic properties, concerning hydrated ionic radius and electronegativity, that are carried by Cu(II), Cd(II) and Pb(II) as shown in **Figure 12** - Ionic properties of Pb(II), Cu(II) and Cd(II). First of all, the hydrated ionic radius plays an important role in the mass transfer of the ions from the ionic solution towards the biomass. The ionic radius determines the degree of resistance to its mass transfer during the sorption process, which is more strongly present for ions with large hydrated radii. Pb(II) has the smallest hydrated radius of 4.01 Å within the multicomponent system. As a result, these ions encounter the least resistance whilst migrating through the solution and are therefore more likely to reach the biomass surface faster in comparison with the other present ions. This resistance increases for Cu(II) with an hydrated ionic radius of 4.19 Å, and is the strongest for Cd(II) ions which have a radius of 4.26 Å. Furthermore, the ionic electronegativity is a measure of the electrostatic attraction between ions and functional groups on the biomass. These interactions are stronger when the difference in electronegativity between the ions in the solution and the counter ions on the biomass is greater. The counter ions in the biomass

which attract the metal ions from the solution are mainly O, N and S with electro-negative values of respectively 3.5, 3.0 and 2.5. Consequently, due to a fixed composition of counter ions in the biomass, the difference in electronegativity whilst interacting is only affected by the nature of the metallic cations. Cd(II) has an electro-negative value of 1.70 and thus experiences the strongest electrostatic attraction by the biomass in comparison to Cu(II) and Pb(II) which have an electro-negative value of 1.90.

From Table 12 it is clear that the initial Cu(II) concentration generates the most important main effect on the sorption process, followed by Pb (II) at position 2 and Cd (II) at position 5 in the ranking, in which the last does not generate a significant effect. It seems logical that the initial Cu(II) concentration is ranked 1st in the analysis since its presence is directly related to the Cu(II) sorption capacity. without the presence of Cu(II) ions in the solution, a process output of 0 would be obtained as there is no Cu(II) available to remove. This also explains the strong increases in S/N ratios whilst increasing the initial Cu(II) concentration. Subsequently, the initial Pb(II) concentration also appears to exert a significant effect on the process. This can be explained by the fact that the biomass has a greater affinity for Pb(II) than for Cu(II), since Cu(II) ions are more hindered during migration due to their larger hydrated ionic radii. An higher concentration of Pb(II) would therefore result in a higher Pb(II) uptake by the biomass, which entails a decrease of the S/N value. At last, it also appears that the lowest initial concentration of Cd(II) ions is most favourable for the overall Cu(II) sorption. This can be explained by the difference in electro-negative value between Cu(II) and Cd(II). Cd(II) ions have a lower electronegative value, which makes the electrostatic attraction more intense. All in all, the effect of this parameter on the sorption process is proven to be non-significant, which implies a rather limited influence on the overall Cu(II) sorption. The reason for this is that the biomass has a higher affinity for Cu(II) than for Cd(II). Although Cd(II) may have a smaller electronegative value, it has a remarkably larger ionic radius than Cu (II), which makes the influence of the resistance more noticeable.

4.1.2   Effect of pH

The pH is ranked by the software analysis as 3rd most influenceable parameter. At pH 5, corresponding to the parameter setting at level 3, a relatively high S/N ratio of 14.2 is found. Nonetheless, from a P-value of 0.05(9) it appears that its effect does not have a significant influence on the process.

The pH setting has an influence on the dissociation rate of the functional groups on the surface of the biomass, the competition between metallic ions in order to bind on active sites and the chemical metallic properties within the ionic solution [42]. It regulates the solubility and speciation of metal ions, which, in turn, affects the degree of surface precipitation and the binding mechanism. The S/N ratio of the process is maximized with increasing values for pH as shown in **Figure 11**. This tendency prevails because at low pH, the present active sites on the surface of the biomass are more protonated, which results in more positively charged sites. These positive charges restrict the approach of Cu(II) ions to the biomass by repulsive forces. When the pH increases, this protonation is lifted, which results in the presence of negative active sites on the artichoke biomass. Because of this, the Cu(II) ions are no longer repelled, but rather electrostatically attracted, making them more likely to be removed out of the solution [25].

4.1.3   Effect of biomass dosage

The biomass dosage is noted to be at rank 4 in the response table and had a maximum S/N ratio of 14.3 at level 1, when 0.5 g/L biomass was added. The corresponding P value of 0.09(8) also refers in this case to a non-significant effect.

The amount of biomass is a crucial parameter for the evaluation of the biosorption performance [25],[32],[42],[46]. Overall, the efficiency of the process decreases when the dosage of biomass increases from 0.5 g/L to 2.0 g/L. In fact, one would expect the opposite tendency as increased biomass

dosage results in the presence of more active sites which, in turn, entail an higher ion uptake. The reason for the reduced efficiency at higher doses throughout this process is due to the overlap of active sites of the added artichokes biomass.

4.1.4 Metal ion interference

Throughout the Taguchi analysis, only interactions between Cu-Cd and Cu-Pb were detected. Interactions between Cu-pH and Cu-D are therefore considered to be non-existent in this sorption process on lignocellulosic biomass of artichokes. The present two-factor interactions between Cu-Pb and Cu-Cd are respectively represented in **Figure 13** and **Figure 15**. Their significance concerning the process is evaluated by their corresponding P-values, obtained from the variance analysis output, which can be seen in Table 13.
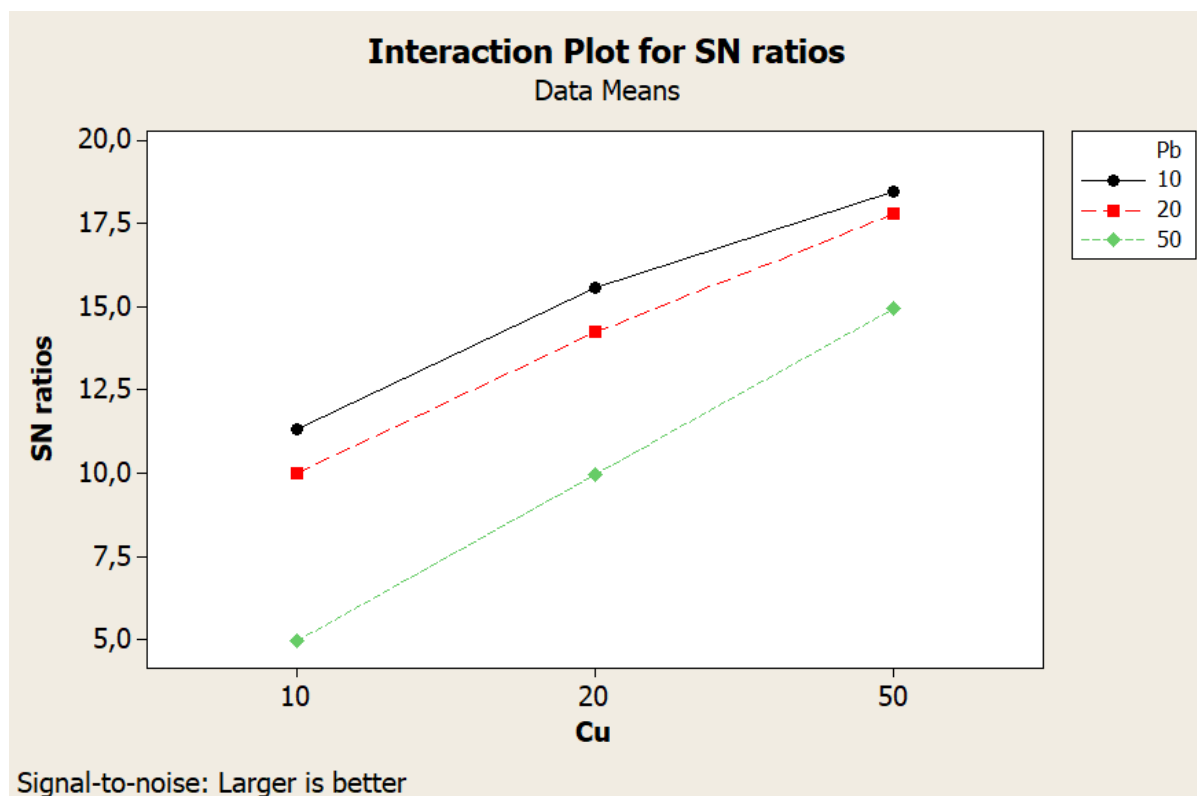
Figure 13 - Interaction plot of Cu-Pb for SN ratios (Larger-Is-Better)

In general, regardless of the Pb(II) concentration, an increasing S/N ratio is obtained whilst increasing the Cu(II) concentration. Furthermore, it appears that the highest S/N ratios are obtained in the presence of 10 mg/L Pb(II). A weak interaction between Cu(II) and Pb(II) is noted upon transition from 20 to 50 mg/L Cu(II) whilst remaining the Pb(II) concentration constant at 10 mg/L. According to the Taguchi analysis, this interaction appears negligible since its P-value of 0.84(5) indicates a non-significant influence.
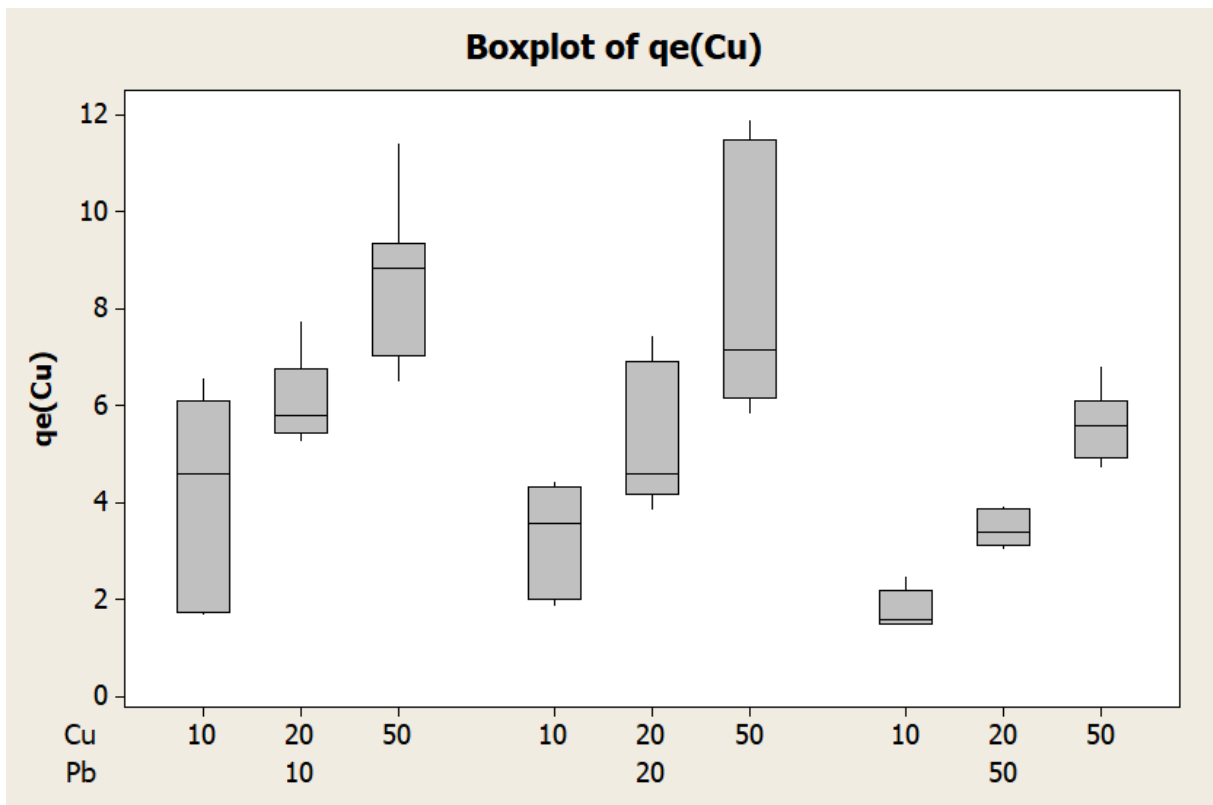
Figure 14 - Sequential boxplot of qe(Cu) for Cu and Pb

The same tendency can be found in the sequential boxplot of the Cu(II) equilibrium sorption, represented in **Figure 14**. At every Pb(II) level, an increasing trend of the average Cu(II) uptake is realised whit increasing Cu(II) concentrations. The highest output values for the performance parameter are found to be achieved at the lowest setting for the Pb(II) concentration. At last, it is noted that a remarkably lower spread is obtained when the highest level of Pb(II) is observed.
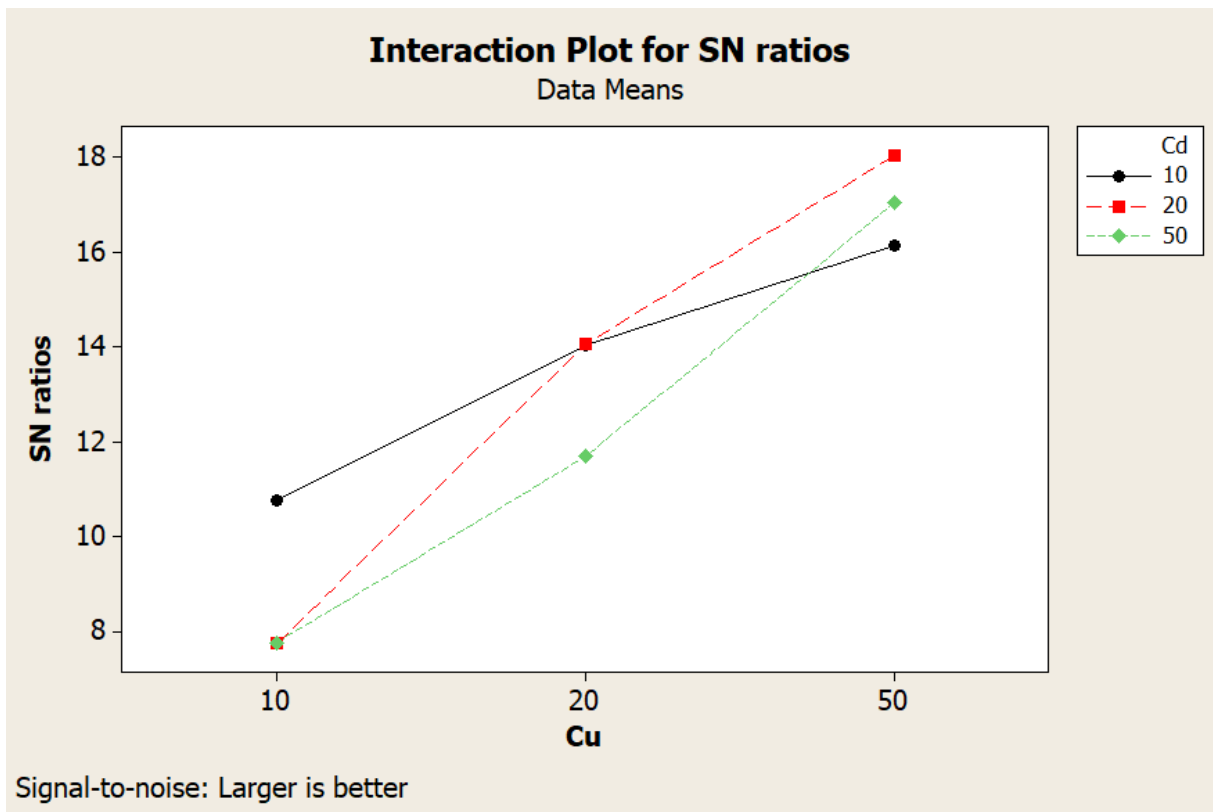
Figure 15- Interaction plot of Cu-Cd for SN ratios (Larger-Is-Better)

The interference between Cu-Cd is apparently of a higher degree than it is between Cu-Pb. This is deduced from the intersection of the 10 mg/L Cd(II) curve with these of 20 and 50 mg/L at transition from Cu(II) level 2 to Cu(II) 3. As a result, the S/N ratio for level 1 of Cd(II) level 3 for Cu(II) reaches a value which is lower than the corresponding Cd(II) levels at the these conditions. However, a P-value of 0.40(7) is linked to the Cu-Cd interaction which, in turn, points to a non-significant influence on the process.
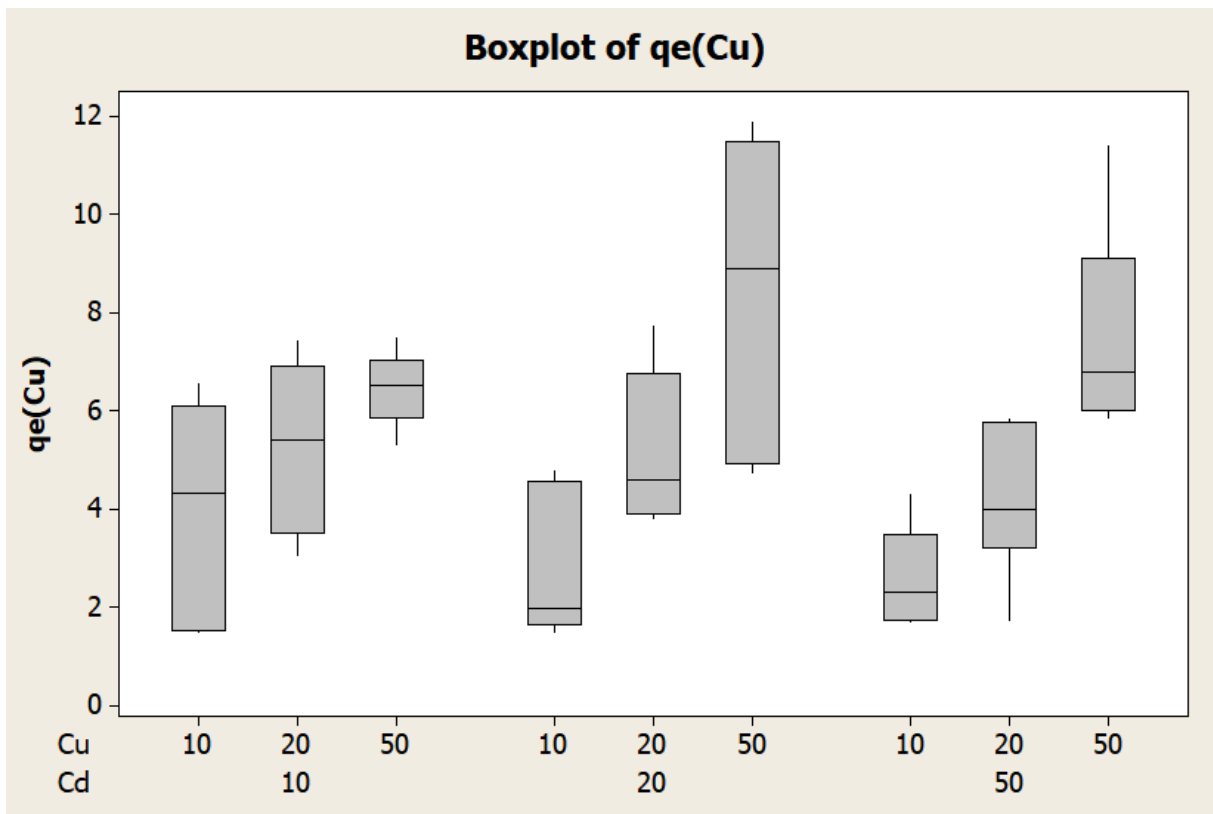
Figure 16 - Sequential boxplot of qe(Cu) for Cu and Cd

The same tendency can be found in the sequential boxplot of the Cu(II) equilibrium sorption, represented in **Figure 16**. At every Cd(II) level, an increasing trend of the average Cu(II) uptake is realised whit increasing Cu(II) concentrations. The highest output values for the performance parameter are found to be achieved at the lowest setting for the Cd(II) concentration. However, for 10 mg/L of Cd (II) and at level 3 for Cu (II), the average Cu(II) uptake is lower than at the corresponding higher Cd(II) concentrations. Therefore, it is noted that the presence of 20 or 50 mg/L of Cd(II) is favourable for the overall Cu(II) sorption capacity at 50 mg/L of Cu(II). At last, regarding the variation on the performance characteristic, one can observe a similar distribution on the sorption capacities at 10 and 50 mg/L of Cu(II), and, moreover, a wider variation on the output values for the 2nd level of Cu(II).

4.2 Equilibrium modelling

Sorption isotherm models are essential in establishing the most suitable sorption equilibrium behaviour, which is indispensable for a reliable estimation of the sorption parameters. These isotherms describe the two-phase interactions between the metal ions (sorbate) and the artichoke biomass (sorbent). Overall, equilibrium modelling is an essential methodology to obtain information about the sorption mechanism, sorption capacity and surface properties of the biomass [60].

For the equilibrium modelling experiment, the suggested optimal parameter settings from the Taguchi analysis were applied. This implies that the initial concentrations of Cu(II), Pb(II) and Cd(II), respectively 50-10-10 mg/L, are desirable for the sorption optimization at pH 5, when 0.5 g/L of biomass is added. The experiment was performed in a 1 L batch at room temperature (25 °C), to which 0.5076 g of weighed biomass was added. Furthermore, the batch was magnetically stirred at 700 rpm throughout the entire process and samples were taken at the predefined times, namely after 1-2-5-10-20-40 min, as well as after 1-1.5-2-2.5-3-3.5-4-5-6-7 h. The Cd(II) concentrations before and after equilibrium were determined by using ICP-OES analysis.

In order to modulate the sorption equilibrium on the basis of the isothermal models, the constants in isotherm equations (1), (2) and (3) need to be defined first. The approximation of the constants was performed by using a linear expressions for Langmuir, Freundlich and Temkin, corresponding to equation (4), (5) and (6) as shown in Figure 17, Figure 18 and Figure 19 respectively. Based on the slopes and the intercepts of the linear regressions on the corresponding isothermal expressions, the constants were determined as represented in
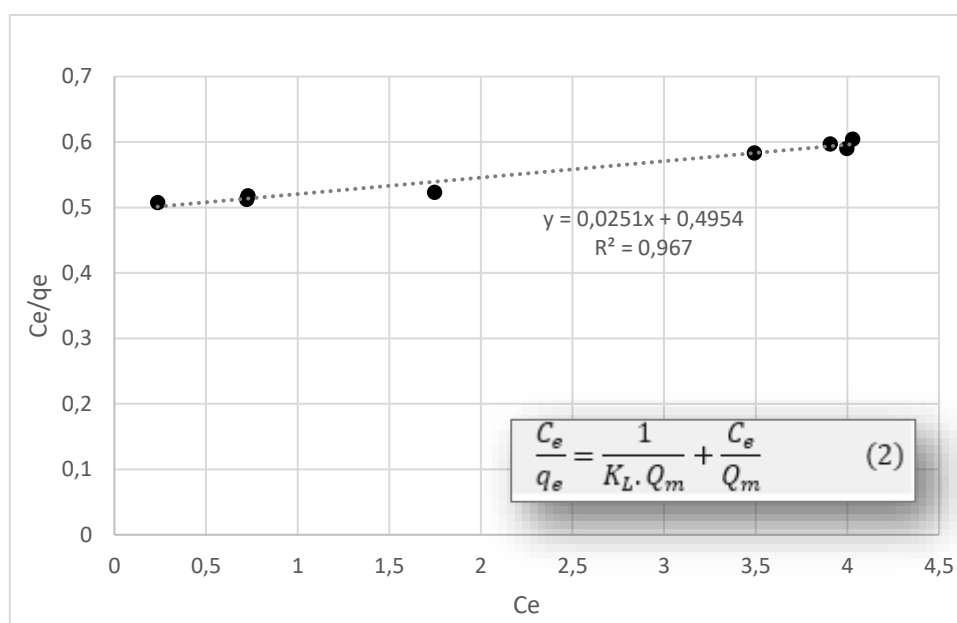
Table **14**.

The chart shows a linear regression with $y = 0{,}0251x + 0{,}4954$ and $R^2 = 0{,}967$, with axes Ce/qe versus Ce.

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot Q_m} + \frac{C_e}{Q_m} \qquad (2)$$

Figure 17 – Linear expression for *Langmuir* isotherm
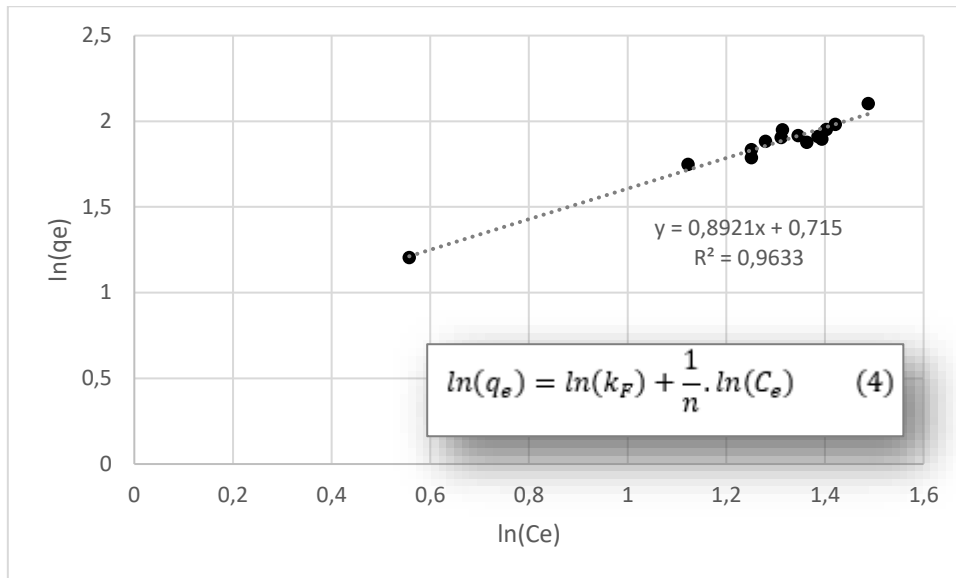
Figure 18 – Linear expression for *Freundlich* isotherm

The plot shows the equation:

$$ln(q_e) = ln(k_F) + \frac{1}{n}.ln(C_e) \qquad (4)$$

with $y = 0{,}8921x + 0{,}715$ and $R^2 = 0{,}9633$.
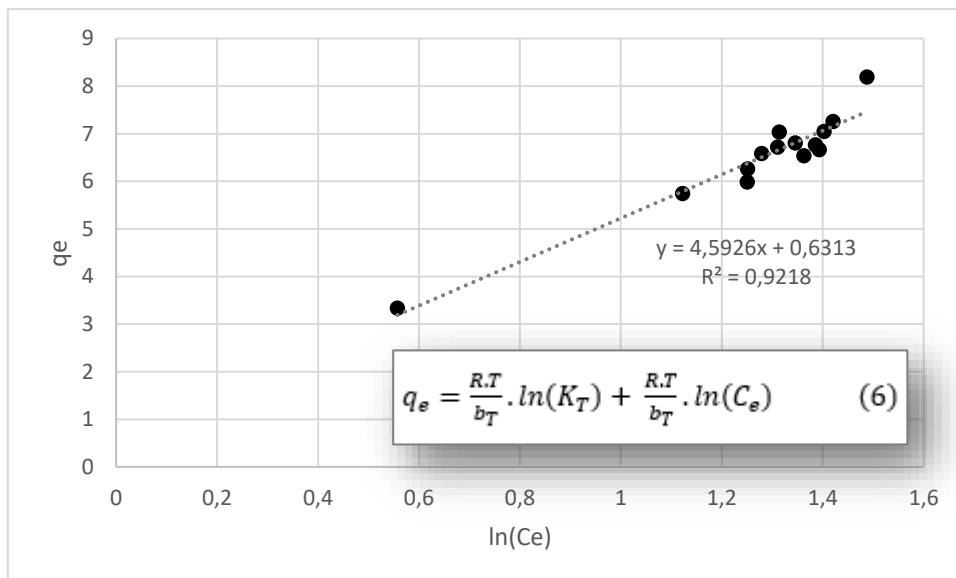
Figure 19 – Linear expression for *Temkin* isotherm

The plot shows the equation:

$$q_e = \frac{R.T}{b_T}.ln(K_T) + \frac{R.T}{b_T}.ln(C_e) \qquad (6)$$

with $y = 4{,}5926x + 0{,}6313$ and $R^2 = 0{,}9218$.

Table 14 – Calculated isotherm parameters

Metal ion	Langmuir			Freundlich			Temkin		
	Q_m $(mg.g^{-1})$	K_L $(mg.L^{-1})$	R^2	K_F $(mg.g^{-1})$	n	R^2	K_F $(g.L^{-1})$	B $(=\frac{RT}{b_T})$	R^2
Cu(II)	39.84	0.05	0.967	2.04	1.12	0.963	1.15	4.59	0.922

Q_m and K_F are both measures for the maximum Cu(II) uptake within the process. As shown in Table 14, the *Freundlich* approach for this value shows a strong deviation relative to the *Langmuir* approach. Furthermore, the *Langmuir* constant K_L was found to be 0.05. This constant is a measure of the affinity of the biomass for the Cu(II) ions and is assessed based on the dimensionless separation factor R_L of which the equation is represented below:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{14}$$

$0 < R_L < 1$ is valid for this sorption process since a value of 0.28 was calculated for the dimensionless separation factor. This connection suggests that the process is thermodynamically favourable, and that consequently a favourable Cu(II) uptake is realized on the biomass. The biomass thus contributes a desired affinity for the Cu(II) sorption. This implies that the artichoke biomass has a certain affinity for the Cu(II) ions. Furthermore there is constant n, which is present in the *Freundlich* isotherm with an estimated value of 1.12. This empirical parameter provides information on the heterogeneity and the intensity of the sorption process by interpretation of the $1/n$ relationship. In this case, $1/n$ corresponds to a value of 0.89 so that the assumption $0 < 1/n < 1$ is valid. This implies that sorption within the process is mainly determined by chemisorption, and consequently adsorption to a lesser extent. Moreover, the value of 0.89 is closer to 1 than to 0, as a result of which the biomass surface can be regarded as relatively homogeneous. At last, the constants K_T and B occur within the Temkin isotherm. This isotherm assumes that variance in sorption-heat is rather linear instead of logarithmic, which is expressed by constant B. K_T is the equilibrium binding constant which corresponds to the maximum Cu(II) binding energy. These constants in were eventually used to approximate the equilibrium behaviour of the process with the aid of the Isotherms as represented in **Figure 20**, **Figure 21** and **Figure 22**.
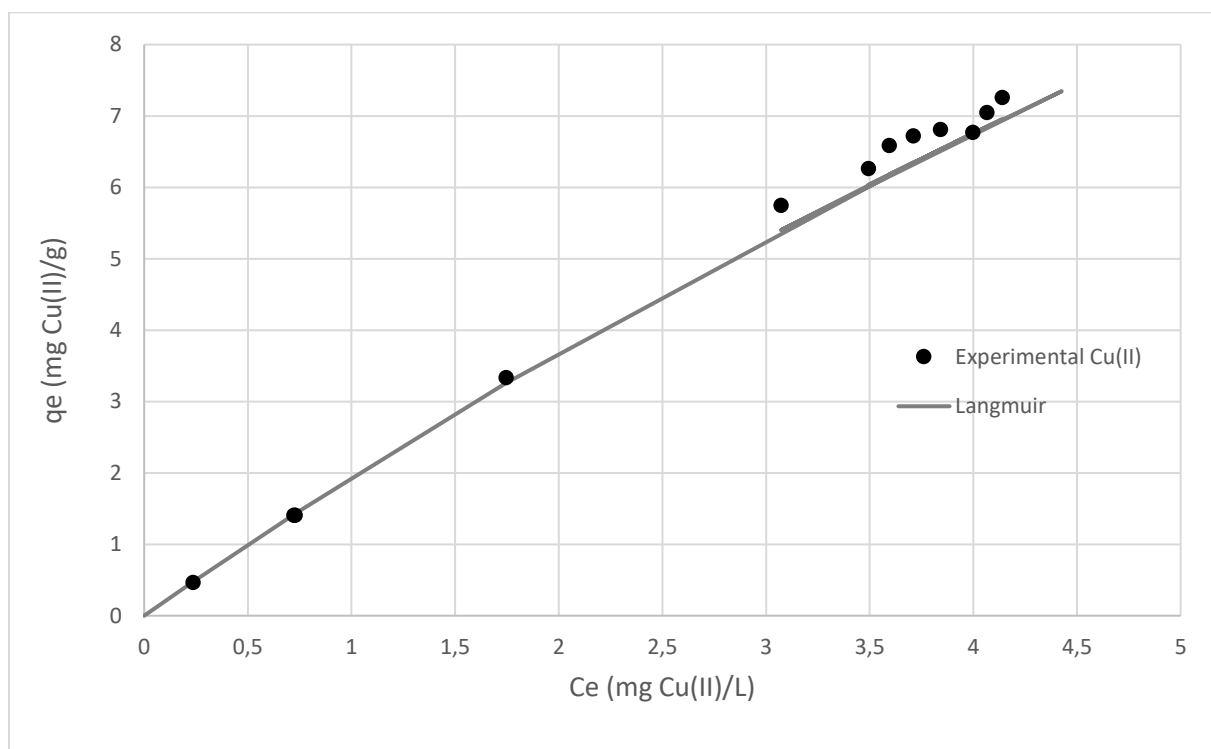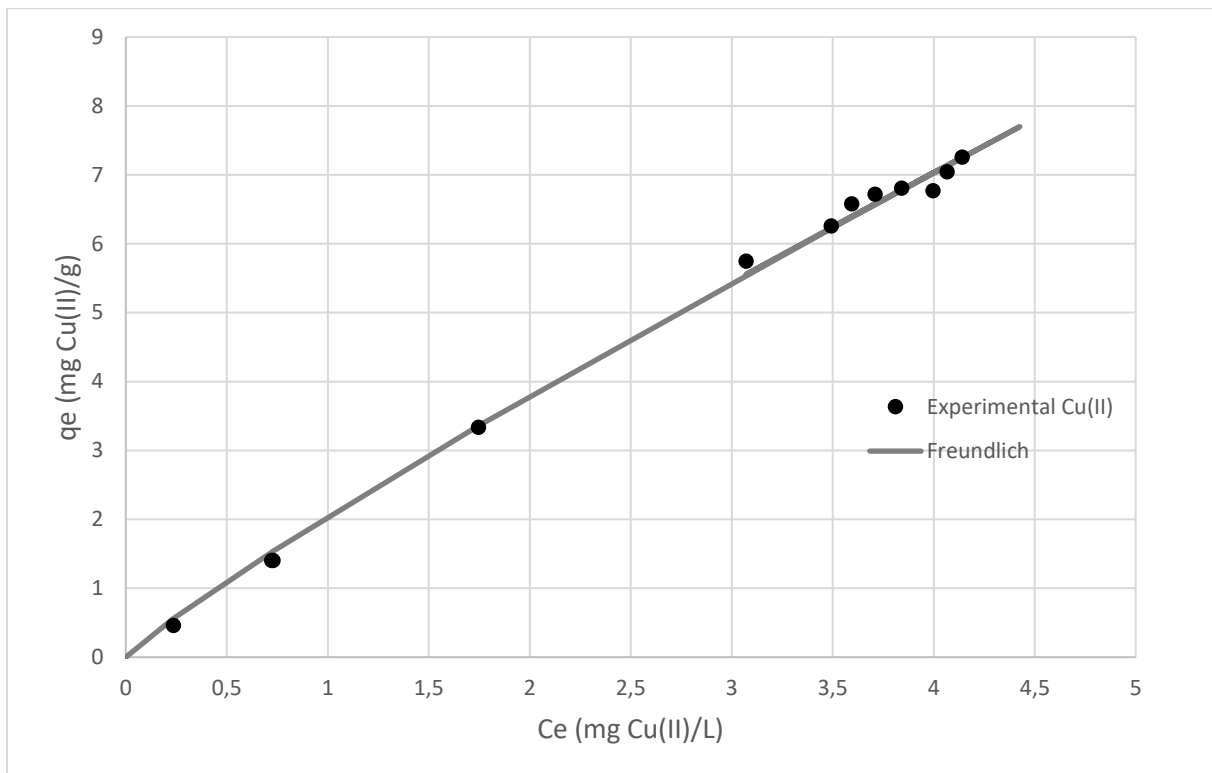

Figure 20 – *Langmuir* Isotherm
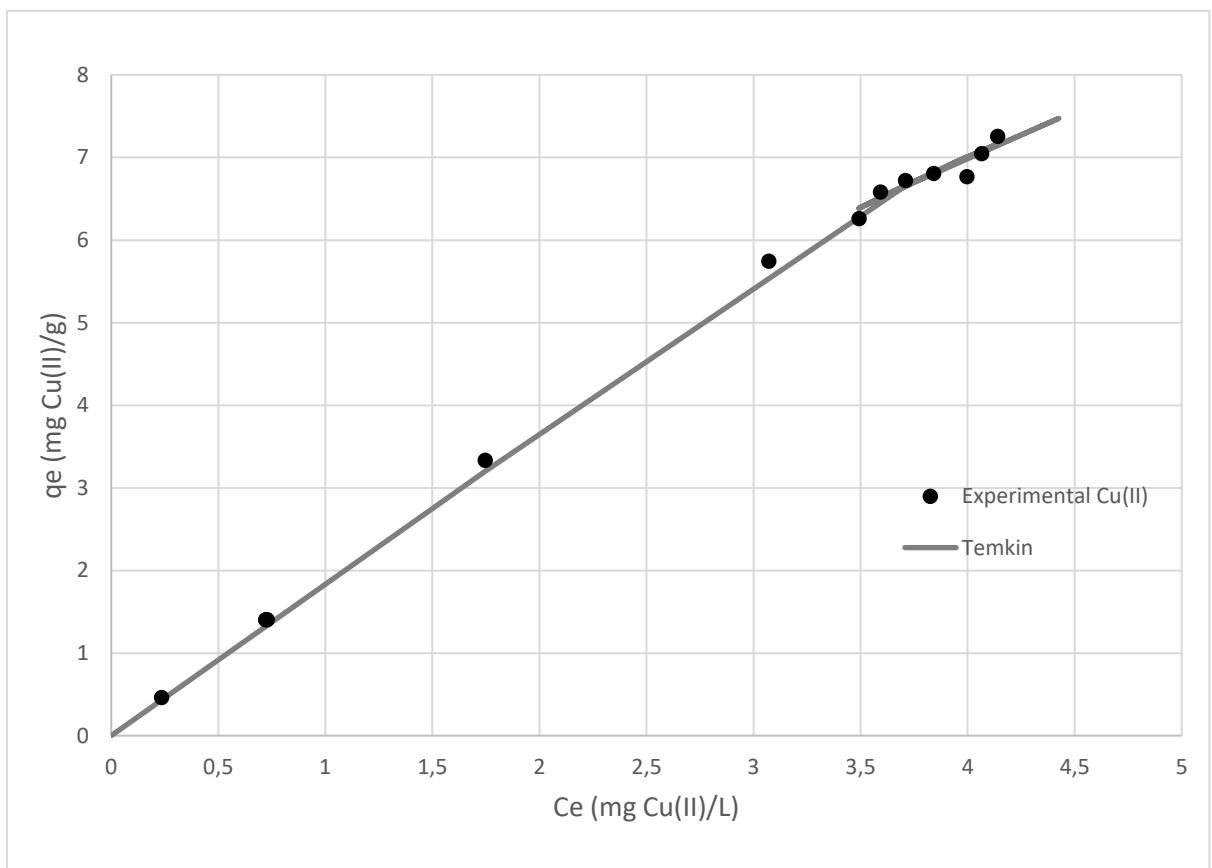
Figure 21 – *Freundlich* isotherm

Figure 22 – *Temkin* isotherm

Based on the correlation coefficients R^2 and on the different isotherm model plots, it appears that each model fits the equilibrium well. The Langmuir isotherm describes the equilibrium conditions the most accurate with a correlation factor of 0.967, followed by Freundlich (0.963) and Temkin (0.922).

Finally, the kinetics of the process were described by using the pseudo-second order equation. For this purpose, linearization was applied in order to determine the constants by the slope (1/qe) and the intercept (1/k.qe²). A maximum Cu(II) sorption capacity of 7.99 mg/g was found whilst the rate constant corresponds to a value of 0.01 min^{-1} as shown in **Fout! Verwijzingsbron niet gevonden.**.

The kinetics modelling, based on the pseudo-second-order equation, is represented in Figure 23 and shows a high degree of fitting thanks to its large correlation coefficient of 0.999.
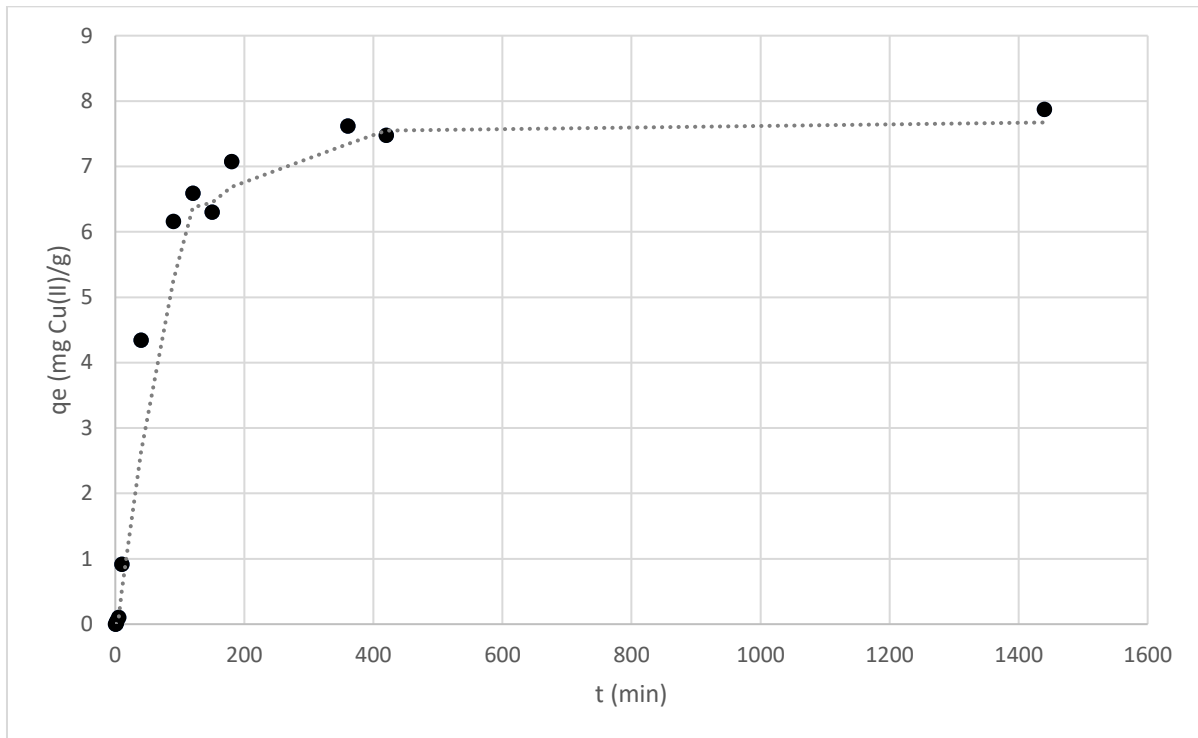

Figure 23 - Pseudo-Second-Order kinetics modelling

Table 15 – Kinetic parameters

Equation	Pseudo-Second-Order		
	$q_e(mg.g^{-1})$	$k\ (min^{-1})$	R^2
$\dfrac{t}{q} = \dfrac{1}{k.q_e^2} + \dfrac{t}{q_e}$	7.99	0.01	0.999

Chapter 5 – Conclusion

5.1   Conclusion

This study has proven that Cu(II), Cd(II) and Pb(II) ions can effectively be removed from aquatic environment by biosorption on low-cost lignocellulosic waste products of globe artichokes (*Cynara scolymus L.*). From the biomass characterization, the presence of alcoholic, amine, sulphonic and carboxyl groups can be noted within the applied lignocellulosic matter. These groups are responsible for the chemisorption processes within the overall physio-chemical sorption mechanism, which implies that mainly ion exchange, complexation and surface precipitation generate the sorption capacity so that adsorption yields a lesser share within the total ion uptake. The fact that chemisorption plays the dominant role during the sorption process is also noted from the *Freundlich* constant *n*. This value provides a 1/*n* ratio of 0.89, which is tending towards 1, and thus indicates that sorption is associated with chemisorption according to *Freundlich*'s methodology. The Taguchi OA design has proved to be a reliable tool in improving the desired Cu(II) removal. It facilitated in understanding the influence of the parameters of interest on the sorption process at 3 different levels. From the Taguchi analysis, it can be concluded that only the initial concentration of Cu(II) and Pb(II) have a significant effect on the overall Cu(II) uptake, in which mainly the initial Cu(II) concentration exerts the most influence. Furthermore, significant two-factor interactions do not appear to be present within the process, although weak interactions between Cu-Cd and Cu-Pb are noted. Optimal parameter settings, in order to maximize the S/N ratio, were found to be at pH 5, [Cu (II)] 50 mg/L, [Cd (II)] 10 mg/L, and [Pb (II)] 10 mg/L. Under these conditions, a remarkably low Cu(II) equilibrium sorption capacity of 6.77 mg/g was obtained. This value is exceeded numerous times by different factor settings throughout the batch sequence and does not outweigh the maximum observed 11.90 mg/g of the Cd2-F experiment. This tendency can be explained by the deviating impact of the capacity due to agitation. Initially, agitation was applied at constant stirring speeds of 300 rpm to avoid overlap due to biomass sedimentation at the bottom of the Erlenmeyer flask. However, the equilibrium modelling experiment was carried out at 700 rpm which caused the formation of a vortex. It is noted that high agitation speeds can hinder external film diffusion due to turbulence which, in turn, lowers the overall Cu(II) uptake [61]. At last, the kinetics of the system appears to be well approached by a pseudo-second-order relationship, as evidenced of the corresponding correlation factor of 0.999. Concerning the equilibrium modelling, the *Langmuir* isotherm fits the equilibrium conditions the most accurately, followed by respectively *Freundlich* and *Temkin.*

5.2   Impetus to further research

The key in this research consisted of understanding the mechanisms that entail sorption properties on the one hand, and of studying the influence of physicochemical parameters on both equilibrium and kinetics on the other hand. Now knowledge about the chemical and physical behaviour of the process has been acquired, the outcome can be further used to elaborate this natural phenomenon into an industrial regime. A first important aspect in this industrialization is further research onto chemical modification of the applied artichoke biomass. As already mentioned, chemical modification can favourably influence the sorption capacity q_e in comparison to raw biomass [24],[25],[27],[28], and thus provides the opportunity to enhance metal-sorbent binding properties. A second aspect that is interesting to investigate is situated in the process automation. In order to apply biomass properties for industrial water purification purposes, it is recommended to move from a batch sorption to a continuous sorption. Continuous processing is, after all, standard practice within chemical industries when a certain scale is exceeded. Moreover, automation entails a reduction in residence and contact time and is more surface efficient in comparison to batch operations [62]. Finally, it is interesting to examine to what extent biomass, whose capacity is fully utilized, is regenerable. In this focus, it is

important to investigate how already bound metal ions can be released again from their sorbent. Moreover, it entails the possibility to investigate recuperation, and thus valorisation, of heavy metals which have been purified from the water.

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3

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