

RECOVERY OF SILVER AND NEODYMIUM FROM AQUEOUS  
SOLUTIONS BY USING MICROALGAE

by

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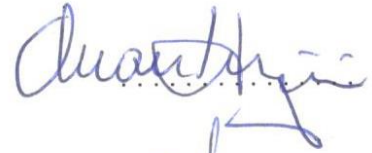
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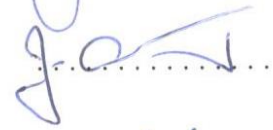
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## ABSTRACT

### RECOVERY OF SILVER AND NEODYMIUM FROM AQUEOUS SOLUTIONS BY USING MICROALGAE

Electronic waste is one of the fastest growing streams of waste due to the increase in electronics production. Electronic waste consists of valuable elements that many governments and companies wish to extract from the waste. Although the increase in the usage of electronic devices is inevitable, eco-friendly and easily operated recovery methods for the valuable elements can be developed. In this study, characterization of electronic waste were carried out by using three different digestion methods; USEPA 3051, USEPA 3050B and Modified Microwave Digestion Method to define focus elements. The recovery of selected elements was carried out by using green microalgae, *Chlorella vulgaris*. Results showed that silver and neodymium were found as major precious metal and rare earth element, respectively. Biosorption capacities were found as 151.7 mg/g for silver, and 296.8 mg/g for neodymium. Bioaccumulation capacities refer to 161.6 mg/g for silver and 239.7 mg/g for neodymium. When there were multi-elements in the solution, the uptake capacities decreased and uptake of selected element can be limited via changing the process parameters. Variations in functional groups were observed that suggests binding of elements to the microalgae. Silver and neodymium were seen on algal surfaces as particles and scattered, respectively. Pseudo-second order kinetics fitted better both to biosorption and bioaccumulation for silver and neodymium. Freundlich isotherm model and linear model was found suitable for biosorption and bioaccumulation, respectively. In the context of sustainability, this study supports the achievement of United Nations Sustainable Development Goals by following Goals: 3, 9, 11, and 12.

## ÖZET

### MİKRO ALG KULLANIMI İLE GÜMÜŞ VE NEODİMYUMUN SIVI SOLÜSYONDAN GERİ KAZANIMI

Elektronik cihazların üretimindeki artış nedeni ile, en hızlı büyüyen atık türlerinden biri elektronik atıklardır. Elektronik atıklar, bir çok devlet ve şirketin atıklardan geri kazanmak isteyeceği değerli elementler ihtiva etmektedir. Elektronik cihazların kullanımındaki artış kaçınılmaz olmasına rağmen, çevreye zarar vermeyen ve kolay uygulanabilen değerli elementlerin geri kazanımı için yöntemlerin geliştirilmesi mümkündür. Bu çalışmada, geri kazanım için seçilecek elementlerin belirlenmesi amacı ile üç farklı parçalama yöntemi; USEPA 3051, USEPA 3050B ve Modifiye edilmiş Mikrodalga Parçalama Yöntemi kullanılarak elektronik atıkların karakterizasyonu yapılmıştır. Seçilen elementlerin geri kazanımı için yeşil mikroalg türü olan; *Chlorella vulgaris* kullanılmıştır. Sonuçlara göre, en çok bulunan değerli metal ve nadir toprak elementi sırası ile gümüş ve neodimyum olmuştur. Biyosorpsiyon kapasitesi gümüş için 151,7 mg/g ve neodimyum için 239,9 mg/g bulunurken, biyoakümülyasyon kapasitesi gümüş için 161,6 mg/g ve neodimyum için 296,8 mg/g olarak bulunmuştur. Solüsyonda çoklu element olduğu zaman, alım kapasiteleri düşmüş ve parametrelerin değiştirilerek belirlenen elementin alımının belirli bir ölçüde sınırladığı gözlemlenmiştir. Fonksiyonel gruplarda değişiklik gözlenmesi elementlerin mikroalgelere bağlandığı sonucunu önermektedir. Gümüşün alg yüzeyinde parçaçık olarak, neodimyum ise tüm yüzeye yayılmış olarak bulunduğu gözlemlenmiştir. Gümüş ve neodimyum biyosorpsiyonu ve biyoakümülyasyonu ikinci derece kinetic modelde gerçekleşmektedir. Freundlich izotermi ve lineer model sırası ile biyosorpsiyon ve biyoakümülyasyon süreçlerine uygun bulunmuştur. Bu çalışma sürdürülebilirlik kapsamında, Birleşmiş Milletler Sürdürülebilir Kalkınma Hedefleri kapsamında Hedef 3, 9, 11 ve 12'yi desteklemektedir.

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS .....	iv
ABSTRACT .....	v
ÖZET.....	vi
TABLE OF CONTENTS .....	vii
LIST OF FIGURES.....	x
LIST OF TABLES .....	xii
LIST OF SYMBOLS/ABBREVIATIONS .....	xiii
1. INTRODUCTION.....	1
2. LITERATURE REVIEW.....	2
2.1. E-waste Characterization.....	4
2.2. Recovery of Metals .....	5
2.2.1. Biosorption and Bioaccumulation .....	6
2.2.2. Factors Affecting Biosorption .....	7
2.2.2.1. pH .....	7
2.2.2.2. Temperature .....	8
2.2.2.3. Initial Metal Concentration .....	8
2.2.2.4. Biosorbent Dosage .....	9
2.2.2.5. Contact Time .....	9
2.2.2.6. Presence of other metals.....	10
2.3. Modelling .....	10
2.3.1. Kinetic Modelling .....	10
2.3.2. Isotherm Modelling .....	11
3. MATERIALS AND METHODS .....	12
3.1. Characterization of E-waste .....	12
3.2. Biosorption by Microalgae.....	14

3.2.1. Cultivation of Microalgae .....	14
3.2.2. Solubility Tests.....	14
3.2.3. Biosorption Experiments.....	15
3.3. Bioaccumulation by Microalgae .....	16
3.3.1. Microalgae Preperation .....	16
3.3.2. Bioaccumulation Experiments .....	17
3.4. Biosorption and Bioaccumulation from Binary Metal Solutions.....	17
3.5. Modelling Studies .....	17
4. RESULTS AND DISCUSSIONS .....	20
4.1. Characterization of E-waste .....	20
4.1.1. Base Metals .....	20
4.1.1.1. PCBs.....	20
4.1.1.2. Screens .....	20
4.1.2. Precious Metals and Rare Earth Elements .....	24
4.1.2.1. PCBs.....	24
4.1.2.2. Screens .....	24
4.1.3. Comparison of the Methods .....	28
4.2. Biosorption.....	28
4.2.1. Single Metal Biosorption .....	28
4.2.1.1. Temperature .....	28
4.2.1.2. pH.....	29
4.2.1.3. Effect of Biosorbent .....	30
4.2.1.4. Effect of Stirring Speed.....	31
4.2.1.5. Remaining Metal Concentration .....	33
4.1.1.6. Uptake as a Function of Time .....	33
4.2.2. Biomass Analysis for Optimum Conditions.....	34
4.2.2.1. SEM-XRD.....	34
4.2.2.2. FTIR .....	35



4.3. Bioaccumulation.....	28
4.3.1. Single Metal Bioaccumulation .....	28
4.3.1.1. Effect of Biosorbent and Initial Metal Concentration .....	36
4.3.1.2. Remaining Metal Concentration .....	38
4.3.1.3. Uptake as a Function of Time .....	38
4.3.2. Biomass Analysis for Optimum Conditions.....	39
4.3.2.1. SEM-XRD .....	39
4.3.2.2. FTIR .....	40
4.4. Biosorption and Bioaccumulation from Multiple Element Solutions.....	41
4.4.1. Binary Element Solution .....	42
4.4.2. Tertiary Element Solution .....	42
5. MODELLING .....	43
5.1. Biosorption.....	43
5.2. Bioaccumulation from Multiple Element Solutions.....	46
6. CONCLUSION .....	50
REFERENCES.....	52

## LIST OF FIGURES

Figure 3.1. Preparation of e-waste samples for analysis .....	12
Figure 3.2. The analyses of biosorption process .....	16
Figure 3.3. Schematic view of the study .....	18
Figure 4.1. Base metals found in e-waste .....	21
Figure 4.2. Precious metals and rare earth elements found in e-waste .....	25
Figure 4.3. Effect of temperature on (a) Ag and (b) Nd biosorption .....	29
Figure 4.4. Effect of pH on (a) Ag and (b) Nd biosorption.....	30
Figure 4.5. Effect of biosorbent dosage on (a) Ag and (Nd) biosorption .....	30
Figure 4.6. Biosorption amounts of Ag and Nd according to time .....	33
Figure 4.7. Algal surface analysis of Ag loaded algae; SEM and XRD analysis (taken by ZEISS EVO 40) .....	34
Figure 4.8. Algal surface analysis of Nd loaded algae; SEM and mapping (taken by ZEISS EVO) .....	34
Figure 4.9. FTIR Analysis of the samples before and after biosorption (taken by Thermo Fisher Nicolet 380 FTIR Spectrometer .....	35
Figure 4.10. Effect of biosorbent dosage on (a) Ag and (b) Nd bioaccumulation .....	37

Figure 4.11. Bioaccumulation amounts of Ag and Nd according to time.....	38
Figure 4.12. Backscatter and XRD analysis for Ag loaded algae (taken by ZEISS EVO 40).....	39
Figure 4.13. Mapping for Nd loaded algae (taken by ZEISS EVO 40) .....	39
Figure 4.14. FTIR Analysis of the samples before and after bioaccumulation (taken by Thermo Fisher Nicolet 380 FTIR Spectrometer).....	40
Figure 4.15. Comparative uptake of metals of biosorption and bioaccumulation .....	41
Figure 4.16 Mapping of binary metal loaded algae (taken by ZEISS EVO 40).....	41
Figure 5.1. First order kinetics for Ag and Nd biosorption.....	43
Figure 5.2. Second order kinetics for Ag and Nd biosorption .....	44
Figure 5.3. Langmuir isotherms for Ag and Nd biosorption.....	45
Figure 5.4. Freundlich isotherms for Ag and Nd biosorption .....	45
Figure 5.5. First order kinetics for Ag and Nd bioaccumulation .....	46
Figure 5.6. C Second order kinetics for Ag and Nd bioaccumulation .....	47
Figure 5.7. Langmuir isotherms for Ag and Nd bioaccumulation .....	48
Figure 5.8. Freundlich isotherms for Ag and Nd bioaccumulation.....	48
Figure 5.9. Nd bioaccumulation linear model.....	49

## LIST OF TABLES

Table 2.1. Metal content of e-waste reported in different studies (g/kg) .....	7
Table 2.2. Biosorption capacities of different metals.....	7
Table 3.1. Determination of optimum conditions .....	15
Table 4.1. Heavy metal content of selected samples according to different digestion methods (g/kg).....	22
Table 4.2. Precious metal and rare earth element content of selected samples according to different digestion methods (g/kg).....	26
Table 4.3. Uptake of experimental data of biosorption of Ag.....	32
Table 4.4. Uptake of experimental data of biosorption.....	32
Table 4.5. FTIR bands coordinates for biosorption .....	35
Table 4.6. Bioaccumulation uptake for Ag and Nd.....	37
Table 4.7. FTIR bands coordinates for bioaccumulation .....	40

## LIST OF SYMBOLS/ABBREVIATIONS

<b>Symbol</b>	<b>Explanation</b>	<b>Unit</b>
$Q$	Uptake amount	mg/g
<b>Abbreviation</b>	<b>Explanation</b>	
E-waste	Electronic waste	
FTIR	Fourier-Transform Infrared Spectroscopy	
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy	
MMDM	Modified Microwave Digestion Method	
PCB	Printed Circuit Boards	
SEM	Scanning Electron Microscope	
TSS	Total Suspended Solids	mg/g
XRD	X-Ray Dispersion	

## 1. INTRODUCTION

As we are surrounded by many types of electronics from mobile phones and laptops to fridges and dishwashers, production of electronic devices increases by 8% per year (JEITA, 2018), making it one of the fastest-growing streams.

The development in technology and the increase in electronics has resulted in advancements in the generation of electronic waste (e-waste), which is one of the highest growing waste streams (Bazargan et al., 2014; Guo et al., 2009; Anshu and Subrata, 2017). The amount of e-waste generation is estimated to be 49.8 million metric tons/year globally (Statista, 2019). Asia has the largest amount of e-waste (18.2 million metric tons per year), followed by Europe (12.3 million metric tons per year) (Baldé et al., 2017).

E-waste contains hazardous substances (Tsydenova and Bengtsson, 2011; Chen et al., 2016; Koliyas et al., 2014; Heacock et al., 2016) as well as valuable elements (Cayumil et al., 2016; Oguchi et al., 2013; Namias, J. 2013; OEKO, 2012). E-waste discarded in 2014 contained silver (Ag), gold (Au), palladium (Pd) with a combined approximate value of US\$52 billion (UN University, 2015) and is expected to worth \$62.5 billion annually (World Economic Forum, 2019). Given the presence of both hazardous substances and valuable elements in e-waste, the content of e-waste becomes crucial for pollution prevention, resource conservation, and overall waste management (Oguchi et al., 2013).

Many methods are being used for the recovery of elements such as hydrometallurgical separation and pyrometallurgical conversion processes (Dodson et al., 2012). These methods have some major disadvantages such as the generation of chemicals and resins that have to be re-treated. Alternatively, biological methods have been receiving attention (Kütahyalı et al., 2010; Das, 2010; Dobson and Burgess, 2007) since they are eco-friendly, low-cost, efficient, and being chemical-free (Bağda et al., 2017; Yi et al., 2016). Biological sorbents such as algae, fungi, and yeast can be used for recovering valuable elements from aqueous solutions. Microalgae is used and tested for binding of elements from aqueous solutions and showed high efficiency for separation of base metals (Karthikeyan et al., 2007; Areco et al., 2012; Maznah et al., 2011). Moreover, algae can be produced in mass amounts easily and is eco-friendly.

So, the research question has arisen as: ‘Is it possible to recover the main valuable elements in e-waste that is projected to increase in future years by using biological means such as the usage of bioprocesses using microalgae?’

For this purpose, metal characterization of mobile phones and laptops’ printed circuit boards (PCBs) and screens was carried out to define focus elements for recovery purposes. Three different digestion methods were applied for e-waste digestion procedure. The characterization includes base metals, precious metals, and rare earth elements to fill the gap regarding e-waste content in literature. The biorecovery of focus elements was carried out by using dried and living microalgae, *Chlorella vulgaris*, as a biosorbent material.

The study aimed to investigate the following areas:

- the optimum characterization method for e-waste that is lack in literature,
- the biosorption and bioaccumulation capacity of dried and living microalgae for specific types of valuable element,
- the biosorption and bioaccumulation capacity of microalgae from binary element solutions.

Scientific value includes;

- There is limited information available for rare earth element content in e-waste. So, the gap was filled.
- There is no commonly used method available in the literature for e-waste characterization. Thus, digestion of e-waste was done by considering several methods, and the most appropriate method for each element was reported.
- Microalgae are of special interest in the search for biosorbents materials because of their available active sites that can bind elements.
- An environment-friendly nature could be adopted for the recovery of precious elements.
- For the development of a circular economy, the recycling of valuable and rare elements is essential (World Economic Forum, 2019).

This study supports the achievement of United Nations Sustainable Development Goals (2019) by following the following headlines:

- Goal 9: Industries, Innovation and Infrastructure; especially in the context of encouraging innovation.

- Goal 12: Sustainable consumption and protection; in the context of efficient usage of natural sources by recovery, reducing waste generation by recycling and reduction.
- Goal 3: Good health and well-being in the context of preventing the materials from spreading to the environment and Goal 11: Sustainable Cities and Communities by providing improving resource use.





## 2. LITERATURE REVIEW

### 2.1. E-waste Characterization

Electronic devices consist of plastics, metals, cables, screens, and PCBs. These parts include hazardous metals (Tsydenova and Bengtsson, 2011; Chen et al., 2016; Koliyas et al., 2014; Heacock et al., 2016) as well as valuable materials such as precious metals and rare earth elements (Cayumil et al., 2016; Oguchi et al., 2013; Namias, J. 2013; OEKO, 2012). The characterization of e-waste is crucial to manage the e-waste appropriately and define suitable recycling and recovery techniques.

The content of metals has been broadly defined by analytical instruments and techniques for more than 30 years. Most used methods refer to flame or electrothermal atomic absorption spectroscopy and Inductively Coupled Plasma Spectrometry (ICP) (Sastre et al., 2002; Güven and Akıncı, 2011). For solid samples, acid digestion procedures are used to convert the sample into liquid extracts for spectroscopic analysis (Silva and Nascimento, 2014). Conventional digestion procedure refers to the extraction of metals under acidic conditions on a heating source. On the other hand, microwave-assisted digestion enables closed digestion that provides higher temperatures and pressure. Commonly used acids and acid mixtures for the extraction process are HNO<sub>3</sub>, HNO<sub>3</sub>-HF, and HNO<sub>3</sub>-HCl (Güven and Akıncı, 2011).

The metal and rare earth element composition of e-waste discussed in literature can be seen in Table 2.1 For the base metals, copper (Cu) has the highest content in all of the studies; representing between 190 – 335 g/kg except for the mobile phone screen sample, which is relatively low as 13.5 g/kg of content. The Cu content is higher in mobile phones compared to laptop and computer samples. Zinc (Zn), nickel (Ni), lead (Pb) and aluminum (Al) are also the main elements found in most of the samples and represents contents between 5-59.2 g/kg, 4.3-26.3 g/kg and 9.8-55.8 g/kg, 2.6-57 g/kg, respectively. Screen shows lower contents of Zn, Ni, Pb, and Al. There is no significant difference observed between mobile phone and laptop samples for these metals. Chromium (Cr) and cobalt (Co) contents are found relatively low in measured samples, representing 0.61 -1.7 g/kg and 0.2 g/kg for mobile phone PCBs, respectively. Cadmium (Cd) content is found as low as 0.002-0.004 g/kg.

When it comes to precious metals and rare earth element contents, Ag, Au and Pd are the main metals present in samples, representing 1.1 – 3.6 g/kg and as high as 1.4 g/kg and 0.2– 0.3 g/kg, respectively.

No Au was found in mobile phone samples in the study conducted by Yamane et al., 2011. No significant difference was observed between e-waste samples. Lastly, there is limited information on platinum (Pt), lanthanum (La), dysprosium (Dy), praseodymium (Pr) and cerium (Ce) and neodymium (Nd) contents of e-waste. It is found that mobile phone screens involve La, Dy, Pr, and Ce.

Table 2.1. Metal content of e-waste reported in different studies (g/kg).

Type of e-waste	Mobile phone PCBs (Mean values)	Mobile phone Screen (Nokia)	Mobile Phone	Mobile Phone	Laptop	Computer
Reference	(Şahan, 2016)	(Şahan, 2016)	(Oguchi et al., 2013)	(Yamane et al., 2011)	(Oguchi et al., 2013)	(Yamane et al., 2011)
Cu	335	13.5	330	344.9	190	201.9
Fe	23.2	-	18	105.7	37	73.3
Zn	19.2	0.24	5	59.2	16	44.8
Ni	25	1.7	-	26.3	-	4.3
Pb	12	0.33	13	18.7	9.8	55.3
Al	14.1	3.8	15	2.6	18	57
Co	0.2	-	-	-	-	-
Cr	1.7	0.27	1.1	-	0.61	-
Cd	-	-	0.004	-	0.002	-
Ag	3.6	0.6	3.8	2.1	1.1	1.6
Au	1.4	0.19	1.5	<	0.63	1.3
Pd	0.3	<	0.3	-	0.2	-
Pt	0.03	-	-	-	-	-
La	-	0.48	-	-	-	-
Dy	-	0.02	-	-	-	-
Pr	-	0.03	-	-	-	-
Ce	-	0.004	-	-	-	-

## 2.2. Recovery of Metals

The hydrometallurgical and pyro-metallurgical methods are widely used to remove metals from a specific surface. Most commonly used processes for removing metals from aqueous solutions include ultradialysis, electrodialysis, phytoremediation (Ahalya et al., 2003), adsorption, coagulation, flotation (Kütahyalı et al., 2010), reverse osmosis, ion-exchange, and chemical precipitation (Ahalya et al., 2003; Kütahyalı et al., 2010). The conventional methods have advantages as well as some major disadvantages such as generation of chemicals and resins. In this sense, the interest in biological means has increased (Limcharoensuk et al., 2015; Kütahyalı et al., 2010; Das, 2010; Dobson and Burgess, 2007).

### 2.2.1. Biosorption and Bioaccumulation

Removal of metals from aqueous solution can be achieved by biosorption or bioaccumulation by using biological sorbents. Biosorption can be defined as a process where biomass such as a solid surface and a sorbate, like an ion, interact with each other in a manner that results in adsorption or absorption of the sorbate to the biomass (Das and Dash, 2017; Gadd, 2008) by various physicochemical mechanisms (Rezaei, 2013). The process requires using inactive or dead cells. Thus, biosorption is growth independent and not limited to toxicity. On the other hand, bioaccumulation is an active process where living microorganisms are used (Limcharoensuk et al., 2015). It can also be called as active biosorption (Flouty and Estephane, 2012), which has two stages. The first stage is biosorption and the second stage is the transport of the sorbate into the living cells (Flouty and Estephane, 2012). The advantages of biosorption and bioaccumulation are cost-effectiveness, regeneration possibility of the biosorbent, and secondary metabolites-free process (Rezaei, 2013; Nadeem et al., 2016).

Several types of biosorbents are available, such as bacteria, fungi, algae, sludges, agricultural materials like rice straws, and chitosan (Das and Dash, 2017; Rezaei, 2013). For bioaccumulation, live microorganisms such as fungi, yeast, algae, and bacteria can be used for uptake of metals (Flouty and Estephane, 2012; Wang and Chen, 2009). Among these biosorbents, algae have high efficiency in terms of metal-binding capacity, since they consist of polysaccharides, proteins, and lipid on the cell wall surface due to various functional groups such as hydroxyl, carboxyl, amino, and sulfate. These groups are able to bind the metal ions present in the aqueous solutions (Bağda et al., 2017; Anastopoulos and Kyzas, 2015). Algae have been used for biosorption 15.3% more than other types of biomass and 84.6% more than bacteria and fungi (Anastopoulos and Kyzas, 2015; Kanchana et al., 2014). The cost efficiency is showed by Herrera et al. 2004; 10 g of  $\text{Ag}^{+2}$  on cellulose phosphate is found as USD 2.

The uptake amount of several metals by different types of algae types can be seen in Table 2.2. Most of the studies in the literature focus on the biosorption of base metals. It can be seen that the uptake amount of the metal varies according to the type of metal, biosorbent type, and the process conditions. The metals in interest are sorbed by the selected type of algae in different efficiency ratios. There is a limited number of studies conducted that addresses the usage of precious metals and rare earth elements for biosorption studies. Brown algae of *Fucus vesiculosus* and *Turbinaria conoides* are able to sorb  $\text{Au}^{+3}$  by 74.072 mg/gr and 24.5 mg/g, respectively (Mata et al., 2009).  $\text{Ag}^{+2}$  sorption was achieved by 333 mg/g by exopolysaccharides (Deschatre et al., 2013). Nd sorption was found as

136.72 mg/g (Palmieri et al., 2000) and 157.50 mg/g (Kucuker et al., 2017) for different experimental conditions.

Table 2.2. Biosorption capacities of different metals.

Type	Metal	Algae Type/EPS	Q: uptake amount (mg/g)	Conditions	Reference
Biosorption	Cr <sup>+6</sup>	<i>Sprogyra species</i> (Green algae)	14.7	5 mg/L IMC*, pH: 2	(Gupta et al., 2001)
Biosorption	Cu <sup>+2</sup>	<i>Ulva fasciata</i> (Green algae)	2.5 73.5	20 mg/L IMC*, pH: 5 500 mg/L IMC*, pH:5	(Karthikeyan et al., 2007)
Bioaccumulation	Cu <sup>+2</sup> Zn <sup>+2</sup> Cd <sup>+2</sup> Hg <sup>+2</sup>	<i>Cladophora fracta</i> (Green algae)	2.38 1.623 0.240 0.228	10 mg/L IMC*, pH:5 10 mg/L IMC*, pH:5 1 mg/L IMC*, pH: 5 1 mg/L IMC*, pH: 5	(Ji et al., 2012)
Biosorption	Cu <sup>+2</sup> Zn <sup>+2</sup> Cd <sup>+2</sup> Pb <sup>+2</sup>	<i>Ulva fasciata</i> (Green algae)	32.80 30 49 54.3	65 mg/L IMC*, pH: 5	(Areco et al., 2012)
Bioaccumulation	Cu <sup>+2</sup> Zn <sup>+2</sup>	<i>Chlorella Sp.</i> (Green algae)	10-14 25-30	20 mg/L IMC*, pH:7	(Maznah et al., 2011)
Biosorption	Cu <sup>+2</sup> Zn <sup>+2</sup>		12-14 30-35	20 mg/L IMC*, pH 7	(Maznah et al., 2011)
Biosorption	Cu <sup>+2</sup> Ni <sup>+2</sup> Cr <sup>+4</sup>	<i>Chlorella vulgaris</i> (Green algae)	46.8 55.6 33.8	291.8 mg/L IMC*, pH:5 259.2 mg/L IMC*, pH: 4.5 263 mg/L IMC*, pH:2	(Dönmez et al., 1999)
Biosorption	Cu <sup>+2</sup> Ni <sup>+2</sup> Cr <sup>+4</sup>	<i>Scenedesmus obliquus</i> (Green algae)	26.8 24.7 30.2	224.4 mg/L IMC*, pH:5 217.8 mg/L IMC*, pH:4.5 230.4 mg/L IMC*, pH:2	
Biosorption	Au <sup>+3</sup>	<i>Fucus vesiculosus</i> (Brown algae)	74.072	133.172 mg/L IMC*, pH:7	(Mata et al., 2009)
Biosorption	Ag <sup>+2</sup>	Exopolysaccharides produced by marine bacteria.	333	500 mg/L IMC*, pH:5.7	(Deschatre et al., 2013)
Biosorption	Nd <sup>+3</sup>	<i>Monoraphidium sp.</i> (Green algae)	136.72	400 mg/L IMC*, pH:1.5	(Palmieri et al., 2000)
Biosorption	Nd <sup>+3</sup>	<i>Chlorella vulgaris</i> (Green algae)	157.4	250 mg/L IMC*, pH:5	(Kucuker et al., 2017)
Biosorption	Au <sup>+3</sup>	<i>Turbinaria conoides</i> (Brown algae)	34.5	100 mg/L IMC*, pH:2	(Vijayaraghavana et al., 2011)

\*IMC: Initial metal concentration

## 2.2.2. Factors Affecting Biosorption

**2.2.2.1. pH.** The pH of the solution affects the biosorption capacity since the chemistry of the metals may change and the activity of the functional groups may be affected according to pH (Zhang and Banks, 2010). Besides the optimum pH value, the uptake amounts are decreased. Biosorption of Cu<sup>+2</sup>, Pb<sup>+2</sup>, and Cd<sup>+2</sup> was tested by using *Chlorella vulgaris* in the range of 2-6. The uptake of the metals has increased from 22.7% to 87.7% for Cu<sup>+2</sup>, and from 29.9% to %96.4 for Pb<sup>+2</sup> as the pH increases from 2 to 5. The efficiency decreased as pH increased further. For Cd<sup>+2</sup>, the uptake increased from 13.7% to 84.7% when the pH increased from 2 to 6. No increase was observed with any further

increase (Goher et al., 2015). Another study conducted by Vilar et al., 2005 showed similar results. The effect of pH ranging from 3 to 5.3 is tested for  $Pb^{+2}$  biosorption by *Gelidium* algae and algal waste. The biosorption efficiency was found as maximum in pH 5.3. As pH increased from 3 to 5.3, the uptake of  $Pb^{+2}$  also increased. The uptake amount was approximately 8 mg/g algal waste and 17 mg/g *Gelidium* at pH 3, whereas the uptake amount is approximately 26 mg/g algal waste and 40 mg/g *Gelidium* for pH 5.3 (Vilar et al., 2005). For biosorption of  $Cu^{+2}$  and  $Zn^{+2}$  by *Sphagnum Moss*, the optimum pH was found as pH 7 and 7.2, respectively. It was observed that, as the pH increased, there was a tendency towards solubilization and leaching of biomass. However, sorption of  $Pb^{+2}$  was found independent in the pH range of 3-8 in the same study (Zhang and Banks, 2005). This may be because of  $Pb^{+2}$ 's solubility or the binding sites selectivity of the biosorbent for  $Pb^{+2}$ .

When the pH value is low,  $H^+$  ions may compete with the metal ions to bind the functional groups (Goher et al., 2015) and the solubility of the metals in the aqueous phase is higher (Al-Homaidan et al., 2013). As the pH gets higher (>3-4), carboxylic groups are negatively charged and this would enhance binding of positively charged metals (Goher et al., 2015; Vilar et al., 2005). After a certain value of pH, the precipitation of metals may occur and this may have negative effect on the uptake amount.

2.2.2.2. Temperature. Stability of the metal ions and solubility of the ions depends on solution temperature. In high temperatures, an increase in active sites of the sorbent may be promoted (Aksu, 2002; Martins et al., 2004). High temperature may also enhance ion exchange and change the size of the pores (Martins et al., 2004). The uptake of  $Ni^{+2}$  by green algae, *Chlorella vulgaris*, was increased by increasing the temperature from 15 ° C to 45 ° C. The results showed that the uptake amount gradually increased as the temperature increased. The uptake value was found as (approximately) 30 mg/g and 48.2 mg/g under 15 ° C and 45 ° C, respectively (Aksu, 2002). Similar results were found by Gupta and Rastogi (2008) for the biosorption of  $Pb^{+2}$  on green algae type *Spirogyra*. As the temperature increased from 25 ° C to 45 ° C, the uptake increased from 96.4 mg/g to 159 mg/g.  $Cd^{+2}$  and  $Zn^{+2}$  biosorption on dried aquatic moss; *Fontinalis antipyretica* was tested under four different temperatures as 5 ° C, 10 ° C, 20 ° C and 30 ° C. Similar results were found for  $Zn^{+2}$  biosorption. The uptake of metal increased with increasing temperature, reaching a maximum of 15 mg/g at 30 ° C. However, for  $Cd^{+2}$ , the biosorption capacity of moss in different temperatures was close to each other; representing around 28 mg/g uptake (Martins et al., 2004).

2.2.2.3. Initial Metal Concentration. As the initial metal concentration increases, the adsorption rate generally increases. More uptake is often achieved in higher concentration since algae have finite

numbers of binding sites (Aksu, 2002), that enables more chances to bind for the biosorbent when there is more metal ions available (Chen et al., 2008). Such a result was observed by Aksu, 2002;  $\text{Ni}^{+2}$  biosorption was increased by increasing initial metal concentration. When the initial metal concentration represents 48 mg/L and 102.1 mg/L and 250 mg/L, the uptake amounts were found as 35.4 mg/g, 48.2 mg/g, and 60.2 mg/g, respectively (Aksu, 2002). The sorption of  $\text{Ni}^{+2}$  onto brown microalgae types; *Cystoseria indica*, *Nizmuddinia zanardini*, *Sargassum glaucescens* and *Padina australis* were tested. Higher uptake was achieved in higher initial metal concentrations. When initial metal concentration is 6.9 mg/L, the uptake amount of the alga changed between 2.7 to 4.4 mg/g. However, when the initial metal concentration was increased to 201 mg/L, the uptake amounts were found between 22 to 45 mg/g (Pahlavanzadeh et al., 2010). Similar results were found by Chen et al., 2008; the sorption of  $\text{Ni}^{+2}$  and  $\text{Cu}^{+2}$  on a type of algae; *Undaria pinnatifida*, was tested. The uptake capacity of  $\text{Ni}^{+2}$  is found as 0.98 mg/g and 11.33 mg/g when initial metal concentration is 5 mg/L and 50 mg/L, respectively. However, no significant change was observed for  $\text{Cu}^{+2}$  sorption (Chen et al., 2008). This may be due to *Undaria pinnatifida*'s binding sites that are not preferable to bind  $\text{Cu}^{+2}$ , or there may be limited functional groups to bind  $\text{Cu}^{+2}$ .

2.2.2.4. Biosorbent Dosage.  $\text{Cu}^{+2}$  sorption is tested under 0.5, 1, 1.5 and 2 g/L of algal biomass; *Spirogyra*. Highest uptake was observed in the case of least amount of biosorbent. It is found that as the biosorbent dosage increases, the uptake of  $\text{Cu}^{+2}$  decreases. 80% removal efficiency was achieved in 0.5 g/L biosorbent dosage, whereas the efficiency has decreased approximately by 60% when the algal dosage is 2 g/L. (Bishnoi et al., 2004). However, in another study, as the algal dosage increased, the uptake of tested metals  $\text{Cu}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Cd}^{+2}$  also increased. The maximum uptake amount was found to be 0.8 g/L compared to 0.2-1 g/L algal dosage. Even though the uptake efficiency has increased, it remains nearly constant after 0.8 g/L (Ibrahim et al., 2016). Different algal sorbent dosage was assessed for biosorption of  $\text{Cd}^{+2}$  and  $\text{Pb}^{+2}$  by *Anabaena sphaerica*. Various dosage of algae from 0.25 to 2.5 g/L was assessed. 1 and 2 g/L of algal dosage was found optimum for  $\text{Pb}^{+2}$  and  $\text{Cd}^{+2}$  removal, respectively (Abdel-Aty et al., 2012). Up to a specific value, uptake increased as the biosorbent dosage increased, and then it remained same, or it decreased. This may be because of more binding sites are available as the dosage increases; thus, the uptake increases. After a particular value, agglomeration of the algae occurs and there is a screening effect that blocks the binding sites (Bishnoi et al., 2004; El-Sikaily et al., 2011).

2.2.2.5. Contact Time. Most of the biosorption studies completed in a very short period of time, representing; 20-120 minutes for different types of metals and biosorbents found in literature (Goher et al., 2015; Aksu, 2002; Gupta and Rastogi, 2007; Bishnoi et al., 2004; Pahlavanzadeh et al., 2010).

2.2.2.6. Presence of Other Metals. When there is another metal ion present in the solution, the uptake amount has decreased. Aksu and Dönmez (2006) showed that the uptake of metals had dropped to 68.5 mg/g from 86.6 mg/g for  $\text{Cd}^{+2}$  and to 28.3 mg/g from 58.4 mg/g for  $\text{Ni}^{+2}$  when co-ion concentration was arranged to 150 mg/L. Similar results were found by Sulaymon et al., in 2013. The uptake amount decreased when there were more metals present. Binary, ternary, and quaternary systems with  $\text{Pb}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Ar}^{+3}$  was tested and it was found that the efficiency gradually decreases as the number of metals increases in the solution.

## 2.3. Modelling

To understand the process mechanisms and analyze experimental data, appropriate models were used. Two main ingredients as equilibrium and kinetic should be known to understand the process. For kinetics, pseudo-first order and pseudo-second order equations were applied, while for equilibrium, Freundlich and Langmuir isotherms were applied to the experimental data obtained from biosorption and bioaccumulation laboratory tests.

### 2.3.1. Kinetic Modelling

Pseudo-first order (Lagergren, 1898 cited in Azizian, 2004) and Pseudo-second order rate equations (Bhattacharya and Venkobachar, 1984) can be seen in Equation 2.1 and 2.2, respectively.

$$\frac{dq}{dt} = k_1(q_e - q) \quad (2.1)$$

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (2.2)$$

where

$q_e$ : the element adsorbed at equilibrium time (mg/g)

$q$ : the element adsorbed at a time (mg/g)

$k_1$ : pseudo-first order adsorption rate constant (L/min)

$k_2$ : and pseudo-second order adsorption rate constant (g/mg min)

Second- order kinetics are widely found in the literature for biosorption process. Some examples include biosorption of  $\text{U}^{+6}$  by *Cladophora hutchinsiae* (Bağda et al., 2017),  $\text{Cu}^{+2}$  and  $\text{Co}^{+2}$  by *Cytoseira indicia* (Akbari et al., 2014),  $\text{Hg}^{+2}$  by red algae *Pophyridium cruentum* (Zaib et al, 2016),  $\text{Cd}^{+2}$  by brown algae *Sargassum fusiforme* (Zou et al, 2014).

### 2.3.2. Isotherm Modelling

Isotherms are widely used to describe the distribution of adsorbate species between the liquid and the sorbent. Langmuir (Langmuir, 1916) and Freundlich isotherms as shown in Equation 2.3 and 2.4, respectively, which are widely used applied to the experimental data. Freundlich isotherm assumes that the adsorption occurs on heterogeneous surfaces, while Langmuir isotherm assumes adsorption occurs as monolayer adsorption (Ebrahimian et al., 2014).

Langmuir Equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2.3)$$

Freundlich Equation:

$$q_e = K_F C_e^{1/n} \quad (2.4)$$

where

$q_e$ : the element adsorbed at equilibrium time (mg/g)

$q_m$ : the element adsorbed at a time (mg/g)

$C_e$ : concentration of solution in equilibrium (mg/L)

$K_L$ : Langmuir constant

$K_F$ : measure of sorption capacity

$1/n$ : sorption intensity

Both Langmuir and Freundlich models are used widely to biosorption studies in the literature. Biosorption of basic blue 9 by tea waste (Ebrahimian et al., 2014),  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Pb}^{+2}$  by *Ulva lactuca* (Areco et al., 2012),  $\text{Cr}^{+6}$  by green algae *Sprogyra* species (Gupta et al., 2001) represents Langmuir isotherm, while  $\text{Cd}^{+2}$  biosorption by *Chlorella vulgaris* (Ali et al., 2016), and  $\text{Pb}^{+2}$  by *Bacillus cereus* (Ray et al., 2005) better fitted for Freundlich isotherm. Both Langmuir and Freundlich isotherms are better fitted for biosorption of  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$  and  $\text{Cr}^{+6}$  by *Chlorella vulgaris*, *Scenedesmus obliquus*, and *Synechocystis sp* (Dönmez et al., 1999).



### 3. MATERIALS AND METHODS

#### 3.1. Characterization of E-waste

Six different types of e-waste samples were examined by three different digestion methods. The selected e-waste samples included.

- I. PCBs of old mobile phones (such as Nokia 3310)
- II. PBCs of smartphones
- III. PBCs of laptops
- IV. Old mobile phone screens
- V. Smartphone screens
- VI. Laptop screens.

The samples were obtained from Hamburg University of Technology, Institute of Environmental Technology and Energy Economics, and the Department of Waste Resources Management. PCBs and screens of the samples were separated by hand and then subject to grinding in two sets; 1.5 mm followed by 0.75 mm sieve size by Retzch Cutting Mill SM 300 after cutting for size reduction as shown in Figure 3.1.



Figure 3.1. Preparation of e-waste samples for analysis.

The homogenized form of e-waste was digested by using the following methods;

- EPA Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils.

- Modified Microwave Digestion Method (MMDM): Rapid Microwave Digestion Procedures for the Elemental Analysis of Alloy and Slag Samples of Smelted Ocean Bed Polymetallic Nodules (Smita et al., 2012).
- EPA Method 3050B: Acid Digestion of Sediments, Sludges, and Soils.

All digestions were performed in duplicates. Regarding EPA Method 3051A and 3050B, each sample was obtained by mixing two samples from the same source to prevent fluctuations in element contents. Reagents used in this study are as follows: hydrochloric acid 37% (Merck, Germany), nitric acid 65% (Merck, Germany), hydrogen peroxide solution 34.5-36.5%. Deionized water was used for dilutions.

EPA Method 3051A: 0.1 g sample was placed into polytetrafluorethylene vessels. 9 mL of HNO<sub>3</sub> and 3 mL of HCl were added. The vessels were placed into the Mars 6 Microwave Reaction System (CEM Cooperation, USA) and heated to 175 °C in 5.30 min and kept at this temperature for 4.5 minutes. After digestion, the samples were cooled and diluted and then filtered for analysis.

MMDM: 0.1 g sample was placed into polytetrafluorethylene vessels. 10 mL of HCl and 3.5 mL of HNO<sub>3</sub> were added. The sample was heated to 100 °C and kept at this temperature for 5 minutes, and then heated to 110 °C and kept at this temperature for a further 10 minutes. Lastly, the sample was heated to 150 °C and kept at this temperature for 25 minutes. The ramp time of each step was as follows; 5.5 minutes and 5 minutes for the last two steps.

EPA Method 3050B: 0.1 g sample was placed into glass vessels. A 10 mL of HNO<sub>3</sub> was added, and the sample was heated to 95 °C ± 5 °C and refluxed for 15 minutes. After the sample was cooled down, 5 mL of HNO<sub>3</sub> was added, and the sample was refluxed again for 2 hours. 2 mL of H<sub>2</sub>O and 3 mL of H<sub>2</sub>O<sub>2</sub> were added to the solution and then it was heated again until the effervescence subsided. The sample was cooled and 1 mL of H<sub>2</sub>O<sub>2</sub> were added until the sample is unchanged. The samples were refluxed again for 2 hours. 10 mL of HCl was added after the sample was cooled down, and it was refluxed for 15 minutes. The digestate was filtered through a Whatman No 41 filter paper and then diluted.

To increase the solubility of Ag, the steps in EPA Method 3050B was followed. 0.1 gr sample was placed into the vessel. 2.5 mL of HNO<sub>3</sub> and 10 mL of HCl were added, and the sample was

refluxed for 15 minutes at  $95\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ . The digestate was filtered through a Whatman No 41 filter paper. The filtrate and the filter were again placed back into the vessel and heated until the filter paper was dissolved. The digestate was filtered again and diluted. After the digestion, the samples were analyzed by using ICP-Optical Emission Spectrometry (OES) after filtered through 0.45 $\mu\text{m}$  pore sized filter. The wavelength of the measured metals are as follows: Cu; 327.393 nm, Fe; 238.204 nm, Ni; 231.604 nm, Al; 396.153 nm, Zn; 206.200 nm, Pb; 220.353 nm, Cr; 267.716 nm, Mn; 257.610 nm, Co; 228.616 nm, Mo; 202.031 nm, Cd; 228.802 nm, Nd; 406.109 nm, Ag; 328.068 nm, Au; 267.595 nm, Pr; 390.844 nm, Dy; 353.170 nm, Pd; 340.458 nm, Pt; 265.945 nm, La; 398.852 nm, Ce; 413.764 nm.

To compare the efficiency of the selected digestion methods, SPSS Statistics Software was used. A general linear model was created to assess the overall performance of individual methods and bootstrapping was applied to determine a pairwise comparison for each parallel.

## **3.2. Biosorption by Microalgae**

### **3.2.1. Cultivation of Microalgae**

A green type of microalgae, *Chlorella vulgaris*, was selected as biosorbent material. Bioreactors consisting of 2 liters were used to grow the algae, that was incubated for 16 hours at an average intensity of  $300\text{ }\mu\text{E m}^{-2}\text{ s}^{-1}$  at room temperature consistently. Bold's Basal Medium (modified) was used (Stein, 1980).  $\text{CO}_2$  was supplied after mixing with air to the reactors to support the growth of the algae. In addition, young algae was supplied to the reactors on a regular basis to support the growth. The temperature and pH were measured daily. When needed, the pH was adjusted by changing the  $\text{CO}_2$  amount. After 20 days, total suspended solids (TSS) content of the reactors was reaching 0.9 g/L, which represented maximum TSS achieved with the reactors. TSS was measured according to Standard Methods (2540). Cultures were harvested and left to sedimentation for dewatering purposes. After dewatering, cultures were dried at  $60^{\circ}\text{C}$ . Dried algae was crushed and sieved for biosorption experiments.

### **3.2.2. Solubility Tests**

Selected metal and rare earth element were ordered in nitrate forms as  $\text{AgNO}_3$  and  $\text{Nd}(\text{NO}_3)_3$ . The solubility of each element was determined before the biosorption experiments since precipitation may affect adsorption results, which could lead to the misinterpretation of the adsorption capacity.

200 mg/L of the focused element was prepared and the pH of the solutions was adjusted by using 1 M HNO<sub>3</sub> and 1 M NaOH. Obtained samples were filtered to remove the suspended solids and analyzed in ICP-OES.

### 3.2.3. Biosorption Experiments

Prepared solutions and algae were poured into Erlenmeyer flasks. Before adding the algae, pH adjustment of the solution was completed by using 1 M of HNO<sub>3</sub> and 1 of M NaOH with a deviation of  $\pm 0.15$ . After the pH was adjusted, a sample was taken to check the metal concentration in the solution. After addition of algae ( $\pm 0.0010$ ) flasks were agitated on a shaker at 300 rpm for 2 hours for determining the metal uptake of the algae. Sampling time was determined according to the results of preliminary biosorption test, which indicated that most of the biosorption reached equilibrium at 2 hours. The parameters and the range of the parameters tested can be seen in Table 3.1.

Table 3.1. Determination of the optimum conditions.

No	Parameter	Range
1	pH	4 - 5 - 6
2	Temperature (°C)	25 - 35 - 50
3	Biosorbent (g/L)	0.5 - 1 - 2
4	Stirring Speed (rpm)	0-300-600
5	Initial metal concentration (mg/L)	15 - 50 - 100 - 200

The supernatant fraction was analyzed for the remaining metal ions by ICP-OES, while the biomass was subjected to Fourier Transform Infrared Spectroscopy (FTIR) with Thermo Fisher Nicolet 380 FTIR Spectrometer to detect the available and used binding sites of the algae. Biomass was also subjected to X-Ray Dispersion (XRD) analysis with Scanning Electron Microscope (SEM) model ZEISS EVO 40 to obtain a picture of element loaded algae. The view of the analysis can be seen in Figure 3.2.

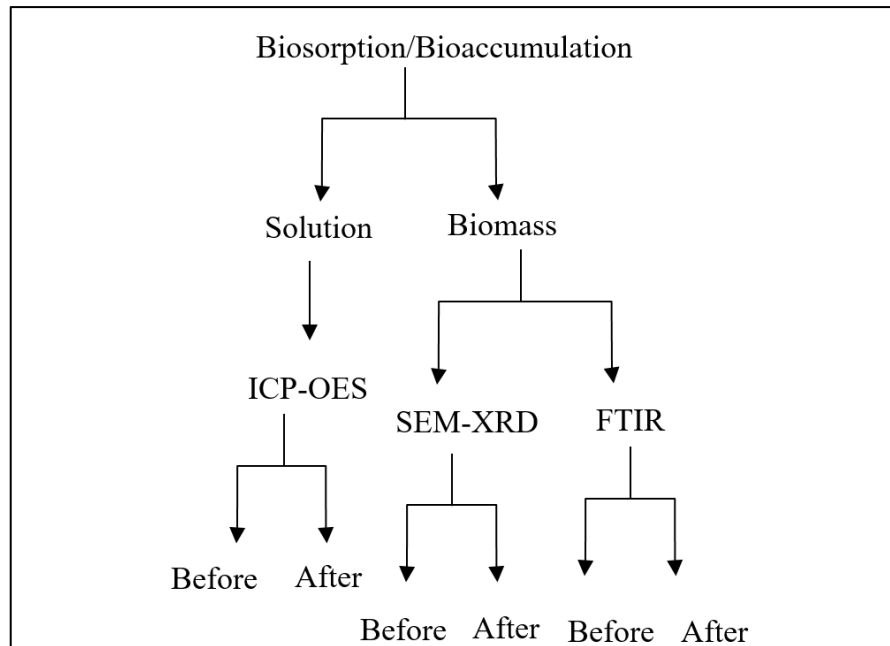


Figure 3.2. The analyses of biosorption process.

The uptake of element by algae is calculated by using Equation 3.1:

$$q_e = \frac{(C_i - C_e)V}{w} \quad (3.1)$$

where

$q_e$ : Metal uptake by algae (mg/g)

$C_i$ : Initial metal solution (mg/L)

$C_e$ : Remaining metal concentration (mg/L)

$V$ : Sample size (L)

$w$ : Biosorbent dosage (g/L)

### 3.3. Bioaccumulation by Microalgae

#### 3.3.1. Microalgae Preparation

To obtain desired concentrations of microalgae, microalgae was sedimented in Imhoff funnel after harvesting. The sediment was taken and then washed with deionized water three times. The TSS concentration was determined and then desired concentrations of algae (0.5 g/L, 1 g/L and 2 g/L) were obtained by dilution using deionized water.

### **3.3.2. Bioaccumulation Experiments**

Bioaccumulation under different biomass dosage (0.5-1-2 g/L) was tested for a variety of initial metal concentrations (15-50-100-200 ppm). The temperature was fixed to room temperature since higher temperature may result in damage of microalgae, and lower temperature may affect the activity of microalgae. pH was also maintained in the same level in all samples (between 7-8). The main purpose of maintaining the temperature and pH in the same level as it is in cultivation was to ensure the algae lived as long as possible. The experiments were conducted in Erlenmeyer flasks containing 50 mL of metal solution and biomass. The flasks were incubated in the shaker at 100 rpm for 72 hours at room temperature (25 °C). Samples were taken at the beginning and pre-determined time intervals (24 h, 48 h, and 72 h) for the residual metal ion concentrations in the solution. Each experiment was performed in duplicates. Optimum conditions as biomass dosage and initial concentration for the bioaccumulation tests were investigated in detail. The supernatant fraction was analyzed for the remaining metal ions by ICP-OES, while the biomass was subjected to FTIR and XRD analysis after drying at room temperature, as shown in Figure 3.2. Uptake amount was calculated by using Equation 3.1.

### **3.4. Biosorption and Bioaccumulation from Binary Metal Solutions**

Optimum parameters obtained from biosorption and bioaccumulation from single element solutions were selected for biosorption and bioaccumulation from binary element solutions. The supernatant fraction was analyzed for the remaining metal ions by ICP-OES, while the biomass was subjected to XRD analysis.

### **3.5. Modelling Studies**

For kinetics, pseudo-first order; Equation 2.1 and pseudo-second order; Equation 2.2 was applied. For equilibrium, Freundlich isotherm; Equation 2.3 and Langmuir isotherm; Equation 2.4 was used to the experimental data. The schematic view of the study can be seen in Figure 3.3.

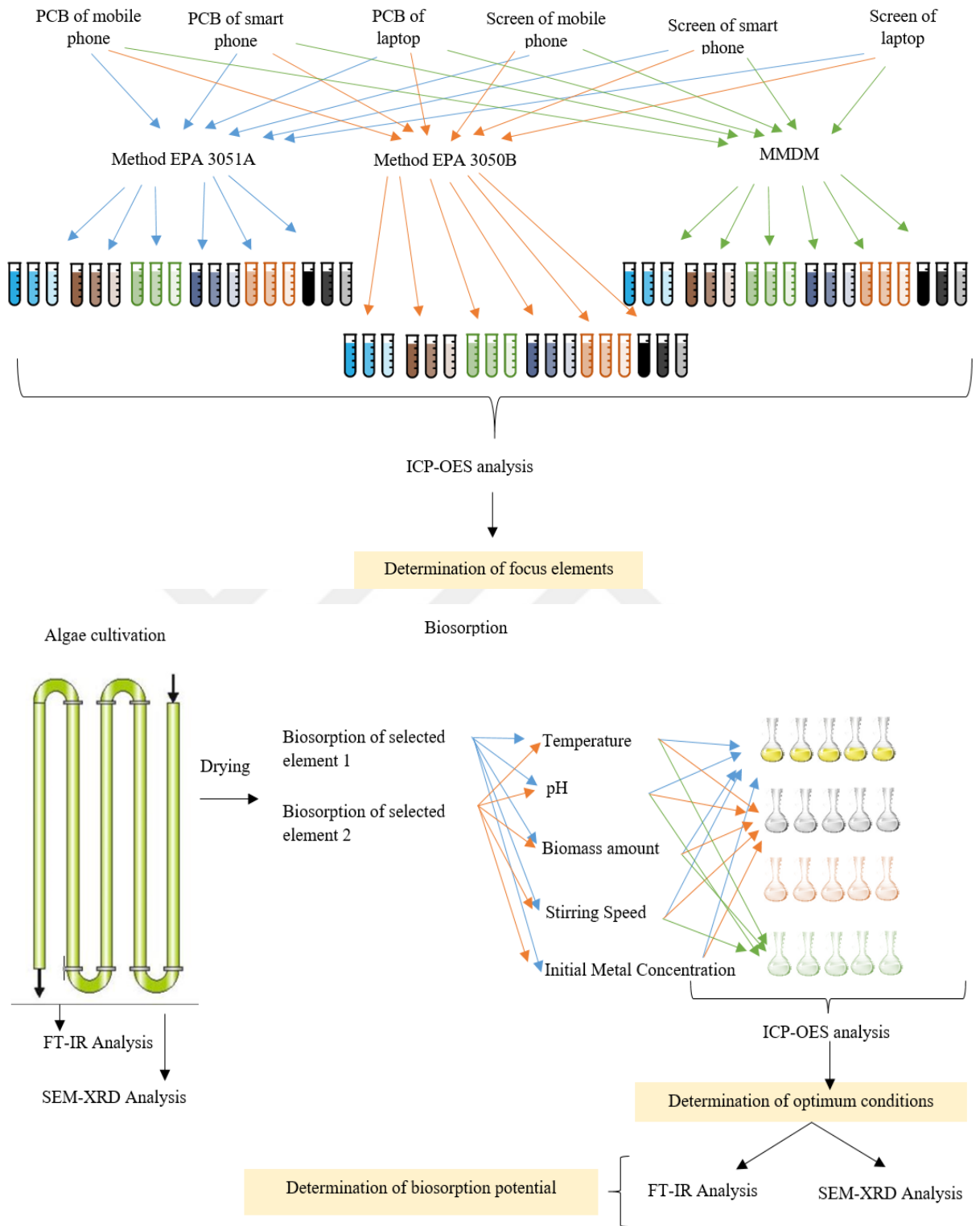


Figure 3.3. Schematic view of the study.

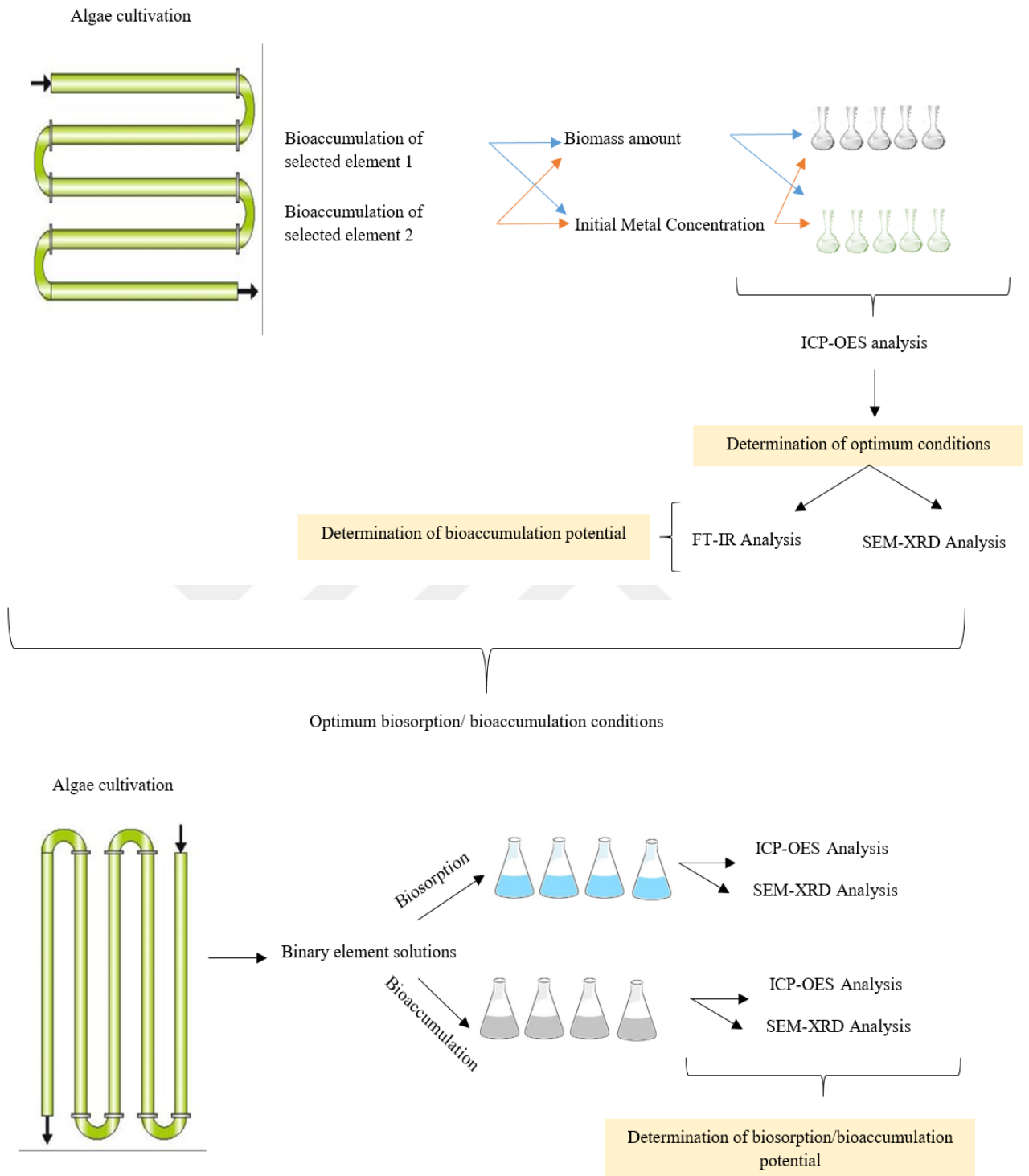


Figure 3.3. Schematic view of the study (continued).



## 4. RESULTS AND DISCUSSIONS

### 4.1. Characterization of E-waste

#### 4.1.1. Base Metals

4.1.1.1. PCBs. The content of heavy metals can be seen in Figure 4.1 and Table 4.1. Cu is the main metal that is found in PCBs of mobile phones and laptops. 288-338 g of Cu can be found in PCBs per kg. Cu is widely used because of its conductivity in electronics. Second common metal is Fe by 37-135 g/kg. Smartphone PCB has the highest amount of Fe, followed by laptop PCB. Ni, Pb, and Al are the other main metals found in PCBs and laptops. Zn is also one of the main metals found in the old mobile phone and laptop PCBs, while it is relatively low in the smartphone PCB. The content of Cr is high in laptop PCB when it is compared to mobile and smartphones. The contents of Co, Mn, Mo were found to be very low in PCBs. Cd was not detected in mobile phones and smartphone PCBs, while very low content was found in laptop PCBs. When the results are compared with the data from the literature as shown in Table 2.1, the values of Cu, Fe, Zn, Ni, Pb, Al, Co, Cd were found comparable, while the content of Cr represents a higher value.

4.1.1.2. Screens. The metal content of base metals in screens is relatively low compared to PCBs. Cu and Fe are the main metals found in screens. Laptop screen has the highest amount of Cu; representing a significantly high value than other screens. The Cr content of the smartphone screen and the Al content of the laptop screen were also significant. However, the contents of other metals were insignificant and represented low amounts.

Since there is a limited study on screens characterization, the comparison was made in a manner similar to a study conducted by Şahan, 2016. The content of Cu, Zn, Ni, Mn, and Co was found to be comparable, while higher Pb and Al and lower Fe and Cr were found.

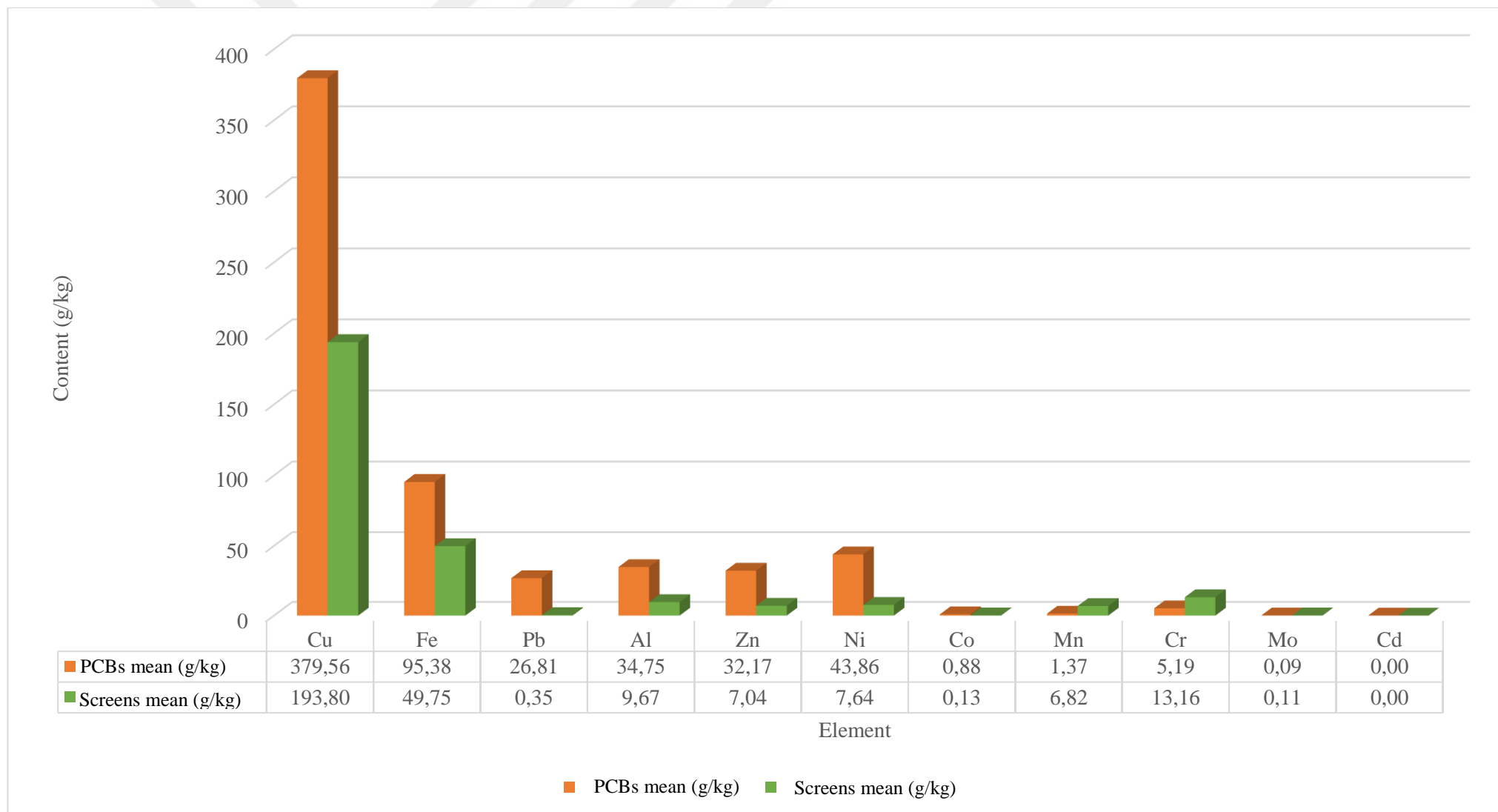


Figure 4.1. Base metals found in e-waste.

Table 4.1. Heavy metal content of selected samples according to different digestion methods (g/kg).

Metal	Mobile PCB		
	EPA Method 3051A	MMDM	EPA 3050B
Cu	493.93 ±46.96	390.22 ±4.65	305.91 ±0.55
Fe	42.77 ±19.21	20.90 ±14.61	37.02 ±20.64
Zn	67.81 ±0.86	66.19 ±6.09	37.45 ±1.47
Ni	67.71 ±1.78	63.20 ±5.14	50.49 ±2.80
Pb	10.85 ±2.03	11.89 ±0.35	23.19 ±2.07
Al	6.65 ±0.74	11.25 ±1.31	27.36 ±3.26
Mn	2.01 ±0.87	1.54 ±0.12	1.06 ±0.21
Co	1.06 ±0.10	0.10 ±0.01	1.49 ±1.41
Cr	0.41 ±0.21	0.43 ±0.28	0.62 ±0.42
Mo	0.03 *	0.06 ±0.01	0.04 *
Cd	ND	ND	ND

Smartphone PCB		
EPA Method 3051A	MMDM	EPA 3050B
163.9 ±1.65	306.72 ±1.01	288.52 ±13.24
76.53 ±12.41	128.06 ±23.45	135.17 ±34.71
1.75 ±0.53	9.65 ±2.15	1.78 ±0.58
6.22 ±0.67	16.59 ±1.68	29.27 ±7.34
1.67 ±0.06	3.82 ±0.03	9.08 ±4.79
9.42 ±0.27	23.20 ±0.93	47.46 ±1.14
0.63 ±0.29	0.82 ±0.03	0.97 ±0.21
0.15 ±0.01	0.28 ±0.01	0.31 ±0.08
1.15 ±0.05	3.04 ±1.36	5.00 ±4.35
0.04 *	0.13 ±0.04	0.13 ±0.07
ND	ND	ND

Laptop PCB		
EPA Method 3051A	MMDM	EPA 3050B
5.72 ±0.28	238.52 ±3.07	338.02 ±32.19
13.39 ±0.46	19.74 ±0.40	108.2 ±78.56
8.72 ±2.05	5.61 ±2.85	19.04 ±15.71
10.39 ±1.54	12.85 ±0.28	34.59 ±19.91
10.49 ±0.38	13.71 ±2.81	48.17 ±2.92
9.37 *	18.71 ±0.21	29.43 ±0.22
0.54 ±0.02	0.72 ±0.23	1.12 ±0.67
0.03 ±<0.006	0.05 ±0.01	0.84 ±0.80
0.64 ±0.02	0.62 ±0.01	9.95 ±9.67
0.03 *	0.03 *	0.07 ±0.04
0.01 *	0.01 *	0.01 *

ND: Not Detected

\*Standard deviation ±<0.005

Table 4.1. Heavy metal content of selected samples according to different digestion methods (g/kg) (continued).

Metal	Mobile Screen			Smartphone Screen			Laptop Screen		
	EPA Method 3051A	MMDM	EPA 3050B	EPA Method 3051A	MMDM	EPA 3050B	EPA Method 3051A	MMDM	EPA 3050B
Cu	5.51 ±5.22	6.42 ±0.74	8.08 ±4.53	16.65 ±6.61	40.90 ±5.79	10.49 ±6.58	448.46 ±8.40	532.41 ±4.4	422.27 ±35.72
Fe	1.73 ±0.32	3.27 ±0.62	2.66 ±0.63	82.37 ±1.60	107.93 ±15.93	97.21 ±26.65	38.04 ±4.15	25.78 ±3.12	34.37 ±24.14
Al	1.20 ±0.48	2.93 ±0.02	1.70 ±0.14	4.84 ±0.63	7.28 ±0.65	2.23 ±0.27	3.82 ±0.30	14.20 ±3.72	18.81 ±14.54
Ni	0.72 ±0.60	1.43 ±0.70	0.45 ±0.04	12.94 ±3.00	12.89 ±1.74	8.10 ±2.91	8.54 ±3.61	5.41 ±0.99	5.05 ±1.97
Pb	0.24 ±0.05	0.46 ±0.07	0.31 ±0.11	0.11 ±0.01	0.27 ±0.14	0.07 ±0.02	0.32 ±0.28	0.07 ±0.02	0.12 ±0.12
Cr	0.10 ±0.09	0.20 *	0.21 ±0.02	26.15 ±0.02	39.2 ±2.08	25.48 ±7.76	0.07 ±0.01	0.04 *	0.05 *
Zn	0.09 ±0.07	0.25 ±0.02	0.22 ±0.05	2.79 ±2.53	0.15 ±0.01	0.10 ±0.01	18.07 ±0.11	6.49 ±1.48	4.04 ±2.54
Co	0.09 ±0.08	0.03 ±0.01	0.02 *	0.21 ±0.02	0.25 ±0.01	0.21 ±0.08	0.05 ±0.02	0.01 ±0.01	ND
Mo	0.09 ±0.07	0.02 *	0.03 *	0.19 *	0.24 ±0.04	0.17 ±0.04	ND	ND	ND
Mn	0.03 ±0.03	0.07 ±0.01	0.06 ±0.01	7.84 ±0.48	10.4 ±5.11	3.91 ±0.74	10 ±0.78	6.76 ±1.94	8.42 ±5.43
Cd	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND: Not Detected

\*Standard deviation  $\pm < 0.005$

## 4.1.2. Precious Metals and Rare Earth Elements

4.1.1.1. PCBs. The precious metal and rare earth element content can be seen in Figure 4.2. and Table 4.2. In the composition of PCBs, one of the most used rare earth elements is Nd. In smartphone PCBs, on average, 9.76 g/kg Nd is present. Additionally, due to the technological advances, the precious metal content of PCBs changed; yet, specific physicochemical characteristics of these metals were required for electronic devices. Among these precious metals, Ag has the highest share in PCBs; 4.81 g/kg in mobile phones, 3.79 g/kg in smartphones, and 2.71 g/kg in laptop PCBs. Ag is followed by Au regarding the presence in e-waste. The contents of Ag, Au, and Pd were similar to those found in literature both in mobile phone PCBs and Laptop PCBs. Pd is also found in old mobile phone PCBs; however, it is not detected in smartphone and laptop PCBs.

4.1.2.2. Screens. When it comes to screens, laptop screens had 1.29 g/kg of Ag higher than other samples, and metals together with Nd content of smartphones, representing 0.85 g/kg. Park and Fray (2009) indicated that the precious metals in PCBs could add up to 80% of the economic value, even though the mixing ratio is less than 1% by weight.

Silica was also included in the study; however, the content of silica was found low, and this is because of silica is not soluble in HCl or HNO<sub>3</sub>. It is only soluble in HF (Bazargan, et al., 2014).

- According to the results, Ag and Nd were selected as focus metals for biosorption and bioaccumulation.
- Nd is a limited element and there is a risk to supply it in future, at the same time there is a serious threat about the scarcity of Ag in the next 100 years (World Economic Forum, 2019).

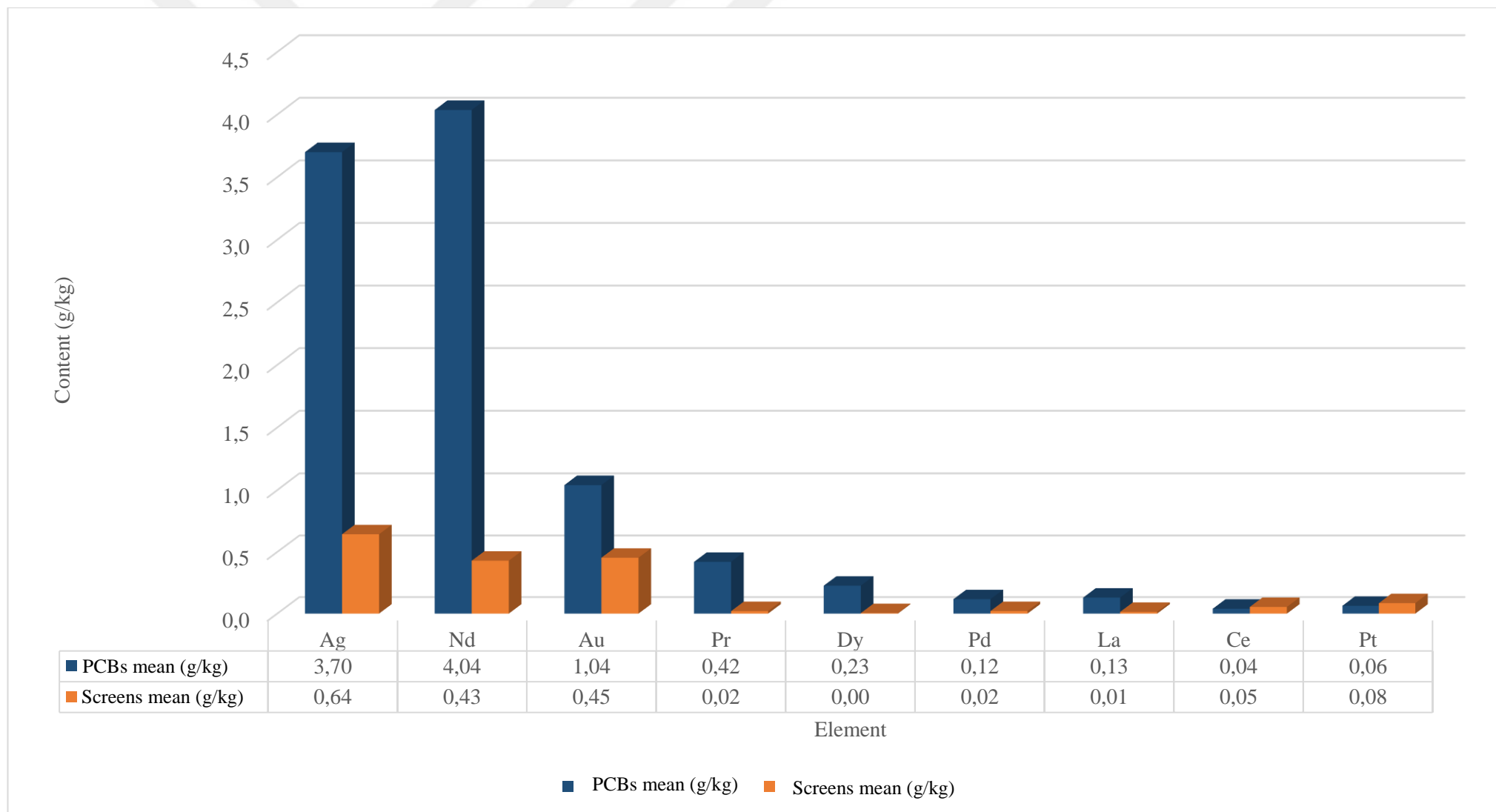


Figure 4.2. Precious metals and rare earth elements found in e-waste.

Table 4.2. Precious metal and rare earth element content of selected samples according to different digestion methods (g/kg).

Metal	Mobile PCB		
	EPA Method 3051A	MMDM	EPA 3050B
Cu	493.93 ±46.96	390.22 ±4.65	305.91 ±0.55
Fe	42.77 ±19.21	20.90 ±14.61	37.02 ±20.64
Zn	67.81 ±0.86	66.19 ±6.09	37.45 ±1.47
Ni	67.71 ±1.78	63.20 ±5.14	50.49 ±2.80
Pb	10.85 ±2.03	11.89 ±0.35	23.19 ±2.07
Al	6.65 ±0.74	11.25 ±1.31	27.36 ±3.26
Mn	2.01 ±0.87	1.54 ±0.12	1.06 ±0.21
Co	1.06 ±0.10	0.10 ±0.01	1.49 ±1.41
Cr	0.41 ±0.21	0.43 ±0.28	0.62 ±0.42
Mo	0.03 *	0.06 ±0.01	0.04 *
Cd	ND	ND	ND

Smartphone PCB		
EPA Method 3051A	MMDM	EPA 3050B
163.9 ±1.65	306.72 ±1.01	288.52 ±13.24
76.53 ±12.41	128.06 ±23.45	135.17 ±34.71
1.75 ±0.53	9.65 ±2.15	1.78 ±0.58
6.22 ±0.67	16.59 ±1.68	29.27 ±7.34
1.67 ±0.06	3.82 ±0.03	9.08 ±4.79
9.42 ±0.27	23.20 ±0.93	47.46 ±1.14
0.63 ±0.29	0.82 ±0.03	0.97 ±0.21
0.15 ±0.01	0.28 ±0.01	0.31 ±0.08
1.15 ±0.05	3.04 ±1.36	5.00 ±4.35
0.04 *	0.13 ±0.04	0.13 ±0.07
ND	ND	ND

Laptop PCB		
EPA Method 3051A	MMDM	EPA 3050B
5.72 ±0.28	238.52 ±3.07	338.02 ±32.19
13.39 ±0.46	19.74 ±0.40	108.2 ±78.56
8.72 ±2.05	5.61 ±2.85	19.04 ±15.71
10.39 ±1.54	12.85 ±0.28	34.59 ±19.91
10.49 ±0.38	13.71 ±2.81	48.17 ±2.92
9.37 *	18.71 ±0.21	29.43 ±0.22
0.54 ±0.02	0.72 ±0.23	1.12 ±0.67
0.03 ±<0.006	0.05 ±0.01	0.84 ±0.80
0.64 ±0.02	0.62 ±0.01	9.95 ±9.67
0.03 *	0.03 *	0.07 ±0.04
0.01 *	0.01 *	0.01 *

ND: Not Detected

\*Standard deviation ±<0.005

Table 4.2. Precious metal and rare earth element content of selected samples according to different digestion methods (g/kg) (continued).

Metal	Mobile Screen			Smartphone Screen			Laptop Screen		
	EPA Method 3051A	MMDM	EPA 3050B	EPA Method 3051A	MMDM	EPA 3050B	EPA Method 3051A	MMDM	EPA 3050B
Cu	5.51 ±5.22	6.42 ±0.74	8.08 ±4.53	16.65 ±6.61	40.90 ±5.79	10.49 ±6.58	448.46 ±8.40	532.41 ±4.4	422.27 ±35.72
Fe	1.73 ±0.32	3.27 ±0.62	2.66 ±0.63	82.37 ±1.60	107.93 ±15.93	97.21 ±26.65	38.04 ±4.15	25.78 ±3.12	34.37 ±24.14
Al	1.20 ±0.48	2.93 ±0.02	1.70 ±0.14	4.84 ±0.63	7.28 ±0.65	2.23 ±0.27	3.82 ±0.30	14.20 ±3.72	18.81 ±14.54
Ni	0.72 ±0.60	1.43 ±0.70	0.45 ±0.04	12.94 ±3.00	12.89 ±1.74	8.10 ±2.91	8.54 ±3.61	5.41 ±0.99	5.05 ±1.97
Pb	0.24 ±0.05	0.46 ±0.07	0.31 ±0.11	0.11 ±0.01	0.27 ±0.14	0.07 ±0.02	0.32 ±0.28	0.07 ±0.02	0.12 ±0.12
Cr	0.10 ±0.09	0.20 *	0.21 ±0.02	26.15 ±0.02	39.2 ±2.08	25.48 ±7.76	0.07 ±0.01	0.04 *	0.05 *
Zn	0.09 ±0.07	0.25 ±0.02	0.22 ±0.05	2.79 ±2.53	0.15 ±0.01	0.10 ±0.01	18.07 ±0.11	6.49 ±1.48	4.04 ±2.54
Co	0.09 ±0.08	0.03 ±0.01	0.02 *	0.21 ±0.02	0.25 ±0.01	0.21 ±0.08	0.05 ±0.02	0.01 ±0.01	ND
Mo	0.09 ±0.07	0.02 *	0.03 *	0.19 *	0.24 ±0.04	0.17 ±0.04	ND	ND	ND
Mn	0.03 ±0.03	0.07 ±0.01	0.06 ±0.01	7.84 ±0.48	10.4 ±5.11	3.91 ±0.74	10 ±0.78	6.76 ±1.94	8.42 ±5.43
Cd	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND: Not Detected

\*Standard deviation  $\pm < 0.005$



### 4.1.3. Comparison of the Methods

The content of each type of e-waste according to the selected digestion method can be seen in Table 4.1 and 4.2. Based on the obtained results from different digestion methods, element concentration of the samples is highly correlated. Hence, compared methods applied for element extraction are reliable (correlation > 0.95) except with Method 3051A on old mobile phone screen samples (correlation = 0.280). This may be due to the heterogeneous content of the screen or may be based on contamination during grinding. Application of different digestion methods enhances the dissolution of certain metals. Therefore, depending on the aim, different digestion method can be selected.

Overall, for most rare earth element, precious metals, and heavy metals USEPA 3050B was found to be the most efficient method for Nd, Pd, Pr, Ag, Dy, Pt, Mn, Ce, Cd, Cr, Co, Al, Pb, and Fe. While Au, Mo, Zn, and Cu, Ni; USEPA 3051A resulted in higher concentrations, MDM was only suitable for La among all other elements.

## 4.2. Biosorption

### 4.2.1. Single Metal Biosorption

Biosorption capacity of algae was assessed in different conditions. The data regarding the uptake of the element by biosorption can be seen in Table 4.3 and Table 4.4.

*4.2.1.1. Temperature.* Three different temperatures were tested under pH 5 and biosorbent dosage of 0.5 g/L. Based on these tests, the maximum element uptake takes place in the most saturated metal solution at 25 °C for Ag and Nd. The maximum metal uptake for Ag and Nd was 151.70 mg/g and 239.75 mg/g, respectively. The effect of temperature on biosorption can be seen in Figure 4.3. As the saturation of the solution increases, the effect of temperature on biosorption also increases. For instance, the temperature has nearly no effect on metal uptake for a solution that has 15 ppm Ag; however, as the temperature increases to 35 °C, there is a change observed in uptake amount. In a study conducted by Bishnoi and Garmina, 2004, the optimum temperature for Cu<sup>+2</sup> biosorption by algal biomass was found at 25 °C, and a decrease was observed in uptake amount with increasing temperature (Bishnoi and Garmina, 2004). Similar results were found by Sulayman et al (2013) for four different metals: Pb<sup>+2</sup>, Cd<sup>+2</sup>, Co<sup>+2</sup>, and Ar<sup>+3</sup>. Maximum metal uptake was achieved at 25 °C. As

the temperature increased, decreases in the metal was also observed. However, optimum temperature for Ni biosorption by *circinella* was found at 40 °C, representing a minimal difference ( $2.51 \times 10^{-4}$  mol/g for 20 °C, and  $2.67 \times 10^{-4}$  mol/g for 40 °C) (Alpat et al., 2010). Generally, a higher temperature may reduce the biosorption efficiency since it provides better solubility for metal ions (Lau et al., 1999). This may be because of solubility of metal ions, biosorbent surface, destruction of binding sites, and a decrease of biosorption forces between the active sites and the sorbate species (Sulaymon et al., 2013).

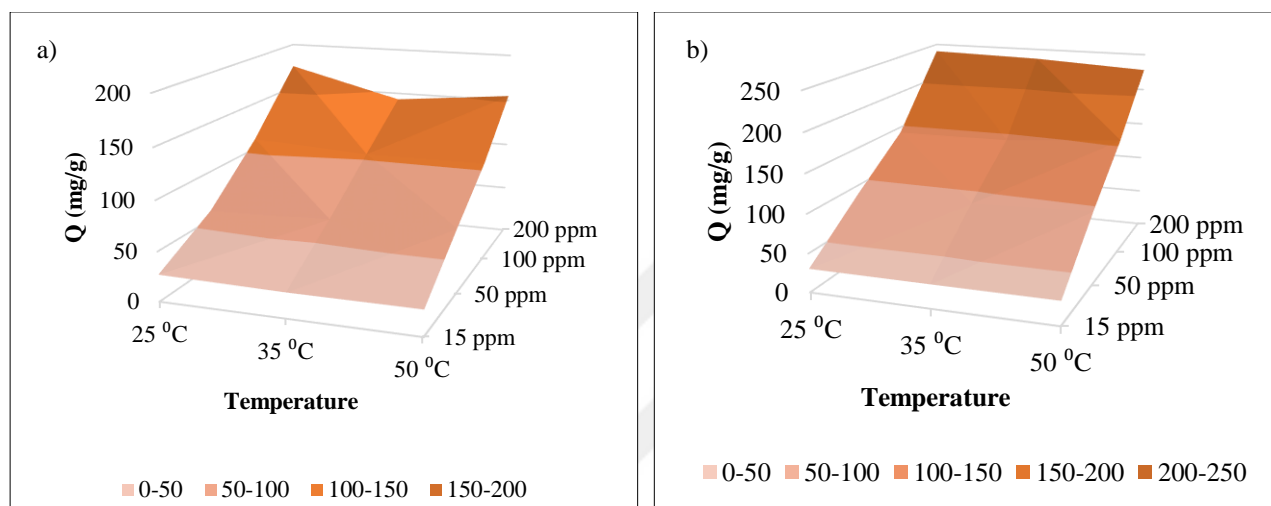


Figure 4.3. Effect of temperature on (a) Ag and (b) Nd biosorption.

**4.2.1.2. pH.** pH 4, 5, and 6 were tested for 25 °C for Ag and Nd with 0.5 g/L biosorbent dosage. The maximum uptake was found at pH 5 both for Ag and Nd. Effect of pH on metal uptake can be seen in Figure 4.4. For Ag, the biosorption efficiency decreased by 20% when the pH was 4 and by 14% under pH 6 compared to pH 5. For Nd, when the pH is 4, the uptake efficiency has decreased by 37% and by 33% when the pH is 6, compared to pH 5. Similar results were found by Ibrahim et al., (2016); optimum pH was found as 4.5, 5, and 5 for  $\text{Cd}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Cu}^{+2}$ ,  $\text{Pb}^{+2}$ , respectively. Maximum biosorption was also achieved at pH 5 for selected heavy metal ions by red macroalgae (Ibrahim, 2011). At low pH, protons may compete with the metals to bind the active sites. For the pH values lower than 4, hydrogen ions compete with the ions (Farhan et al., 2015). In addition, the different groups of amino, hydroxyl, carboxyl, and sulfate on the algal surface may be affected by the change in pH (Sari et al., 2008). When the pH is increased, because of depressed electrostatic repulsions between the adsorbent and the metal ions, the biosorption efficiency may increase. As pH gets higher (6-8), precipitation may occur or negatively charged anionic species in solution, and negative surface charge of the sorbents may decrease the biosorption efficiency (Ibrahim, 2011).

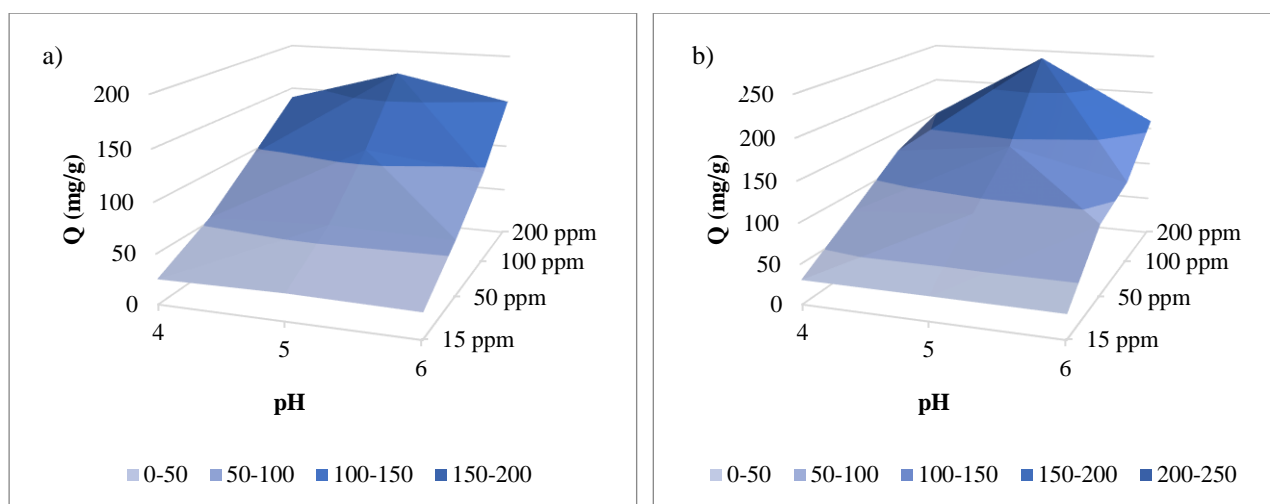


Figure 4.4. Effect of pH on (a) Ag and (b) Nd biosorption.

**4.2.1.3. Effect of Biosorbent.** 0.5, 1 and 2 g/l of biosorbent dosage were tested. Ag and Nd uptake were highest in most saturated solutions with the lowest biosorbent dosage under pH 5 and 25 °C, as shown in Figure 4.5. For 200 ppm Ag solution, the metal uptake was found as 151.7, 99.2 and 79.8 for 0.5, 1 and 2 g/L biosorbent dosage, respectively. For 200 ppm Nd solution, the metal uptake was found as 239.75, 148.89, and 98.21 for 0.5, 1 and 2 g/L biosorbent dosage, respectively. As the dosage increases, the metal uptake decreases in both cases. Similar trend was found for  $\text{Cu}^{+2}$  biosorption by 0.5 g/L biomass dosage in literature. Higher biomass concentrations showed lower efficiency since the shell effect may limit the binding of the metals to the active sites (Rome and Gadd, 1987). As biomass dosage increases, surface area and binding sites increases. However, after equilibrium is reached, overlapping or aggregation of the biosorbent results in a decrease in biosorption efficiency (Al-Homadian et al., 2014), this is similar to a study conducted by Alpat et al. (2010).

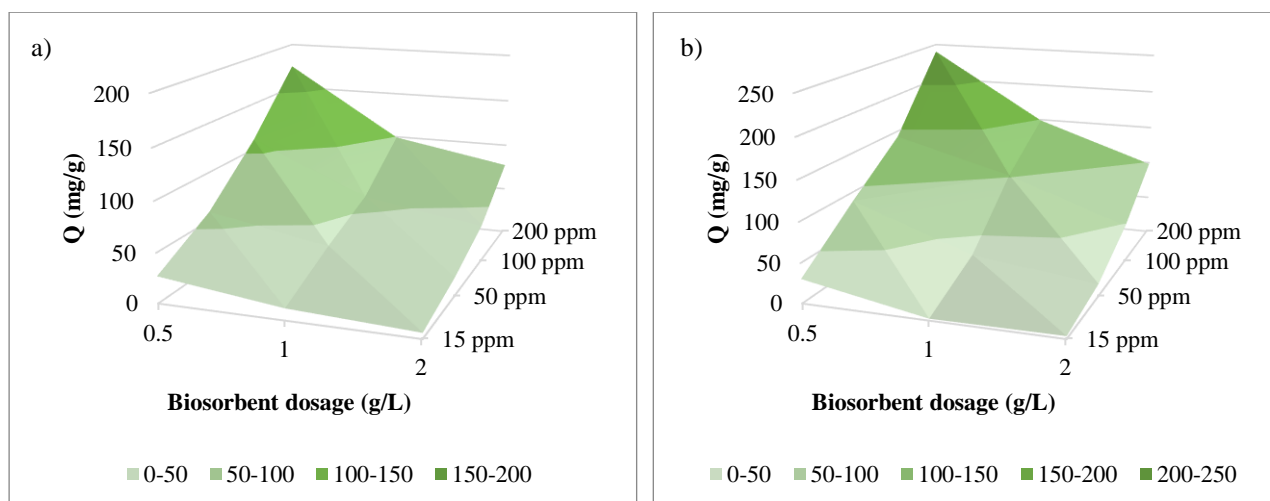


Figure 4.5. Effect of biosorbent dosage on (a) Ag and (b) Nd biosorption.

4.2.1.4. Effect of Stirring Speed. For Ag and Nd, optimum conditions for stirring speed is found as moderate; representing 300 rpm. The uptake of Ag decreased by 39% for no stirring and 19% for high stirring conditions. For Nd, it decreased by 53% for no stirring and 46% for high stirring conditions. The stirring speed may have an effect on the penetration of the algae to the solution. When there is no stirring, the algae cannot bind the elements since it cannot reach all of the ions. In the case of high stirring, the algae may not be able to bind the elements since there maybe not enough time for the active sites to bind the ions or the elements maybe desorbed from the biomass again.



Table 4.3. Uptake of experimental data of biosorption of Ag.

Temperature	25 °C	35 °C	50 °C	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C
pH	5	5	5	4	6	5	5	5	5
Biosorbent Dosage (g/L)	0.5	0.5	0.5	0.5	0.5	1	2	0.5	0.5
Stirring speed	moderate stirring	moderate stirring	moderate stirring	moderate stirring	moderate stirring	moderate stirring	moderate stirring	no stirring	high stirring
Uptake Amount (mg/g)	Q	Q	Q	Q	Q	Q	Q	Q	Q
15 ppm	27.12	25.39	25.75	25.15	25.62	11.80	5.80	-	-
50 ppm	59.37	62.79	66.42	54.06	57.66	36.70	18.90	-	-
100 ppm	110.51	103.75	104.59	96.27	96.07	57.90	38.50	-	-
200 ppm	151.70	143.1	154.9	139.45	150.15	99.30	77.30	108.30	144.10

-.:Not conducted.

Table 4.4. Uptake of experimental data of biosorption of Nd.

Temperature	25 °C	35 °C	50 °C	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C
pH	5	5	5	4	6	5	5	5	5
Biosorbent Dosage (g/L)	0.5	0.5	0.5	0.5	0.5	1	2	0.5	0.5
Stirring speed	moderate stirring	moderate stirring	moderate stirring	moderate stirring	moderate stirring	moderate stirring	moderate stirring	no stirring	high stirring
Uptake amount (mg/g)	Q	Q	Q	Q	Q	Q	Q	Q	Q
15 ppm	30.48	30.42	30.61	30.52	30.09	2.32	3.47	-	-
50 ppm	88.54	90.57	96.00	76.87	91.12	34.43	15.74	-	-
100 ppm	142.57	143.47	155.33	124.18	107.67	101.90	48.61	-	-
200 ppm	239.75	236.25	228.12	150.07	160.35	148.89	98.21	112.00	128.80

-.:Not conducted.

**4.2.1.5. Remaining Metal Concentration.** This term represents the amount of the ions left in the solution. This parameter can be used when designing a pilot-scale or real scale plants. It was found that as the concentration of the solution increases, the remaining metal concentration increases both for Ag and Nd. When the initial metal concentration was 15 ppm, 90.1% of the Ag and 96.9% of the Nd ions were removed by the algae that mean 9.9% of Ag and 3.1% of Nd remained in the solution. When the initial metal concentration was increased to 50 ppm, 40.7% of Ag, and 11.3% of Nd ions remained in the solution. The data of 100 ppm solution refers to 44.8% of Ag, and 30.3% of Nd stayed in the solution. When the initial metal concentration of 200 ppm was tested, the remaining amount of the ions in the solutions refers to 55.5% of Ag and 39.9% of Nd. The data of remaining metal concentration in the solution can be used when modeling gradual biosorption processes.

**4.2.1.6. Uptake as a Function of Time.** The uptake amounts of Ag and Nd according to time can be seen in Figure 4.6 as a function of time. A significant amount of biosorption completes within 60 minutes both for Ag and Nd.

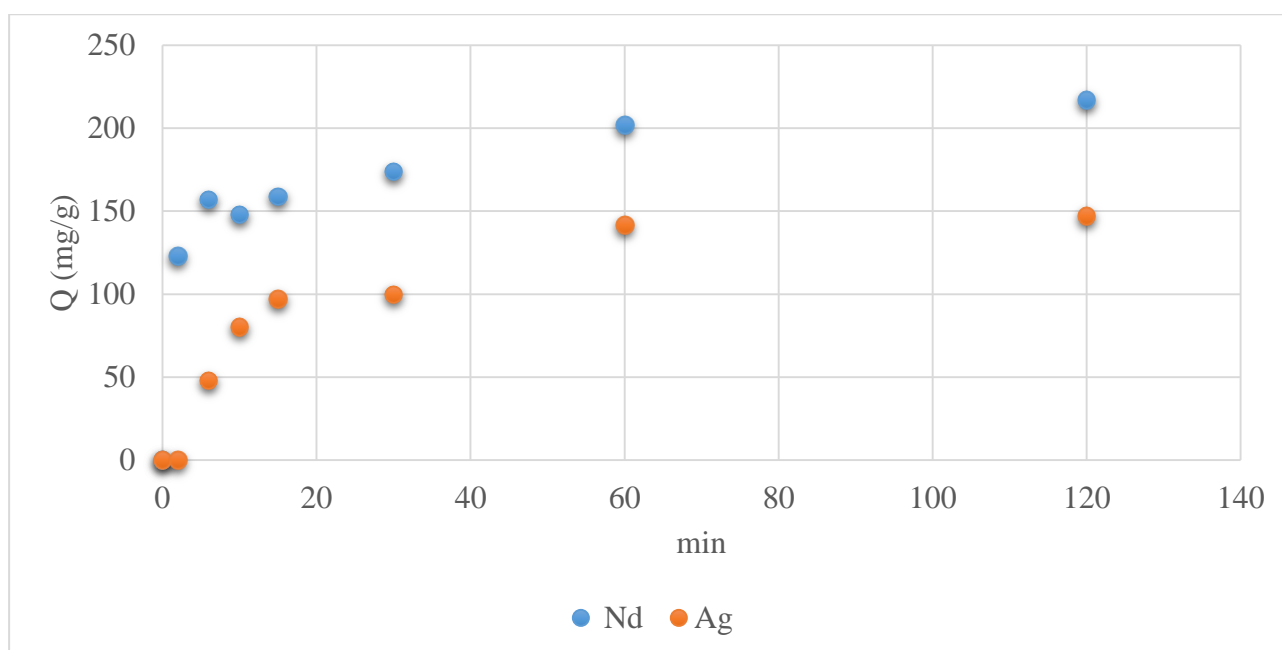


Figure 4.6. Biosorption amounts of Ag and Nd according to time.

Additional: Adherence of the metals to the Erlenmeyer was also tested. The data showed 2% deviation for Ag and 11-13% deviation for Nd. Since reading deviation of ICP-OES for Ag and Nd was found to be 2% and 20%, respectively. It is concluded that there is no adherence of metals to the glass.

The factor of error for determination of Ag and Nd is %0–5% and 15%-20%, respectively.

## 4.2.2. Biomass Analysis for Optimum Conditions

**4.2.2.1. SEM-XRD.** In both cases, Ag and Nd were found on algae surface. The XRD analysis of Ag and Nd loaded algae can be seen in Figure 4.7. Sphere shaped particles were observed in Ag loaded algae. When these particles were subject to XRD analysis, Ag was detected. Unlike Ag, Nd was found scattered on the algae's surface as seen in Figure 4.8.

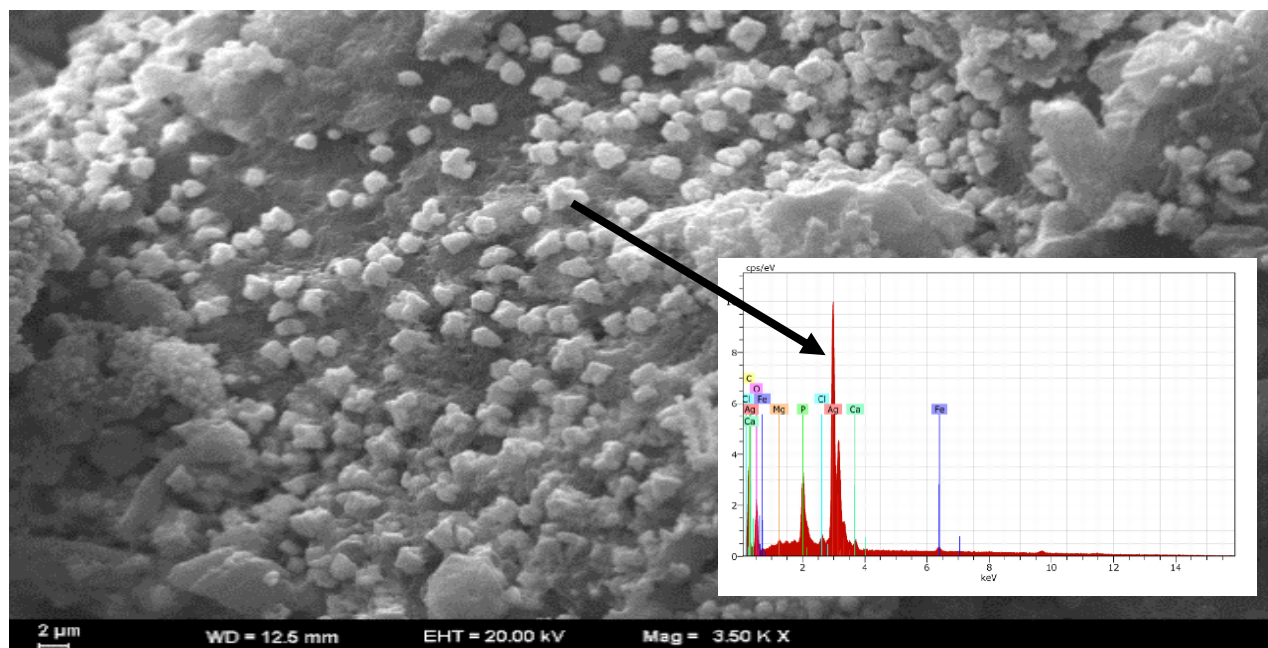


Figure 4.7. Algal surface analysis of Ag loaded algae; SEM and XRD analysis (taken by ZEISS EVO 40).

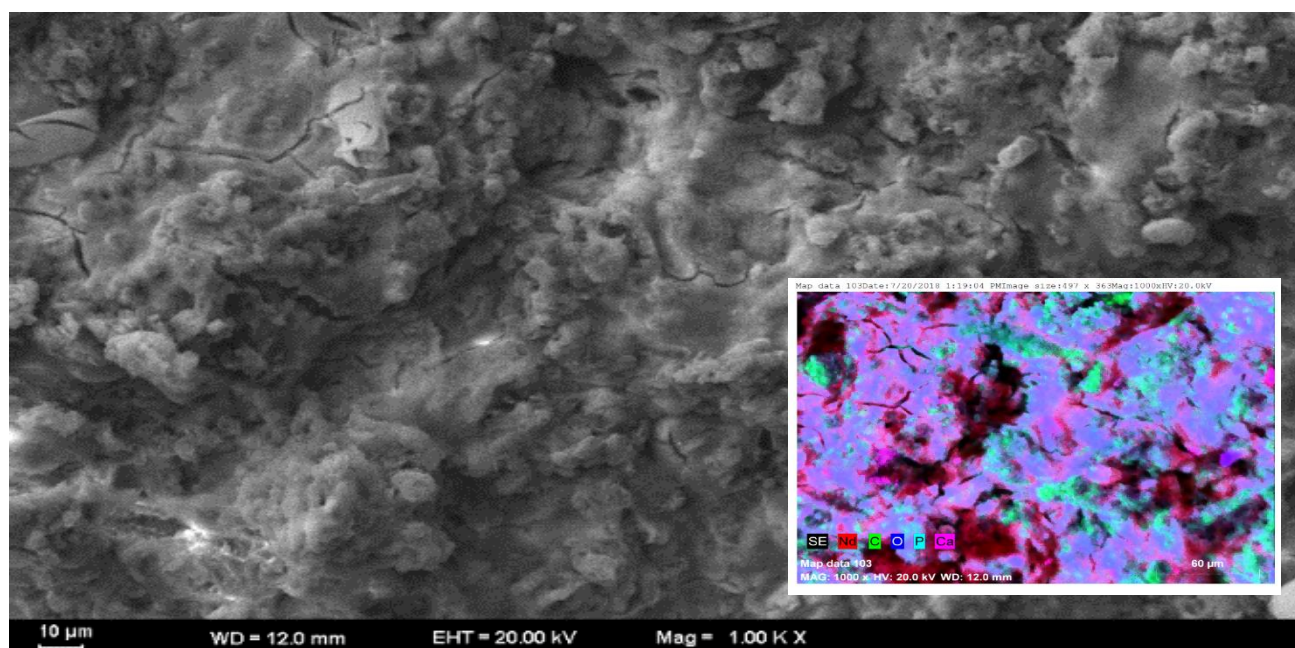


Figure 4.8. Algal surface analysis of Nd loaded algae; SEM and mapping (taken by ZEISS EVO 40).

**4.2.2.2 FTIR.** The spectrum of unloaded algae contains the wide band at  $3256\text{ cm}^{-1}$ , which corresponds to -OH and -NH<sub>2</sub> stretching vibration (Sulaymon et al., 2013). Two peaks at  $2915$  and  $2842\text{ cm}^{-1}$  are stretching vibrations of C-H bond of lipids (Kenne and Merwe, 2013). The minor peak at  $1725\text{ cm}^{-1}$  corresponds to the vibration of ester fragments of phospholipids (Laurens and Wolfrum, 2011). Two peaks at  $1642$ ,  $1538$ ,  $1225\text{ cm}^{-1}$  may be considered as respective bands “amide-I” and “amide II” “amide III” (weak) - asymmetric and symmetric vibration of C=O groups, indicating the protein presence. The complex of bands between  $1045$  and  $1006\text{ cm}^{-1}$  are assigned to the stretching of alcohol C-OH groups of polysaccharides (Sheng et al., 2004).

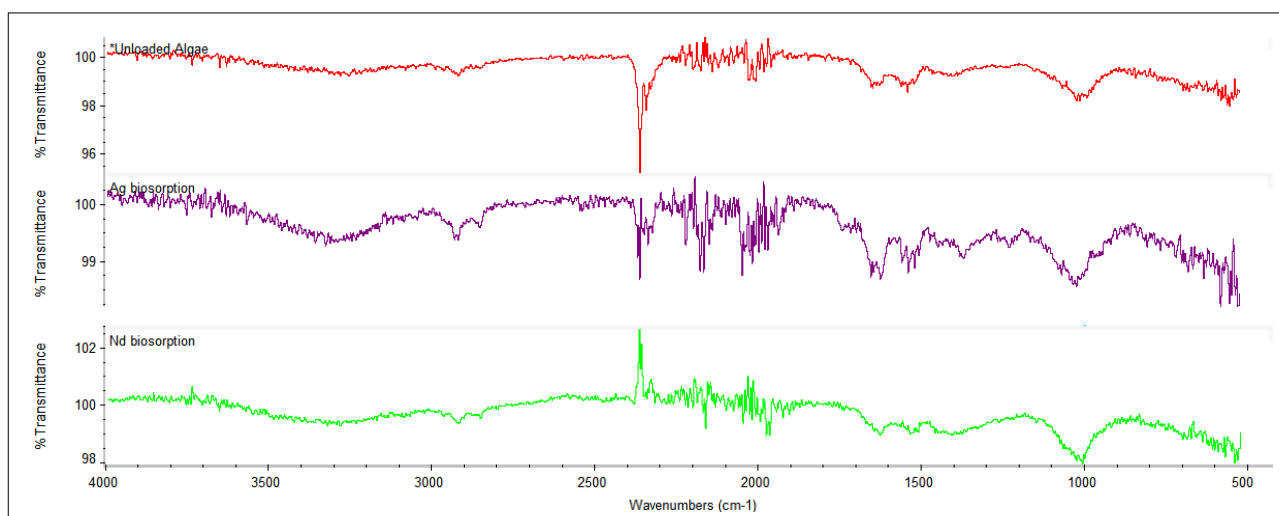


Figure 4.9. FTIR Analysis of the samples before and after biosorption (taken by Thermo Fisher Nicolet 380 FTIR Spectrometer).

Table 4.5. FTIR bands coordinates for biosorption samples.

Band	Unloaded algae	Ag - loaded	Nd-loaded
OH and NH stretching	3256	3314	3314
Alkyl CH stretching	2915	2925, 2915	2915
Alkyl CH stretching	2842	2842	2842
C=O ester (phospholipids)	1725	1735, 1706	1721 (weak)
amide-I (proteins)	1638	1638, 1616	1648, 1616
amide II (proteins)	1548, 1535, 1512	1544, 1523, 1506	1541, 1520, 1505
amide III (proteins)	1225	1214	n/a
C-OH stretching (polysaccharides)	1045	1059	1048
C-OH stretching (polysaccharides)	1006	1006	1002

The loading of both Ag and Nd metals ions as seen in Figure 4.9 and Table 4.5 leads to the increase of the intensity of OH and NH stretching band. The alkyl CH bonds remain almost at the initial state. In the case of Ag loading the intensity of  $1725\text{ cm}^{-1}$  peak; C=O bands increases and it



shifts left. Together with that, all carboxylic amide bands shifting right, which may be explained by metal complex formation. The position of OH polysaccharide bands, in contrary, changed slightly right. In the case of Nd loading the bands shifting is close to the Ag loading case, but the band intensity change is less. By the use of FTIR spectroscopy, it was confirmed that during the processes of biosorption on algae metal ions interacting with its hydroxyl, amino, ester and alcohol groups.

### 4.3. Bioaccumulation

#### 4.3.1. Single Metal Bioaccumulation

*4.3.1.1. Effect of Biosorbent and Initial Metal Concentration.* 0.5, 1 and 2 g/L algae dosage was tested for 15, 50, 100, and 200 ppm of initial metal concentrations. Highest metal uptake was found in 0.5 g/L algae dosage in 200 ppm of solution for Nd. Similar result was found for Ag; however, the results of 1 g/L algae dosage was found very close to the uptake in 0.5 g/L algae dosage. Since less biosorbent dosage is preferable, and the error of Nd determination for ICP-OES was found around 15%- 20%, 0.5 g/L algae dosage. As the saturation of the solution increases the uptake of metal ions increases; however, biosorption efficiency decreases as it can be seen from Table 4.6 and Section 4.3.1.2. As the biosorbent dosage increases, the bioaccumulation decreases as it can be seen from Figure 4.10. The results on single metal bioaccumulation were found similar to the results found for biosorption. The algae accumulated nearly all of the Nd present in aqueous phase. No Nd was found for 15, 50, 100 and 200 ppm of initial metal concentration when 1 g/L and 2 g/L biomass was used. This means that more binding sites are available and more metal can be sorbed. When 0.5 g/L biomass was used, no metal remained in 15, 50, and 100 ppm of initial metal solution. However, 36% of the metal remained in the 200 ppm initial metal solution case. When the uptake amounts were observed, it was found highest in 200 ppm solution for 0.5 g/L. The experiments were not repeated by using more concentrated solutions since Nd is a rare earth element and selected range is broad enough to test the bioaccumulation of Nd content of e-waste. Ag and Nd accumulation was found highest in the most saturated solution with lowest biosorbent dosage.

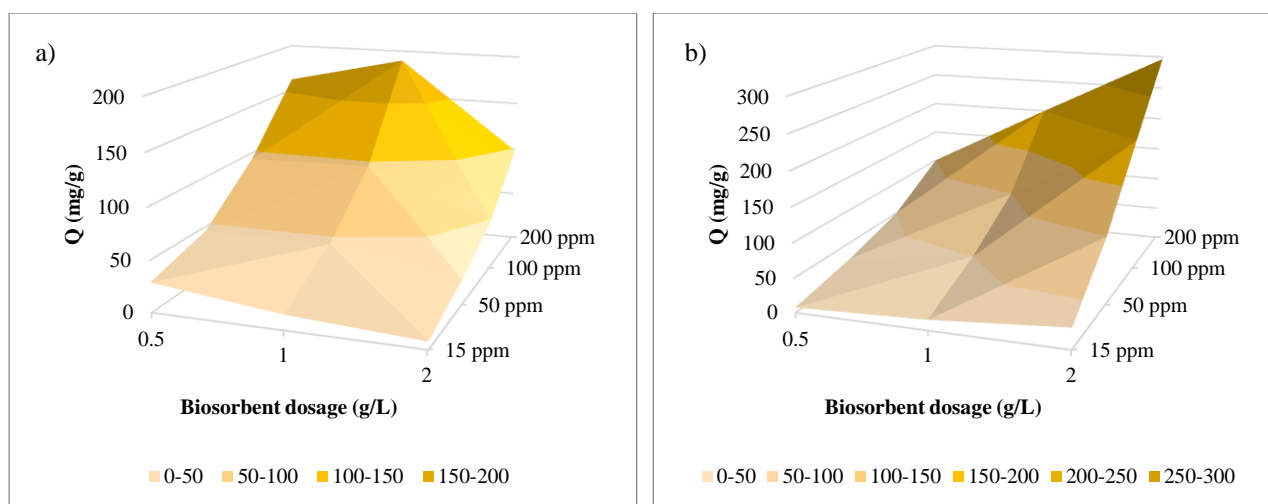


Figure 4.10. Effect of biosorbent dosage on (a) Ag and (b) Nd bioaccumulation.

Table 4.6. Bioaccumulation uptake for Ag and Nd.

Biosorbent Dosage (g/L)	Initial Metal Concentration (ppm)	Ag	Nd
		Q (mg/g)	Q (mg/g)
2 g/L	15	7.5	7.5
	50	24.8	25.0
	100	48.6	50.0
	200	97.9	100.0
1 g/L	15	14.7	15.0
	50	45.7	50.0
	100	96.3	100.0
	200	189.6	199.0
0.5 g/L	15	29.1	30.0
	50	45.7	100.0
	100	93.5	200.0
	200	161.6	296.8

**4.3.1.2. Remaining Metal Concentration.** For Ag, when the initial metal concentration is 15 ppm, 2.9% of the metal ions remained in the solution, while it is 54.2% for 50 ppm, 53.3 % for 100 ppm, 59.6% for 200 ppm solutions. For Nd, all of the metal ions were sorbed by algae in the case of 15, 50, and 100 ppm solutions. When the initial metal concentration was 200 ppm, 25.8% of the metal ions were left in the solution. For Nd biosorption, these results suggest that the removal efficiency is very high. The data of remaining metal concentration in the solution can be used when modeling gradual bioaccumulation processes.

*4.3.1.3. Uptake as a Function of Time.* Bioaccumulation amounts as a function of time can be seen in Figure 4.11. The uptake of Ag and Nd completes in a short period of time, around 5-10 minutes after algae addition. The uptake of Nd is higher than the uptake for Ag. Bioaccumulation also shows faster uptake compared to biosorption both for Ag and Nd. Fast process of uptake suggests adsorption rather than accumulation in the cell, for which longer time is required.

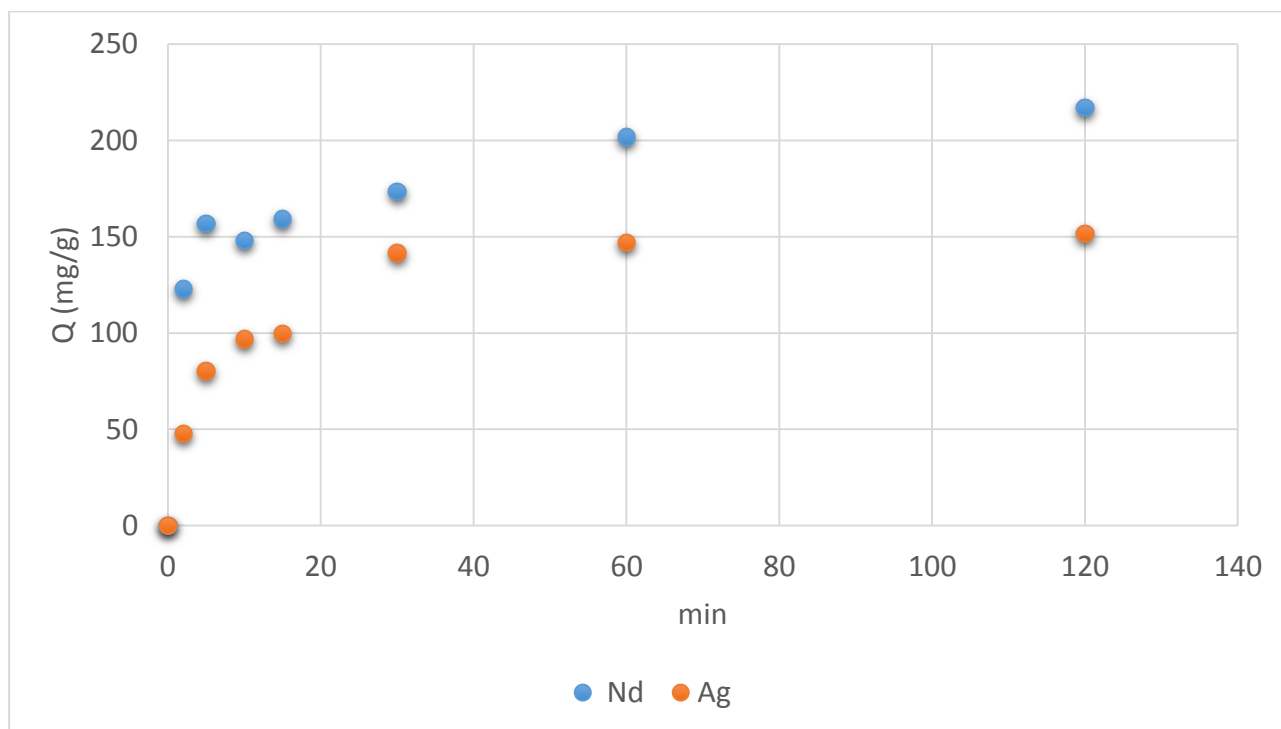


Figure 4.11. Bioaccumulation amount of Ag and Nd according to time.

A control group without metal addition was also maintained. Only microalgae were added to the Erlenmeyer, and it remained for 72 hours. The TSS content was measured after 72 hours, and no change or minor change (<0.1) was observed.

Adherence of the metals to the Erlenmeyer was also tested since glass Erlenmeyer was used. The data showed 2% deviation for Ag and 11-13% deviation for Nd. Since reading deviation of ICP-OES for Ag and Nd was found between 2% and 20%, it is concluded that there is no adherence of metals to the glass.

### 4.3.2. Biomass Analysis for Optimum Conditions

**4.3.2.1 SEM-XRD.** In both cases, Ag and Nd were found on the algae's surface. Backscatter analysis was applied for Ag loaded algae. The image and the XRD Analysis can be seen in Figure 4.12. Mapping for Nd can be seen in Figure 4.13.

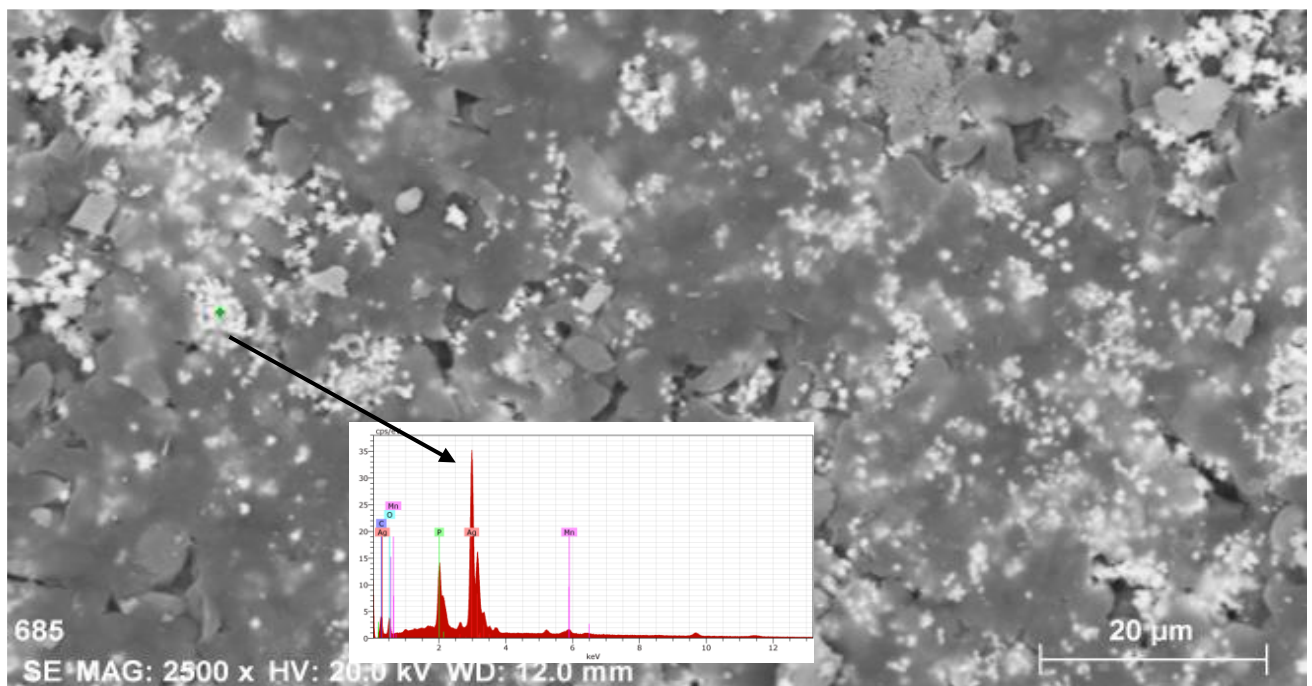


Figure 4.12. Backscatter and XRD analysis for Ag loaded algae (taken by ZEISS EVO 40).

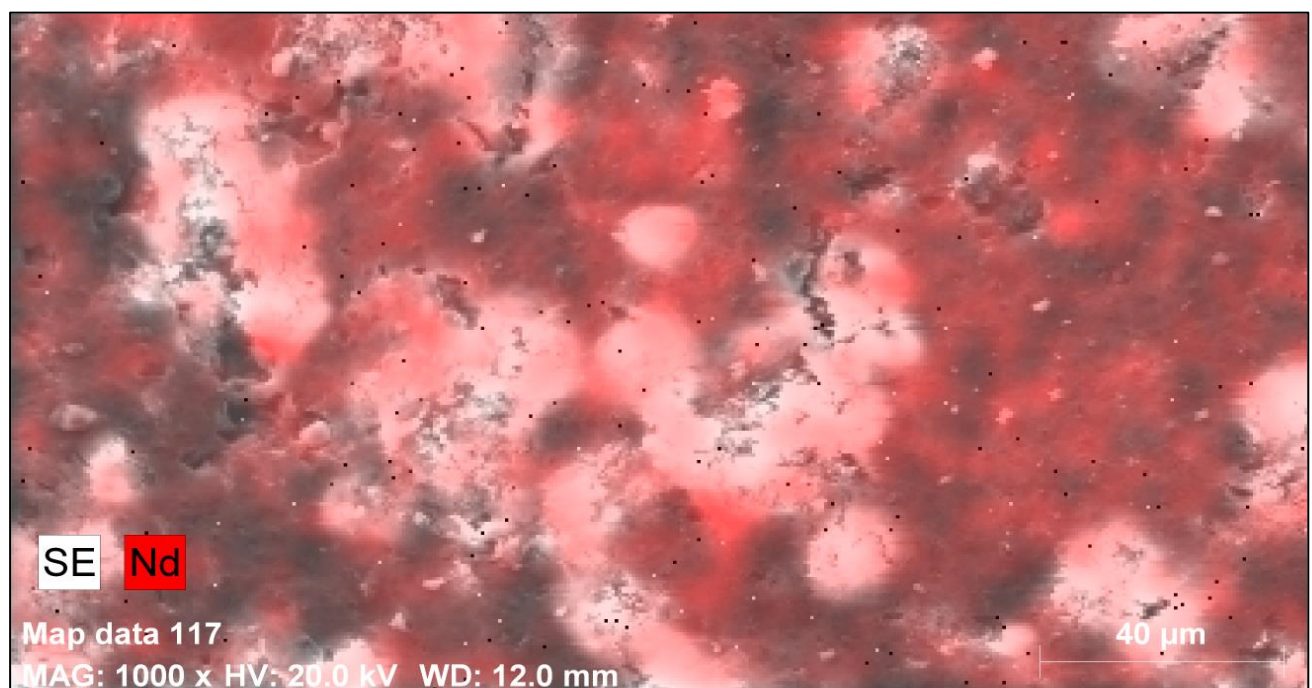


Figure 4.13. Mapping for Nd loaded algae (taken by ZEISS EVO 40).

**4.3.2.2. FTIR.** The position of OH, NH broad absorption band shifted for Ag and Nd samples in comparison to unloaded algae 40 and 30  $\text{cm}^{-1}$  right respectively. The CH vibrational bands at 2915 and 2842  $\text{cm}^{-1}$  remained unchanged. In the case of Ag loading, the slight shift of C=O band at 1725  $\text{cm}^{-1}$  10  $\text{cm}^{-1}$  left is observed. The shift of OH bands of alcohol groups 60  $\text{cm}^{-1}$  right is detected. The Nd loading results in shifting of the first amide band 10  $\text{cm}^{-1}$  left and subsequent shifting right of amide II band as it can be seen from Table 4.7 and Figure 4.14. By the use of FTIR spectroscopy, it was confirmed that during the processes of bioaccumulation on algae, metal ions interacting with its hydroxyl, amino, ester and alcohol groups.

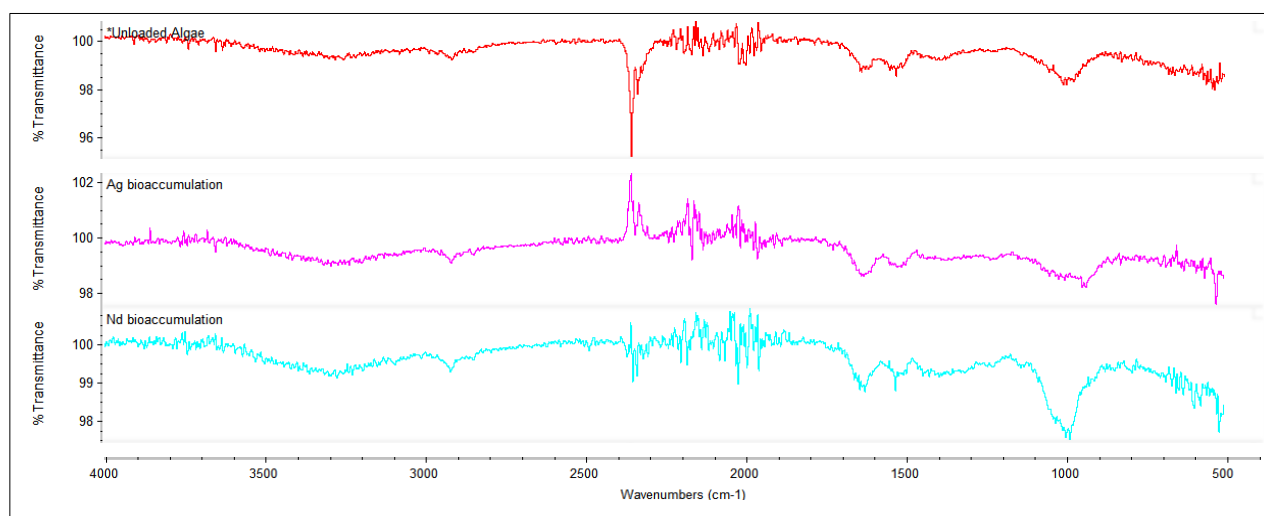


Figure 4.14. FTIR Analysis of the samples before and after bioaccumulation (taken by Thermo Fisher Nicolet 380 FTIR Spectrometer).

Table 4.7. FTIR bands coordinates for bioaccumulation samples.

<b>Band</b>	<b>Unloaded algae</b>	<b>Ag - loaded</b>	<b>Nd-loaded</b>
OH and NH stretching	3256	3296	3285
Alkyl CH stretching	2915	2915	2915
Alkyl CH stretching	2842	2842	2842
C=O ester (phospholipids)	1725	1735	1721
amide-I (proteins)	1638	1635, 1613	1648, 1624
amide II (proteins)	1548, 1535, 1512	1544, 1523, 1504	1530, 1520, 1505
amide III (proteins)	1225	1225	1231
C-OH stretching (polysaccharides)	1045	1052	1042
C-OH stretching (polysaccharides)	1006	941	987



## 4.4. Biosorption and Bioaccumulation from Multiple Element Solutions

### 4.4.1. Binary Element Solution

Biosorption and bioaccumulation were conducted by using Ag and Nd in one solution. For biosorption, following optimum conditions were applied: pH: 5, T: 25 °C, initial metal concentration: 200 ppm, biosorbent dosage: 0.5 g/L. For bioaccumulation, 200 ppm solution and 0.5 g/L biosorbent dosage were used at pH: 5, T: 25 °C. The results can be seen in Figure 4.15. Uptake of metals decreased when there were two elements present in the solution. The reason for that may be the competition between the ions to bind and the decrease in the number of available binding sites. Nd uptake was found higher than Ag uptake for both cases. The efficiency of uptake of elements was higher in bioaccumulation compared to biosorption, especially for Nd.

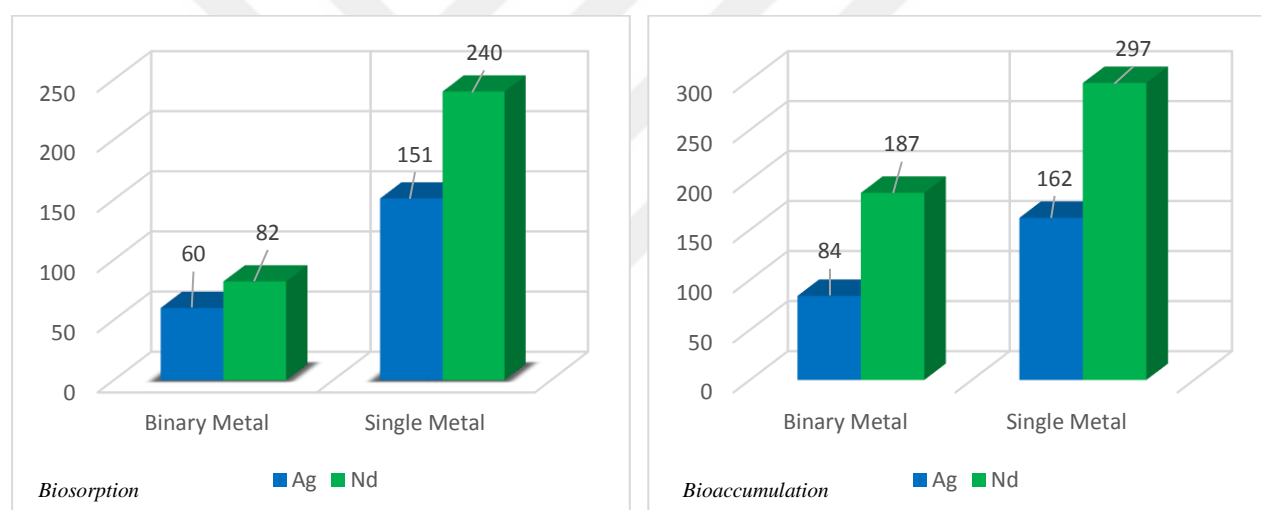


Figure 4.15. Comparative uptake of metals of biosorption and bioaccumulation.

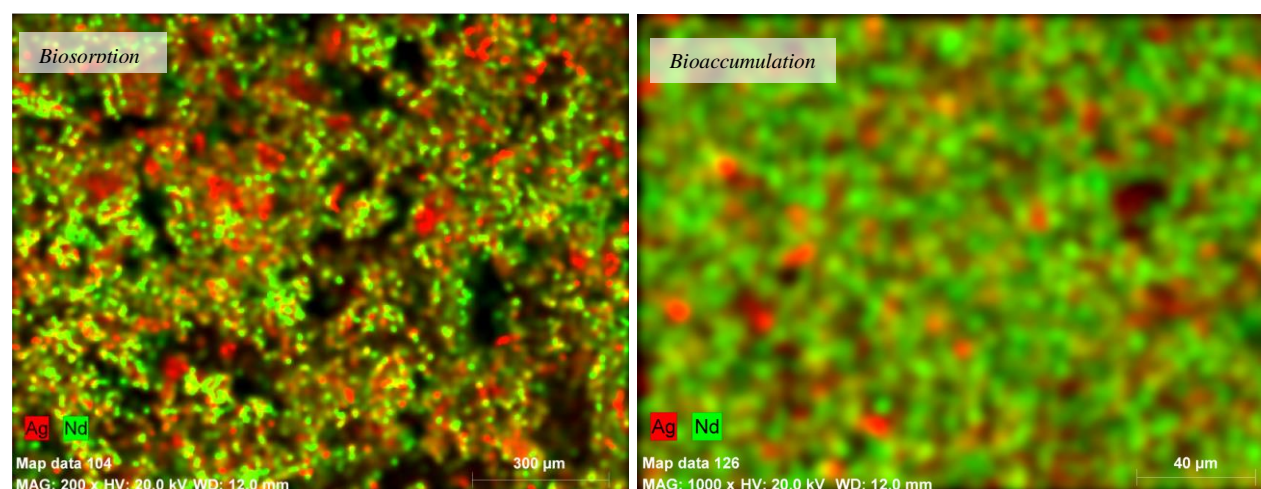


Figure 4.16. Mapping of binary metal loaded algae (taken by ZEISS EVO 40).

#### 4.4.2. Tertiary Element Solution

Biosorption and bioaccumulation under a tertiary element solution were also carried out with Nd, Ag, and Au. For this purpose, the optimization of Au biosorption and bioaccumulation were conducted. The maximum uptake of Au was found as 165.5 mg/g within the following conditions: pH:3, T: 50 °C, initial metal concentration: 200 ppm, biosorbent dosage: 0.5 g/L and moderate stirring speed. The maximum bioaccumulation capacity was found as 191.4 mg/g under pH 3 and T: 50 °C.

Ag was precipitated by using chloride and then filtered from the solution. Two different conditions for the experiments were applied. First, the pH was adjusted to 5 at 25 °C; that represents optimum conditions for Nd removal. Second, the pH was adjusted to 3 at 50 °C; that refers to optimum removal conditions for Au. The results showed that, under pH 5 and T 25 °C, the uptake of Au is very low; representing 45.9 and 86.4 mg/g for biosorption and bioaccumulation, respectively. When the conditions changed to pH 3 and T 50 °C, the uptake amount of Au increased to 165.8 and 191.5 mg/g for biosorption and bioaccumulation, respectively. The changing conditions affected the uptake of Au in a significant way. The uptake for Nd was found close to each other in both conditions and represented a minor (2.6-9.7%) variation. This result showed that, when focusing on the recovery of a specific type of element, changing the conditions may prevent an undesired element from being sorbed by the algae.

## 5. MODELLING

The aim of modeling is to test the applicability of the isotherms and kinetic models of biosorption and bioaccumulation of metals to non-living and living *Chlorella vulgaris*, respectively. The kinetic data of biosorption and bioaccumulation was modeled by using pseudo-first order and pseudo-second order kinetic models. For the equilibrium data, Langmuir and Freundlich isotherm models were used.

### 5.1. Biosorption

The first and second order models can be seen in Figure 5.1 and Figure 5.2 for biosorption. The regression correlation for Ag and Nd were 0.9231 and 0.8022 for pseudo-first order kinetics, respectively. When the pseudo-second order kinetic model was applied to the experimental data, regression correlation coefficients were 0.9964 for Ag and 0.9957 for Nd. The regression correlation coefficient from first order was found to be lower both for Ag and Nd when compared to second order regression correlations. This indicates the mechanism of recovery of Ag and Nd by *Chlorella vulgaris* follows second order kinetics for biosorption.

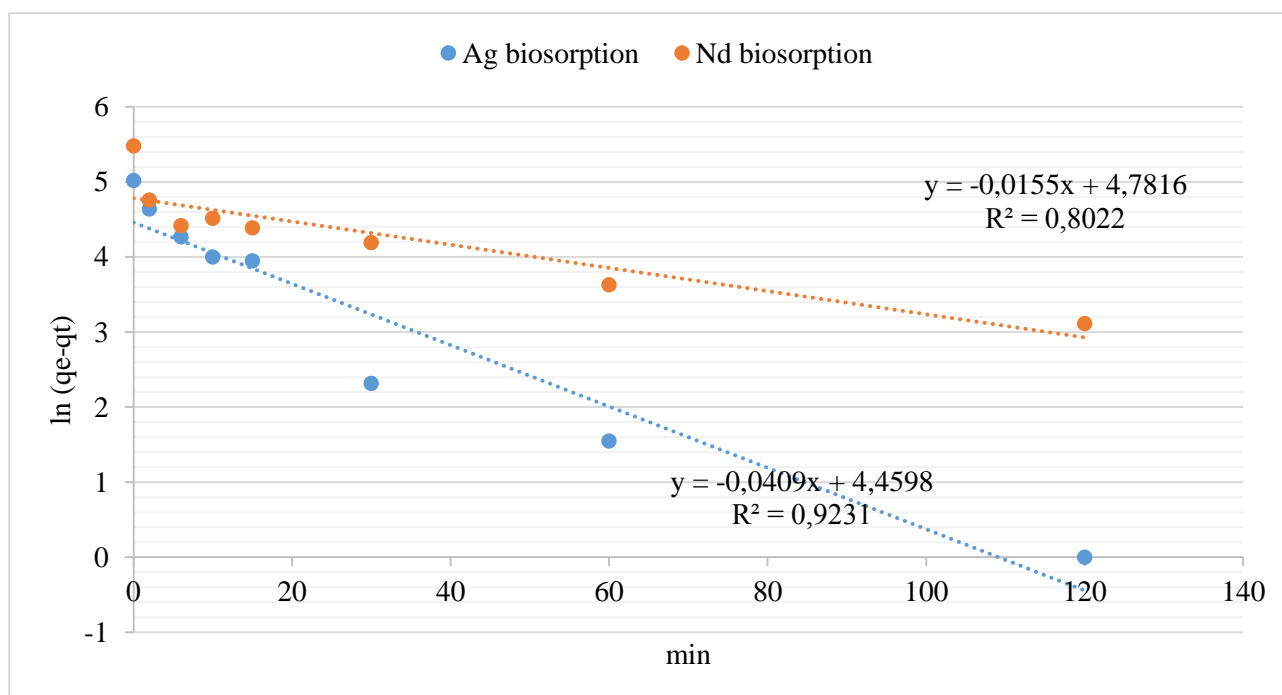


Figure 5.1. First order kinetics for Ag and Nd biosorption.



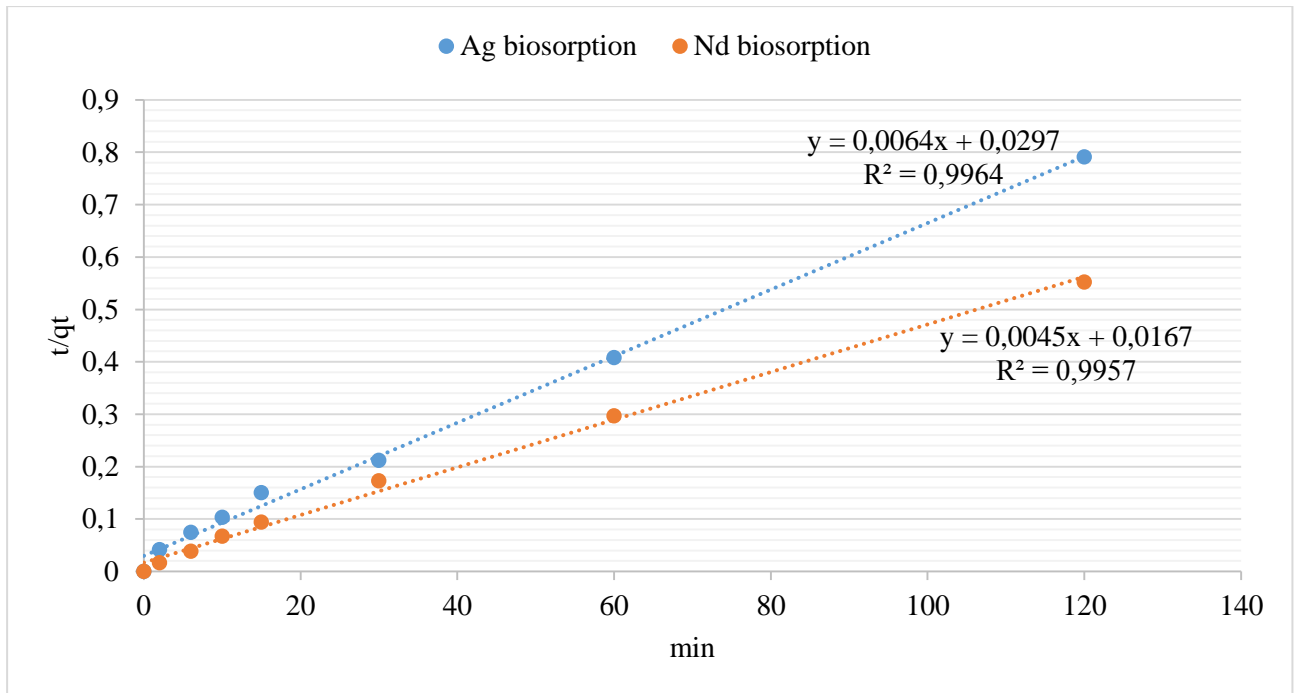


Figure 5.2. Second order kinetics for Ag and Nd biosorption.

Isotherm constants and the models can be seen in Figure 5.3 and 5.4. Regression correlations for Langmuir were found to be 0.9281 for Ag and 0.9748 for Nd, whereas, for Freundlich, they were 0.967 for Ag and 0.9911 for Nd. The results showed that isotherms fitted the experimental data showing better correlation for Nd biosorption and Ag biosorption for the Freundlich isotherm.

Freundlich refers to adsorption to heterogeneous surfaces, unlike the Langmuir model that assumes adsorption on a monolayer (Dada et al., 2012; Igwe and Abia, 2007). The value ' $n$ ' represents the selectivity and capacity of adsorption. When it is between 1 and 10, this shows beneficial adsorption (Mckay et al., 1982). The  $n$  values for Ag and Nd biosorption were found to be 2.494 and 2.564, respectively. This confirms the biosorption of Ag and Nd by *Chlorella vulgaris* is beneficial adsorption.

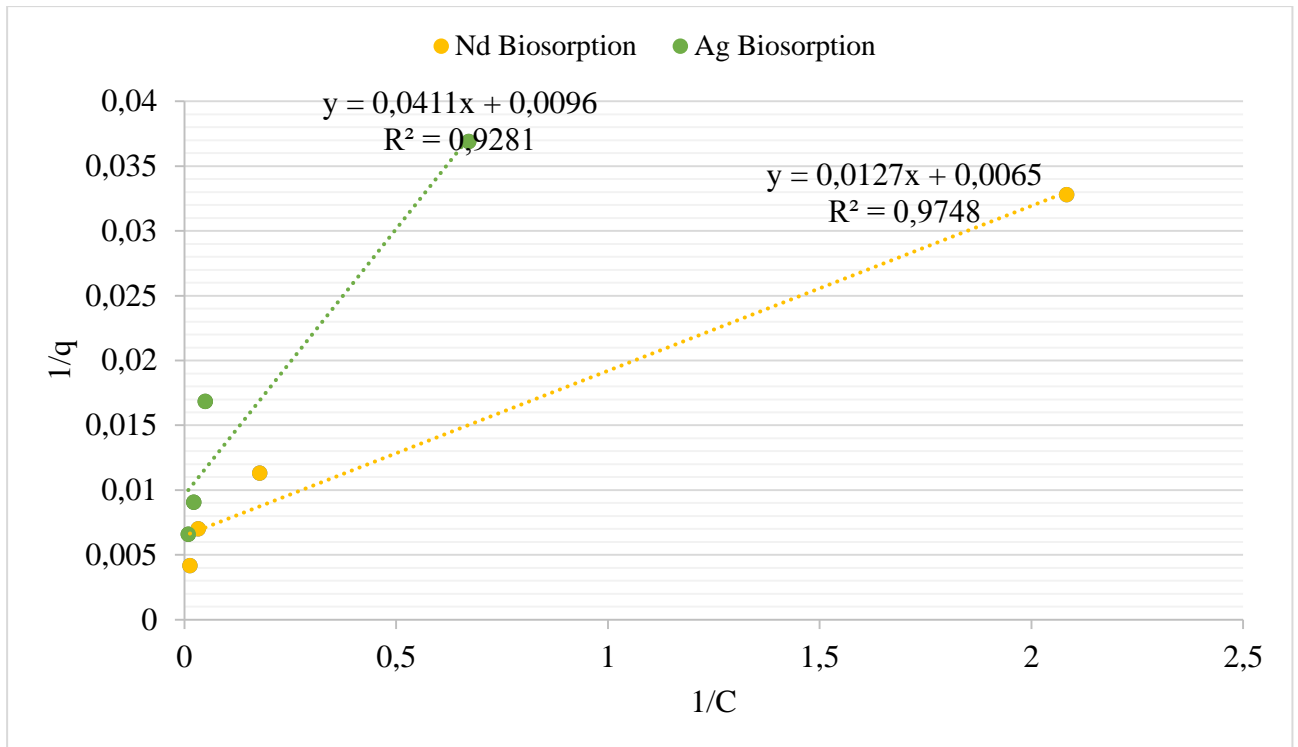


Figure 5.3. Langmuir isotherms for Ag and Nd biosorption.

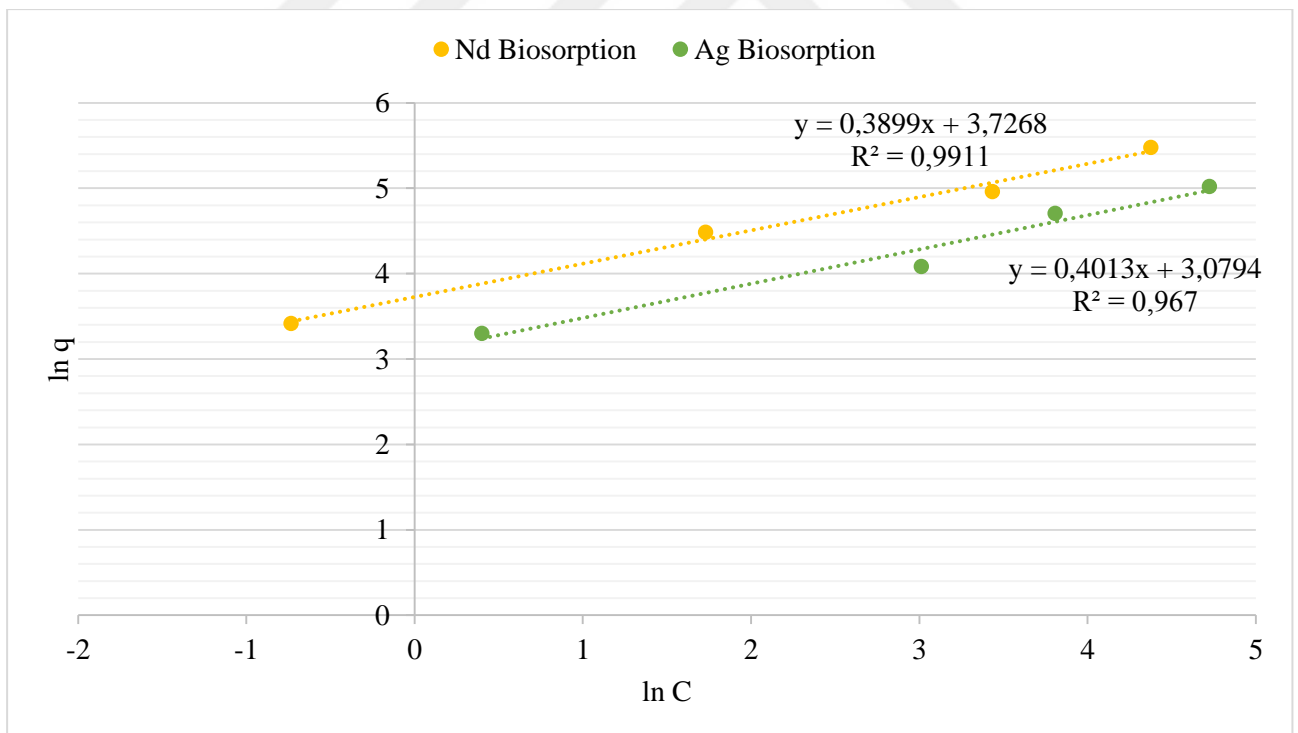


Figure 5.4. Freundlich isotherms for Ag and Nd biosorption.

## 5.2. Bioaccumulation

Pseudo first and second order models applied to experimental data can be seen in Figure 5.5 and Figure 5.6. The regression correlation for first order kinetics was found very low; representing 0.5924 and 0.7710 for Nd and Ag, respectively. The regression correlations for second order kinetics were 0.9999 and 0.9997 for Ag and Nd, respectively. This indicates bioaccumulation process also follows pseudo-second order kinetics.

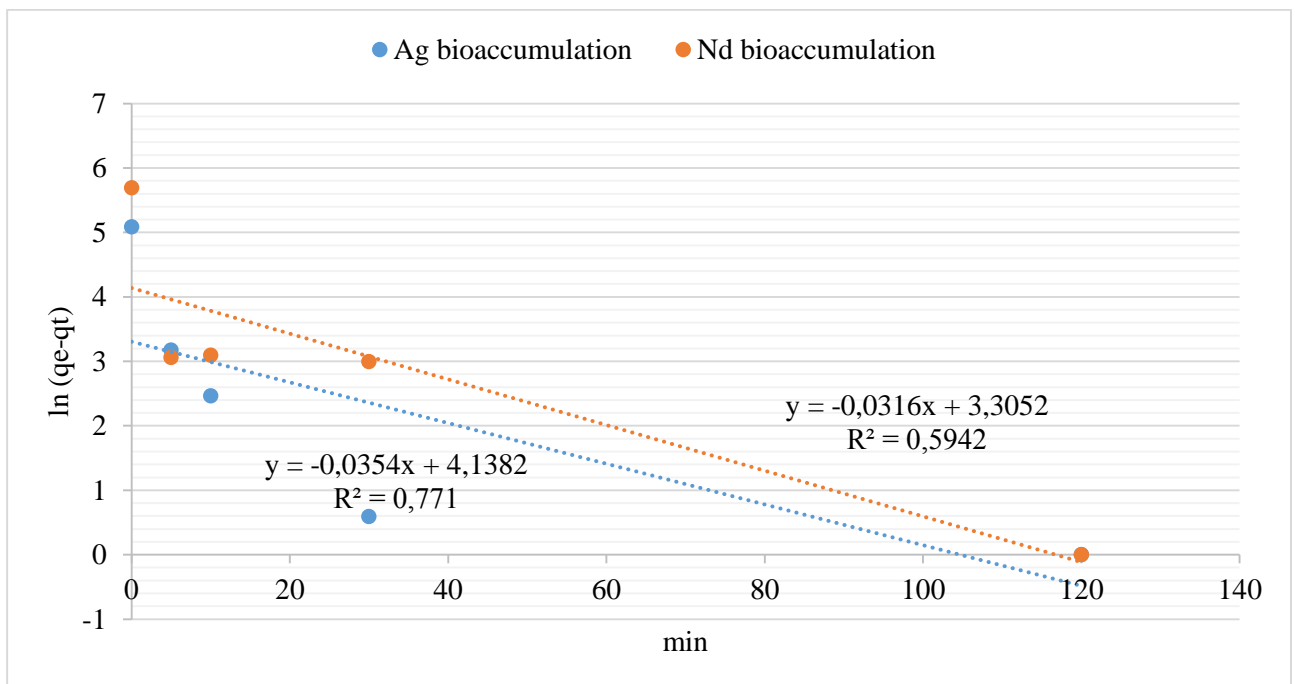


Figure 5.5. First order kinetics for Ag and Nd bioaccumulation.

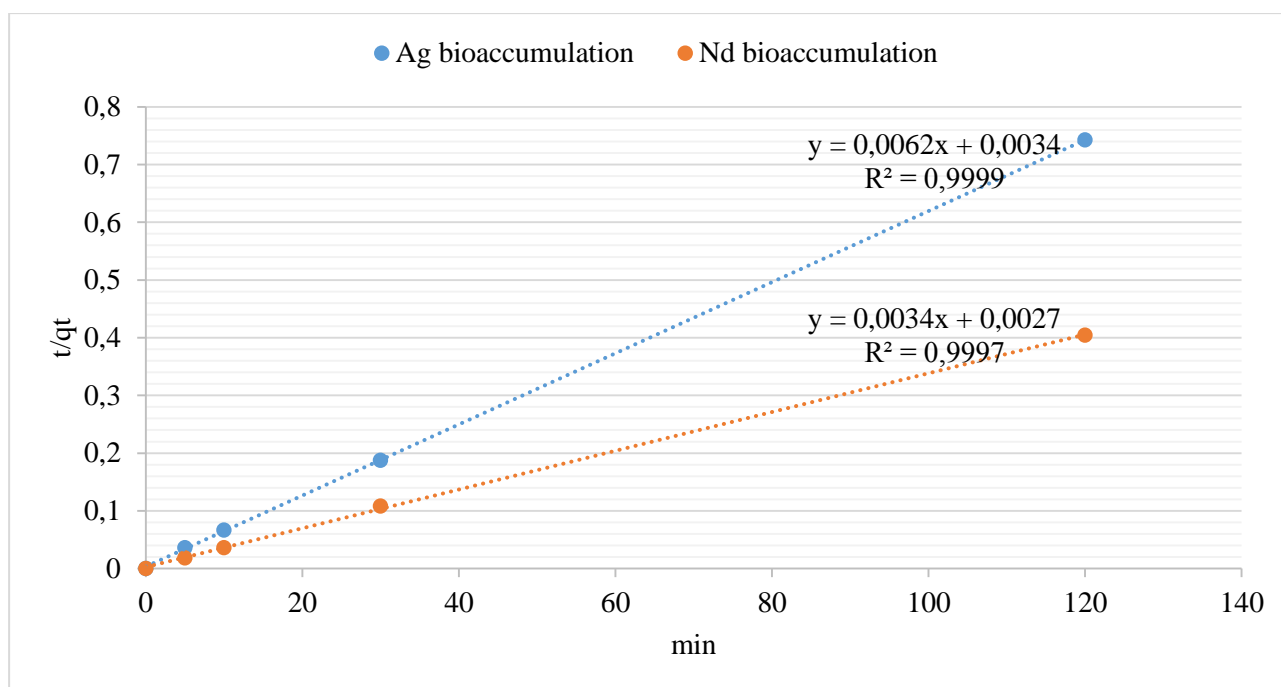


Figure 5.6. Second order kinetics for Ag and Nd bioaccumulation.

For the isotherms, Langmuir and Freundlich isotherms were applied to the experimental data as it can be seen from Figure 5.7 and Figure 5.8. The regression correlation values were 0.7335 and 0.2102 for Ag and Nd bioaccumulation for the Langmuir Model. The regression correlation was found as 0.7631 and 0.3918 for Ag and Nd bioaccumulation. For Ag, the Freundlich isotherm fitted better to the data, that confirms adsorption took place on heterogenous site. The  $n$  value was found as 3.762 for Ag bioaccumulation, representing beneficial adsorption of the metals to the algal surface.

For Nd, since Langmuir and Freundlich isotherms did not fit to the data, the linear model was applied as shown in Figure 5.9. The regression correlation coefficient was found as 0.9176 for Nd and 0.9886 for Ag. This may be due to the lack of element, especially for Nd in the solution for bioaccumulation. If the experiment had been conducted with more saturated solution, an isotherm would probably fit the data. However, since Nd is a rare earth element and found in limited concentrations, and the extent of the selected concentrations is wide enough, there is no need to conduct the experiment with the more saturated solution.

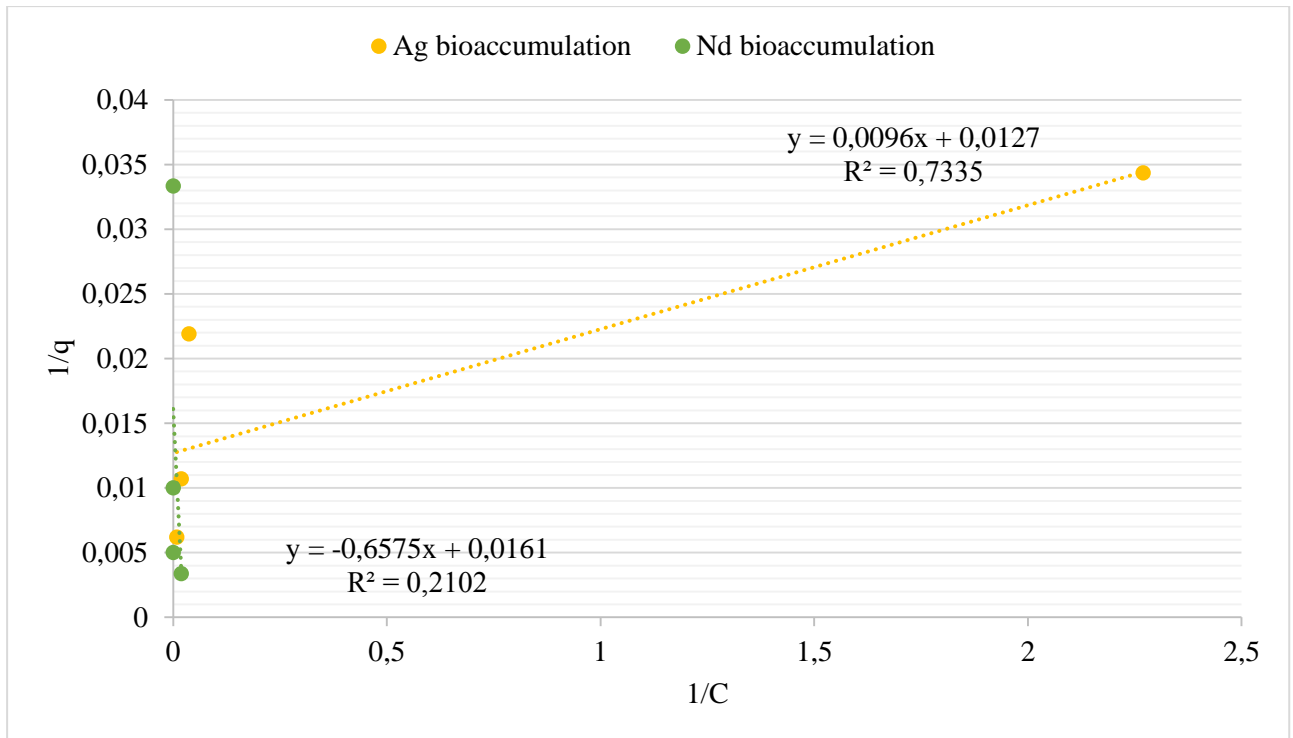


Figure 5.7. Langmuir isotherms for Ag and Nd bioaccumulation.

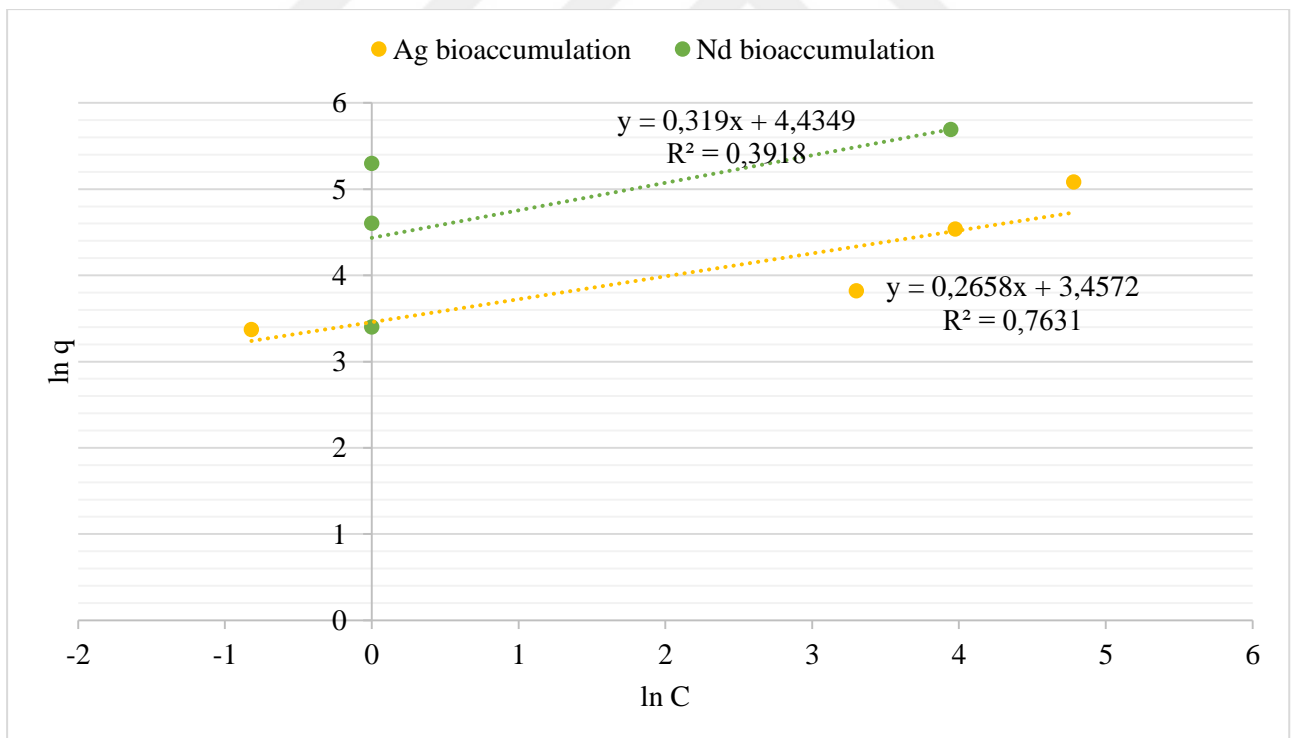


Figure 5.8. Freundlich isotherms for Ag and Nd bioaccumulation.

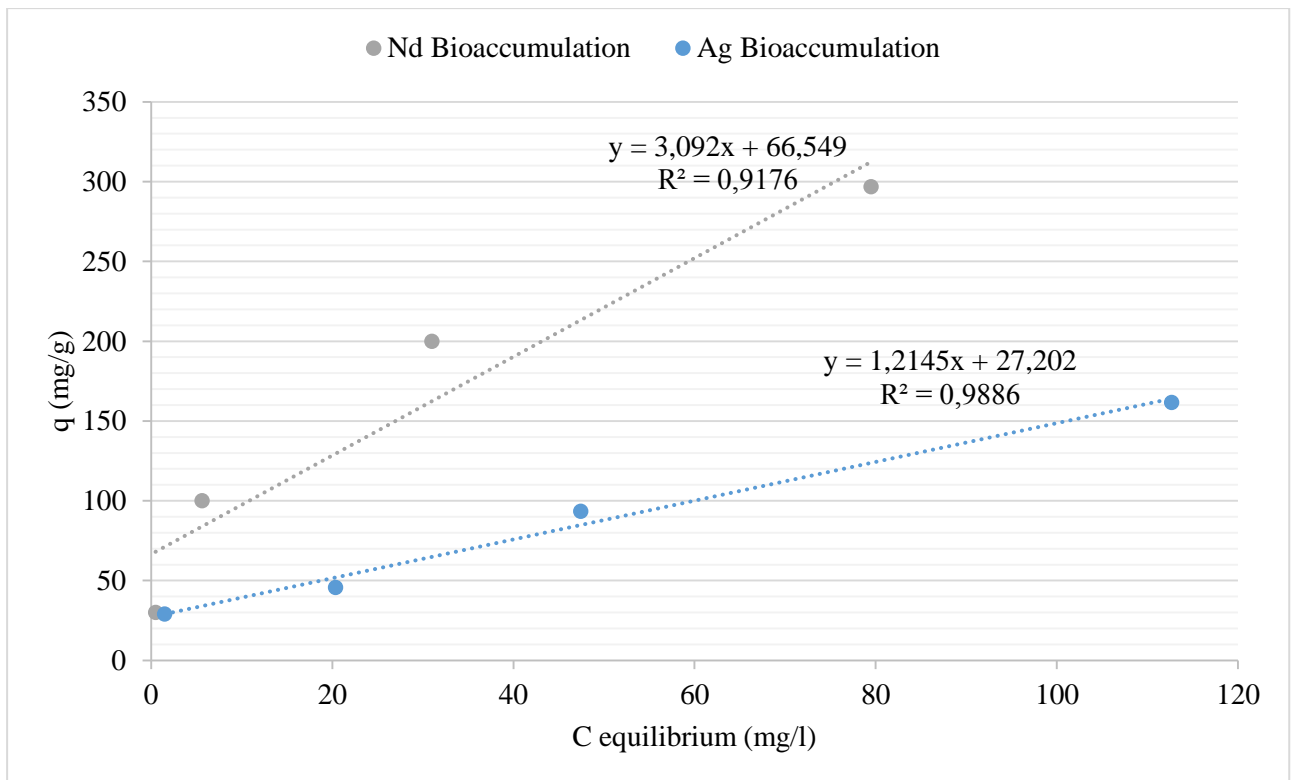


Figure 5.9. Linear model of Ag and Nd bioaccumulation.

## 6. CONCLUSION

This study reveals the metal content of different e-waste in PCBs and screens. Base metals, precious metals, as well as rare earth element contents are assessed by using three different digestion methods prior to ICP-OES analysis. The results showed that with varying methods of digestion, various metals could be dissolved in the aqueous phase. Method USEPA 3051A is recommended for Au, Mo, Zn, and Cu, Ni, while USEPA 3050B is recommended for Nd, Pd, Pr, Ag, Dy, Pt, Mn, Ce, Cd, Cr, Co, Al, Pb, and Fe. La had the best average concentrations when digestion method was MMDM. Since most of the metals are recovered with USEPA 3051A, this method is recommended when all of the elements are in focus in mixed e-waste samples. Cu, Fe, and Al were found as main base metals in all of the samples. Ag and Nd were found as the major precious metal and rare earth elements for each sample, respectively.

For biosorption, dried microalgae was found to be very useful for recovery of Ag and Nd from aqueous solutions. Optimization of focus elements was completed, and the following conditions were determined to be optimum: 25 °C, pH: 5, initial metal concentration: 200 ppm, biosorbent dosage: 0.5 g/L, stirring speed: moderate. As the parameters increase or decrease, the uptake of metal decreases. The process was completed within 60 minutes. Maximum biosorption capacity was found as 151.7 mg/g for Ag and 239.7 mg/g for Nd.

For bioaccumulation, living microalgae was also found to be very useful to recover the metals. Optimum conditions for bioaccumulation for Ag and Nd were found as follows: Initial metal concentration: 200 ppm, biosorbent dosage: 0.5 g/l. As the parameters increase or decrease the uptake amount decreases. The process was completed in approximately 5-10 minutes. Maximum bioaccumulation capacity was found as 161.6 mg/g for Ag, 296.8 mg/g for Nd.

When two elements were present in the binary solutions, the uptake amounts decreased by around 65% and 22-48% for biosorption and bioaccumulation, respectively. When the efficiency of bioaccumulation and biosorption from binary metal solutions are compared, bioaccumulation yielded 38.8% and 127.5% more efficiency for Ag and Nd, respectively. Tertiary element biosorption and bioaccumulation revealed that it is possible to prevent sorption of the selected type of element by changing the process parameters. This may open new visions for research based on selective biosorption and bioaccumulation.

Shifting of functional groups was observed in the FTIR Analysis, which showed that the elements were bound to the active sites of algae. Ag and Nd were observed in algae samples after biosorption in SEM-XRD analysis. Ag was found as particles on the algal surface, while Nd was found on all over the surface; in a more scattered pattern. This result proves that algae uptake the focused elements.

For the modeling studies, biosorption and bioaccumulation of Ag and Nd followed pseudo-second order kinetics. For the isotherm models, the Freundlich model better fitted for Ag and Nd biosorption. Ag bioaccumulation was found suitable for Freundlich isotherm, while the linear model was fitted best to Ag and especially Nd bioaccumulation data.

To conclude;

*Ag and Nd are the main elements present in e-waste. Recovery of these metals can be achieved by using dried and living microalgae, Chlorella vulgaris, with efficient, fast, and environmentally friendly method.*



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