

T.R.
EGE UNIVERSITY
Graduate School of Applied and Natural Science

**NICKEL BIOSORPTION USING A FIXED BED
COLUMN AND KINETIC MODELLING**

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Chemical Engineering Second Cycle Programme

İzmir
2019

Melek Yasemin BAHAR tarafından Yüksek Lisans tezi olarak sunulan “Sabit Yataklı Kolonda Nikel Biyosorpsiyonu ve Kinetik Modellemesi” başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 22.05.2019 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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EGE ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ

ETİK KURALLARA UYGUNLUK BEYANI

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22.05.2019

Melek Yasemin BAHAR

ÖZET**SABİT YATAKLI KOLONDA NİKEL BİYOSORPSİYONU VE
KİNETİK MODELLEMESİ**

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Mayıs 2019, 66 Sayfa

Nikel, canlılar için gerekli bir metaldir; ancak, ortamdaki konsantrasyon artışının kanser riskini arttırdığı bilinmektedir. Anti-inflamatuar ve anti-aging alanında da kullanılan, kırmızı makro alg *Gracilaria verrucosa*, biyosorbent olarak ağır metal gideriminde de kullanılmaktadır. Bu çalışmada, Nikel ağır metalinin sulu çözeltiden uzaklaştırılabilmesi için sabit yataklı kolonda gerçekleştirilmiş ve kurutulmuş *Gracilaria verrucosa* kullanılmıştır. Başlangıç konsantrasyonu, akış hızı ve adsorbent miktarı incelenmiştir. Optimum biyosorpsiyon değeri; 0,6 g adsorbent kullanıldığında, 0,2 ml/dak akış hızında ve 200 ppm Ni konsantrasyonunda bulunmuştur.

Toplanan veriler, üç farklı kinetik model; Thomas, Adams-Bohart ve Yoon-Nelson ile tanımlanmış olup, MATLAB Surface Fitting Tool kullanılarak modellenmiştir. Modelleme verilerine göre, sistemin Thomas modeline uyum gösterdiğine karar verilmiştir. Kolondan temizlenen *Gracilaria verrucosa*'nın, biyosorpsiyon sonrasında ne şekilde değerlendirileceği araştırılmış, yapılan kalori analizleri sonucunda atıktan türetilmiş yakıt teknik özelliklerine uygun olduğu ve çimento tesislerinde ek yakıt olarak değerlendirilebileceği öngörülmüştür.

Sonuç olarak, sürekli sistemde yapılan deneylerde, kullanılan Ni kirliliğindeki algal biyokütle *Gracilaria verrucosa*'nın etkin bir giderim sağladığı görülmüş, deneyler sonrasında oluşan atığın ek yakıt olarak değerlendirilebileceği sonucuna varılmıştır.

Anahtar sözcükler: *Gracilaria verrucosa*, nikel, biyosorpsiyon, kinetik modelleme, algal biyokütle.

ABSTRACT**NICKEL BIOSORPTION USING A FIXED BED COLUMN AND
KINETIC MODELLING**

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May 2019, 66 Pages

Nickel is a necessary metal for living beings; however, the increase in concentration is known to increase the risk of cancer. Red macro algae *Gracilaria verrucosa* which is used in anti-inflammatory and anti-aging areas, is also used as a biosorbent for removal of heavy metal. In this study, experiments were tested in order to remove Nickel heavy metal from aqueous solution using a fixed bed column with dried *Gracilaria verrucosa* as an adsorbent. Nickel studies with biological material in continuous system; initial concentration, flow rate and dosage were investigated using fixed bed column. Optimum biosorption value is found by using 0,6 g biosorbent at 0,2 ml/min flow rate and 200 ppm Ni concentration.

Collected experimental data were defined by three different kinetic models which are Thomas, Adams-Bohart and Yoon-Nelson, and modeled by using MATLAB Surface Fitting Tool. According to collected modeled data, it is decided that system adapted and showed better fit to Thomas model. Removed *Gracilaria verrucosa* was investigated for evolution. Following calorie analysis of microorganism, it is forested since the *Gracilaria verrucosa* is appropriate for refused dried fuel and it is evaluated as an additional fuel for cement industry.

Eventually, with the aid of column experiments, used algal biomass *Gracilaria verrucosa* showed an effective removal from Ni contamination. It is resulted hat waste microorganism occurred after experiments can be recycled as an additional fuel.

Keywords: *Gracilaria verrucosa*, nickel, biosorption, kinetic modeling, algal biomass.

ÖNSÖZ

İnişli çıkışlı birçok döneme şahitlik eden bu uzun soluklu yolculuğa çıkma kararının, çalıştığım firmada bulunan arıtma ünitesine adsorban araştırmasıyla başladığını anımsıyorum. Küçük bir satınalma işleyişinden bir araştırma konusu elde etmiş olmak gerçekten çok heyecan verici.

Çalıştığım işletmenin atık yönetimi üzerine faaliyet göstermesi ile en baştan beri desteğini ve profesyonel bakış açısını üzerimden eksik etmeyen danışmanımın biyokütlelerle yapılacak çalışmaya olan ilgisi, bu çalışmanın olgunlaşmasındaki en büyük şansımdır.

Çalışmanın; ağır metal içerikli atık suların arıtılması ve arıtım sonrası üretilen atığın değerlendirilmesi konusunda hem sektör yöneticilerine hem de literatüre değerli bilgiler sunacağını bilmek kendi adıma mutluluk vericidir.

İZMİR

22/05/2019

Melek Yasemin BAHAR

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NOMENCLATURE

<u>Symbol</u>	<u>Statement</u>
k_{AB}	Kinetic constant in the Adams-Bohart model
k_{TH}	Kinetic constant in Thomas model
k_{YN}	Kinetic constant in the Yoon-Nelson model
N_o	Saturation concentration in the Adams-Bohart Model
m_{total}	Total amount of adsorbate sent to column
q_{eq}	Equilibrium uptake per g of adsorbent in column
q_{total}	Total adsorbed quantity of adsorbate in column
q_0	Thomas model constant
Q	Flow rate
t	Flow time
t_{break}	Time at breakthrough
t_{total}	Total flow time
V_{eff}	Effluent volume
Z	Column height
τ	Time required for 50% adsorbate breakthrough

1. INTRODUCTION

Incorrect use of water resources causes increase in water pollution and decrease in sea creatures and quality of drinking/using water resources, day after day. Water pollution, which means contamination of water as physically, biologically and chemically, occurs not only directly pollute in water, but also pollute in air and soil. In the Figure 1.1, groundwater quality is considered to be a major threat due to excessive use of natural resources and human activities (Bodrud-Doza et al., 2016).



Figure 1.1 Groundwater pollution due to natural and anthropogenic activities

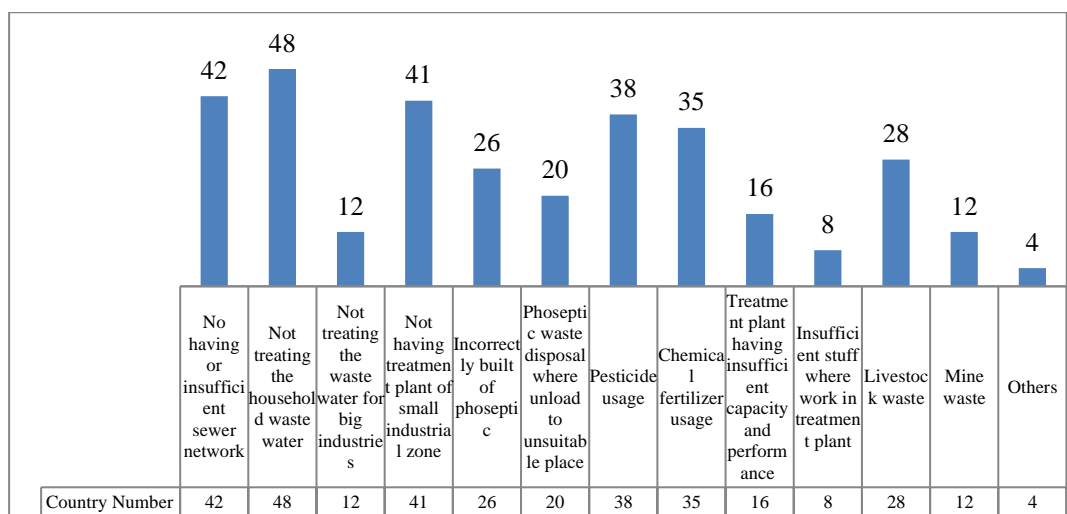


Figure 1.2 Reasons of water pollution at Centers

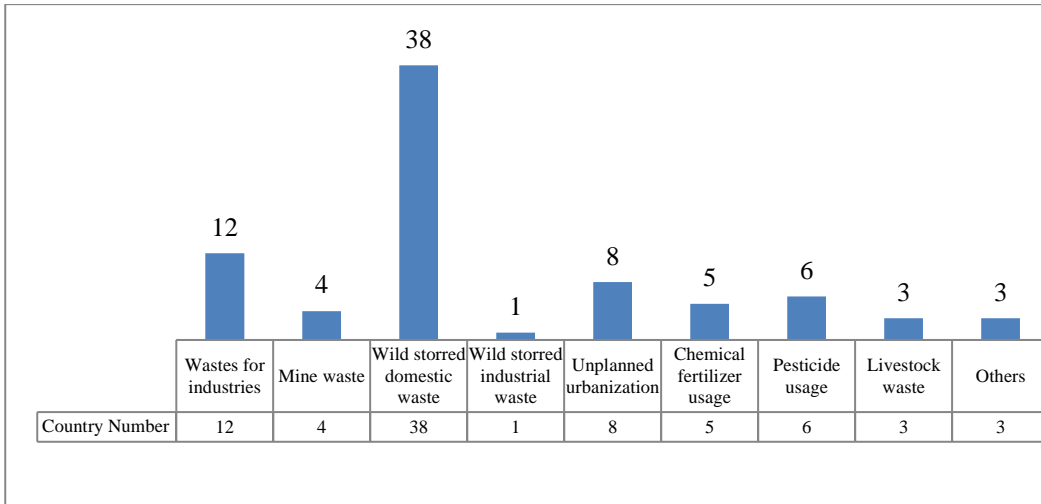


Figure 1.3 Reasons of soil pollution at Centers

According to the study of Ministry of Environment and Urbanization in 2014, negative role of industry (total of big and small industrial areas) on environment is more than other factors such as sewer network etc. in Figure 1.2 and Figure 1.3 can be read as both industrial and domestic waste problem are the main environmental problem of Turkey (Ministry of Environment and Urbanization, 2014).

Heavy metals in waste water cause toxic effect on living organisms in proportion to the concentration. The most common heavy metals which are potentially harmful even if including trace amount are Cu, Cd, Cr, Pb, Mn, Hg, Zn, Ni. Effects of heavy metals concentration changes on from one living to another.

In order to prevent pollution of water resources, environmental regulations obligate industry to minimize heavy metal concentrations in waste water to lower discharge limits in developed countries. It is known that many states and organizations (such as the United States, Canada, EU Countries and WHO) set standards to regulated pollution values that may be present in drinking water to keep consumers at risk of high contamination (Nalcaci et al., 2006).

The seriousness of heavy metal effects on not only livings but also environment accelerates removal of heavy metals from wastewater. Due to growing environmental concerns with the growth of the economy, the issue of removal or recovery of heavy metals from wastewater is becoming increasingly important (Kaminari et al., 2007).

It is recommended that the applications of biosorption technology in industrial scale both reduce the operating costs of the biomass to a great extent and the biomass should be used with a continuous system to ensure the absorption of different metals (Mehta and Gaur, 2005, Sharma and Singh, 2013).

The aim of the study is to investigate the heavy metal of Ni biosorption by *Gracilaria verrucosa* in continuous system and modeling this process.



2. BACKGROUND INFORMATION

2.1 Statement of Heavy Metal Contamination

Metals are the indispensable materials of industrial processes, although; wastes are discharged to the environment as a result of industrial processes (Chowdhury et al., 2016). According to USGS, Table 2.1 represents the usage areas of some specific heavy metals.

Table 2.1 Usage areas of some specific heavy metals

Metal	Usage Area
Chromium	World resources are greater than 12 billion tons of shipping-grade chromites and Chromium production amounts are 3,500 tones for each 2015 and 2016 (USGS, 2017)
Copper	Copper and copper alloy products were used in building construction, 44%; transportation equipment, 19%; electric and electronic products, 18%; consumer and general products, 12%; and industrial machinery and equipment, 7% (USGS, 2017)
Nickel	Approximately 45% of the primary nickel consumed went into stainless and alloy steel products, 36% into nonferrous alloys and super alloys, 7% into electroplating, and 12% into other uses (USGS, 2017).

In Table 2.2, selected heavy metals used in major industries are listed. Waste water from these industrial processes usually contains a higher proportion of heavy metals than the discharge criteria specified by the legislation. (Kaminari et al., 2007).

Although it is known that the negative effects it has on health, still heavy metals are exposed and this exposure has increased especially in less developed countries and it has been observed that it has decreased in many developed countries in the last 100 years (Jarup, 2003). Limit values and health risks of some specific heavy metals are tabulated in Table 2.3.

Table 2.2 Chosen some heavy metals used in already or older industries

Industry	Meade, 1995		* USGS, 2017 ** Cechinel et al., 2016 ***Gupta et al., 2010
	Chromium	Copper	Nickel
Machinery products	x	x	
Paint pigment and ink	x	x	x ***
Electroplating and battery manufacturing	x	x	x *
Textile mill	x	x	
Wood, pulp and paper	x	x	
Organic chemicals	x		
Inorganic chemicals	x	x	
Rubber manufacturing	x		
Iron and steel foundries	x		x *
Nonferrous metal foundries		x	x *
Leather processing	x		
Petroleum refining	x	x	x **
Steam-generation power plants	x	x	x ***

Table 2.3 Limit values and health risks of some specific heavy metals

Metal	NIOSH REL TWA mg/m ³	OSHA PEL TWA mg/m ³	Health Risk OSHA
Metallic Chromium, Cr (II) compounds	0,5	1	Allergic skin rash Lung disorders
Cr (III) compounds	0,5	0,5	Allergic skin rash Lung disorders
Cr (VI) compounds	0,001 (as Cr)	0,005 (as CrO ₃)	Lung disorders, Asthma, Cough, Shortness of breath, Allergic skin rash, Anemia, Ulcer, Sperm damage
Copper (dusts and mists, as Cu)	1	1	Irritation-Eye, Nose, Throat, Skin Cumulative Lung Damage
Ni metal and other compounds (as Ni)	0,02	1 (Metal and insoluble compounds)	Lung and Sinus cancers Sensitization dermatitis, Allergic skin rash
		0,1 (Soluble compounds)	

2.1.1 Regional heavy metal contamination amounts

The impact of the large amount of polluted wastewater (including toxic metals, metalloids, radionuclides, various organic pollutants) produced by the human impact on the nature combined with industrialization has increased the pressure on the environment (Fomina and Gadd, 2014). In Table 2.4, some heavy metal contamination values are tabled for Gediz River and Eğri Stream regions.

Table 2.4 Regional Heavy Metal Contamination Based on Water Contamination

	Station	Pb (mg/L)	Ni (mg/L)	Cr (mg/L)	Cu (mg/L)	Zn (mg/L)
Gediz River (Öner et.al., 2011)	Nif Çayı	27	78	21	25	21
	İstanbul Köprüsü	29	42	16	28	37
	Karaçay	68	289	29	59	158
	Muradiye Köprüsü	94	43	38	90	60
	Menemen Yolu	99	29	35	71	98
Eğri Stream (Çekim et.al., 2014)	-	0,214 – 0,549	0,965 – 4,490	0,068 – 0,602	1,490 – 4,570	0,292 – 1,91
Maximum Permissible Concentrations (MPC) of Various Metals in Natural Waters For the Protection of Human Health (EPA, 1987)	-	5	13,4	50	-	-

By the way, the heavy metal contamination of soil can be measured by Lichens which are also called biomonitors, are used to monitor the metal contamination in the atmosphere (by in situ sampling of the organism or using the transplantation technique) (Ölgen and Gür, 2012).

Table 2.5 represents heavy metal concentration of lichen samples which are collected different areas close to Yatağan Coal Fired Power Plant (Ölgen and Gür, 2012). Bold values show where the concentrations pass over the limit value. Toxic

metal-containing soils are harmful to plants and animals because they are the main material with a high metal concentration (Sarwar et al., 2017).

Table 2.5 Heavy metals in samples collected around Yatağan ($\mu\text{g/g}$) (Ölgen and Gür, 2012)

	Hg	Ni	Pb	Cu	Zn
Min	110	9,4	7,29	9,43	46,10
Max	235	21,2	25,11	19,40	89,90
Average	141,2	13,9	12,98	13,24	65,86
Limit Value	20 – 200	0,1 – 5	0,1 – 10	4 – 15	8 – 400

2.1.2 Regulations in Turkey

Legislative regulations on the discharge of pollutants into the environment are becoming more stringent (Bermúdez et al., 2011). There are some regulations about waste and waste water management in Turkey, such as;

- Water Pollution Control Regulation (31.12.2004 date and 25687 numbered Official Newspaper)
- Urban Wastewater Treatment Regulation (08.01.2006 date and 26047 numbered Official Newspaper)
- Water Pollution Control Regulation Administrative Producers Communiqué (10.10.2009 date and 27372 numbered Official Newspaper)
- Soil Pollution Control and Regarding Contaminated Soil Regulation (08.06.2010 date and 27605 numbered Official Newspaper)
- Waste Incineration Regulation (06.10.2010 date and 27721 numbered Official Newspaper)
- Regulation on the Regular Storage of Wastes (26.03.2010 date and 27533 numbered Official Newspaper)
- Communiqué on Technical Procedures for Wastewater Treatment Plants (20.03.2010 date and 27527 numbered Official Newspaper)
- Waste Management Regulation (02.04.2015 date and 29314 numbered Official Newspaper)

The risk of polluting of soil by contaminated water, the main regulation where discharge criteria are determined is Water Pollution and Regulation. According to

sector and connection point of waste water to discharge area; deep sea discharge, river etc. (Table 2.6).

Table 2.6 Discharge Limits of Some Metals

Metal	Regulations in Turkey (mg/L)*
Metallic Chromium, Cr (II) compounds	0,5 – 5**
Cr (III) compounds	0,5 – 5**
Cr (VI) compounds	0,05 – 0,5**
Copper (dusts and mists, as Cu)	0,3 – 5**
Ni metal and other compounds (as Ni)	1 – 5**

*Water Pollution Control Regulation

**Changes according to sector and connection point of waste water to discharge area

2.1.3 Effects of Ni Contamination on Living Health

Nickel, Ni, is a heavy metal whose atomic number and atomic weight are 28 and 58.69, respectively. It is a transition metal and belongs to group of 7B in periodic table. Because of its electron sequence, its oxidation state tends to gain +2 values, although +3 and +4 are also known.

Due to its chemical properties (i.e. hardness, high melting point, ductility, malleability, ferromagnetic, fair conductor of heat and electricity) it is much suitable to form alloy with Nickel (IARC, 2012). Nickel alloys have very limited use (EPA, 1992); and, Table 2.7 (NTP, 2000) represents according to producing and using industries, exposure concentrations of Nickel data are listed.

Table 2.7 Nickel risks in nickel producing and using industries

Industry Sector	Range of exposure concentrations (mg Ni/m ³) ¹	Range of mean aerosol exposure concentrations (mg Ni/m ³) ²	Predominant species ³
Mining	0 – < 1,0	0,003 – 0,15	SU, O ⁴
Milling	0,001 – 4,0	0,01 – < 0,70	SU
Smelting	0,001 – 77,0 ⁵	0,01 – < 3,0	SU, O ⁶
Refining	0,001 – 20,0 ⁷	0,003 – ~1,50 ⁸	SU, O, M, SO ⁹
Stainless and alloy steels	0 – < 1,0	0,001 – 0,10	O, M
Nickel alloy steels	0,001 – 9,0 ¹⁰	0,002 – ~0,50 ¹¹	O, M
Welding and hot cutting	Trace – 7,0 ¹²	0,001 – ~0,5 ¹³	O, M ¹⁴

¹ Total nickel, unless otherwise indicated

² Total nickel, unless otherwise indicated

³ M = metallic nickel, O = oxidic nickel, NC = nickel carbonyl, SU = sulphidic nickel, SO = soluble nickel salts

⁴ Dependent upon the type of ore

⁵ Upper limits of ranges for most data sources did not exceed 2.0 mg Ni/m³

⁶ Dependent upon the type of ore

⁷ Upper limits of ranges for most data sources did not exceed 5.0 mg Ni/m³

⁸ A few mean aerosol concentrations exceeded 1.5 mg Ni/m³. The highest mean value reported was 4.84 mg Ni/m³

⁹ Dependent upon the operation and job

¹⁰ Upper limits of ranges for most data sources did not exceed 1 mg Ni/m³

¹¹ A few mean aerosol concentrations exceeded 0.5 mg Ni/m³. The highest mean value reported was 3.2 mg Ni/m³

¹² Upper limits of ranges for most data sources did not exceed 1 mg Ni/m³

¹³ A few mean aerosol concentrations exceeded 0.5 mg Ni/m³. The highest mean value reported was 3.58 mg Ni/m³

¹⁴ In some instances, soluble nickel was noted to be present, although it was not the predominant form of nickel found

Nickel plating	Trace – ~3,0 ¹⁵	0,0004 – ~0,10 ¹⁶	SO
Production of chemicals	0,001 – ~3,0	0,02 – ~1,50	SO, O, OM
Nickel catalysts	0 – 26,0 ¹⁷	0,004 – ~1,0 ¹⁸	SO, O, OM ¹⁹
Nickel-cadmium batteries	0 – ~2,0	0,005 – ~0,50	O, M, SO
Others	Trace – 14,0	Trace – 0,5 ²⁰	Mixed

Condition of nickel exposure (inhalation, oral and/or dermal); while it causes developmental effects in human and animals, death, systematic, immunological and lymphoreticular, neurological, reproductive and cancer. Because of the differences in the chemical forms of heavy metals, the human body can cause disorders (hematogenesis and the central nervous, cardiovascular and urogenital systems) are variable. (Tepanosyan et al., 2017).

Table 2.8 (ATSDR, 2005) listed exposure amounts of Nickel by inhalation, oral and dermal ways. According to exposure time; acute, intermediate or chronic, effects can be observed as different diseases.

Insoluble nickel, nickel-producing industries are seen in predominant exposure; soluble nickel is observed to be predominantly exposed in nickel-using industry (IARC, 2012). It is known that occupational nickel exposure is seen by not only inhalation and dermal but also oral ways. Occupational exposure to nickel is measured by monitoring air and blood serum, plasma, or urine (NTP, 2000).

¹⁵ A few mean aerosol concentrations exceeded 0.5 mg Ni/m³. The highest mean value reported was 3.2 mg Ni/m³

¹⁶ In instances where speciation was conducted, insoluble nickel compounds were noted to be present although they were not the predominant forms of nickel found

¹⁷ Upper ranges for most data sources did not exceed 4.0 mg Ni/m³

¹⁸ A few mean aerosol concentrations exceeded 1.0 mg Ni/m³. The highest mean value reported was 1.55 mg Ni/m³

¹⁹ In addition to potential exposures to oxidic and/or metallic nickel species, sulfidic nickel also is believed to be present in the spent nickel catalyst

²⁰ A few mean aerosol concentrations exceeded 0.5 mg Ni/m³. The highest mean value reported was 4.1 mg Ni/m³

Table 2.8 Discussion of Health Effects by Route of Exposure

EXPOSURE Acute (≤ 14 days) Intermediate (15 - 364 days) Chronic (≥ 365 days)			EFFECTS						
			Death	Systemic	Immunological and Lymphoreticular	Neurological	Reproductive	Developmental	Cancer
Inhalation	Human	Acute	382 mg Ni/m3	-	-	-	-	-	-
		Chronic	-	0.75 mg Ni/m3	-	-	-	-	1 - 10 mg Ni/m3
	Animal	Acute	1.4 - 12.2 mg Ni/m3	0.11 - 7.9 mg Ni/m3	0.25 - 1.4 mg Ni/m3	0.635 mg Ni/m3	1.4 - 23.6 mg Ni/m3	-	-
		Intermediate	-	0.11 - 3.9 mg Ni/m3	0.15 - 9.2 mg Ni/m3	-	0.44 - 3.9 mg Ni/m3	1.6 mg Ni/m3	-
		Chronic	0.06 - 15 mg Ni/m3	0.06 - 0.7 mg Ni/m3	0.11 - 1 mg Ni/m3	-	0.11 - 2 mg Ni/m3	-	0.7 - 1 mg Ni/m3
Oral	Human	Acute	570 mg Ni/Kg/Day	0.057 - 7.1 mg Ni/Kg/Day	-	7.1 mg Ni/Kg/Day	-	-	-
		Intermediate	-	0.02 mg Ni/Kg/Day	-	-	-	-	-
	Animal	Acute	39 - 140 mg Ni/Kg/Day	62.5 mg Ni/Kg/Day	-	-	23 mg Ni/Kg/Day	45.3 - 90.6 mg Ni/Kg/Day	-
		Intermediate	8.6 mg Ni/Kg/Day	5.75 - 150 mg Ni/Kg/Day	14.4 - 44 mg Ni/Kg/Day	8.6 mg Ni/Kg/Day	1.1 - 30 mg Ni/Kg/Days	1.3 - 160 mg Ni/Kg/Day	-
		Chronic	-	62.5 - 187.5 mg Ni/Kg/Day	62.5 - 187.5 mg Ni/Kg/Day	62.5 - 187.5 mg Ni/Kg/Day	-	-	-
Dermal	Human	Acute	-	1 mg Ni/cm2/weeks	-	-	-	-	-
	Animal	Acute	-	-	% 1 (concentration)	-	-	-	-
		Intermediate	-	40 - 100 mg Ni/Kg/Day	-	-	40 - 60 mg Ni/Kg/Day	-	-

2.2 Treatment Methods of Heavy Metals

Evaluation of treatment methods of heavy metals shows us too much study has been done for last half century. Since heavy metals are biologically insoluble, it is very difficult to clean contaminated water and soil; and as heavy metal containing wastes are released more and more in the nature environment in many parts of the world, the appropriate technological approaches to be developed for the effective cleaning of contaminated water and soil are of great importance (He and Chen, 2014)

There are many purification techniques that can be used to remove heavy metals not only from soil but also from water. The performance of each technique can be considered normal; however, there are a few drawbacks; and, in particular, they do not work very well in processing heavy metal containing water with varying concentrations (He and Chen, 2014).

2.2.1 Removal or recovery of heavy metals from soil

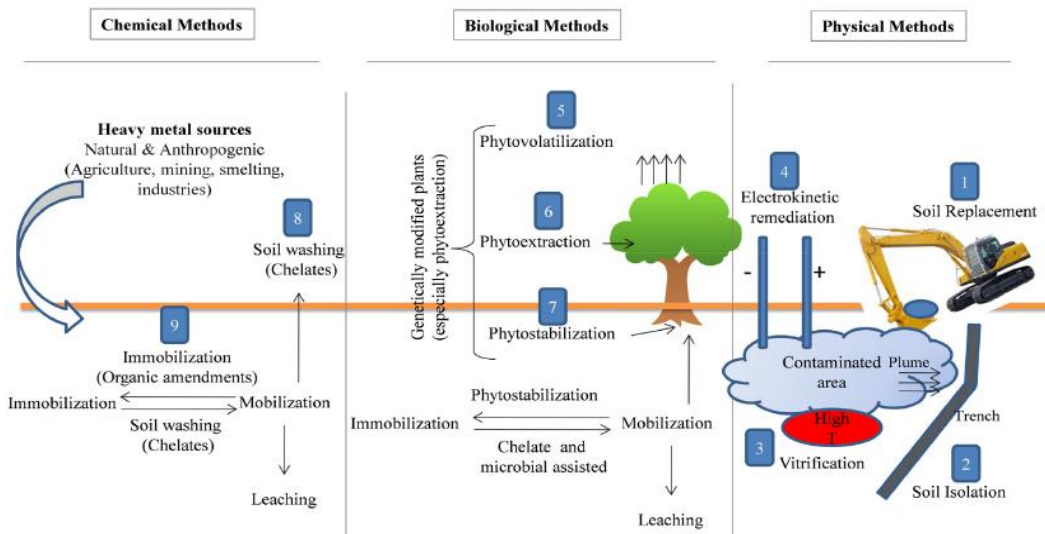


Figure 2.1 Three different soil cleaning methods

In Figure 2.1, Soil improvement methods; physical, chemical and biological groups. Physical remediation methods include (1) soil replacement, (2) soil isolation, (3) vitrification, and (4) electrokinetic; biological methods generally include (5) phytostabilization, (6) phytoevaporation and (7) phytoextraction, and chemical methods contain (8) immobilization and (9) soil washing. However, biological and chemical methods should be applied together with the type of

pollutant metal, soil and plant according to chemical reagent. Furthermore, the healing of soil can be improved by the effectiveness of different plant breeding techniques (microbial-, chelate- and genetic-assisted remediation) (Khaldi et al, 2017).

Pollution is known to cause loss of land as a resource and hence the loss of property (Burlakovs and Vircavs, 2011). There are methods used to treat heavy metals from the soil. These methods are grouped in three parts by Khaldi et al, (2017); as physical, biological and chemical methods (Figure 2.1).

2.2.1.1 Physical methods

Soil replacement which is the oldest remediation method refers that replacing the contaminated soil by uncontaminated. Replacement process dilutes the concentration of heavy metals.

The process of separating the soil contaminated by heavy metal from uncleaned soil is called soil insulation; and, auxiliary engineering measures are needed to completely separate heavy metal from soil (Khaldi et al., 2017).

Vitrification is the process of high temperature at which the organic matter is melted when the mineral substance is burned; the slag must be cooled rapidly to obtain the vitrification product in the vitreous state (Mallampati et al., 2015). Thinking about vitrification is a classical remediation method is an incorrect approach.

In order to improve the soil by electrokinetic method, it is necessary to place the electric field gradient with the appropriate density on both sides of the electrolytic tank (Khaldi et al., 2017).

2.2.1.2 Biological methods

Phytostabilization is a method where heavy metals are stabilized by using plants. As heavy metals are not easy to remove from the soil, phytostabilization is not a permanent solution; however, it should be monitored regularly (Sarwar et al., 2017).

Phytoextraction refers that metals are absorbed from soil by roots of plant, and accumulated in biomass. By phytoextrusion, heavy metals are transferred from the soil to the plant; it is therefore relatively easy to recycle heavy meal into the soil by biomass of the plant (Khaldi et al., 2017).

The heavy metal Hg is transformed into a less toxic mercuric ion by phytovolatilation (Sarwar et al., 2017).

2.2.1.3 Chemical methods

Soil washing is one of the frequently used engineering techniques where some specific reagents and extractants are selecting for leaching with heavy metal contaminated soil. Washing of the soil can be defined as the mixing of both metal and soil with a suitable solution (Khaldi et al. 2017).

Immobilization is a method where heavy metal mobility minimized by using special agents. Soil rehabilitation that immobilizes the metal triggers various processes (such as adsorption, surface precipitation, forming complexes with organic ligands and ion exchange) (Mahmoud and El-Kader, 2015).

Table 2.9 represents advantages and disadvantages of remediation methods; physical, biological and chemical.

Table 2.9 Advantage and disadvantages of remediation methods (Khaldi et al., 2017)

Remediation Methods	Advantage	Disadvantage
Physical Methods	Laborious and costly methods	Can be applied to high contaminated sites
Biological Methods	Economical, eco-friendly methods	Time consuming and limited to moderately contaminated sites
Chemical Methods	Rapid and effective methods	Depend on the type of soil, chemical and metal

2.2.2 Removal or recovery of heavy metals from water

Physicochemical methods (chemical precipitation, adsorption, ion exchange, membrane separation, etc.) used to remove heavy metals from wastewater are considered as priorities (Mehta and Gaur, 2005). In addition to physical and/or chemical methods, biological methods for extracting or recovering heavy metals from water are also considered.

2.2.2.1. Chemical methods

The use of chemicals for the removal of heavy metals from water is a classical and often expensive method; furthermore, the removal of pollutants from the water is not sufficient, since these toxic pollutants also cause the problem of disposal with concentrated sludge deposition (Ahmaruzzaman, 2011).

Coagulation – Flocculation is the processes completed in two steps where the particles neutralize the forces that first separate them (coagulation) and then the unstable neutral particles are agglomerated in a second stage (flocculation) (Bilal et al., 2013).

Chemical precipitation is a widely applied technique where metals turn to complex compounds by using chemical agents. The chemical precipitation method is used to treat wastewater with high concentrations and heavy metal ions; but, when the metal ion concentrations are low, precipitation is ineffective (Bilal et al., 2013).

Conventional oxidation methods by using oxidizing agents modifies surface of adsorbents and improves adsorption capacity. Another oxidizing method which is named ozonation in which metals are oxidized is applied with gaseous form of ozone.

Electrochemically treatment is newly method in which contaminated waste water is passed through in a magnetic field. Irradiation, electroflotation, electrocoagulation can be counted as ways of electrochemical treatment methods.

2.2.2.2 Biological Methods

When compared with physical and chemical methods, biological methods are frequently more preferred and alternative way. Biological methods are generally preferred for the treatment of industrial wastewater, because preferred microorganisms (such as bacteria, yeasts, algae and fungi) can be used for many contaminants (Ahmaruzzaman, 2011).

2.2.2.3 Physical methods

Filtration using a membrane such as nanofiltration, reverse osmosis, electrodialysis is a pressure-based method and it is known to perform depending on the size of heavy metals (Bilal et al., 2013).

Adsorption is the known method for treating wastewater containing low concentrations of heavy metals (Bilal et al., 2013). Ion exchange of precious metal ions back from the wastewater (Bilal et al., 2013) is a branch of adsorption techniques, one of the physical treatment methods.

According to large-scale literature studies, it is seen that liquid-phase adsorption is one of the popular methods for removing toxic pollutants from waste water, because if the adsorption process is design appropriately, it is known that high-quality processed waste water will be produced (Ahmaruzzaman, 2011).

In Table 2.10 advantages and disadvantages of physical, chemical and/or biological process are listed for comparing current treatment technologies.

Table 2.10 Current treatment technologies for heavy metals removal involving physical, chemical and/or biological processes (Ahmaruzzaman, 2011)

Physical and/or chemical methods	Advantages	Disadvantages
Oxidation	Rapid process for toxic pollutants removal	High energy costs and formation of by products
Ion exchange	Good removal of a wide range of heavy metals	Absorbent requires regeneration or disposal
Membrane filtration technologies	Good removal of heavy metals	Concentrated sludge production, expensive
Adsorption	Flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants	Adsorbents requires regeneration
Coagulation/flocculation	Economically feasible	High sludge production and formation of large particles
Electrochemical treatment	Rapid process and effective for certain metal ions	High energy costs and formation of by products
Ozonation	Applied in gaseous state: alteration of volume	Short half life
Photochemical	No sludge production	Formation of by products
Irradiation	Effective at lab scale	Required a lot of dissolved O ₂
Electrokinetic coagulation	Economically feasible	High sludge production
Fentons reagents	Effective and capable of treating variety of wastes and no energy input necessary to activate hydrogen peroxide	Sludge generation
Biological treatment	Feasible in removing some metals	Technology yet to be established and commercialized

2.3 Adsorption Theory

Numerous physical, chemical and biological processes known to occur between the boundaries of the two phases are initiated at that interface. The change of the concentration of a particular substance at the interface in the neighboring phases is called adsorption. Depending on the phases in contact with each other, this process can be evaluated in liquid-gas, liquid-liquid, solid-liquid and solid-gas systems (Ova and Övez, 2013; Dabrowski, 2001).

If the process where molecules are deposited at the interface, the term “adsorption” is used; the term “absorption” should be used if it is to be mentioned that molecules penetrate into the solid phase (Ova and Övez, 2013). If both adsorption and absorption occur or cannot be distinguished in the system, the term ‘sorption’ is used (Ova and Övez, 2013; Dabrowski, 2001).

2.3.1 Adsorption types

According to the bonding interaction between surface and molecule; adsorption can result in one of two ways; chemical adsorption (Chemisorption) or physical adsorption (Physisorption). The term of adsorption can be named as physical, if weak Van der Waal’s force can be seen as a binding force. In chemical adsorption, process can be considered as if chemical process.

Different from physical adsorption, adsorption saturation can be seen as a monolayer in chemical adsorption. Figure 2.2 shows the presentation of adsorption processes (Lyubchik et al., 2011). It is known as a rule that the adsorption process is a reversible process that takes place at a temperature close to the critical temperature of an adsorbed material (Ova and Övez, 2013).

In contrast to physical adsorption, in chemisorption, electron density in the region between the adsorbate and the substrate rises and a chemical bond occurs (Kumar et al. 2004). Exothermic physical adsorption is due to the fact that the reduction in free energy is accompanied by entropy of the system (Ova and Övez, 2013; Dabrowski, 2001).

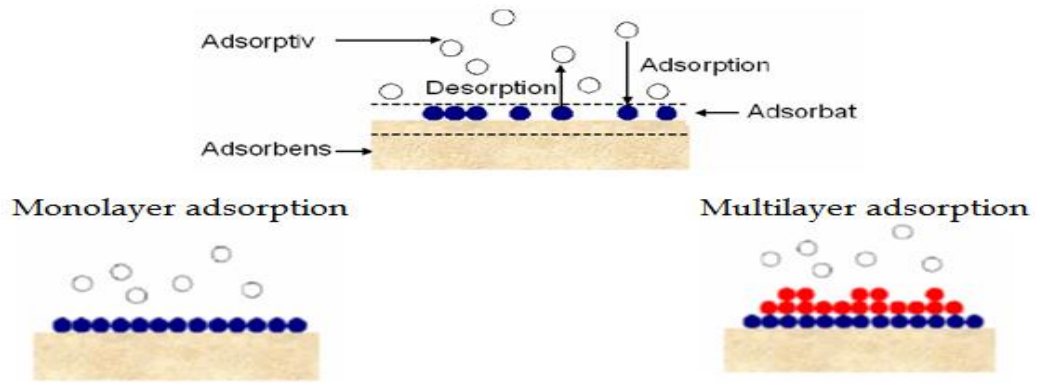


Figure 2.2 Presentation of the typical adsorption process

Kumar et al. (2004) and Ova and Övez (2013) were tabled the typical characteristics of both physical and chemical adsorption processes in Table 2.11

Table 2.11 Typical properties of adsorption processes

Characteristics	Physical Adsorption	Chemical Adsorption
Binding Force	Van der Waal's adsorption	Activated adsorption
Adsorption Saturation	Monolayer/Multilayer	Monolayer
Adsorption Kinetics	Fast, non-activated process	Activated process
Adsorption Temperature	Near or below boiling point temperature of adsorbate	Unlimited range
Nature of adsorption	Non-dissociative and reversible	Dissociative and irreversible
Crystallographic Specificity	Independent of surface geometry	Marked difference for between crystal planes
Adsorption Enthalpy	1 Kcal/mole	50 – 100 Kcal/mole
Potential Force	Lennard-Jones Potential	Morse Potential

2.3.1.1 The physical adsorption (physisorption) theory

There are isotherm equations obtained by physical, mathematical, and experimental studies in literature studies. As different types of adsorption (solid-

gas, solid-liquid, and liquid-gas) have different properties, it is thought that they should be explained by different physical pictures and mathematical operations (Ova and Övez, 2013). Thus, isotherm equations, physical adsorption, mathematical modeling, are the thermodynamic infrastructure (Ova and Övez, 2013; Toth, J., 2001).

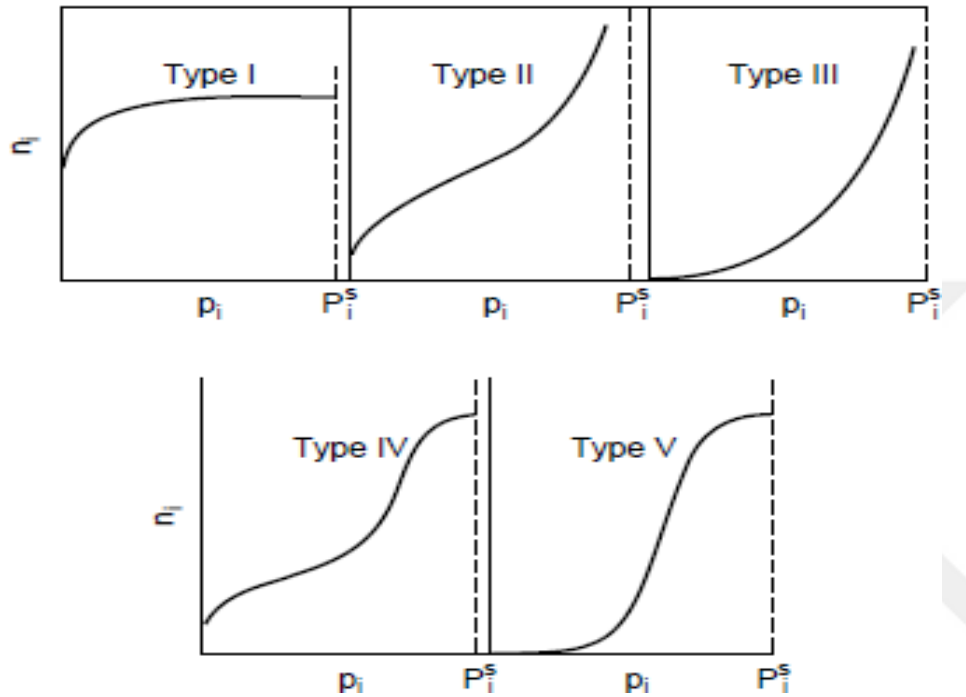


Figure 2.3 Classification of physisorption isotherms where p_i and P_i^s represent pressure and vapor pressure of solute, respectively

According to Perry et al. (1999) there are five classes of physical adsorption isotherms; illustrated in Figure 2.3. listed the statement of physisorption isotherm types represented in Table 2.12 (Thommes et al., 2015).

Table 2.12 Statement of isotherm types

Isotherm Types	Statement
Type I	Typically Langmuir type of monolayer adsorption. -Isotherms are given by microporous materials having mainly narrow micropores (of width < 1 nm) - Isotherms are found with materials having pore size distributions over a broader range including wider micropores and possibly narrow mesopores (< 2,5 nm)
Type II	A multilayer adsorption isotherms are given by the physisorption of most gases on nonporous or macroporous adsorbents
Type III	A multilayer adsorbent-adsorbate interactions are now relatively weak and the adsorbed molecules are clustered around the most favorable sites on the surface of a nonporous or macroporous solid
Type IV	A multilayer adsorption isotherms is a final saturation plateau, of variable length (sometimes reduced to a mere inflexion point) - Capillary condensation is accompanied by hysteresis. This occurs when the pore width exceeds a certain critical width, which is dependent on the adsorption system and temperature - Isotherms are also given by conical and cylindrical mesopores that are closed at the tapered end
Type V	Isotherm shape is very similar to that of Type III and this can be attributed to relatively weak adsorbent–adsorbate interactions

Type I is designated as “favorable isotherm” because curve is concave downward throughout while Type III which is concave upward throughout is “unfavorable isotherm”. Others which are Type II, Type IV, and Type V have one or more inflection points. The “favorable” and “unfavorable” terms refer to fixed-bed continuous systems while the isotherm is known to maintain its compact waveform. During uptake period, a favorable isotherm behaves as an unfavorable isotherm because of the discharge step. This is particularly important for the presence of a favorable regenerative procedure for the effective functioning of the regenerative process (Perry et al, 1999).

2.3.1.2 The chemical adsorption (chemisorption) theory

According to Shustorov (1988), processes related to the interaction energies of atomic and/or molecular chemical bonds on solid surface can be defined as

chemisorption. When the transition metal surfaces are evaluated, the value measured as the chemical adsorption temperature is evaluated as metal-adsorbed binding energy (10-150 kcal/mol). Due to interaction, a new chemical can be observed on the surface of adsorbent; corrosion event is a striking example.

Because of the specificity of material, chemical adsorption may varies from system to system depending on the structure of the chemical and its surface (Ova and Övez, 2013).

In order to understand the surface adsorption of chemical, surface chemistry and heterogeneous catalysis should be understood (Shustorov, 1988). If the catalyst is in solid phase in the chemisorptions process, it is very important for the role of heterogeneous catalysis in the transition metal catalyst (Ova and Övez, 2013).

2.3.2 Adsorbent materials

There are many types of adsorbent materials used for Ni (II) adsorption in literature (Table 2.13) represents adsorption capacities of various organic, inorganic and biological types of adsorbents for processes of Ni (II) adsorption. It may be seen that q_{\max} values vary widely when different adsorbents are evaluated.

Table 2.13 Adsorbents used in the adsorption process of Ni (II) heavy metal

Adsorbate	Material	Adsorbent	q_{max}^* (mg/l/g)	Investigated Parameters	Reference
Ni (II)	Organic	Waste Tea	18,42	Adsorbent dose Concentration pH Agitating rate Temperature	Malkoç et al., 2005
		Waste Tea	120,50	pH Contact time Adsorbent dose	Shah et al., 2015
		Ion-imprinted (IIP) Non-imprinted (NIP) polymers	16,90 5,70	Concentration	Lenobe et al., 2015
		Waste apricot AC	101,01	Concentration pH	Erdoğan et al., 2005
		Coconut coirpith AC	-	pH	Kadirvelu et al., 2001
		Bagasse fly ash	6,49	pH Contact time Single and binary systems	Srivastava et al., 2006
		Rice husk ash	0,083	pH Single and binary systems	Srivastava et al., 2009
		Bael tree leaf powder	1,088	Concentration Adsorbent dose Contact time	Kumar et al., 2009
		Sawdust AC	94,49	Concentration pH Flow rate Temperature Time Reagent type	Nayak et al., 2017
		Pecan nutshell (Carya illinoensis) AC	-	Activation method	Aguayo-Villarreal et al., 2017
	Biological	AC Silica/ AC (2:3) Silica	400	Concentration Adsorbent type	Karnib et al., 2014
		Phragmites australis AC	34,04	Activation method	Guo et al., 2016
	Inorganic	Baker's yeast	11,4	pH Initial metal ion concentration	Padmavathy et al., 2003
		Surface-imprinted silica gel	12,61	pH Flow rate	Jiang et al., 2006
	Molecular imprinting adsorbent, SMIA	6,80	pH Concentration Flow rate Bed height	Li et al., 2007	

* Experimental values

2.4 Continuous Fixed Bed Studies

In order to treated large volume of waste water, continuous processes are generally selected for industries. Fixed bed columns are usually selected for continuously adsorption of pollution (heavy metals, organic pollutants etc.) processes.

When pollutant containing waste water passes through a fixed bed column where the porous adsorbate is unmovable during the sorbate flows through it, initially, most of pollutant is caught on by adsorbent. Pollutant concentration of waste water which leaves the column is almost very low. As adsorption continues, the pollutant concentration in the wastewater is slowly rising and suddenly accelerates after a certain time; and the flow is stopped as soon as this sudden rise or breakthrough occurs (Ova and Övez, 2013). In studies with fixed bed columns, the solution enters the column filled with the sorbent continuously and leaves the system. As a result, at any stage in the system, a complete balance between the solute present in the solution and the adsorbed amount cannot be mentioned (Chowdhury et al., 2015).

In Figure 2.4, considering the zones formed in a fixed bed column, it is known that the flow of contaminated water forms a wave in front of the adsorbent bed and that the wave covering the region near the inlet side is called the mass transfer zone (MTZ). Sorption occurs in the region of mass transfer (Chowdhury et al., 2015).

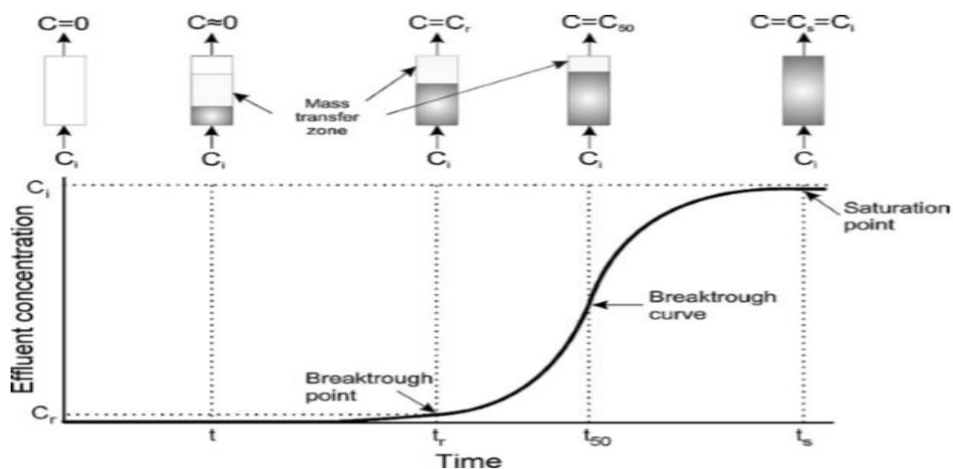


Figure 2.4 Schematic representation of a Breakthrough Curve in fixed bed column (Calero et al., 2009)

If it is desired to make an identification for the breakthrough point, the point at which the ratio between inlet concentration C_0 (mg/L) and outlet concentration C_t (mg/L) at t is from 0,05 to 0,90 as illustrated in Figure 2.5 (Chowdhury et al., 2015). The breakthrough curve is known to indicate the loading behavior during separation from the mixture using a fixed bed and is generally known to be expressed in the normalized concentration defined as the ratio of exit contaminant concentration of the mixture from the column at time t to inlet contaminant concentration (C_t/C_0) with respect to volume of effluent (V_{eff}) or time at fixed bed height (Ova and Övez, 2013).

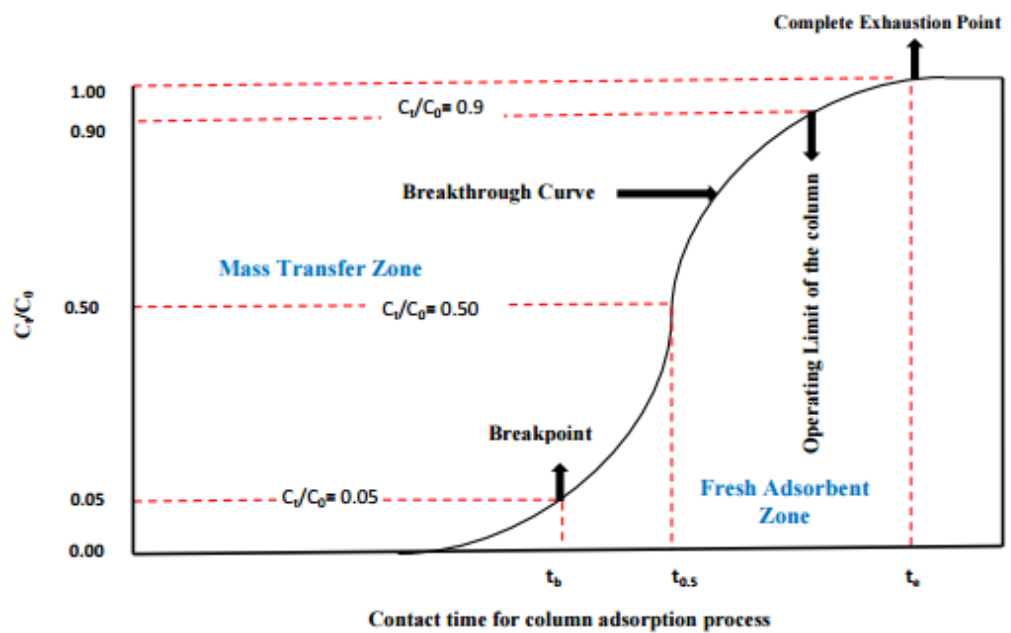


Figure 2.5 Breakthrough curve properties in the fixed bed system as a function of time

Effluent volume is calculated as;

$$V_{eff} = Q t_{total} \quad (1.1)$$

where Q and t_{total} are the volumetric flow rate (mL/min) and time (min), respectively.

The area which is situated under the breakthrough curve (A) can be calculated by integration of adsorbed concentration, C_{ad} (mg/L) with respect to time, t (min) graph is used to determine the maximum column capacity, q_{total} (mg);

$$q_{total} = \frac{Q A}{1000} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad} dt \quad (1.2)$$

m_{total} which represents the total amount of adsorbate sent to column can be calculated as;

$$m_{total} = \frac{C_0 Q t_{total}}{1000} \quad (1.3)$$

Performance of the column (Total removal) versus flow volume can be calculated as;

$$Total\ removal\ \% = \frac{q_{total}}{m_{total}} \times 100 \quad (1.4)$$

Maximum capacity of the column, q_{eq} represents the adsorbate uptake at equilibrium in the column, and is calculated as;

$$q_{eq} = \frac{q_{total}}{X} \quad (1.5)$$

where, q_{total} is the total amount of adsorbate sorbed per gram of sorbate X at the end of total flow time.

C_{eq} (mg/L) is the unadsorbed adsorbate concentration at equilibrium in the column can be calculated as;

$$C_{eq} = \frac{m_{total} - q_{total}}{V_{eff}} \times 1000 \quad (1.6)$$

If the fixed bed column is to be successfully designed, the concentration time profile of system (breakthrough curve) needs to be carefully analyzed. It is naturally difficult to develop a model that accurately identifies the dynamic behavior of adsorption for a fixed bed system (Ova and Övez, 2013). Adsorbate concentration moves through the bed, because of the inoperative process conditions at steady state. It is difficult to derive fundamental transport equations in order to model the fixed bed systems which have to require complex numerical methods to finalize. These referred numerical solutions are not generally hard; however, constantly does not match experimental results, very well. It is known that full-time analytical solutions are not available to differential equation-based models of generally proposed rate mechanisms, except in very restrictive situations. For this reason,

some mathematical models are designed to understand the dynamism in the column and it is known that the models used to determine the performance of the column can be obtained from literature (Aksu and Gönen, 2004; Ova and Övez, 2013).

There are some fixed bed studies represented in Table 2.14 in order to compare the available mode of studies in literature.

In order to analyzed effect of feed flow rate on breakthrough capacity, Bed Volume (mL solution/mL) and Space Velocity (min⁻¹) were calculated as;

$$BV = \frac{Q t}{V} \quad (1.7)$$

$$SV = \frac{Q}{V} \quad (1.8)$$

where, Q is the solution flow rate (mL/min), t is time (min) and V is the wet volume of adsorbent (Recepoglu et.al, 2018).

Table 2.14 Some continuous fixed bed studies

Adsorbent Form	Adsorbent Surface Area (m ² /g)	Adsorbate	Investigated Parameters	Conclusion	Reference
AC	1411,75	Ni (II)	Flow rate pH Concentration	At pH is 4, 20 mg/L initial concentration and 2 ml/min flow rate is effective	Orhan and Erdem, 2017
Powdered AC Fly Ash Bagasse	710,0 485,0 419,5	Ni (II) Cr (VI)	pH Concentration Partical size	Powdered AC has more adsorption capacity for Cr (VI) and Ni (II) removal than bagasse and Fly Ash. Bagasse obtained from a local sugar factory is effective for the removal of chromium. Bagasse and fly ash are efficiently working for the Cr (VI) removal between the pH 6.0–7.0	Raoa et al., 2002
Waste Tea	0,39	Ni (II)	Adsorbent dose Concentration pH Agitating rate Temperature	The capacity of heavy metal raised up with increasing temperature and pH. The max adsorption capacity was obtained at pH 4.0 The lower adsorption capacity of waste tea for heavy metal was obtained in column experiments	Malkoç and Nuhoglu, 2005
Rubber wood sawdust	1400	Pb (II)	Concentration Flow rate Bed height pH	Adsorption capacities were high at the flow rate of 15 mL/min, bed depth of 7 cm, influent concentration of 30 mg/L, and pH of 5.2 Max adsorption capacity is 38.56 mg/g	Biswas and Mishra, 2015
Lignocellulosic Waste	-	Cu (II)	Concentration Bed height Flow rate	The removal efficiency of Cu (II) was found to increase with an increase in sorbent amount (bed height) but decrease with an increase in both inlet concentration and flow rate of the adsorbate	Chowdhury et al., 2015
<i>Sargassum Tenerrimum</i>	-	Cu (II)	Bed height Flow rate	Column studies proved the suitability of this algae and its potential to withstand extreme conditions without losing its metal sorption capacity	Sivaprakash et al., 2010
<i>Sargassum baccularia</i>	-	Cu (II)	Bed height	The breakthrough curves obtained in this study exhibited a very broad trailing edge due to slow intraparticle diffusion within the pores of the PVA-immobilized biomass beads	Hashim et al., 2000

2.4.1 Kinetic adsorption modeling of continuous fixed bed column

2.4.1.1 The Thomas Model

The Thomas solution is one of the most commonly used methods in column performance theory (Ova and Övez, 2013). The Thomas equation is given as;

$$\frac{C_t}{C_0} = \frac{1}{1 + e^{\left[k_{TH} \frac{(q_0 x - C_0 V_{eff})}{v} \right]}} \quad (1.9)$$

where Thomas rate constant is k_{TH} , mL/min.mg; equilibrium adsorbate per gram of adsorbent q_0 , mg/g; amount of adsorbent in column x , g; effluent volume V_{eff} , mL; influent concentration C_0 , mg/L; effluent concentration C_t , mg/L; flow rate v , mL/min.

When the Thomas model is linearized as follow;

$$\ln \left(\frac{C_0}{C_t} - 1 \right) = \frac{k_{TH} q_0 x}{v} - \frac{k_{TH} C_0 V_{eff}}{v} \quad (1.10)$$

k_{TH} and q_0 can be found from plot of $\ln \left(\frac{C_0}{C_t} - 1 \right)$ versus V_{eff} .

2.4.1.2 The Yoon-Nelson Model

Yoon-Nelson model was developed based on the assumption that the rate of adsorption for each adsorbate molecule is proportional to likelihood of adsorb adsorption and the likelihood of adsorbate adsorption on the adsorbate (Ova and Övez, 2013).

The Yoon-Nelson equation is;

$$\ln \frac{C_t}{C_0 - C_t} = k_{YN} t - \tau k_{YN} \quad (1.11)$$

where t represents the breakthrough time, min; τ the required time for 50% breakthrough, min; k_{YN} the rate constant, L/min.

k_{YN} and τ can be estimated by plotting $\ln \frac{C_t}{C_0 - C_t}$ versus t . If the mathematical model correctly accurately describes experimental data, plot should show a straight

line with slope of k_{YN} and intercept $\tau \times k_{YN}$ (Ova and Övez, 2013; Aksu and Gönen, 2004).

2.4.1.3 The Adams-Bohart Model

The Adams–Bohart adsorption model is one of the most general methods in column performance theory, and assumes that the adsorption rate is proportional to not only the residual capacity of the adsorbent, but also the concentration of the inlet solutions (Li et al., 2007).

The Adams-Bohart model is known to be used to describe the first part of the breakthrough curve (Ova and Övez, 2013; Aksu and Gönen, 2004).

The mass transfer rates;

$$\frac{\partial q}{\partial t} = -k_{AB}qC_b \quad (1.12)$$

$$\frac{\partial C_b}{\partial Z} = -\frac{k_{AB}}{U_0}qC_b \quad (1.13)$$

where kinetic constant is represents as k_{AB} ; L/mg.min. When it is assumed that the concentration is considered to be low; $C < 0,15C_0$, and for $t \rightarrow \infty$, $q \rightarrow N_0$, where N_0 represents saturation concentration; mg/L. According to assumption, following equation can be derived with parameters N_0 and k_{AB} ;

$$\ln \frac{C_t}{C_0} = k_{AB}C_0t - k_{AB}N_0 \frac{Z}{U_0} \quad (1.14)$$

where C_0 represents the inlet concentration, mg/L; C_t effluent concentration, mg/L; Z column height, cm; U_0 superficial velocity, cm/min; N_0 saturation concentration of the Adams-Bohart model, mg/L; k_{AB} Adams-Bohart kinetic constant which is mass transfer coefficient, L/mg.min. A straight line was obtained for the system by plotting $\ln \frac{C_t}{C_0}$ versus t , where slope gives the value of k_{AB} (Ova and Övez, 2013; Aksu and Gönen, 2004).

Table 2.15, Table 2.16, Table 2.17 represent parameters evaluated in different studies including kinetic models of Thomas, Yoon-Nelson and Adams-Bohart, respectively.



Table 2.15 Thomas Model parameters evaluated in different studies

Adsorbent	Adsorbate	Thomas Model				References
		k_{TH} (mL/min.mg)	q_0 (mg/L)	Variables	R^2	
Olive Stone	Cr (III)	0,179	0,330	C_i (50 mg/L)	0,80	Calero et al., 2009
Oil palm frond (NaOH modified)	Cu	1,241	0,192	Hydraulic retention time (12 min)	0,98	Salamatinia et al., 2008

Table 2.16 The Yoon - Nelson Model parameters evaluated in different studies

Adsorbent	Adsorbate	Yoon-Nelson Model				References
		k_{YN} (mL/min.mg)	τ (min)	Variables	R^2	
Olive Stone	Cr (III)	7,510	56,900	C_i (50 mg/L)	0,80	Calero et al., 2009
Oil palm frond (NaOH modified)	Cu	0,039	257,000	Hydraulic retention time (12 min)	0,98	Salamatinia et al., 2008

Table 2.17 Adams-Bohart Model parameters evaluated in different studies

Adsorbent	Adsorbate	Adams-Bohart Model				References
		k_{AB} (mL/min.mg)	N_0 (mg/L)	Variables	R^2	
Molecular imprinting adsorbent, SMIA	Ni (II)	0,449	175,000	Flow rate pH Concentration	0,99	Li et al., 2007
Olive Stone	Cr (III)	2,110	95,900	C_i (50 mg/L)	0,93	Calero et al., 2009
Oil palm frond (NaOH modified)	Cu	1,390	2652,000	Hydraulic retention time (12 min)	0,94	Salamatinia et al., 2008

3. MATERIALS AND METHODS

3.1 Materials

Used macro algae, *Gracilaria verrucosa* whose botanical classification is *Rhodophyte*, was collected from İzmir Bay, Izmir, Turkey.

By dissolving the powdered $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Nickel (II) Nitrate Hexahydrate) in deionized water, a stock Nickel solution of 200 mg/L was prepared (Bermudez et.al, 2011); and nickel solutions at different concentrations were set by diluting stock solution.


pH is set at 6 by using 0,1 M HCl (Hydrochloric Acid fuming 37%) or NaOH solution.

3.2 Conditioning of Biomass

The collected algae were washed with deionized water and dried under shadow for 24 h. After drying at ambient temperature, algae were dried in oven at 30 °C till constant weight was obtained. After drying period in oven, particles stored in polyethylene bottles. Properties of *Gracillaria verrucosa* in the 500 mesh-range previously measured by Ovez (2006) were tabulated in Table 3.1 and used directly without any modification.

Algae are filled in column at ambient temperature. Prior filling the *Gracillaria verrucosa* to column, it was hold in distilled water until algae release its reddish color to the water. The purpose of the algae to be kept in water was to observe the swelling prior to column study.

Table 3.1 Properties of *Gracillaria verrucosa*

Properties	<i>Gracillaria verrucosa</i>
Stature	
Color	Red
o.d.(x10 ⁻² m)	0,04
Length (x10 ⁻² m)	2,19
Surface Area (x10 ⁻⁴ m ²)	0,584
Volume (x10 ⁻⁶ m ³)	0,0047
Density (kg/m ³)	1,05
Surface area (m ² /m ³)	12.425,53
C; H; N (%)	29,2; 4,4; 1,3
Protein ²¹ (μg/g)	2700

3.3 Experimental Set-Up

In order to analyze the column performance of *Gracilaria verrucosa*, on removal of Ni (II) from synthetic contaminated water, continuous mode adsorption studies were performed. Figure 3.1 represents the experimental setup used in laboratory.

During the experiments, a glass column having 1 cm inner diameter was used and the tests were carried out under room temperature with up-flow mode by using peristaltic pump with no effluent recycle. The column was cleaned with distilled water before the experiments. Prior to experiment, packed bed was washed with distilled water in up-flow mode in order to remove trapped air in it.

²¹ It is reported that values were obtained after experiments and protein values were reported to be zero denitrification experiments (Ovez, 2006)

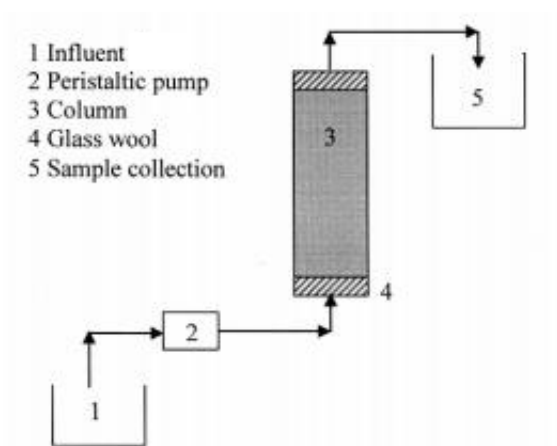


Figure 3.1 Experimental set-up of up-flow fixed bed operation

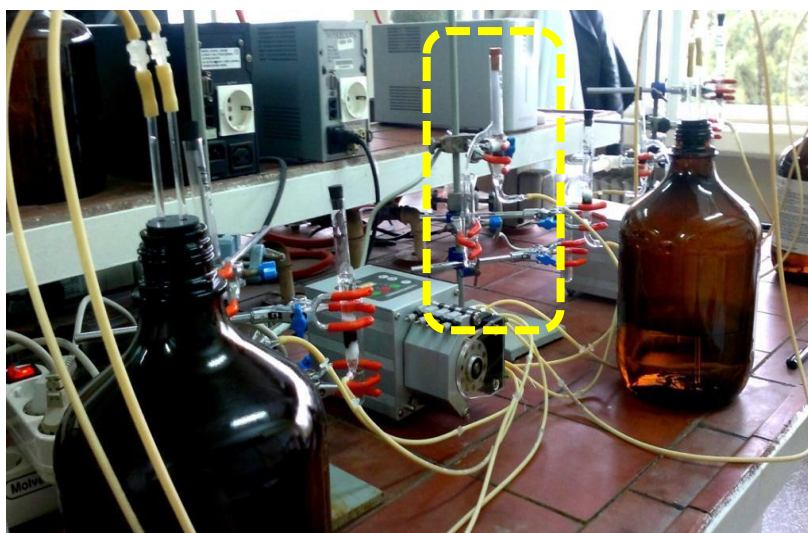


Figure 3.2 Experimental set up of Ni (II) biosorption by *Gracillaria verrucosa*

Metal solutions were pumped through the column by up-flow mode at different flow rates by using a peristaltic pump. Periodically samples were collected at scheduled time intervals.

Experimental set up and test parameters of Ni (II) biosorption by *Gracillaria verrucosa* are represented in Table 3.2 and Figure 3.2, respectively.

In order to research the influence of important parameters on system; initial concentration, flow rate, sorbent amount (in other words bed height, mm) were investigated.

Table 3.2 Test parameters of Ni (II) biosorption by *Gracillaria verrucosa*

Initial concentration (ppm)	10; 50; 100; 200
Flow rate (ml/min)	0,2; 0,3; 0,4; 0,6
Sorbent amount (g)	0,2; 0,4; 0,6; 0,8

3.4 Analysis of Ni (II)

3.4.1 Quantitative analysis by atomic absorption spectrometry

The Ni (II) concentration in the filtered solutions were analyzed by using atomic absorption spectrometry (AAS, VarianspectrAA 10 plus) at a max wavelength of 232 nm.

Before beginning measurement of absorbance of collected samples, the absorbance of 10, 20, 30, 40 and 50 ppm Ni (II) of standard solutions were analyzed in order to plot the calibration curve which was procured prior to each measurement (Figure 3.3).

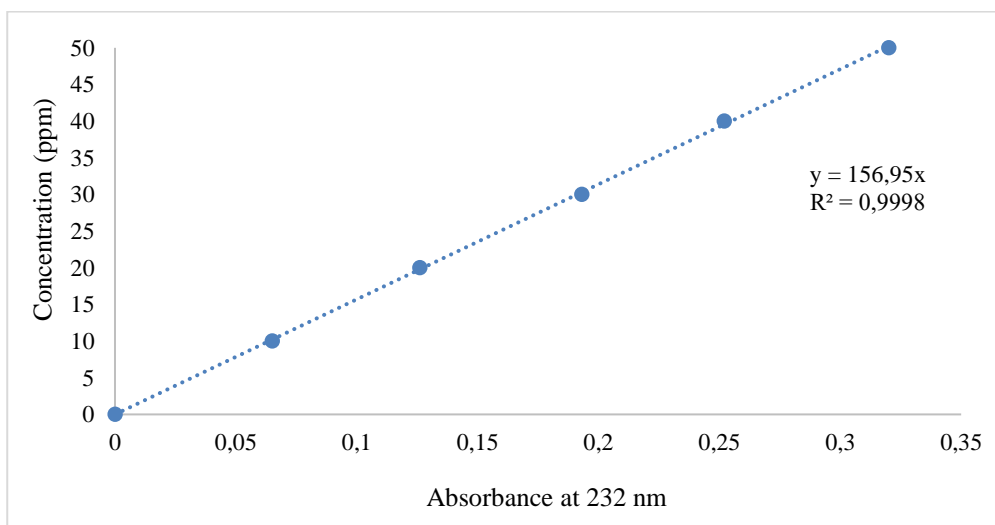


Figure 3.3 The calibration curve for Ni (II) analyzed by using AAS

3.4.2 Computer modeling by MATLAB

Non-linear regression for modeling each setup with including the model parameters is evaluated by using MATLAB R2016B Surface Fitting Tool. Although limit (upper and lower) of model constants varies in terms of each model, all constant is positive because of having their physical quantities. The screen shot of user interface of MATLAB R2016B Surface Fitting Tool represented in Figure 3.4.

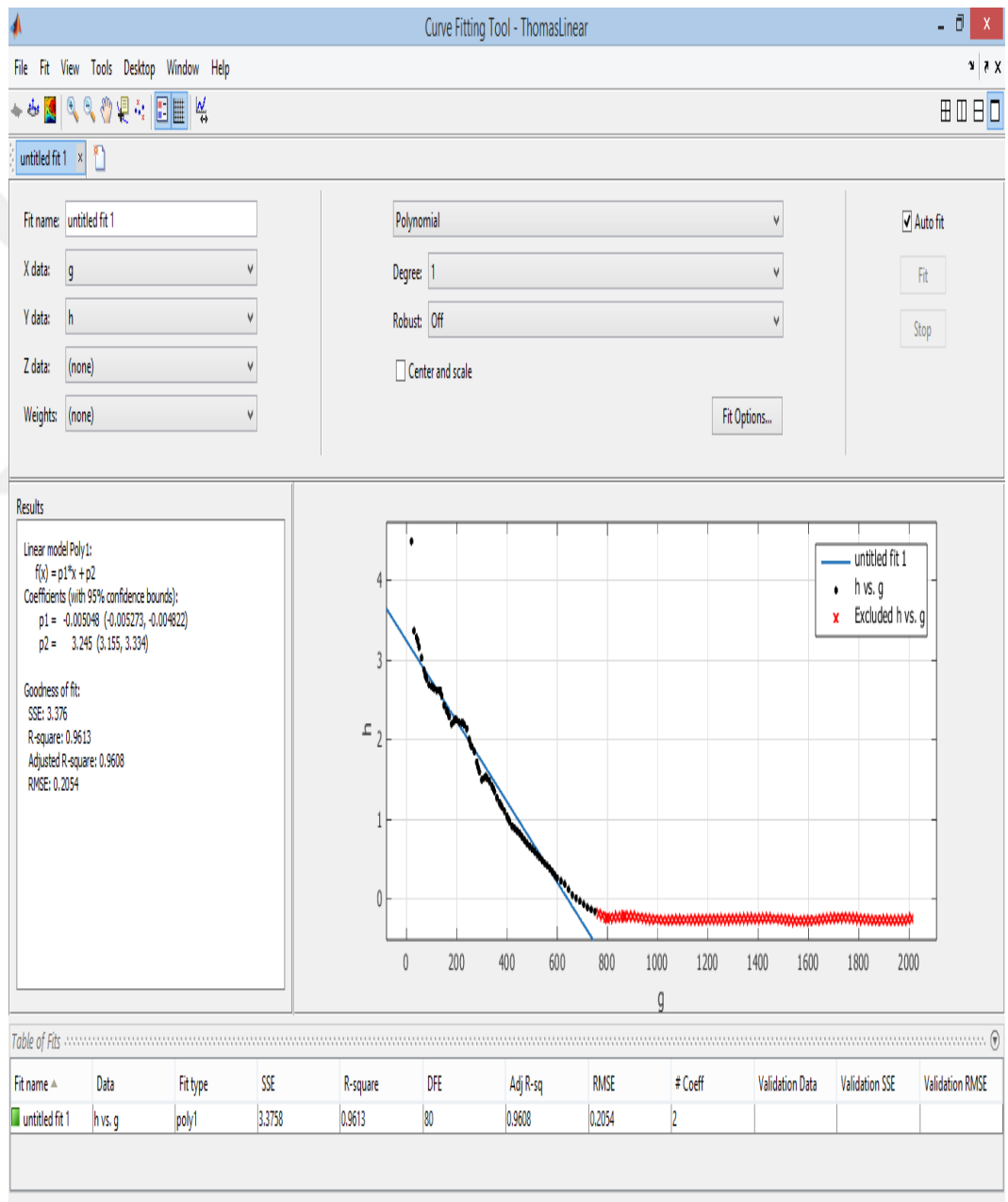


Figure 3.4 Screen-shot of MATLAB Surface Fitting Tool

3.5 Analysis of Adsorbent

3.5.1 Calorimetric analysis of contaminated biomass *Gracillaria verrucosa*

Calorimeter was used to find created heat by burned liquid or solid samples in which closed vessel includes an oxygen rich medium, which is surrounded by water. Figure 3.5 shows the overview of the parts of the calorimeters. The results helped to make decisions according to quality, physiological, physical and chemical substances as well as financial results related to the product.

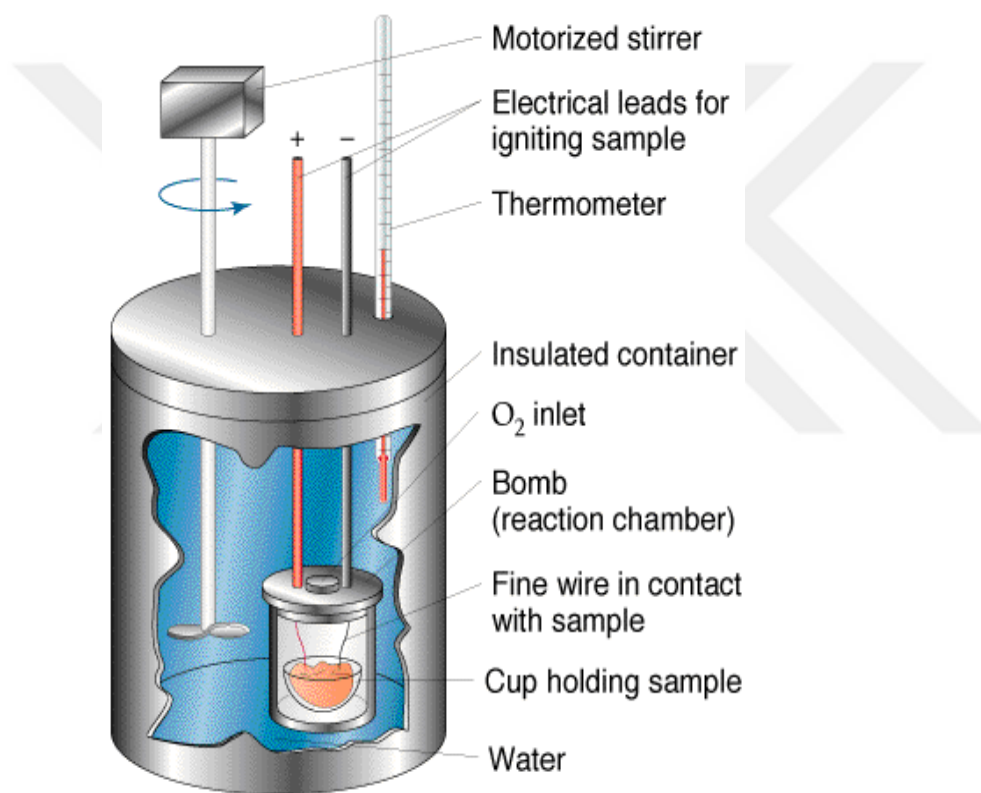


Figure 3.5 Overview of the parts of calorimeter

IKA C 200 model calorimeter was used to analyze calorie of algae. Figure 3.6 represented the calorimeter used at Aten Brantner Waste Management Co. in which sample collection processes of experiments was done.

About 1 g of alga was weighed into crucible and placed into the bomb. The bomb was filled with 30 bars of oxygen (quality 3,5; technical oxygen 99,95 %). The sample was ignited cotton rope which is thread by connection to solid ignition wire inside the bomb. While combustion, temperature can reach to 1000 °C the

pressure increases. All organic materials were burned, and also oxidized, under these conditions.



Figure 3.6 Calorimeter used at Aten Brantner Waste Management Co. in which sample collection processes was completed waste acceptance laboratory

4. RESULTS AND DISCUSSIONS

4.1. Effect of Initial Metal Concentration

In order to investigate the change in Ni (II) concentration, flow rate (also space velocity) and adsorbent amount were kept constant for each state. There are four different initial concentration values; 10 ppm, 50 ppm, 100 ppm and 200 ppm were selected. Breakthrough curves of Ni (II) sorption at different concentration are represented in Figure 4.1.

Primarily, the adsorption occurred rapidly due to the presence of a large number of empty areas. When the initial concentration is increased, it causes a greater impulse to be able to overcome the mass transfer resistance in the liquid phase and the areas rapidly depleted, so the treated water volume is also reduced (Patel, 2019).

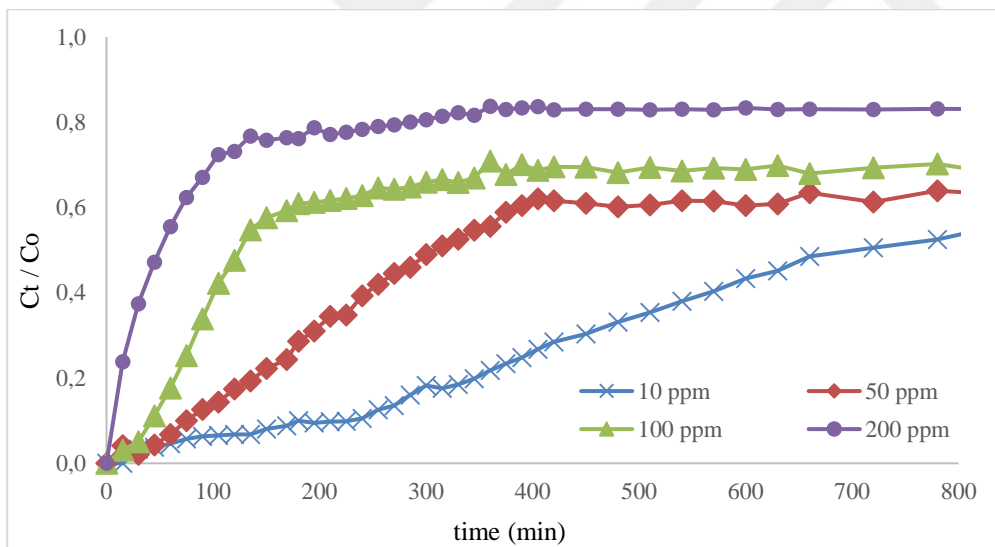


Figure 4.1 Breakthrough curves of Ni (II) sorption by *Gracilaria verrucosa* at different Ni (II) concentration where 0,4 ml/min flow rate and 0,6 g biosorbent amount

It is seen in Figure 4.1, when the initial concentration gets higher, breakthrough time gets smaller, slope of the curve gets sharper; and the highest removal percentage was calculated at 200 ppm concentration as % 89,58 total removal (Table 4.1).

Table 4.1 Calculated q_{eq} values according to different Ni (II) Concentration

Ni (II) Concentration (ppm)	q_{eq} (mg/g)	% Total Removal
10	1,71	82,14
50	1,84	80,77
100	3,14	79,17
200	6,29	89,58

According to activated carbon batch study of *Gracilaria*, similar result was reported where maximum q_{eq} (1,62 mg/g) was observed by using increasing initial Ni (II) concentration from 30 to 70 mg/L (Esmaeili and Ghasemi, 2009). These literature data were similar to this study.

4.2 Effect of Flow Rate on Ni (II) Sorption

In order to verify the effect of flow rate, the inlet concentration of Ni (II) and adsorbent amount were kept constant for each test. There are four different flow rate values; 0,2 ml/min, 0,3 ml/min, 0,4 ml/min and 0,6 ml/min. Breakthrough curves of Ni (II) sorption at different flow rates are shown in Figure 4.2.

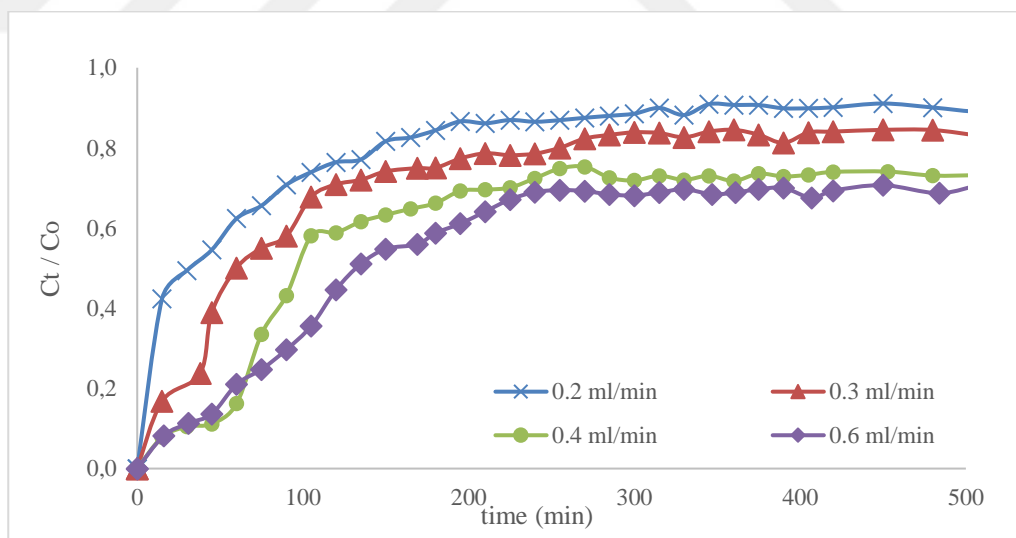


Figure 4.2 Breakthrough curves of Ni (II) sorption by *Gracilaria verrucosa* at different flow rates where 200 ppm Ni concentration and 0,2 g biosorbent amount

It is seen in Figure 4.2, when the flow rate rose up, the breakthrough curves rose up, too. When the low speed flow was evaluated, it was thought that the solution has more time for contact with the biomass and that the solution was kept at a higher rate in the column.

The mass transfer rate is increased so that the amount of adsorbed Ni (II) depending on the height of the unit bed (mass transfer region) increases with the increased flow rate leading to faster saturation (Patel, 2019). This may lead to a reduction in the time required to achieve the breakthrough concentration (Recepoğlu et.al., 2018).

Sorption capacities and % removal data were given in Table 4.2 for each flow rate and the maximum sorption condition was found at 0,2 ml/min flow rate with % 80,00 total removal.

Table 4.2 Calculated q_{eq} values according to different Flow Rate and Space Velocity

Flow Rate (mL/min)	Space Velocity (min ⁻¹)	q_{eq} (mg/g)	% Total Removal
0,2	0,02	13,64	80,00
0,3	0,03	11,82	76,92
0,4	0,04	12,61	78,37
0,6	0,06	12,83	78,74

According to Mangaleshwaran et al., 2015, in the study of Ni (II) adsorption by using treated polyurethane foam in a fixed bed column study, when flow rate was decreased from 60 mg/L, maximum q_{eq} was observed as %78 at 50 mg/L. Besides, similar result was found by using active carbon prepared from grape stalk in a fixed bed column (Orhan and Erdem, 2017); when flow rate was increased from 1 to 4 mL/min, Ni (II) sorption of q_{eq} was decreased from 1,61 to 0,94 mg/g. These literature data were similar to this study.

4.3 Bed Height Effect

In order to examine the bed height effect, influent Ni (II) concentration and flow rate were kept constant for each test. There are four different bed height values; 5 mm, 10 mm, 15 mm and 20 mm which coincide with show the same values as 0,2 g, 0,3 g, 0,4 g and 0,6 g of sorbent amount, respectively. Breakthrough curves of Ni (II) sorption at different bed heights are in Figure 4.3.

It is seen in Figure 4.3, when the bed height gets smaller, the breakthrough curve shifted to left. The time elapsed for the biomass and the interaction increased with the increased amount of adsorbent (Patel, 2019).

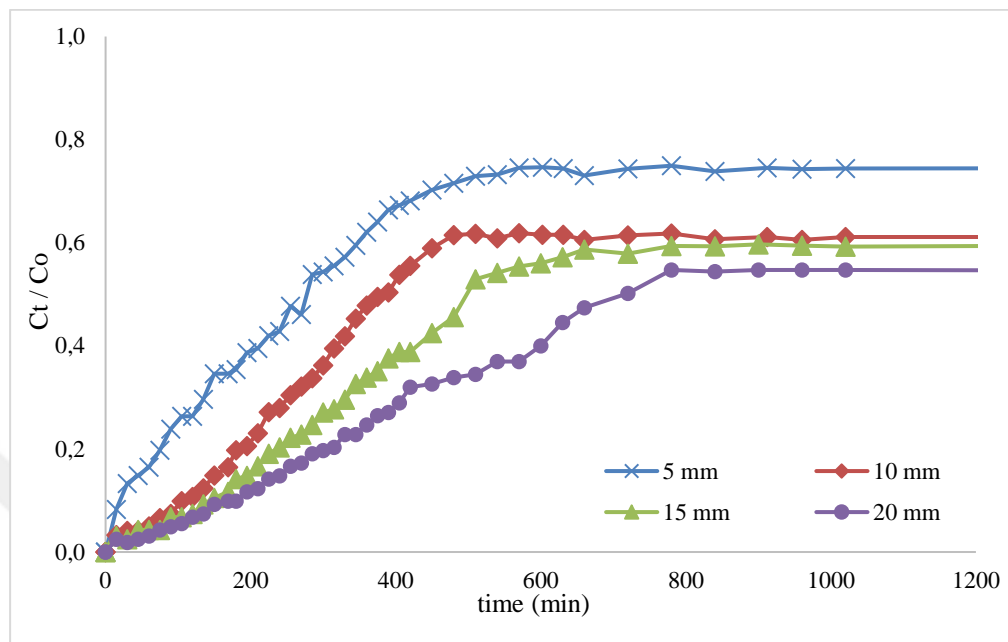


Figure 4.3 Breakthrough curves of Ni (II) sorption by *Gracilaria verrucosa* at different bed height where 0,6 ml/min flow rate and 10 ppm Ni concentration

Wet volume with respect to bed height is a parameter that can be evaluated to interpret with a different perspective. When the wet volume increased from 0,10 to 1,57 mL, % total removal has a tendency to rise.

Table 4.3 Calculated q_{eq} values according to different Bed Height, Sorbent Amount and Wet Volume

Bed Height (mm)	Sorbent Amount (g)	Wet Volume (mL)	q_{eq} (mg/g)	% Total Removal
5	0,2	0,10	28,87	92,06
10	0,3	0,39	29,46	94,44
15	0,4	0,88	34,92	95,83
20	0,6	1,57	44,26	96,79

Calculated values were showed in Table 4.3 for each bed height, sorbent amount and wet volume. Optimum bed height was found as 20 mm with % 96,79 total removal.

According to the sorption study of Ni (II) by using modified rice straw in literature (Sharma and Singh, 2013), when bed height, was selected as 1,5 and 2 cm, it reported that the bed height of 2 cm was provided optimum % total removal. These literature data were similar to this study.



4.4 Application of Models for Thomas, Yoon-Nelson and Adams-Bohart

As mentioned by Salamatina et al. (2008) these models were suitable only for the breakthrough curve, the whole sorption process data is not used. The column data for breakthrough curve part were set to models in order to find constants and other model parameters.

It is seen that model parameters at different conditions, for Thomas Model, when concentration scales up, adsorption capacity of the bed; q_0 , scales up, but rate constant; k_{TH} scale down; when flow rate increase, constant; k_{TH} rises up, but q_0 , is reduced. Since increase in flow rate affects retention time in decreasing trend, ions do not able to spend more time for contacting with bed; as a result, adsorption capacity of bed tends to decrease. Scaling up concentration produces a suitable condition for touching more ions with bed; so, adsorption capacity of bed increases. When the flow rate is minimized and inlet concentration is maximized, the adsorption capacity of bed; q_0 , is maximized. When the flow rate is maximized and inlet concentration is minimized, the adsorption capacity of bed; q_0 , is minimized.

Table 4.4 Using Linear Forms of Kinetic Models for Calculation of Values According to Optimum Condition

Model	Nonlinear Form	Linear Form	Calculated Values According to Optimum Condition (0,2 ml/min; 200 ppm Ni; 0,6 g adsorbent or 2 mm bed height)	
Adams-Bohard	$\frac{C_t}{C_0} = \frac{1}{e^{k_{AB}n_0 \frac{Z}{U} - k_{AB}C_0t} + 1}$	$\ln \frac{C_t}{C_0} = k_{AB}C_0t - k_{AB}N_0 \frac{Z}{U_0}$	$\ln \left(\frac{C_t}{200} - 1 \right) = 0,00016365 \cdot 3157,116 \cdot \frac{Z}{U} - 0,00016365 \cdot 200 \cdot t$	$C_t = \frac{C_0}{e^{(5,7804 - 0,319t)} + 1}$
		$\ln \left(\frac{C_t}{C_0} - 1 \right) = \frac{k_{BA}N_0 \frac{Z}{U} - k_{BA}C_0t}{-k_{BA}C_0t}$		
Thomas	$\frac{C_t}{C_0} = \frac{1}{1 + e^{\left[\frac{k_{TH}(q_0x - C_0V_{eff})}{v} \right]}}$	$\ln \left(\frac{C_0}{C_t} - 1 \right) = \frac{k_{TH}q_0x}{v} - \frac{k_{TH}C_0V_{eff}}{v}$	$\ln \left(\frac{200}{C_t} - 1 \right) = \frac{0,00011625 \cdot 11,940x}{v} - 0,00011625 \cdot 200 \cdot t$	$C_t = \frac{C_0}{e^{(4,164 - 0,02325t)} + 1}$
		$\ln \left(\frac{C_0}{C_t} - 1 \right) = \frac{k_{TH}q_0x}{v} - k_{TH}C_0t$		
Yoon-Nelson	$\frac{C_t}{C_0} = \frac{1}{e^{k_{YN}(\tau - t)} + 1}$	$\ln \frac{C_t}{C_0 - C_t} = k_{YN}t - \tau k_{YN}$	$\ln \left(\frac{200}{C_t} - 1 \right) = 0,0317 \cdot 149,8581 - 0,0317 \cdot t$	$C_t = \frac{C_0}{e^{0,0137(149,8581 - t)} + 1}$
		$\ln \left(\frac{C_0}{C_t} - 1 \right) = k_{YN}\tau - k_{YN}t$		

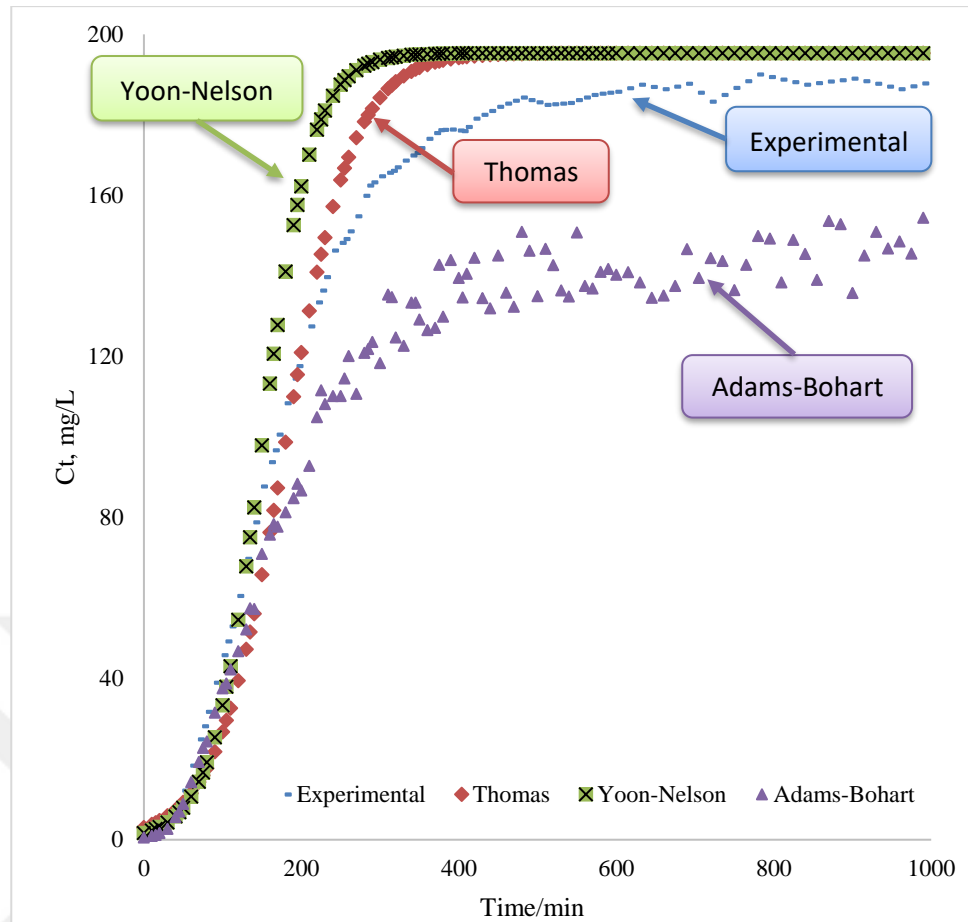


Figure 4.4 Kinetic Models at Optimum Condition where 200 ppm initial Ni Concentration; 0,2 ml/min flow rate; 0,6 g sorbent amount

Table 4.4 represents nonlinear and linear forms of kinetic models with calculated values according to optimum condition. Figure 4.4 also represents a comparison graph with linearized forms of model equations in Table 4.4. When models are compared each of them, Yoon-Nelson and Thomas could be selected more suitable kinetic models more than Adams-Bohart Model.

Those results show the accuracy of flow rate and concentration differences mechanisms. The same result was concluded by Malkoç and Nuhoğlu (2006) for removal of Ni (II) ions from aqueous solutions using waste of tea factory and Ova and Övez (2013) for modeling the potential of microorganisms on the removal of 2,4-dichlorophenoxyacetic acid from aqueous solutions by adsorption. Additionally, when the bed height is increased, rate constant; k_{TH} is decreased and the adsorption capacity of bed is increased.

For Yoon-Nelson Model; the inlet concentration and flow rate scale up, frequently, rate constant; k_{YN} scale up and required time for 50% adsorbate breakthrough; τ scale down. τ has a minimum value at parameters of 200 ppm initial concentration and 0,4 mL/min flow rate, since increase in flow rate decreases retention time of solution in the column and increase in concentration increases the chance of come across of ion and adsorbate as a result capacity of bed loaded sharply. τ has a maximum value at parameters of 10 ppm initial concentration and 0,2 mL/min flow rate, since decrease in flow rate increased retention time of solution in the column and decrease in concentration decreases the chance of come across of ion and adsorbate as a result capacity of bed loaded slowly. The same results were observed by Aksu and Gönen (2004) for biosorption of phenol by immobilized activated sludge in a continuous packed bed. Additionally, when the bed height increased, rate constant of k_{YN} decreased and τ increased. Maximum τ was investigated when operational condition at maximum bed height with minimum rate constant.

For Adams-Bohard Model; increase in flow rate maximizes the kinetic constant; k_{AB} ; since in the primary part of adsorption, external mass transfer is dominant for overall system kinetics. Maximum adsorption capacity (N_o) scales up with scaling up inlet concentration. Because of that, the maximum N_o is observed at 200 ppm inlet concentration as verified by Aksu and Gönen (2004) for biosorption of phenol by immobilized activated sludge in a continuous packed bed. Additionally, k_{AB} and N_o reduce with rising up the height of bed. N_o was observed by the maximum bed height with minimum k_{AB} .

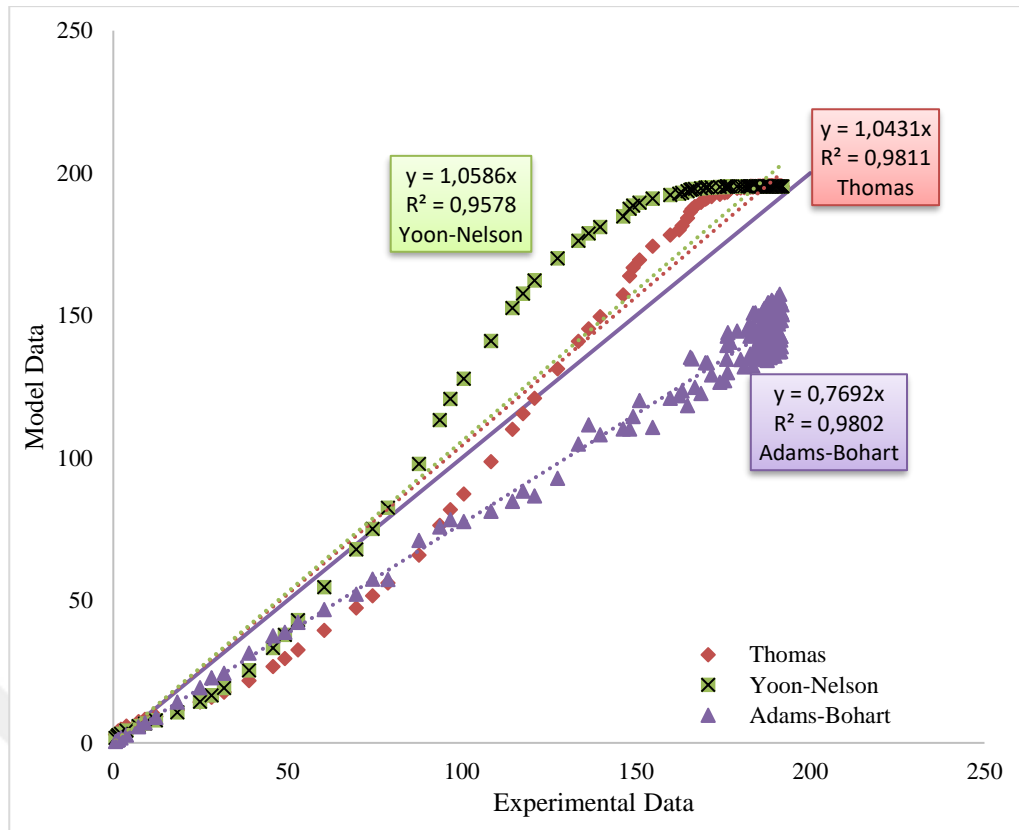


Figure 4.5 Kinetic Models vs. Experimental Data at Optimum Condition where 200 ppm initial Ni Concentration; 0,2 ml/min flow rate; 0,6 g sorbent amount

Figure 4.5 shows the comparison of kinetic models vs. experimental data according to kinetic models. The linear equations of Thomas and Adams – Bohart Kinetic Models have highest R^2 values when compared with Yoon – Nelson Kinetic Model.

In order to find the best fitted model, error function analysis was used. Error function analysis is an optimization method used to evaluate the compatibility of experimental data with the most accurate model (Biswas and Mishra, 2015).

Root Mean Square Error (RMSE) was utilized in order to determine the best fitted model. RMSE was calculated (Mentaschi et.al., 2013);

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (S_i - O_i)^2} \quad (3.1)$$

where, S_i is the i th simulated data, O_i i th observation and N is the number of observations available for the analysis.

Table 4.5 Error function values of selected kinetic models at optimum condition

Adams – Bohart		Thomas		Yoon – Nelson	
RMSE	R ²	RMSE	R ²	RMSE	R ²
0,589	0,909	0,444	0,919	0,468	0,931

The adequacy of the fitted sorption isotherm models can be evaluated by means of the coefficient of determination (R^2), the root mean squared error (RMSE), or sum of square errors (SSE). The R^2 quantifies the proportion of total variation explained by the regression. The closer the R^2 values are to 1, the better is the fit. The RMSE and the MRD are both measures of the deviation between the experimental and predicted data. Low values for the RMSE and SSE indicate a high ability of the model to describe the experimental behavior (Ruiz-Lopez and Herman Lara, 2009). Since R^2 is a relative measure of fit and RMSE is an absolute value for the experimental and predicted data, Thomas Model can be suggested as the best fitted model (Table 4.5).

4.5 Determination of Calorific Value of Biomass

In order to compare results of calorific value of *Gracilaria verrucosa*, data taken from Aten Brantner Waste Management Co. waste acceptance laboratory were utilized and tabulated in Table 4.6 where calorific test of *Gracilaria verrucosa* was done after biosorption process where alga having Ni (II) ions.

Waste acceptance laboratory of Aten Brantner Waste Management Co. works for testing the industrial wastes in order to send them a facility focus to prepare refused dried fuel (RDF). RDF facilities work for preparing an alternative fuel according to coal types for cement plants by using industrial wastes. Preparing of RDF includes, simply, a resizing and mixing process of wastes; however, reaction and interaction of wastes must be considered.

Information in Table 4.6 was important for both RDF facilities which combine wastes and waste supplier Aten Brantner Waste Management Co, since calorific value of materials was dominant criteria when compare advantage of waste type.

Table 4.6 Results of calorific value tests done at Aten Brantner Waste Management Co. waste acceptance laboratory

Type	Organic Material	Calorific value (Kcal/Kg)
Waste Type	Ni Contaminated <i>Gracilaria verrucosa</i>	3.770 (this study)
	Dye sludge waste	2.000 – 3.500
	Contaminated clothes	3.000 – 10.000
	Washing wastes	2.500 – 3.500
	Sewage sludge	2.500 – 3.500
Coal Type	Lignite coal	3.000
	Soma coal	5.500
	Imported coal	6.000

As a result, cement plants accepted criteria which is seen in Table 4.7, *Gracilaria verrucosa* including Ni (II) ions has an acceptable calorific value when compare the other organic both waste materials which combine for preparing RDF and coals.

Table 4.7 Waste (as a Refused Dried Fuel, RDF) accepted criteria of Cement Plants

Criteria	Value
Calorific Value	3.000 – 3.500 Kcal/Kg
Halogen	Max %1 (w/w)
Humidity	Max %20 (w/w)

According to Table 4.7, if *Gracilaria verrucosa* including Ni (II) ions halogen free upper limit %1 (w/w) and dried with maximum %20 (w/w) humidity, it is a desired organic material for RDF menu.

5. CONCLUSION

The contamination of water sources with various materials, especially heavy metals which poise not only human but also other species and environment is a major interest, recently.

In this thesis, removal of Ni (II) ions from synthetic waste water with dried alga using adsorption technique was analyzed. Continuous mode studies were investigated.

Optimum initial concentration was found as 200 ppm. These results show that change in concentration slope operates the breakthrough time and saturation rate. It means that there is a concentration dependent diffusion process. When the initial concentration rises up, the Ni (II) loading rate improves; however, it is seen decrease in mass transfer driving force where decrease in the adsorption zone length, too.

Optimum flow rate was found as 0,2 ml/min. It means that increase in flow rate adsorption capacity of the system get reach the equilibrium faster. As a result of this, mass transfer efficiency of Ni (II) ions affected, negatively. At lower inflow, breakthrough time achieving saturation gets faster. At higher inflow, the breakthrough curves approach as vertical, and, the break point time is reduced like as adsorbed ion concentration. As a result, in order to reach the maximum adsorption capacity, lower flow rate and higher inlet concentration conditions should be preferred in continuous systems.

Optimum bed height was selected 20 mm; other words, optimum sorbent amount is 0,6 g. Increment of bed height results increment of breakthrough time. Rising up total bed capacity affects the retention time in an upward direction. Since these reasons affect, extended breakthrough time process and bed capacities were achieved higher adsorbent masses.

It was observed that the bed capacity rises up, if the inlet Ni (II) concentration and bed height are raised up, the flow rate is reduced. The breakthrough time reduced with increment of loading time of ions.

The experimental data were examined according to three mathematical continuous models which are Thomas, Yoon-Nelson and Adams-Bohard. When the correlation coefficient was compared, between these three kinetic models, Thomas Model preferable suited to experimental data. For the Thomas Model, the highest adsorption capacity of bed was investigated at highest bed height with the lowest rate constant, since adsorbate amount and retention time were increased.

The calorific value of used adsorbate was analyzed and compared with not only industrial waste but also coal types. According to cement plants waste accepted criteria, it is considered that used adsorbate would be a desired organic material for RDF menu.

As a conclusion, dried and grinded red marine algae *Gracilaria Verrucosa* has been found to be useful and effective biosorbent material under the optimum conditions. Additionally, it was seen that there was a calorific value of waste after biosorption and it was a desired organic material for RDF menu.

After the adsorption studies, Ni (II) content on to the surface of the adsorbent should be recovered by desorption for the purpose of regain Ni (II) content and investigate reusability of the adsorbent. Additionally, by using same adsorption material, multi-metal system and/or real industrial waste water should be investigated.

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ACKNOWLEDGEMENT

I would like to express my deepest gratitude to my advisor Prof. Dr. Bikem Övez for her valuable mentorship, supervision, continuous support and encouragement throughout this study.

I sincerely wish to thank Prof. Dr. Oğuz Bayraktar for leading, trusting and supporting me to start and complete the study.

I heartily wish to thank Dr. Chemical Engineer Duygu Ova Özcan for her assistance and MSc. Chemical Engineer Ayça Ata for her support.

I would also give my special thanks to my former managers who support me to start and make possible the conditions for carrying all experiments at Aten Brantner Waste Management Co. Laboratory.

I am greatly very thankful to my parents Fatma Sermin Karacığa and Yasin Karacığa; and also, my brother Korgün Ersin Karacığa who are always ready to help, encourage and support me from start to final of the study.

Lastly, I am special thankful to my colleague Chemical Engineer Yusuf Azmi Akbaş who support and encourage me.

Finally, I would like to thanks to my husband Ramazan Bahar and my little son Arda Bahar for understanding, encouraging and supporting me to complete the study.

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