MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES

MATHEMATICAL MODELING OF Ni^{2+} BIOSORPTION BY *SCHIZOSACCHAROMYCES POMBE* USING UNIVERSAL SIGMOID APPROACH

RUMEYSA BÜKCÜ

M.S. THESIS
Department of Bioengineering

ADVISOR
Prof. Dr. Ahmet Alp SAYAR

ISTANBUL, 2014

MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES

Rumeysa Bükcü, a Master of Science student of Marmara University Institute for Graduate Studies in Pure and Applied Sciences, defended her thesis entitled "**Mathematical Modelling of Ni^{2+} Biosorption by *Schizosaccharomyces pombe* using Universal Sigmoid Approach**", on September 4, 2014 and has been found to be satisfactory by the jury members.

Jury Members

Prof. Ahmet Alp SAYAR (Advisor)
Marmara University .....(SIGN).....

Prof. Dilek KAZAN (Jury Member)
Marmara University .....(SIGN).....

Prof. Arif Nihat GÜLLÜOĞLU (Jury Member)
Marmara University .....(SIGN).....

APPROVAL

Marmara University Institute for Graduate Studies in Pure and Applied Sciences Executive Committee approves that Rümeysa Bükcü be granted the degree of Master of Science in department of Bioengineering, Bioengineering Program on 10.10.2014
(Resolution no:2014/22-04)

Director of the Institute
Prof. Prof. Dr. Uğur YAHŞİ
Müdür

ACKNOWLEDGEMENT

It would not have been possible to write this doctoral thesis without the help and support of the kind people around me, to only some of whom it is possible to give particular mention here.

This thesis would not have been possible without the help, support and patience of my principal supervisor, Prof. Ahmet Alp SAYAR, not to mention his advice and unsurpassed knowledge. His mentorship was paramount in providing a well-rounded experience consistent my long-term career goals. I am not sure many graduate students are given the opportunity to develop their own individuality and self-sufficiency by being allowed to work with such independence.

The good advice and support of Prof. Dr. Dilek KAZAN has been invaluable on both an academic and a personal level, for which I am extremely grateful. Also special thanks go to Assistant Professor N. Alpagu SAYAR who helped me to materialize this Project.

I would like to thank the jury members of my thesis for their attention.
This thesis would not have been possible without the help, good advice, support and friendship of Selçen DURMAZ ŞAM for which I am extremely grateful.

I would also like to thank all of my friends especially Nilay BÜDEYRİ GÖKGÖZ, Ceyda KULA in Bioengineering Department Laboratory for their support and friendship during the project.

Above all, I would like to thank my daughter Neva for her love and great patience at all times. My parents have given me their unequivocal support throughout, as always, for which my mere expression of thanks likewise does not suffice. I would like to acknowledge the financial, academic and technical support of the Marmara University Scientific Research Committee (Project No: FEN-C-YLP-040712-0280).

TABLE OF CONTENTS

	PAGE
ACKNOWLEDGEMENT	**i**
TABLE OF CONTENTS	**iii**
ÖZET	**iv**
ABSTRACT	**vi**
SYMBOLS	**vii**
ABBREVIATIONS	**viii**
LIST OF FIGURES	**ix**
LIST OF TABLES	**x**
1. INTRODUCTION	**1**
1.1 Heavy Metals	1
1.2 Nickel as Heavy Metal	2
1.3 Physicochemical Properties Affecting Toxicity of Nickel	3
1.3.1 Solubility	4
1.4 Biosorption	5
1.5 Biosorption Mechanism	6
1.5.1 Physical Adsorption	9
1.5.2 Ion Exchange	9
1.5.3 Complexation	11
1.5.4 Precipitation	12
1.5.5 Reduction	13
1.5.6 Co-ordination	13
1.5.7 Chelation	13
1.6 Biosorption Equilibrium Models	14
1.6.1 Langmuir Isotherm Model	15
1.6.2 Freundlich Isotherm Model	16
1.6.3 Sips Isotherm Model	17
1.6.4 Redlich-Peterson Isotherm Model	18
1.6.5 Radke–Prausnitz Isotherm Model	19
1.6.6 Kahn Isotherm Model	19
1.6.7 BET Isotherm Model	20

1.6.8 Dubinin–Radushkevich Isotherm Model 20
1.6.9 Aim and Scope 21
2. MATERIAL AND METHOD 22
2.1 Biosorption Experiments 22
2.1.1 Stock solutions 22
2.1.2 Detection of Ni (II) concentration 22
2.1.3 Best Fit Curve Analysis 23
2.1.3.1 The Levenberg-Marquardt Method 23
2.2 Model Development 24
2.3 Model Validation 25
2.3.1 Chi-Square Test 25
3 RESULTS AND DISCUSSION 26
3.1 Biosorption Experiments 26
3.2 Effect of pH 26
3.3 Effect of initial Ni (II) concentration 28
3.4 Effect of temperature 29
3.5Equilibrium Studies 31
3.6Biosorption Kinetics 38
3.7 Model Parameters and Simulation Results 40
3.8Model Verification and Validation 40
4. CONCLUSIONS 41
REFERENCES 44
ÖZGEÇMİŞ

ÖZET

Metallerle kirlenmiş atık suların uygun olmayan yöntemlerle arıtımı ve bertarafı toprak ve su kirliliği problemlerine yol açmaktadır.Çevrenin toksik ağır metaller ile kirlenmesi endüstriyel gelişme nedeniyle giderek artan dünya çapında bir sorundur.Ağır metallerin, canlı tarafından dokularda biriktirilebilmesi ve metabolizmada bu ağır metallerin neden olabileceği toksik etkiler tartışılmaz bir gerçektir.Bu durum çevre ve insan sağlığını olumsuz yönde etkilemektedir. Ağır metallerin gerek endüstriyel atık sulardan ve gerekse ağır metal ile kirlenmiş/kirletilmiş çevresel su kaynaklarından uzaklaştırılmasında çeşitli kimyasal ve fiziksel süreçler kullanılmaktadır. Ancak bu yöntemlerin ekonomik olmayışları ve elde edilen arıtım düzeyinin yeterli olmaması nedeniyle bu alanda önemli bir potansiyele sahip mikroorganizmaların etkin bir şekilde kullanıldığı ve tercih edildiği görülmektedir (Volesky, 1990). Mikroorganizmalara özgü hücre yüzeyi özellikleri sıvı fazdaki ağır metal iyonlarının tutulmasını sağlamaktadır. Biyosorpsiyon –inaktif hücreler tarafından belirli molekül ve iyonların tutulması- ve biyobirikim –canlı mikroorganizma hücreleri tarafından belirli molekül ve iyonların tutulması- süreçleri konvansiyonel metotlara karşı belirgin avantajlara sahiptir. Bu işlemler sonunda kimyasal içerikli çamur açığa çıkmaz, işletimi kolaydır ve düşük konsantrasyonlarda kirletici içeren çok miktarda atıksuyun arıtımı için bile daha az masraflıdır. Mikroorganizmaların sahip oldukları biyomoleküller gerek canlı ve gerekse ölü biyokütlelerin yüksek bir metal ilgisine sahip olmasını sağlamakta ve dolayısıyla çok yüksek bir biyosorpsiyon kapasitesi sunmaktadırlar. Bu amaçla çeşitli bakterilerin, fungusların ve alglerin kullanıldığı bilinmektedir (Kapoor ve Viraraghavan, 1998; Brady ve Duncan 1994).Ağır metal gideriminde kullanılacak olan mikroorganizmanın iyi bir biyosorbant olmasının yanı sıra ekonomik olaraküretilebilmesi de önemlidir. Pek çok endüstriyel alanda yaygın olarak kullanılan mayalar ekonomik olarak üretilebilmeleri, kolay elde edilebilir olmaları, çevresel değişimlere karşı hassas olmamaları gibi nedenlerle ağır metal giderim amacıyla kullanılabilecek önemli bir kaynaktır (Gupta ve ark. 2006).Bu çalışmada tek hücreli mayaların bir türü olan *Schizosaccharomyces pombe*, Ni^{2+} ayırma yöntemi için biyokütle olarak kullanılmıştır. Biokütle, artan Ni^{2+} konsantrasyonu ve değişen sıcaklık, ajitasyon hızı vb. gibi deneysel koşulları değiştirilerek, ilgili verileri değerlendiren matematiksel bir model

geliştirilmiştir. Modelin güvenilirliği vedoğruluğu istatistiksel ki-kare yöntemi ile test edilmiştir. Bu yaklaşım, incelenen işlemin önemli bir simülasyon açıklaması olmuştur.

ABSTRACT

The utilization of microorganisms as biosorbents for the removal and recovery of heavy metals from industrial wastewaters has become a major alternative to conventional methods. Biosorption is one of those methods which implement microorganisms for that purpose. Microorganisms, active or inactive, can adsorb dissolved metals by courtesy of their special membrane characteristics. The design of the appropriate equipment and the estimation of optimum process input values have a great importance concerning the analysis and synthesis of the process under investigation. In order to obtain a dependable optimization scheme, the evaluation of a wide collection of biosorption data is required. Instead of using a time consuming and expensive database matrix, the development of a suitable mathematical model depending on process principles and a truncated experimental data may be more efficient approach to establish an optimization result.A satisfactorily accurate model of a system can be used to predict outcomes under varying conditions without the need for actual experimentation and observation. In this study, the inactiveand dried biomass of *Schizosaccharomycespombe*, a species of unicellular yeasts, was used as biomass for the bioremoval of Ni^{2+}.S.pombe (972) was grown at its optimum media.Biosorption experiments were done at varying experimental conditions such as pH, temperature, metal concentration. The biomass was added to a 100 mL Ni (II) solution at predetermined initial metal (1, 2, 5, 10, 50 mg g^{-1}), temperature(25, 30, 35, 50 C°)and pH (4.0, 5.0, 6.0) values to get a mixture of 1 g L^{-1}sorbent content. Biosorption operations were performed in 250 mL Erlenmeyer flasks which were agitated in an incubator shaker at 150 rpm for a total period of 2 h. As a result, effects of temperature, starting metal concentration and pH were investigated during the experiments. Autofit 3.0 program was used for the equilibrium studies by trying different isotherms running with different algorithms such as Levenberg-Marquardtand Maximum Inherit Optimization.A mathematical model was developed to evaluate the relevant data. Reliability and accuracy of the model were tested using chi-square statistical method. This approach is a significant simulated description of examined process.

SYMBOLS

C_i : initial Ni (II) concentration, mg/L

C_f : final Ni (II) concentration in solution, mg/L

C_e : residual Ni (II) concentration at equilibrium, mg/L

q_e : Ni (II) uptake at equilibrium, mg/g

Q^0 : the maximum metal uptake, mg/g

K_L : Langmuir isotherm equilibrium constant, L/mg

K_F : Freundlich isotherm constant, (mg/g) $(mg/L)^{-1/n}$

n_F : Freundlich isotherm exponent

K_S : Sips isotherm constant, (mg/g) $(mg/L)^{-\beta}$

a_S : Sips isotherm constant, $(L/mg)^{\beta}$

β_S : Sips isotherm exponent

K_{RP} : Redlich-Peterson isotherm constant, L/g

a_{RP} : Redlich-Peterson isotherm constant

β_{RP} : Redlich-Peterson isotherm exponent

b_K : Khan isotherm constant

n_K : Khan isotherm exponent

K_{BET} : BET isotherm constant

n_{BET} : BET isotherm exponent

B_{DR} : Dubinin–Radushkevich isotherm constont

R^2 : correlation coefficient

χ^2 : Pearson's cumulative test statistic

ABBREVIATIONS

GA1 : The given name for mutant *S. pombe* strain by the generators

AAS : Atomic Absorption Spectrophotometer

BET : Brunanuer-Emmett-Teller isotherm model

RMSE : Root Mean Square Error

REL :Reference Exposure Level

AAS : Atomic Absorption Spectrometry

EPS : Exo-PolySaccharides

LIST OF FIGURES

SAYFA

Figure 3.2: The effect of pH on the equilibrium uptake of Ni (II) by *S. pombe* (Temperature: 25 ^{o}C ; initial Ni (II) conc.: 10 mg/L ; biosorbent dose: 1.0 g/L ; agitation rate: 150 rpm.) 27

Figure 3.2.1: The effect of pH on the equilibrium uptake of Ni (II) by *S. pombe* (Temperature: 25 ^{o}C ; initial Ni (II) conc.: 10 mg/L ; biosorbent dose: 1.0 g/L ; agitation rate: 150 rpm.) 27

Figure 3.2.2: The effect of pH on the equilibrium uptake of Ni (II) by *S. pombe* (Temperature: 30 ^{o}C ; initial Ni (II) conc.: 10 mg/L ; biosorbent dose: 1.0 g/L ; agitation rate: 150 rpm.) 28

Figure 3.2.3: The effect of pH on the equilibrium uptake of Ni (II) by *S. pombe* (Temperature: 35 ^{o}C ; initial Ni (II) conc.: 10 mg/L ; biosorbent dose: 1.0 g/L ; agitation rate: 150 rpm.) 28

Figure 3.2.4: The effect of pH on the equilibrium uptake of Ni (II) by *S. pombe* (Temperature: 50 ^{o}C ; initial Ni (II) conc.: 10 mg/L ; biosorbent dose: 1.0 g/L ; agitation rate: 150 rpm.) 28

Figure 3.3: The effect of initial Ni (II) concentration on equilibrium uptakes of*S. pombe* at various temperatures with the fit lines generated by Freundlich sorption model (pH= 5.0; biosorbent dose: 1.0 g/L; agitation rate: 150 rpm 29

Figure 3.5.1: Equilibrium biosorption data obtained at pH 4.0 and 25 ^{o}C with fit lines created by Langmuir and Freundlich isotherms. 32

Figure 3.5.2: Equilibrium biosorption data obtained at pH 4.0 and 30^{o}C with fit lines created by Langmuir and Freundlich isotherms. 33

Figure 3.5.3: Equilibrium biosorption data obtained at pH 4.0 and 35^{o}C with fit lines created by Langmuir and Freundlich isotherms. 33

Figure 3.5.4: Equilibrium biosorption data obtained at pH 4.0 and 30^{o}C with fit lines created by Langmuir and Freundlich isotherms. 34

Figure 3.5.5: Equilibrium biosorption data obtained at pH 5.0 and 25 ^{o}C with fit lines created by Langmuir and Freundlich isotherms. 34

Figure 3.5.6: Equilibrium biosorption data obtained at pH 5.0 and 30^{o}C with fit lines created by Langmuir and Freundlich isotherms. 35

Figure 3.5.7: Equilibrium biosorption data obtained at pH 5.0 and 30^{o}C with fit lines created by Langmuir and Freundlich isotherms. 35

Figure 3.5.8: Equilibrium biosorption data obtained at pH 5.0 and 50^{o}C with fit lines created by Langmuir and Freundlich isotherms. 36

Figure 3.5.9: Equilibrium biosorption data obtained at pH 6.0 and 25^{o}C with fit lines created by Langmuir and Freundlich isotherms. 36

Figure 3.5.10: Equilibrium biosorption data obtained at pH 6.0 and 30^{o}C with fit lines created by Langmuir and Freundlich isotherms. 37

Figure 3.5.11: Equilibrium biosorption data obtained at pH 6.0 and 35^{o}C with fit lines created by Langmuir and Freundlich isotherms. 37

Figure 3.5.12: Equilibrium biosorption data obtained at pH 6.0 and 50^{o}C with fit lines created by Langmuir and Freundlich isotherms. 38

Figure 3.8: The graphical diagonal test that compares experimental and modeled results. 41

LIST OF TABLES

SAYFA

Table 1.6: Frequently used single-component adsorption models 14

Table 3.4: Equilibrium Ni (II) uptake and % removal values for *S. pombe* at each temperature and initial Ni (II) concentration studied. 30

Table 3.5.1. Langmuir Isotherms correlating experimental data for pH 4.0,5.0,6.0 31

Table 3.5.2: Freundlich Isotherms correlating experimental data for pH 4.0,5.0,6.0 32

Table 3.6.1 Kinetic models frequently applied to biosorption data in literature. 39

Table 3.6.2 Pseudo-second order kinetic model parameters for *S. pombe* at various initial Ni (II) concentrations and temperatures. 39

Table 3.7 The estimated numerical values for model parameters and computed statistics 40

1. INTRODUCTION

1.1 Heavy Metals

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals that are harmful to humans include nickel, mercury, lead, and arsenic. Chronic exposal of these metals can have heavy health consequences. Inhalation of air pollutants, consumption of contaminated drinking water, exposure to contaminated soils or industrial waste, or consumption of contaminated food lead humans to be exposed through heavy metals. Food sources such as vegetables, fruits, fish and shellfish can become polluted by diffusing metals from surrounding soil and water. Heavy metal exposure results in serious health effects which includes reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals may also cause development of autoimmunity. This can lead to conjoin diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system.

Metals are especially toxic to the rapidly developing systems of fetuses, infants, and young children. Some heavy metals can easily cross the placenta and damage the fetal brain. Childhood exposal of heavy metals can cause learning difficulties, behavioral problems such as aggressiveness and hyperactivity, memory impairment and damage to the nervous system. Some of heavy metals can cause irreversible brain damage at higher doses.

The main danger to human health from heavy metals is caused by exposure to nickel, lead, cadmium, mercury and arsenic. These metals have been widely studied and their risks on human health revised by WHO. Heavy metals have been used by humans for thousands of years. Even though various negative health effects of heavy metals have been known for a long time, exposure to heavy metals continues. It is even increasing in some parts of the world, such as less developed countries. Cadmium containing compounds are generally used in re-chargeable nickel-cadmium batteries. During the 20th century, cadmium emissions have considerably increased. First reason is that although cadmium-containing products are not frequently re-cycled, they are often dumped together with household waste. One of the major sources of cadmium exposure is cigarette smoking. In non-smokers, food is the main source of cadmium exposure. Recent data shows that negative health effects of cadmium exposure may be at lower exposure levels than previously detected, especially in the form of kidney damage but possibly also bone effects and fractures.

The general population is primarily exposed to mercury via food, fish being a major source of methyl mercury exposure, and dental amalgam. The general population does not face a

considerable health risk from methyl mercury, even though certain groups with high level fish consumption may attain blood levels associated with a low risk of neurological damage to adults. Because there is a risk to the fetus, pregnant women should avoid a high intake of certain fish like shark, swordfish and tuna; fish (such as pike, walleye and bass) taken from polluted fresh waters should be avoided. There has been a research on the safety of dental amalgams and it is stated that mercury from amalgam may cause a variety of diseases. However, there are no studies so far which have been able to show any relations between amalgam fillings and ill health. In general population is exposed to lead from air and food in almost equal proportions.

During the last century, lead emissions to ambient air have caused serious pollution, mainly because of petrol. Due to high gastrointestinal uptake and the permeable blood-brain barrier, children are especially susceptible to lead exposure. Recent data shows that there may be neurotoxic effects of lead at lower levels of exposure than previously detected. Even though lead in petrol has considerably decreased, so that reducing environmental exposure, phasing out any remaining uses of lead additives in motor fuels should be encouraged. The use of lead-based paints should be forbidden. Food containers shouldn't be consist of lead and public should be warned about it. Exposure to arsenic is generally caused by the intake of food and drinking water. In particular food is the most important source in most populations. Long-term exposure to arsenic in drinking-water may increase the risks of skin cancer. Also some other cancers, as well as other skin lesions such as hyperkeratosis and pigmentation changes. Exposure to arsenic by inhalation is generally related with lung cancer.

1.2 Nickel as Heavy Metal

Nickel causes a variety of non-carcinogenic toxic effects that includes occupational contact dermatitis, occupational asthma, and reproductive toxicity in humans. Researches in experimental animals exhibit immune suppression, nephrotoxicity, pneumotoxicity, perinatal mortality and altered gene expression. The most sensitive effects appear to be in the lung and immune system.

1.3 Physicochemical Properties Affecting Toxicity of Nickel

As a result of dust storms, forest and grass fires, vegetation, sea spray, vehicular and industrial emissions, and atmospheric chemical reactions cause the formation of aerosols in other words liquid or solid particulate matter (PM) in the air (Rostami, 2009). Anthropogenic activities results in the formation of 10% of atmospheric aerosols. The toxicity levels of inhaled

aerosols depends on many reasons such as the extent of deposition in the head or extra-thoracic region, upper and lower airways of the lung (bronchi and alveoli), chemical composition, and as well as subsequent fate, including clearance. Physical properties, the size or diameter of the particle (and distribution thereof), the concentration, and the density effects the deposition of airborne particles. The clearance of deposited particles also is affected by location of deposition, solubility, and the mass deposited or burden. Generally, deposited PM is more rapidly discarded from the upper airways (tracheobroncheal region, TB) than from the pulmonary region (alveoli) and soluble particles are more rapidly cleared than insoluble particles. Engulfment by alveolar macrophagesis required for removal of particles from the alveoli. Various computational models are made for the prediction of airway deposition and clearance (Jarabek et al., 2005; Rostami, 2009).

The inhalation studies stated in the Nickel Exposure Levels by Office Of Environmental Health Hazard Assessment in 2012. In this document nickel particles are described as having a mass median aerodynamic diameter (MMAD) in μm, a geometric standard deviation (for lognormal size distribution), and a particle density in g/cm3. These three parameters and the aerosol concentration are used as inputs in the Multiple Path Particle Dosimetry (MPPD2) model.

Kleeman and Cass (1999) concluded that PM2.5 from several stationary sources ranged from 11 to 50% of total PM emissions (tons/day), the remainder essentially was PM10. Particle size distributions (PSDs) and elemental partitioning with three coal types and residual fuel oil combusted in three different systems simulating process and utility boilers by Linak et al. (2000). Uncontrolled PM emissions from the three coals ranged from 3800 to 4400 mg/m3 compared to 90 to 180 mg/m3 for fuel oil. The mass and composition of particles between 0.03 and >20μm in aerodynamic diameter indicated that the combustion of these fuels for PM produced different bimodal and trimodal PSDs.

Krudysz et al. (2008) searched spatial variation of PM in an urban area affected by local and regional PM sources. Size-segregated (<0.25, 0.25-2,5, and >2,5 μm) PM samples were gathered every week in the winter of 2005 in the Long Beach, California area. For size-fractionated PM mass, organic and elemental carbon, sulfur and 18 other metals and trace elements coefficients of divergence analyses were managed. Generally for many metal species the highest concentrations were present in the coarse particles (>2,5μm), followed by the 0.25 to 2,5 μm fraction with considerably lower concentrations in the <0.25μm fraction. In contrast, vanadium, nickel, cadmium, zinc and lead concentrations were highest in the <0.25μm and 0.25 to 2,5μm fractions. In addition to that nickel concentrations in the three

fractions were almost about 2 ng/m^3, <0.25µm; 1 ng/m^3, 0.25-2,5µm; and 1,5 ng/m^3,>2,5µm. Therefore the researchers concluded that the particle size distributions used in the animal studies are a reasonable surrogate for PM2.5 and PM10 emitted from stationary and possibly mobile sources.

1.3.1 Solubility

The aqueous solubility of nickel compounds has an important effect on their uptake and also on tissue distribution. In recent studies about solubility of different water soluble and insoluble compounds, the water soluble compounds (e.g., $NiSO_4$, $NiCl_2$, Ni $(NO_3)_2$) were generally found in 10 to 100 fold higher concentrations in lung, liver, kidney, heart, brain and blood than the water insoluble compounds (e.g., NiS, Ni_3S_2, NiO). Insoluble compounds have solubility less than 0.01 mol/L, soluble compounds have solubility more than 0.1 mol/L and slightly soluble compounds range between 0.01 and 0.1 mol/L. In addition insoluble nickel compounds have solubility products that range from about 1 x 10-9 to 1 x 10-31 (National Institute for Occupational Safety and Health, September, 1995)

1.4 Biosorption

Biosorption is a physiochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure (Volesky, 1990). Even though the use of biomass in environmental cleanup has been in practice for a while, researchers are hoping this phenomenon will be an economical alternative for removing toxic heavy metals from industrial wastewater and aid in environmental remediation. Since biosorption is a metabolically passive process which does not require energy, and the amount of contaminants a sorbent can remove is depends on kinetic equilibrium and the composition of the sorbents cellular surface (Velásquez L, Dussan J, 2009). Biosorption is a process in which contaminants are adsorbed onto the cellular structure. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1992). On the other hand, bioaccumulation is an active metabolic process driven by energy from a living organism and requires respiration. Biosorption became an alternative way of removing of toxic metals by metal binding capacities of various biological materials as a result of

searching for new technologies. (Velásquez L, Dussan J, 2009; Vijayaraghavan K, Yun YS, 2008)Algae, bacteria and fungi and yeasts have proved to be potential metal biosorbents (Volesky, 1986). The major advantages of biosorption over conventional treatment methods mentioned at below (Kratochvil and Volesky, 1998 a):

- It is a low-cost method;
- It provides high efficiency;
- It minimize the chemical and biological sludge;
- It requires no additional nutrient;
- It enables the regeneration of biosorbent;
- And there is the possibility of metal recovery.

There are two phases in the biosorption process; a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Because of the higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there with different mechanisms. When the equilibrium established between the amount of solid-bound sorbate species and its portion remaining in the solution, the biosorption process is completed. The distribution between the solid and liquid phases is determined by the degree of sorbent affinity for the sorbate. Biosorption displays some unique characteristics. As it is mentioned above, it can effectively sequester dissolved metals from very dilute complex solutions with high efficiency. This makes biosorption an economical alternative for the treatment of high volume low concentration complex waste-waters. Because of the cost of formulating the biomass into an appropriate biosorbent material, pilot applications have shown the limitations associated with inactive microbial biomass.

On the other hand, the negative effect of co-ions in the solution on the uptake of the targeted metals by the immobilized microbial biomass, and the reduced resilience of the biological material, made recycling and reuse of the biosorbent more difficult. One should take in account of the contribution of biosorption as a parallel mechanism together with other metabolically mediated mechanisms such as bioprecipitation and bioreduction in cases of metabolically active microbial cells, in biological reactors. For this reason, biosorption should always be considered as a metal immobilization process in every case of metal bearing water streams treatment technology which is based on the interactions of microbial cells with soluble metal species. Therefore biosorption can also be defined as the selective sequestering of metal soluble species that result in the immobilization of the metals by microbial cells.

Metal sequestering by different parts of the cell can occur via various processes: complexation, chelation, coordination, ion exchange, precipitation, reduction.

During biosorption, the first cellular structure that comes in contact with the soluble metal species in the extracellular environment is usually the cell wall. Of course this is the case if the possibility of interaction and retentionof metal species by extracellular excretions produced by some microbial cells is excluded (Tsezos et al., 2006; Wang and Chen, 2009).A microbial cell wall can be defined as is a polymeric matrix located just outside the plasma membrane of a cell. Cell wall enable the formation of increased mechanical strength and resistance and also can be composed of polysaccharides, proteins, lipids, or a combination of these compounds. These compounds are part of the structure of eubacteria, archaebacteria, fungi, algae, and plants. Peptidoglycan is the most frequently found cell wall containing a polysaccharide in eubacterial species. The differences in cell wall structure are a major feature used in classifying the eubacteria into two main groups: Gram Positive and Gram-negative bacteria.

Different from eubacteria, the cell walls of archaebacteria are being composed of different polysaccharides and proteins, with no peptidoglycan. Manyarchaebacteria have cell walls that are composed of the polysaccharide pseudomurein. Fungal cell walls are typically made of the polysaccharides chitin and cellulose. Also the cell walls of algae and plants are composed mainly of the polysaccharide cellulose.

Proteins, polysaccharides and nucleic acids are the three major polymer groups ubiquitous in the living world, being found in all members of the animal, plant, protozoan and microorganism groups (Beveridge et al. 1976; Beveridge et al. 1980; Flemming, 1995; Kapoor, A. and T. Viraraghavan, 1997).Important potential of metal binding is provided by these biopolymers, constituents of the cell wall and the other parts of the cell. (Diels et al. 1995; Tsezos, M. and E. Remoundaki, 1997).Furthermore, proteins and DNA as an intracellular biopolymers, may also contribute to metal immobilization. Participation in metal immobilization can be observed in many cases like extracellular polymeric substances such as Exo-PolySaccharides (EPS) that are closely related to the cell membrane (Diels, 1995).

As a generalization, Simple ion-exchange and the formation of complexes (co-ordination compounds) which may be chelates are two of the binding of metal ions to biopolymers. Due to the complexity of most biopolymers, generally more than one processes of binding take place in a system at the same time.

Here is two examples are explained;

_ metal-ion exchange: via cation-binding with ionisable functional groups found in biopolymers such as carboxyl, organic phosphate and organic sulphate;

_ complex formation by organic molecules (ligands) with metal atoms: where one or more lone electron pairs of the ligand are donated to the metal. The most likely electron donor atoms in biopolymers are neutral trivalent nitrogen atoms and neutral divalent oxygen or sulphur atoms.

1.5 Biosorption Mechanism

The description of the mechanism of biosorption is necessary to enable the technology to be developed (Tsezos et al. 1990; Tsezos et al. 1989; Tsezos et al. 1986).

Such mechanisms are complicated and not fully understood(Tsezos, M. and B. Volesky 1982; Tsezos, M. and B. Volesky, 1981). One can find an extensive literature about the mechanism and modeling of biosorption which refers to specific elements and microbial strains (Pujol et al. 1992). There are some significant factors that control and characterize these mechanisms;

_ the type of biological ligands available for metal sequestering;

_ whether the biomass is living or non-living;

_ the chemical, stereo chemical and coordination characteristics of the targeted

metals and metal species (Remoudaki, Eet al. 1999; Tsezos, M. et al. 1995);

_ the characteristics of the metal solution such as pH and the presence of competing co-ions (Esposito, A. et al. 1992; Fourest, E. et al. 1994).

Microorganisms have some functional groups that can passively adsorb metal ions. This adsorption process may include various passive, i.e. non-metabolic, mechanisms such as: complexation; chelation; co-ordination; ion exchange; precipitation; reduction. The complex structure of microorganisms indicates us that there are several ways for metal uptake by the microbial cell. The biosorption mechanisms are very complex so that they are not fully understood. They may be classified according to various criteria.

When considered the dependence on the cell's metabolism, biosorption mechanisms can be divided into two groups:

1. Metabolism dependent and
2. Non -metabolism dependent.

And the location where the metal removed from solution is found may also divide the biosorption into three:

1. Extra cellular accumulation/ precipitation
2. Cell surface sorption/ precipitation and

3. Intracellular accumulation.

Intracellular accumulation is yielded as a result of transport of the metal across the cell membrane. This process is dependent on the cell's metabolism which means that this kind of biosorption may take place only with viable cells. The active defense system of the microorganism, which reacts in the presence of toxic metal, is related to this process. When bioaccumulation is not the case, metal uptake is by physico-chemical interaction between the metal and the functional groups present on the microbial cell surface. Here the main process is about physical adsorption, ion exchange and chemical sorption, which is not dependent on the cells' metabolism. As it is mentioned before, cell walls of microbial biomass, mainly composed of polysaccharides, proteins and lipids have abundant metal binding groups such as carboxyl, sulphate, phosphate and amino groups. So it is non-metabolism dependent biosorption and relatively rapid and reversible (Kuyucak and Volesky, 1988). The metal transport systems may be negatively affected by the same charged metal ions or ions with same ionic radius associated with essential ions. However, mechanism of that kind process is not metabolism dependent. Biosorption by living organisms can be divided into two steps:

1. Metabolism independent binding where the metals are bound to the cell walls.
2. Metabolism dependent intracellular uptake, whereby metal ions are transported across the cell membrane(Costa, et.al., 1991, Gadd et.al., 1988).

1.5.1 Physical adsorption

When it becomes to precipitation, the process may take place both in the solution and on the cell surface (C. Ercole, et al. 1994). Also, in the presence of toxic metals, microorganism produces some compounds to favor the precipitation process which is cell metabolism-dependent biosorption. Precipitation may not be dependent on the cells' metabolism, if it occurs after a chemical interaction between the metal and cell surface. Physical adsorption takes place mainly with the help of van der waals forces. According to Kuyucak and Volesky 1988 electrostatic interactions between the metal ions in solutions and cell walls of microbial cells enable dead biomasses to take uranium, cadmium, zinc, copper and cobalt biosorption. In the study of Aksu et al. 1992, it is stated that electrostatic interactions have been demonstrated to be responsible for copper biosorption by bacterium *Zoogloea ramigera* and alga *Chiarella vulgaris*, for chromium biosorption by fungi*Ganoderma lucidum* and *Aspergillus niger*.

1.5.2 Ion Exchange

The ion Exchange process in biosorption may be explained by following example. The gram-positive bacteria, principally members of the genus *Bacillus*, have enhanced capacity for metal binding because of a significant negative charge density. Because of the structure of the cell wall with teichoic and teichuronic acids that cause an attachment to the peptidogly can network. There are phosphodiesters of teichoic acid and the carboxylate groups of the teichuronic acid. These groups contribute ion-exchange capacity to the cell wall.

As it is mentioned above, cell walls of microorganisms contain polysaccharides and bivalent metal ions exchange with the counter ions of the polysaccharides. For example, the alginates of marine algae occur as salts of K+, Na+, Ca^2+, and Mg^2+ can exchange with counter ions such as CO^2+, Cu^2+, Cd^2+ and Zn^2+ resulting in the biosorptive uptake of heavy metals (Kuyucak and Volesky 1988). Another example of ion exchange mechanism is the biosorption of copper by fungi *Ganoderma lucidium* (Muraleedharan and Venkobachr, 1990) and *Aspergillus niger*.

In biopolymers the most likely cation binding ionisable groups can be classified as carboxyl, organic phosphate and organic sulfate. Firstly, carboxylic acids are primarily distributed in biopolymers. These groups are most commonly found as side-chain constituents of proteins, the uronic, neuraminic and muramic acids, and related substituted monosaccharides of polysaccharides. Phosphodiester links give away negative charge to the nucleic acid backbone. On the other hand, both diester and monoester groupings are found most commonly in bacterialpolysaccharides and related macromolecules. Another example of structures containing phosphodiester as part of the lipid moiety are lipoprotein and lipopolysaccharides.

In connective tissue and algal polysaccharides the sulphate esterification to carbohydrate hydroxyl groups is common. This provides the greatest negative charge density, at very low pKa, among the charged biopolymers. In proteins ester sulfate and phosphomonoester groupings may also occur. Specific translational modifications can be achieved by hydroxyl groups of serine, threonine and tyrosine. In addition, weak negative charge and binding potential are provided by phenolic hydroxyl.

A variety of organic-nitrogen-based groupings may be the source of anion Exchange on biopolymers. In proteins, as a source of positive charge, amino (lysyl side chain and N-terminal) imidazole (histidyl) andguanidine (arginyl) groupings can be mentioned. The protonation of amino groups on purine or pyrimidinerings or the protonation of heterocyclic nitrogen atoms can serve as centers of positive charge in nucleic acids.

Polysaccharides, on the other hand, can be acidic or neutral macromolecules with basic functional groups. And they are rare and arising as un-acetylated amino sugars. Chitin is As a notable example, chitin where a proportion of glucosamine residues are reportedly un-acetylated and which provides on deacetylation chitosan with a high proportion of protonisable positive charge centers.

There are many examples of an ion exchange mechanism in metal on removal by biosorption (Veglio, F. and F. Beolchini, 1997; Davis, T.A et al., 2003; Vasudevan, P et al., 2002; Schneider, A et al. 2001). However, researchers agree that ion exchange is neither the sole nor the main mechanism for metal biosorption (Brady, J.M. and J.M. Tobin, 1995).

1.5.3 Complexation

Complex formation of metal ions with organic molecules involves the ligand centers in the organic species. Complexation may occur as electrostatic or covalent formation. The simplest example is complexation by a mono-dentate ligand such as RNH_2. Hard-soft acid-base classification (Pearson's classification) is an important part of the recent advances in biosorption which can be used to explain the biosorption mechanism.

"Hard acids" bind to oxygen containing hard bases. These hard acids are mostly essential for microbial growth. Metals such as Na, K, Ca, Mg can be given as an example of hard acids. Hard bases are ligands such as OH^-, HPO_4^{2-}, CO_3^{2-}, $R\text{-}COO^-$, and =C=O. And soft acids bound covalently to the cell wall by soft bases. Soft acids are generally metals such as the precious metals Ag, Au, Pt, Pd and soft bases are ligands containing nitrogen or sulfur. As it is mentioned above, there are several mechanisms might be involved in the immobilization of metals. Many authors admitted that the biosorption of precious metals has two steps. First is covalent bonding and second is *in-situ* reduction. Also there are borderline ions on the "hard/soft" classification like Mn^{2+},Zn^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}. These transition metals present an important degree of covalent bonding with nitrogen or sulfur containing "soft" ligands. After the interaction between the metal and the active groups the complex formation may occur on the cell surface. Aksu et al. 1992 studied the biosorption of copper and claimed that biosorption takes place through both adsorption and formation of coordination bonds between metals and amino and carboxyl groups of cell wall polysaccharides by C. *vulgaris* and Z. *Ramigera.* In addition, for calcium, magnesium, cadmium, zinc, copper and mercury accumulation complexation was found to be the only mechanism responsible by *Pseudomonas syringae.* Organic acids may be produced by microorganisms and these organic acids (e.g., citric, oxalic, gluonic, fumaric, lactic and malic acids), which may chelate toxic

metals result in the formation of metallo-organic molecules. Originally, these organic acids enable metal compounds to be soluble and to leach from their surfaces. Carboxyl groups placed in microbial polysaccharides and other polymers both can cause biosorption ofmetals or form complexes with metals..

1.5.4 Precipitation

Metal precipitation is another process that biosorption may include. There are two possibilities of precipitation during biosorption. First is formation of adremain in contact with or inside the microbial cells. Second is to be independent of the solid phase of the microbial cell where the presence of the solid phase-microbial cellular biofilm also plays a favorable role in the phenomenon of precipitation.

Precipitation generally includes the formation off insoluble inorganic metal precipitates. In another opportunity, organic metal precipitates may also be formed (Macaskie, L.E et al. 1992).

Extracellular Polymeric Substances (EPS) is bounded by metals and excreted by some prokaryotic (bacteria, archaea) and eukaryotic (algae, fungi) microorganisms. When cells are isolated and products are purified such as glucan, mannan, and chitin accumulate greater quantities of cations than the intact cells, proving that biomolecules can form metal precipitates.

Precipitation may be divided into two groups: cellular metabolism-dependent and non-metabolism-dependent precipitation. In the former case, biosorption is mostly related to active defense system of the microorganisms. In the presence of toxic material metabolism favors same products to precipitate with metals in the solution. In the latter case, it may be a consequence of the chemical interaction between the metal and the cell surface. Several kind of biosorption mechanisms mentioned above can take place simultaneously.

Another precipitation example is the use of recombinant bacteria for metal removal. In that case adsorbents from water and wastewater are strongly influenced by physico-chemical parameters such as ionic strength, pH and the concentration of competing organic and inorganic compounds. Recently, recombinant bacteria are being investigated for removing specific metals from contaminated water.

1.5.5 Reduction

In literature there are many studies about reduction during biosorption process. The removal of toxic hexavalent chromium from aqueous solution by biosorption by different biomass

types has been extensively reported (Umesh K. Garga, M.P. Kaura, V.K. Gargb, 2007). This removal is often related to the simultaneous reduction of Cr(VI) to Cr(III), thus inactivated fungal biomass e.g.*Aspergillus niger*, *Rhizopus oryzae*, *Saccharomyces cerevisiae* and *Penicilliumchrysogenum* remove Cr(VI) from aqueous solutions by reduction to Cr(III) when contacted with the biomass.

Some sites on and within the cell wall act like nucleation points for the reduction of metals and growth ofcrystals and elemental gold and palladium have been obtained. This occurs because of soft metals' binding to these sites and these sites are acting as nucleation points. To remind, the biosorption mechanism is a two-step process: initiation of the uptake at discrete points by chemical bonding, then reduction of the metal ions.

1.5.6 Co-ordination

Apart from the preferences of binding to specific donor atoms ("hard/hard" / "soft/soft"), metal atoms are affected by the stereo chemical arrangements that play an important role in the binding with the available ligands on the microbial cell. However, there is limited information of surface complexation models, based on the theory of surface co-ordination chemistry. And it is available to describe metal biosorption; however, observed metal biosorption capacities and to elucidate biosorption mechanisms can be explained by the preferences of the metal species.

1.5.7 Chelation

If there are more than one functional group with donor electron pairs in organic molecules, it can simultaneously donate these to a metal atom. As a result chelation which is the formation of a ring structure involving the metal atom is occurred. Often, chelated compounds are more stable than complexes involving monodentateligands since a chelating agent may bond to a metal ion in more than one place simultaneously. The more the number of chelating sites available on ligands, the more stable the chelation. This is why the chelation of metals by donor ligands of biopolymers leads to the formation of stable species.

1.6 Biosorption equilibrium models

The equilibrium sorption isotherms are used to describe the capacity of the adsorbent. The isotherm is characterized by certain constants whose values express the surface properties and affinity of the adsorbent. The solid liquid sorption system can be examined and tested by two types of investigations. First, the equilibrium batch sorption tests and second, dynamic

continuous flow sorption studies. The equilibrium of the biosorption process is often described by fitting the experimental points with models. They are usually used for the representation of isotherm adsorption equilibrium. Widely accepted and linearized equilibrium adsorption isotherm models for single solute system are given by the following:

Table 1.6: Frequently used single-component adsorption models

Isotherm	Equation	Advant.	Disadvant.	Refer.
Langmuir	$q = \frac{bq_m C_e}{1 + bC_e}$	Interpretable parameters	Not structured, Monolayer sorption	Langmuir (1918)[2]
Freundlich	$q = KC_e^{1/n}$	Simple expression	Not structured, no leveling off	Freundlich (1915)[3]
Combination (Langmuir-Freundlich)	$q = \frac{bq_m C_e^{1/n}}{1 + bC_e^{1/n}}$	Combination of above	Unnecessarily complicated	Sips (1948)[4]
Radke and Prausnitz	$\frac{1}{q} = \frac{1}{aC_e} + \frac{1}{bC_e^{\beta}}$	Simple expression	Empirical, uses 3 parameters	Radke & Prausnitz (1972)[5]
Reddlich – Peterson	$q = \frac{aC_e}{1 + bC_e^{n}}$	Approaches Freundlich at high concn.	No special advantages	Jossens *et al.*, (1978)[6]
Brunauer (BET)	$q = \frac{BCQ^{o}}{(C_s - C)[1 + (B-1)C/C_s]}$	Multilayer adsorption; Inflection pt.	No "total capacity" equivalent	Brunauer (1938)[7]
Dubinin-Radushkevich	$\frac{W}{W_o} = \exp[-k(\frac{\varepsilon}{\beta})^2]$ (volume adsorbed)	Temperature independent: Polanyi pot'l. theory	Not limited behavior in the Henry's Law regime	Dubinin, (1947)[8]

1.6.1 Langmuir Isotherm Model

Langmuir isotherm is probably the most widely applied adsorption isotherm. According to this model, adsorption takes place at specific homogeneous sites within the adsorbents is the basic.

The isotherm is expressed as:

$$q_e = \frac{Q^0 K_K C_e}{1 + K_L C_e} \qquad (1.6.1)$$

where;

Q^0 is the maximum sorbate uptake under the given conditions (mg/g),

K_L is a coefficient related to the affinity between the sorbent and sorbate.

Some limitations of Langmuir isotherm can be titled as follow:

1. Since the adsorbed gas has to behave ideally in the vapor phase, this condition can be fulfilled at low pressure conditions only. Therefore, Langmuir Equation is valid under low pressure only.

2. Langmuir Equation explains adsorption as a monolayer system. But, the only possibility that monolayer is formed is when the pressure is low. Since the gas molecules attract more molecules to each other, high pressure conditions breaks down the assumption of Langmuir Equation.

3. Langmuir isotherm also assumes that all the sites on the solid surface are equal in size and shape and have equal affinity for adsorbate molecules i.e. the surface of solid if homogeneous. However, in reality solid surfaces are heterogeneous.

4. Another assumption made by Langmuir Equation is that molecules do not interact with each other. But, this is impossible as weak force of attraction exists even between molecules of same type.

5. Decrease in randomness has to be zero ($\Delta S = 0$). In practice, this is not possible because on adsorption liquefaction of gases taking place, which results into decrease in randomness but the value, is not zero.

Because of the mentioned facts above, Langmuir equation is valid under low pressure conditions.

Irving Langmuir developed the Langmuir isotherm in 1916 to describe the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature. Whilst the Langmuir isotherm is one of the simplest, it still provides a useful insight into the pressure dependence of the extent of surface adsorption. In general, the capacity of an adsorbent can be described by its equilibrium sorption isotherm. It provides the characterization by certain constants whose values express the surface properties and affinity of the adsorbent.

1.6.2 Freundlich Isotherm Model

In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. Simply it relates the curve of the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. As it is mentioned above there are basically two well established types of adsorption isotherm: the Freundlich adsorption isotherm and the Langmuir adsorption isotherm. Here the amount of mass that is adsorbed is plotted against the temperature which gives an idea about the variation of adsorption with temperature. Freundlich isotherm describes the non-ideal and reversible adsorption that is not restricted on monolayer. Also it is known as the earliest adsorption relationship (H.M.F. Freundlich, 1906). Multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface may be examined by this empirical model (Md. Ahmaruzzaman, 2008). The development reason was the adsorption of animal charcoal, demonstrating that the ratio of the adsorbate onto a given mass of adsorbent to the solute was not a constant at different solution concentrations (A.W. Adamson, A.P. Gast; 1997). This means, amount of adsorption on all sites is equal to the amount of adsorption in total. First, adsorption sites with the stronger binding sites are occupied, until adsorption energy are exponentially decreased upon the completion of adsorption process (Zeldowitsch,1934). Nowadays, for heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves Freundlich isotherm is widely used. The measure of adsorption intensity or surface heterogeneity is shown by the slope ranging between 0 and 1.It becomes more heterogeneous as its value gets closer to zero. On the other hand, below the value of unity indicates chemisorption where 1/n above one is an indicative of cooperative adsorption (F. Haghseresht, G. Lu;1998). Since it is not approaching the Henry's law at vanishing concentrations Freundlich isotherm is said to be lack of a fundamental thermodynamic basis. (Y.S. Ho, J.F. Porter, G. Mckay;2002).
The isotherm is expressed as:

$$q_e = K_F C_e^{1/n_F} \qquad (1.6.2)$$

where;

K_F and n_F are Freundlich constants related to adsorption capacity and adsorption intensity, relatively (Freundlich, 1906). Some limitations of Freundlich isotherm can be titled as follow:

1. Freundlich equation is not based on a theoretical basis and it is an empirical formula.

2. Extent of adsorption depends on pressure and it is valid up to a certain pressure rate that is saturation pressure. Adsorption reaches to saturation point even after applying higher pressure. Therefore Freundlich Adsorption Isotherm failed at higher pressure.
3. The constants K and n are temperature dependent parameters that vary with temperature.
4. If the adsorbate concentration is very high Freundlich's adsorption isotherm fails.

1.6.3 Sips Isotherm Model

The Sips isotherm is a combination of the Langmuir and Freundlich isotherms and is given in the following general form:

$$q_e = \frac{K_s C_e^{\beta_s}}{1+(a_s C_e)^{\beta_s}} \qquad (1.6.3)$$

where;

K_s is Sips isotherm constant (mg/g)(L/mg)$^{-\beta}$,

a_s is Sips isotherm constant (L/mg)$^{\beta}$,

β_s is Sips isotherm exponent.

The Sips isotherm has an advantage of reducing the Freundlich isotherm at low pressures and approaches the monolayer capacity at high pressure similar to the Langmuir isotherm. A Nelder-Mead simplex algorithm may be employed to fit the Sips isotherm model. As it is mentioned above Sips isotherm is a combined form of Langmuir and Freundlich expressions (R. Sips, 1948) derived for predicting the heterogeneous adsorption systems (A. Gunay, E. Arslankaya, I. Tosun; 2007). Also by this isotherm model the limitation of the rising adsorbate concentration associated with Freundlich isotherm model is reduced. At high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm and at low adsorbate concentrations, it reduces to Freundlich isotherm; while. Generally, the operating conditions such as the alteration of pH, temperature and concentration affects the equation.(A.B. Pérez-Marín, V. Meseguer Zapata, J.F. Ortuno, M. Aguilar, J. Sáez, M.
Llorens, 2007).

1.6.4 Redlich-Peterson Isotherm Model

Redlich–Peterson isotherm (O. Redlich, D.L. Peterson, 1959) is a combination isotherm model stands for both Langmuir and Freundlich isotherms, which incorporate three parameters into an empirical equation (R.K. Prasad, S.N. Srivastava, 2009). In the numerator there is a linear correlation with concentration and in dominator there is an exponential function dependency (J.C.Y. Ng, W.H. Cheung, G. McKay, 2002). Because of its versatility model can be applied to both homogeneous and heterogeneous systems and by this way, one can represent adsorption equilibria over a wide concentration range (F. Gimbert, N. Morin-Crini, F. Renault, P.M. Badot, G. Crini, 2008). At high concentrations when the exponent tends to zero, it approaches to Freundlich isotherm model. On the contrary, al low concentrations when the values are all close to one, it approaches to Langmuir isotherm (L. Jossens, J.M. Prausnitz, W. Fritz, E.U. Schlünder, A.L. Myers, 1978). The Redlich-Peterson isotherm is a hybrid of the Langmuir and Freundlich isotherms. The numerator is from the Langmuir isotherm and has the benefit of approaching the Henry region at infinite dilution. The denominator has the hybrid Langmuir-Freundlich form.A Nelder-Mead simplex algorithm may be employed to fit the Redlich-Peterson isotherm model.

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta_{RP}}} \qquad (1.6.4)$$

where;

K_{RP} is the Redlich-Peterson isotherm constant (L/g),

a_{RP} is the Redlich-Peterson model constant (L/mg),

β_{RP} is the Redlich-Peterson model exponent.

The exponent, β_{RP}, lies between 0 and 1. There are two limiting behaviours: Langmuir form β_{RP}=1 and Henry's law from for β_{RP}=0.

1.6.5 Radke–Prausnitz Isotherm Model

The correlation of Radke–Prausnitz isotherm is usually predicted well by the high RMSE and chi-square values. aR and rR are referred to the model constants and the model exponent is represented by R.

1.6.6 Kahn Isotherm Model

Multicomponent adsorption model was generated by Kahn and modified into a single solute system in order to describe adsorption of aromatics by activated carbon (Khan et al., 1997). Kahn isotherm model can be expressed in the following simplified form:

$$q_e = \frac{Q^0 b_K C_e}{(1 + b_K C_e)^{n_K}} \tag{1.6.6}$$

where;

Q^0 is the maximum metal uptake (mg/g)

b_K and n_K are Kahn isotherm constant and exponent, respectively.

1.6.7 BET Isotherm Model

Gas-solid equilibrium systems are mostly evaluated by Brunauer–Emmett–Teller (BET) isotherm which is a theoretical equation (S. Bruanuer, P.H. Emmett, E. Teller, 1938). It was first generated in order to derive multilayer adsorption systems with relative pressure ranges from 0.05 to 0.30 corresponding to a monolayer coverage lying between 0.50 and 1.50. Model can be expressed as follow:

$$q = q_{\mathrm{m}} \frac{K_L C_e [1 - (n+1)(K_S C_e)^n + n(K_S C_e)^{n+1}]}{(1 - K_S C_e)[1 + (\frac{K_L}{K_S} - 1) K_S C_e - (\frac{K_L}{K_S})(K_S C_e)^{n+1}]} \tag{1.6.7}$$

where;

q is the amount of adsorbate adsorbed on the solid surface, mg/g,

q_m is the amount of adsorbate corresponding to complete monolayer adsorption, mg/g,

K_L is the equilibrium constant of adsorption for 1st layer in Langmuir and BET isotherms, $(\mathrm{mg/L})^{-1}$,

K_S is the equilibrium constant of adsorption for upper layers in BET isotherm, $(\mathrm{mg/L})^{-1}$,

n is maximum number of adsorbed layers on solid surface in BET isotherm,

C_e is equilibrium liquid phase concentration of sorbent (mg/L).

1.6.8 Dubinin–Radushkevich Isotherm Model

Dubinin–Radushkevich isotherm is an empirical model. The adsorption mechanisms with a Gaussian energy distribution (A. Gunay, E. Arslankaya, I. Tosun, 2007)onto a heterogeneous surface are mostly defined by this isotherm model (O. Altin, H.O. Ozbelge, T. Dogu, 1998).Although model has often successfully fitted high solute activities and the intermediate range of concentrations data well, as a limitation the model has some unsatisfactory asymptotic properties and does not predict the Henry's law at low pressure (O. Altin, H.O. Ozbelge, T. Dogu, 1998). The model enable to distinguish the physical and chemical adsorption of metal ions (M.M. Dubinin, 1960).

E which is per molecule of adsorbate defines removing a molecule from its location in the sorption space to the infinity and can be expressed by the following relationship (J.P. Hobson, 1969):

$$E = \left[1/\sqrt{2B_{DR}}\right] \tag{1.6.7.1}$$

where B_{DR} is denoted as the isotherm constant.

The equation parameterε can be correlated as follow:

$$\varepsilon = RT\ln\left[1+1/C_e\right] \tag{1.6.7.2}$$

where R, T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively. Dubinin–Radushkevich isotherm model is temperature-dependent. A function of logarithm of amount adsorbed vs the square of potential energy defines the adsorption data at different temperatures and all suitable data will lie on the same curve, named as the characteristic curve.

1.6.9 Aim and Scope

This thesis can be divided into two major parts. First part presents the experimental data array for the sigmoid model under research and does not have an aim to characterize the biosorption process of wild type of *S. pombe*. Reliable data matrix was obtained which was used in multiple inputs when computing the sigmoid model in the second part. For this reason, dried inactive biomass was utilized as biosorbent at various solution pHs, temperatures and initial metal concentrations. The varying concentrations of Ni (II) removal was determined by metal ion analyses of samples using Atomic Absorption Spectrophotometer. The biosorption

phenomena were expressed employing two-parameter isotherm models on data. Even though this is not the major point, kinetic descriptions of biosorption data were also carried out. In the second part, by using Auto2fit 3.0® softwarewith suitable algorithm the experimental data was regressed and optimized. The best convergence parameters were found when using the Levenberg-Marquardt algorithm. After the optimization, parameters and the experimental data were simulated. In addition, the last step was the use of chi-square test in order to validate the sigmoid model.

2 MATERIAL AND METHOD

2.1 Biosorption experiments

The biosorption data of Ni (II) onto dead wild type S. pombe (972 h^-) through a batch equilibrium process have been observed originally for this work at various *T* and *pH* conditions of 25, 30 , 35, 50 ^{0} C and 4, 5 and 6, respectively. The equilibrium values of Ni (II) uptake by the biomass, q_e, mg (g dry weight)$^{-1}$ were calculated using

$$q_e = (C_i - C_e)V / m \qquad (2.1.1)$$

WhereC_i, C_e, *V* and *m* denote, initial Ni (II) concentration of the aqueous phase (mg L^{-1}), equilibrium Ni (II) concentration of the aqueous phase (mg L^{-1}), volume (L) of the solution contacted by the sorbent and the amount of the sorbent expressed as dry mass (g), respectively. The wild-type (972 h^{-1}) *S. pombe* strain used in this work was obtained from the Department of Molecular Biology and Genetics, University of Istanbul. This strain was grown in aqueous medium containing 30 g L^{-1} glucose and 5 g L^{-1}yeast extract, both furnished by Merck. Biosorption experiments were performed exactly through an elaborate procedure recently published study of Durmaz Sam, S. (2011). Each experiment was conducted as three trials and arithmetic averages were taken. Filtered samples were analyzed in triplicate with Perkin Elmer AAS 400 atomic absorption spectrophotometer to measure the concentration of not adsorbed Ni(II) species remaining in aqueous medium.

2.1.1 Stock solutions

Stock Ni(II) solution was prepared by dissolving $NiCl_2.6H_2O$ (GR for analysis, Merck (Darmstadt)) in ultrapure grade water to give a concentration of 1.0 g/L. Ni(II) solutions with required initial metal concentration were prepared by diluting the stock solution with

appropriate amounts of ultra-pure grade water. In order to obtain solutions of required pH values, 0.1 and 1.0 M HNO_3 or NaOH solutions were used.

2.1.2 Detection of Ni(II) concentration

Atomic absorption spectrometry is a useful method for measuring the concentrations of elements down to parts per billion of a gram (μg/L) in a sample. During biosorption experiments Scientific i3500 flame AAS was used to measure initial and residual Ni (II) concentrations of samples. Working principle of AAS is based on the use of the wavelengths of light specifically absorbed by an element. For calibration at least three different solutions with different Ni(II) metal ion concentrations were prepared with 0.1% (v/v) ultra pure grade HNO_3solution and commercial 1000 mg/L Ni (II) solution with high purity. A hallow cathode lamp was used for nickel with air-acetylene flame with the flame temperature of 2300 ^oC. For back ground correction Deuterium lamp was used. Blank reagent was the dilution solution (0.1% (v/v) ultra pure grade HNO_3 solution)in order to set the spectrophotometer to zero absorbance at 232 nm. Triplicate measures were conducted and calibration of the device was renewed at every 15-18 measurements.

2.1.3 Best Fit Curve Analysis

As optimizing software Auto2fit 3.0® was used with Maximum Inherit Optimization and Levenberg– Marquardt algorithms. Isotherm and model parameters, kinetic models, regression statistics were computed. These algorithms gave the best result in rapid and reproducible convergence for global maxima. The square of the correlation factor, R^2 and the root mean square error, RMSE values were used to validate the representing performance of the models.

2.1.3.1 The Levenberg-Marquardt Method

Non linear least squares methods are referenced when the function in question is not linear in the parameters. These are iterative methods that decrease the sum of the squares of the errors between the function and the data points. The Levenberg- Marquardt method is a mathematical approach generally used in order to solve non-linear least square problems, especially curve fitting for a given data matrix. LM is consisting of steepest descent and the Gauss-Newton method. The algorithm behaves like a steepest descent method in the case of current solution far from the correct one. This results in slow, but guaranteed to converge. As an example, each parameter starting from the initial values at each iteration is increased and

the sum of squares is checked if it increases or decreases. If the sum decreases it continues to increase the parameter values. Or else it decreases them. It behaves as a Gauss-Newton method when the current solution is close to the correct solution. Least squares function is assumed to be locally quadratic and the Gauss-Newton method aims to find the minimum of the quadratic. Error between the function and the data points are calculated as follows:

$$E(a,b) = \sum_{n=1}^{N} (y_n - (ax_n + b))^2$$

The optimized values of a and b parameters which minimizes the error, are aimed to be found in the method of least squares.

2.2. Model Development

Input and output correlation can be done between process variables by the use of simple but versatile universal sigmoid function (N.A. Sayar et al. 2009; N.A. Sayar et al. 2007). The independent multiple input variables are related as the forcing variables to the process response to a certain quality of fit. The useful applicability of Jacobian and Hessian operations provides an advantage to this function. Therefore universal sigmoid function becomes more simple and robust for future mathematical optimization procedure.

In this study selected process inputs are determined as C_e, T and pH and the resulting output as % q_e.

$$\%q_e = 100 - [a_1 exp^{a_2 P} + a_6 exp^{a_7 P}] \qquad (2.2.1)$$

where

$$P = (C_e)^{a_3} (T)^{a_4} (pH)^{a_5} \qquad (2.2.2)$$

$$\%q_e = (q_e)_{act} / (q_e)_{max} \qquad (2.2.3)$$

Where $(q_e)_{act}$ is the simulated value for the given input and $(q_e)_{max}$ is the highest value in the whole simulated data matrix. The use of percentage expression which is a dimensionless normalized form, results in good fit of chi-square test.

For each separate case that is at each temperature, pH and initial metal concentration, $(q_e)_{max}$ is provided by the correlation of $q_e$versus C_e with Freundlich isotherms. With a 60 elemented input-output array the best estimation of model parameters has been done by using a numerical optimization solver Auto2fit 3.0 (CPX-Software, Copyright © 7D-Software).

Sigmoid model has 7 parameters, $a_{i=1 \text{ to } 7}$ and input-output array of 62 elements consists of different $C_e$values varying from 0 .48 to 50 mg $L^{-}1$, T from 25 to 50 ^{0}C and $pH$from 4 to 6.

2.3Model Validation

2.3.1 Chi-Square Test

is a statistical test applied to sets of categorical data to evaluate how likely it is that any observed difference between the sets arose by chance. It is suitable for unpaired data from large samples. The value of the test-statistic is

$$\chi^2 = \sum_{i=1}^{n} \frac{(O_i - E_i)^2}{E_i}$$

where

χ^2 = Pearson's cumulative test statistic, which asymptotically approaches a χ^2 distribution.

O_i = an observed frequency;

E_i = an expected (theoretical) frequency, asserted by the null hypothesis;

n = the number of cells in the table.

Since the chi-square distribution is typically used to develop hypothesis tests and confidence intervals and rarely for modeling applications, we omit any discussion of parameter estimation. The chi-square distribution is used in many cases for the critical regions for hypothesis tests and in determining confidence intervals. Two common examples are the chi-square test for independence in an RxC contingency table and the chi-square test to determine if the standard deviation of a population is equal to a pre-specified value. The chi-square test is always testing what scientists call the null hypothesis, which states that there is no significant difference between the expected and observed result. The agreeability of block model and simulation results can be statistically assessed by the use of two-sided chi-square, $\chi 2$, test (N.A. Sayar et al. 2009). The test requires a null hypothesis which in this case presumes zero difference between block model and simulation results. Degrees of freedom (df) refers to the number of values that are free to vary after restriction has been placed on the data. For instance, if you have four numbers with the restriction that their sum has to be 50, and then three of these numbers can be anything, they are free to vary, but the fourth number definitely is restricted. For example, the first three numbers could be 15, 20, and 5, adding up to 40; then the fourth number has to be 10 in order that they sum to 50. The degrees of freedom for these values are then three. The degrees of freedom here is defined as N - 1, the number in the group minus one restriction (4 - 1).

3 RESULTS and DISCUSSION

3.1 Biosorption Experiments

In Ni (II) biosorption experiments, wild type strain (972 h^-) of the yeast *S. pombe* were used. The effects of pH, temperature and initial metal concentration on equilibrium Ni (II) uptake were investigated. In all biosorption experiments, agitation rate was adjusted to 150 rpm, which was one of the most frequently encountered mixing rate in the biosorption literature (Aksu et al., 1999; Ferraz et al., 2004; Veit et al., 2005; Chen and Wang, 2008). The studies, which focused on the effect of agitation rate on metal biosorption, showed that 150 rpm is an optimum rate to achieve effectual mixing (Dilek et al., 2002; Shinde et al., 2012).

3.2 Effect of pH

Solution pH is one of the most important parameters for biosorption. In the study of Durmaz-Sam S., Sayar N.A., Topal-Sarikaya A., Sayar A.A. ;2011, the optimum pH for Ni (II) biosorption by wild-type *S. Pombe* was determined by conducted experiments at five different pH values in the range of 2.0-6.0. Detected optimum pH value at each temperature was showed in the figure3.2, 3.4, 3.5, 3.6. During experiments biomass concentration was kept at 1.0 g/L at each trial. No further nickel (II) uptake was detected over pH 5.0. In addition, in an alkali solutions, at pH 7.0 and higher pH values, precipitation of Ni $(OH)_2$occurs. Since the sequestration mechanism of the collection of the metal species is not straight, the formation of (micro) precipitates becomes more complicated. In another study, the case of lead was investigated and found out that the danger starts at pH values above5.0 for lead and pH 6.7 for nickel. pH adjustment in the study of sorption systems becomes complicated due to the formation of amphoteric lead hydroxides. Hydrolytic reaction is caused by metal ions coordinated by water molecules (B. Volesky and Z.R. Holan, 1995). Adsorption mechanisms are affected by the initial pH of adsorption medium and they shows the nature of the physicochemical interactions of the species in solution and the adsorptive sites of adsorbent(Aksu et al 2002).

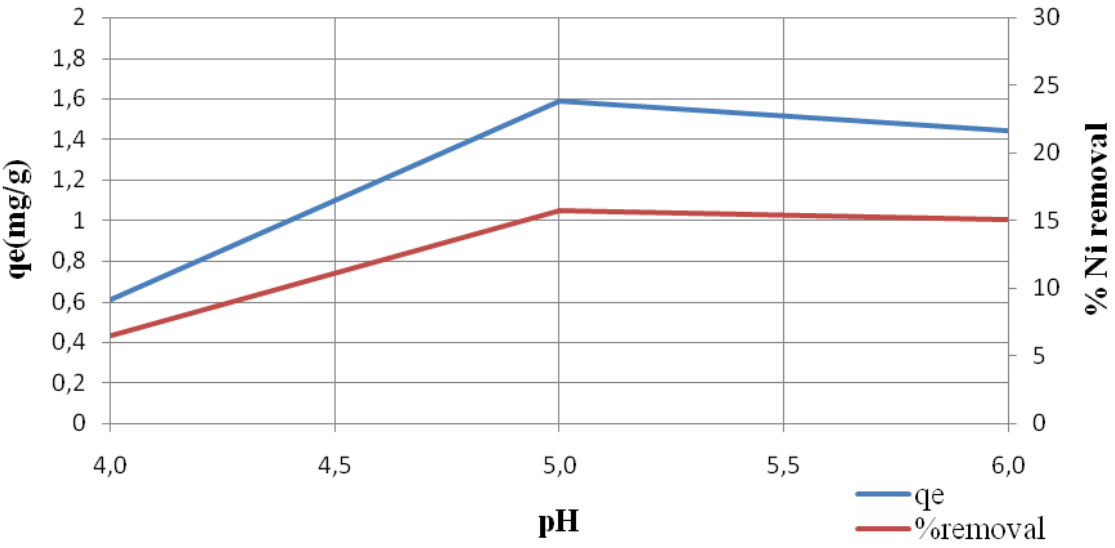

Figure 3.2.1: The effect of pH on the equilibrium uptake of Ni (II) by *S. pombe* (Temperature: 25 ^{o}C ; initial Ni (II) conc.: 10 mg/L ; at 1 hour; biosorbent dose: 1.0 g/L ; agitation rate: 150 rpm.)

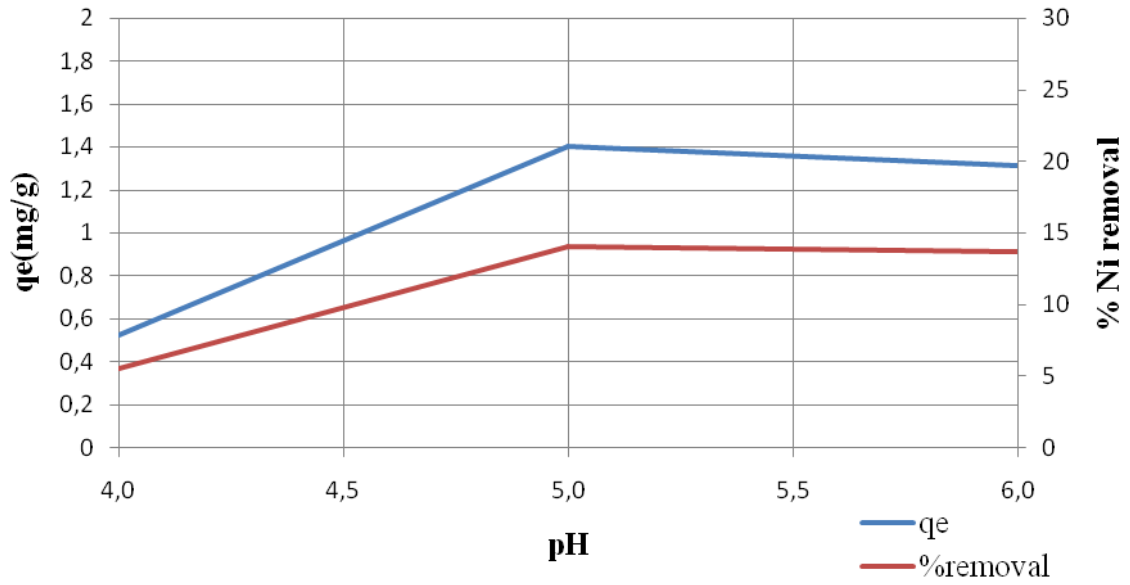

Figure 3.2.2: The effect of pH on the equilibrium uptake of Ni (II) by *S. pombe* (Temperature: 30^{o}C ; initial Ni (II) conc.: 10 mg/L ; at 1hour; biosorbent dose: 1.0 g/L ; agitation rate: 150 rpm.)

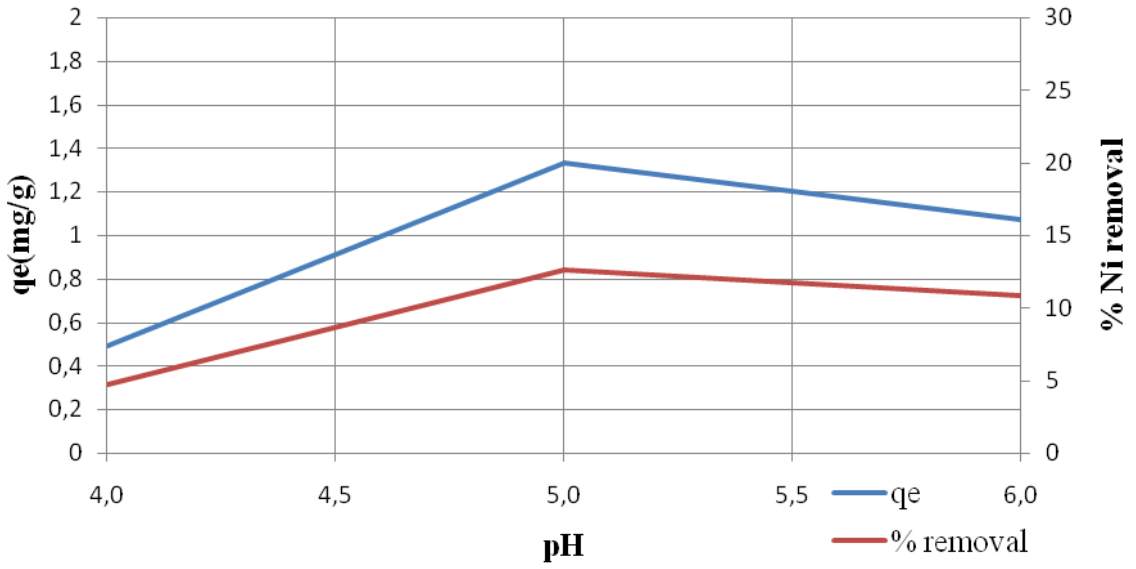

Figure 3.2.3: The effect of pH on the equilibrium uptake of Ni (II) by *S. pombe* (Temperature: 35 ^{o}C ; initial Ni (II) conc.: 10 mg/L ; at 1 hour; biosorbent dose: 1.0 g/L ; agitation rate: 150 rpm.)

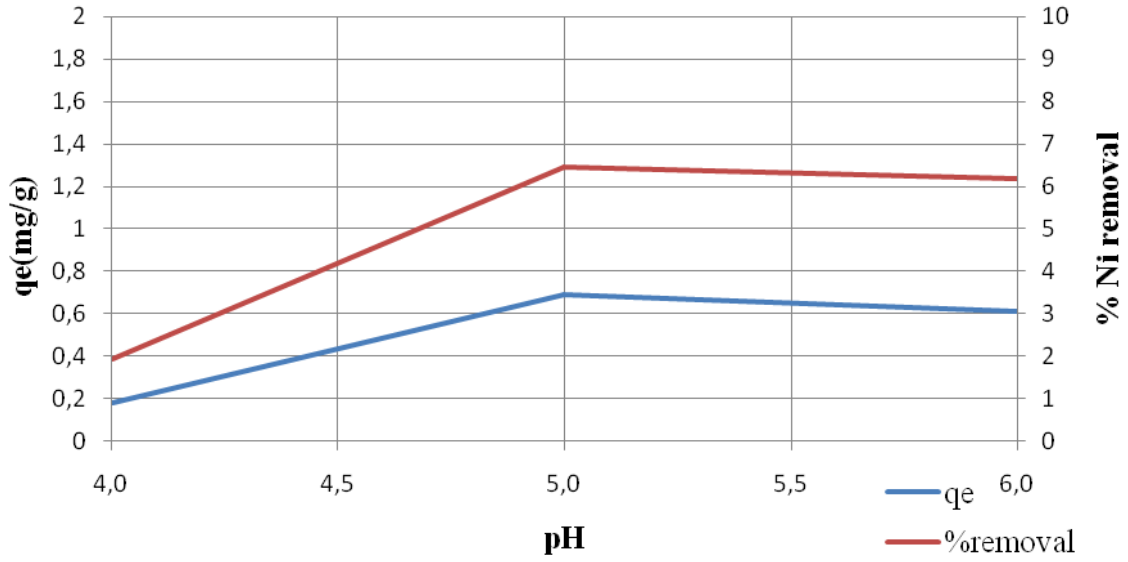

Figure 3.2.4: The effect of pH on the equilibrium uptake of Ni (II) by *S. pombe* (Temperature: 50^{o}C ; initial Ni (II) conc.: 10 mg/L ; at 1 hour; biosorbent dose: 1.0 g/L ; agitation rate: 150 rpm.)

3.3 Effect of initial Ni (II) concentration

Initial concentration provides an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases (Aksu and Balibek, 2006). The increase in the initial metal concentration results in an increase in the biosorption rate. The Freundlich parameters have been optimized using appropriate experimental data. The rate of

the saturation of binding sites on cell surface increases at high metal ion concentrations. It is assumed that under optimum initial metal concentrations and pH condition (pH 5.0) no precipitation of metal ion as hydroxides occurs.

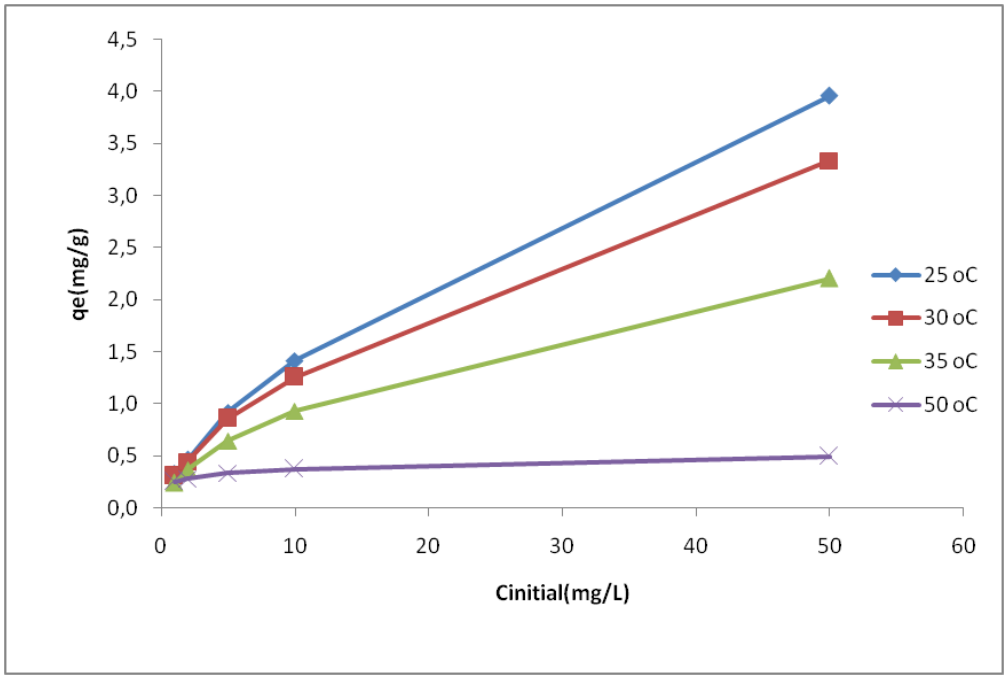

Figure 3.3: The effect of initial Ni(II) concentration on equilibrium uptakes of *S. pombe* at various temperatures with the fit lines generated by Freundlich sorption model (pH= 5.0; biosorbent dose: 1.0 g/L; agitation rate: 150 rpm)

3.4 Effect of temperature

Since Ni (II) biosorption onto biosorbent has had an exothermic nature, as the temperature increased Ni (II) uptake capacity decreases. For this reason, the lowest metal removals were observed at 50 ^{o}C.

The temperature range that the biosorption of Ni (II) ions from aqueous media by S. pombe was investigated was between 25–50 ^{o}C at varying initial Ni (II) concentrations. Experiments showed that at each concentration studied when the temperature increases from 25 to 50 ^{o}C, metal uptake portion. Furthermore, maximum initial adsorption rate of Ni (II) ions to *S. pombe* was reached at temperature 25 ^{o}C.

The reason for the decrease of metal uptake at higher temperatures is probably because of the thermal sensitivity of the surface of *S. pombe* and therefore the physical degeneration of the sorbents. In some cases temperature increase may affect the sorption reaction in a positive way, i.e. endothermic reactions (Aksu, 2002). Sorption rate is increased as a result of the increased surface activity and kinetic energy of the solute at higher temperatures

(Vijayaraghavan and Yun, 2007; Dhankbar and Hooda, 2011). However, temperatures close to room temperature are always desirable to conduct biosorption as this condition is easy to replicate.

Table 3.4: Equilibrium Ni (II) uptake and % removal values for wild-type *S. pombe* at 1 hour and at ph values 4.0, 5.0, 6.0, temperature and initial Ni (II) concentration studied.

3.5 Equilibrium studies

	25°C		30 °C		35 °C		50 °C	
C_i (mg/L)	q_e (mg/g)	% Ni (II) removal	q_e (mg/g)	% Ni (II) removal	q_e (mg/g)	% Ni (II) removal	q_e (mg/g)	% Ni (II) removal
1	0,28	34,34	0,26	20,36	0,10	12,18	0,08	9,87
2	0,36	19,36	0,33	18,05	0,38	19,45	0,14	7,46
5	0,37	7,80	0,39	8,27	0,24	5,02	0,11	2,23
10	0,61	6,50	0,52	5,49	0,49	4,74	0,18	1,92
50	1,17	2,44	1,02	2,06	1,05	2,03	0,84	1,65

	25°C		30 °C		35 °C		50 °C	
C_i (mg/L)	q_e (mg/g)	% Ni (II) removal	q_e (mg/g)	% Ni (II) removal	q_e (mg/g)	% Ni (II) removal	q_e (mg/g)	% Ni (II) removal
1	0.41	46,02	0.29	31,59	0.29	39,24	0.27	27,09
2	0.63	33,29	0.61	32,79	0.36	21,55	0.36	20,11
5	0.95	18,37	0.93	17,41	0.88	16,70	0.54	10,84
10	1.59	15,74	1.40	14,07	1.33	12,59	0.69	6,44

	25°C		30 °C		35 °C		50 °C	
C_i (mg/L)	q_e (mg/g)	% Ni (II) removal	q_e (mg/g)	% Ni (II) removal	q_e (mg/g)	% Ni (II) removal	q_e (mg/g)	% Ni (II) removal
1	0,38	49,51	0,33	32,29	0,25	69,81	0,15	14,80
2	0,46	27,52	0,42	24,12	0,37	21,18	0,20	11,13
5	1,01	21,03	0,81	16,19	0,49	10,48	0,38	7,73
10	1,44	15,07	1,31	13,68	1,07	10,88	0,61	6,19
50	3,48	6,82	3,33	6,61	2,19	4,30	0,39	0,77

The two-parameter Langmuir and Freundlich models have been applied to compare the adequacy and the reliability for representing the biosorption of Ni (II) by *S. pombe*. Auto2fit 3.0® has been used to compute the relevant regression statistics for the validated models each at different temperatures. Maximum Inherit Optimization and Levenberg–Marquardt algorithms were evaluated in order to obtain rapid and reproducible convergence for global maxima. Although the square of the correlation factor, R^2, was used to validate the representing performance of the models, it is well known that R^2 values do not always constitute a sufficient criterion for the evaluation especially in the case of nonlinear models.

In order to test the performance of models, the root mean square error, RMSE values have also been used. The results for pH 4.0,5.0 and 6.0are given in Table 3.5.1.

Among the adsorption models with only two parameters, Freundlich isotherm was found to be the best relationship to correlate the experimental results. The related isotherm parameters representing the observed data are given in Table 3.5.2.

It has to be noted that the experimental results concerning the metal uptake exhibit a slight discrepancy with the previously published data (Durmaz-SamS**.**, Sayar N.A., Topal-Sarikaya A., Sayar A.A., 2011), possibly due to random mutagenesis of the available *S.pombe* strain generated from the original source.

Table 3.5.1: Langmuir Isotherm correlating experimental data for pH 4.0, 5.0, 6.0.

pH 4.0

Adsorption Model	T (^{0}C)			R^2	RMSE
		K_L	Q^0		
Langmuir	25	0.11395	1.35666	0.91608	0.12511
	30	0.13586	1.11271	0.88592	0.10826
	35	0.07068	1.31207	0.89246	0.12011
	50	0.01711	1.81530	0.97978	0.04916

pH 5.0

Adsorption Model	T (^{0}C)			R^2	RMSE
		K_L	Q^0		
Langmuir	25	0.30233	2.06297	0.91675	0.14198
	30	0.31130	1.83412	0.95321	0.08942
	35	0.21144	1.95254	0.97621	0.07545
	50	0.66448	0.77011	0.99903	0.00552

pH 6.0

Adsorption Model	T (^{0}C)			R^2	RMSE
		K_L	Q^0		
Langmuir	25	0.04368	5.86342	0.99512	0.12496
	30	0.04971	4.73595	0.99549	0.10007
	35	0.06551	2.86807	0.98381	0.10566
	50	0.59269	0.51921	0.65246	0.09687

Table 3.5.2: Freundlich Isotherms correlating experimental data for pH 4.0, 5.0, 6.0

$$q_e = K_F C_e^{1/n}$$

n	K_F	R^2	n	K_F	R^2	n	K_F	R^2	n	K_F	R^2
25 ^{0}C			30 ^{0}C			35 ^{0}C			50 ^{0}C		
			pH=4								
2.632	2.628	0.96938	2.700	0.237	0.97805	2.213	0.175	0.93314	1.4	0.050	0.98182
			pH=5								
1.980	0.523	0.97054	1.939	0.452	0.98680	2.213	0.173	0.93314	2.891	0.317	0.98182
			pH=6								
1.707	0.415	0.99989	1.780	0.383	0.99895	1.992	0.313	0.98310	6.062	0.260	0.34823

According to bivariate comparison, Freundlich model has been found to be the best performing equation among the two-parameter isotherms used in this study. Higher correlation coefficients and lower RMSE values were obtained with Freundlich model. K_F values, representing the affinity between the sorbent and sorbate, decreased with increasing temperature. In addition, Q^0 values indicate that the maximum Ni (II) uptake at each temperature may be observed at higher initial Ni (II) concentrations than those applied in this study.

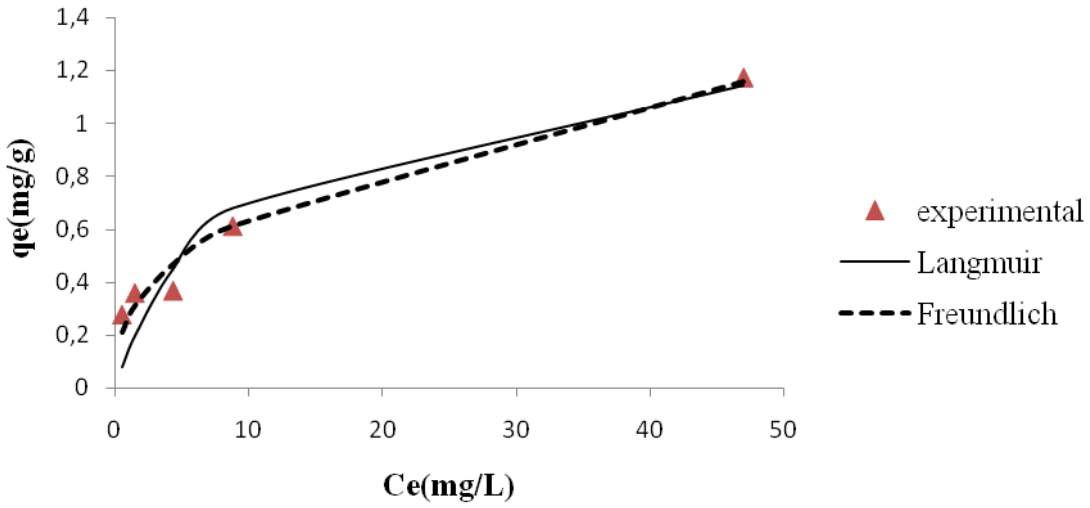

Figure 3.5.1: Equilibrium biosorption data obtained at pH 4.0 and 25 ^{o}C with fit lines created by Lan<gmuir and Freundlich isotherms.

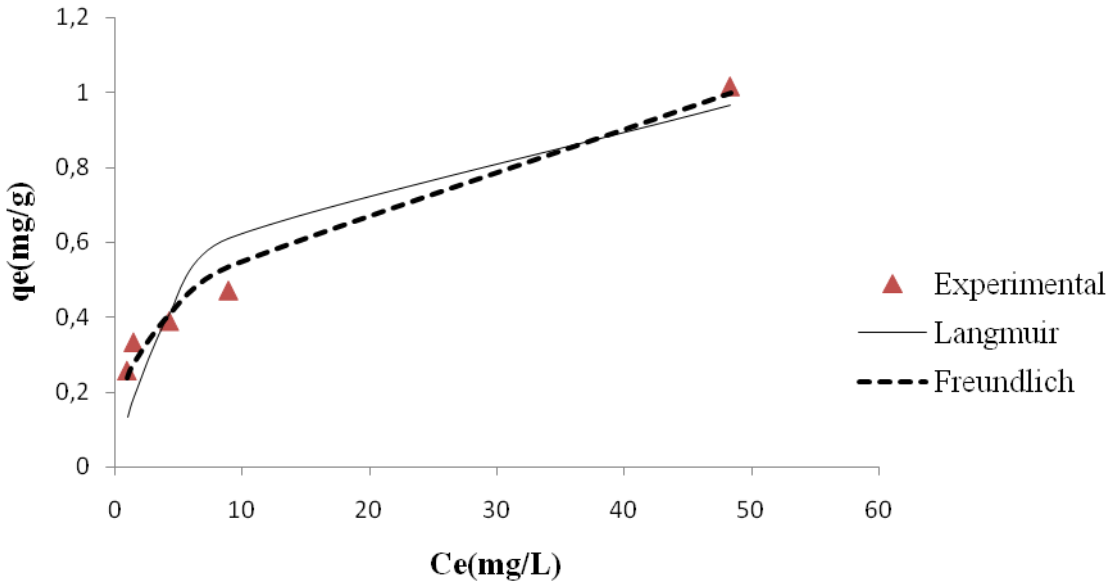

Figure 3.5.2: Equilibrium biosorption data obtained at pH 4.0 and 30°C with fit lines created by Langmuir and Freundlich isotherms.

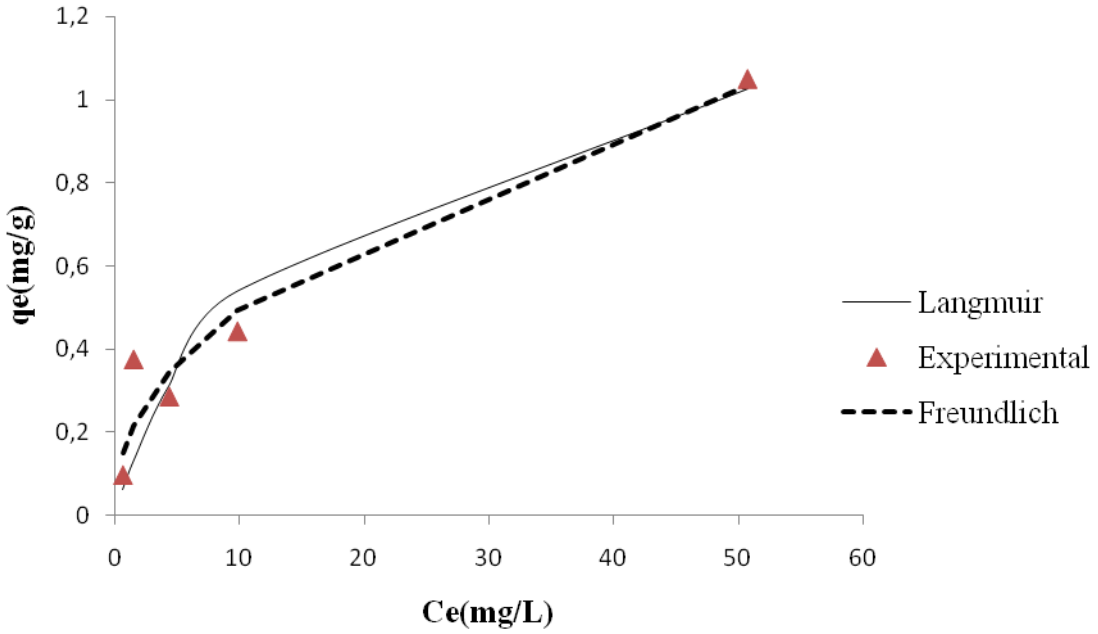

Figure 3.5.3: Equilibrium biosorption data obtained at pH 4.0 and 35°C with fit lines created by Langmuir and Freundlich isotherms.

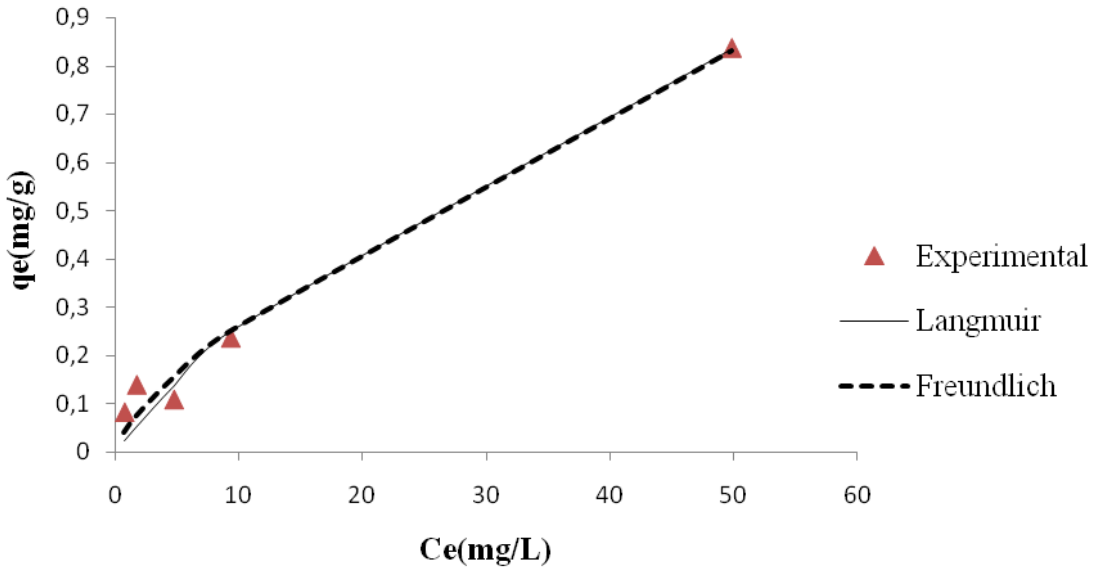

Figure 3.5.4: Equilibrium biosorption data obtained at pH 4.0 and 50°C with fit lines created by Langmuir and Freundlich isotherms.

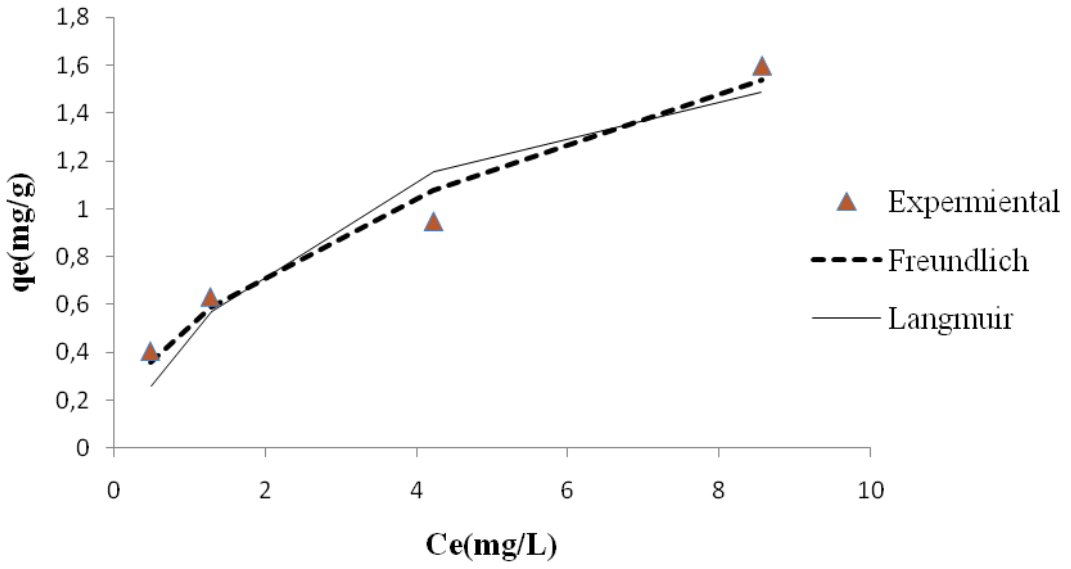

Figure 3.5.5: Equilibrium biosorption data obtained at pH 5.0 and 25 °C with fit lines created by Langmuir and Freundlich isotherms.

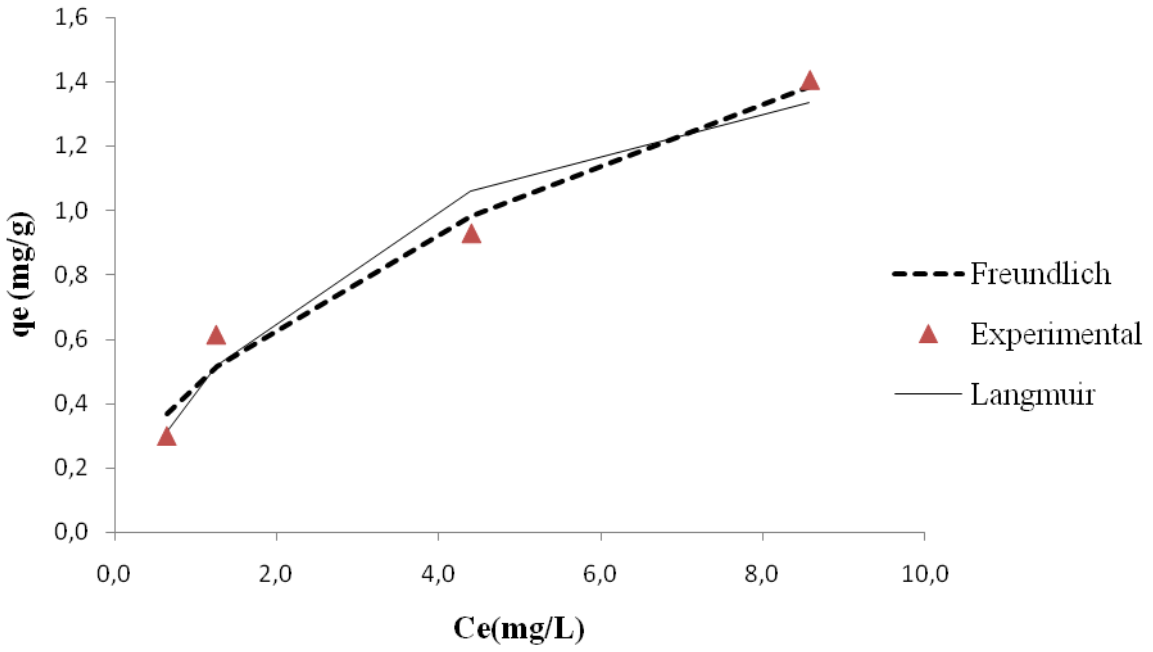

Figure 3.5.6: Equilibrium biosorption data obtained at pH 5.0 and 30°C with fit lines created by Langmuir and Freundlich isotherms.

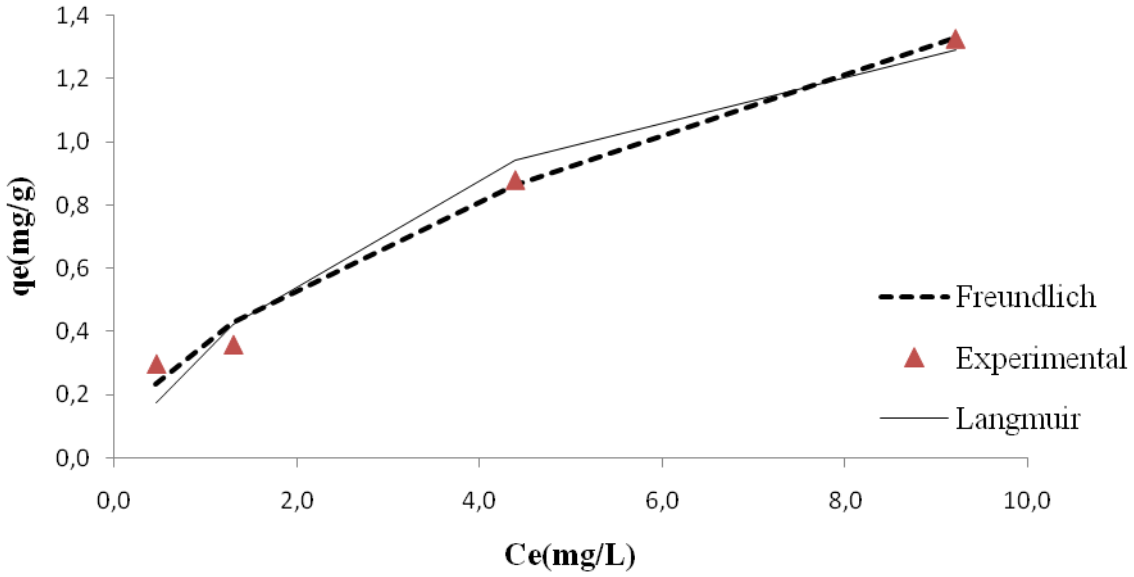

Figure 3.5.7: Equilibrium biosorption data obtained at pH 5.0 and 35°C with fit lines created by Langmuir and Freundlich isotherms.

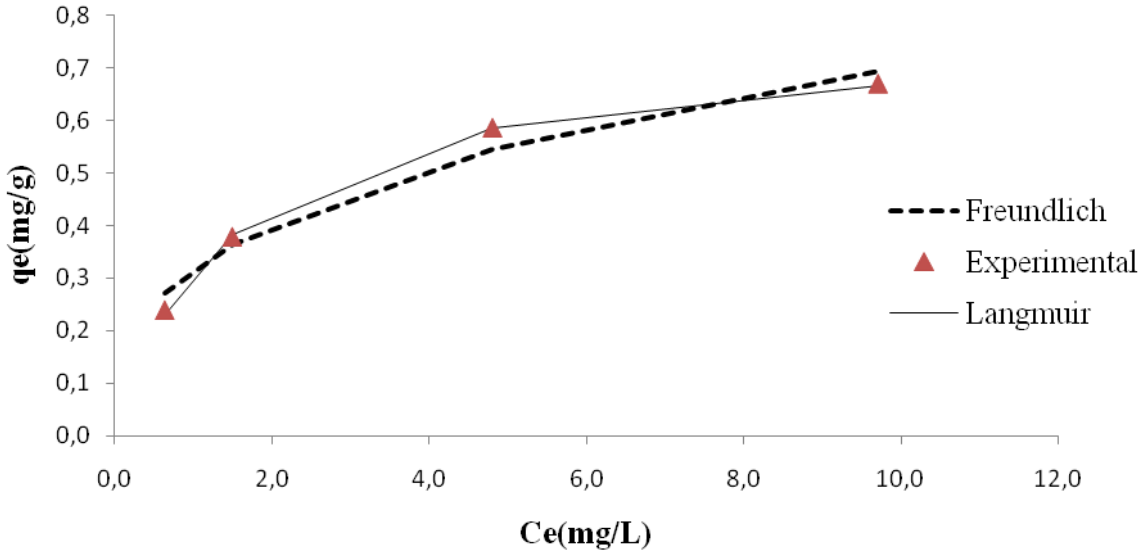

Figure 3.5.8: Equilibrium biosorption data obtained at pH 5.0 and 50^{o}C with fit lines created by Langmuir and Freundlich isotherms.

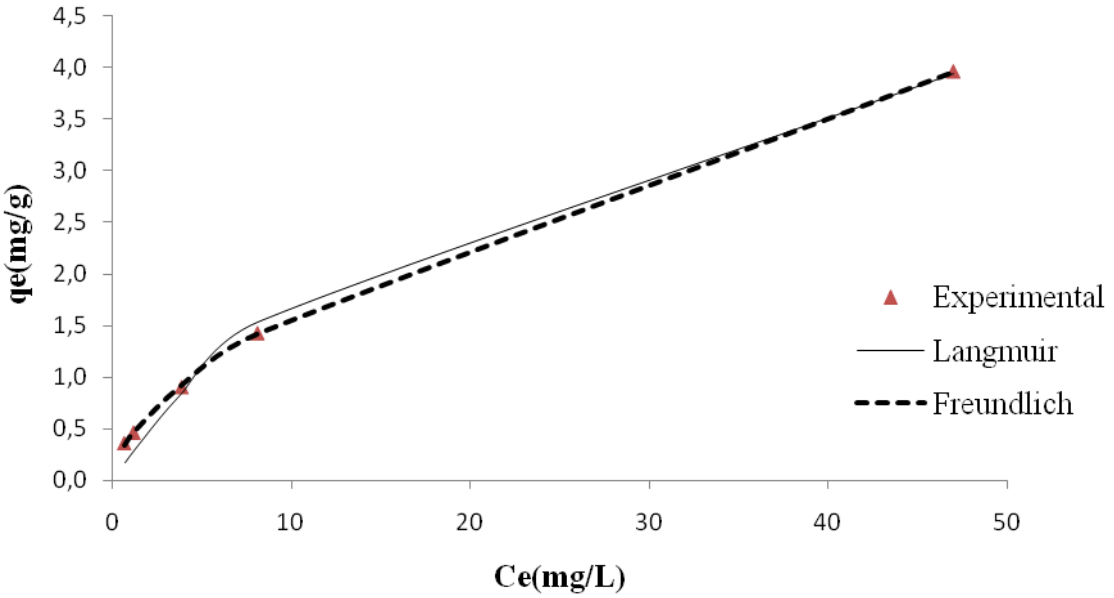

Figure 3.5.9: Equilibrium biosorption data obtained at pH 6.0 and 25 ^{o}C with fit lines created by Langmuir and Freundlich isotherms.

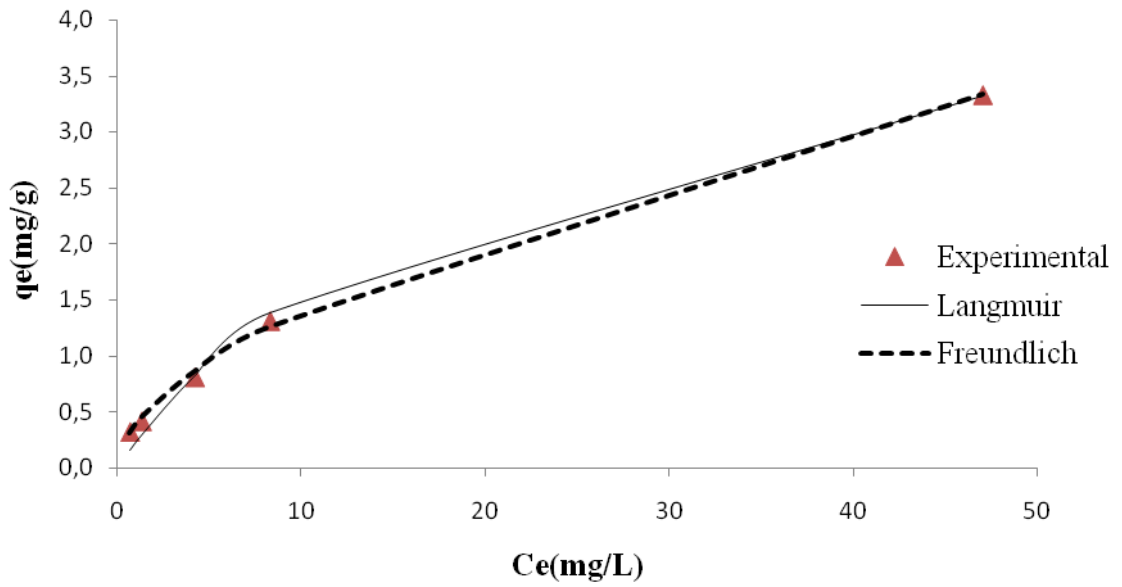

Figure 3.5.10: Equilibrium biosorption data obtained at pH 6.0 and 30°C with fit lines created by Langmuir and Freundlich isotherms

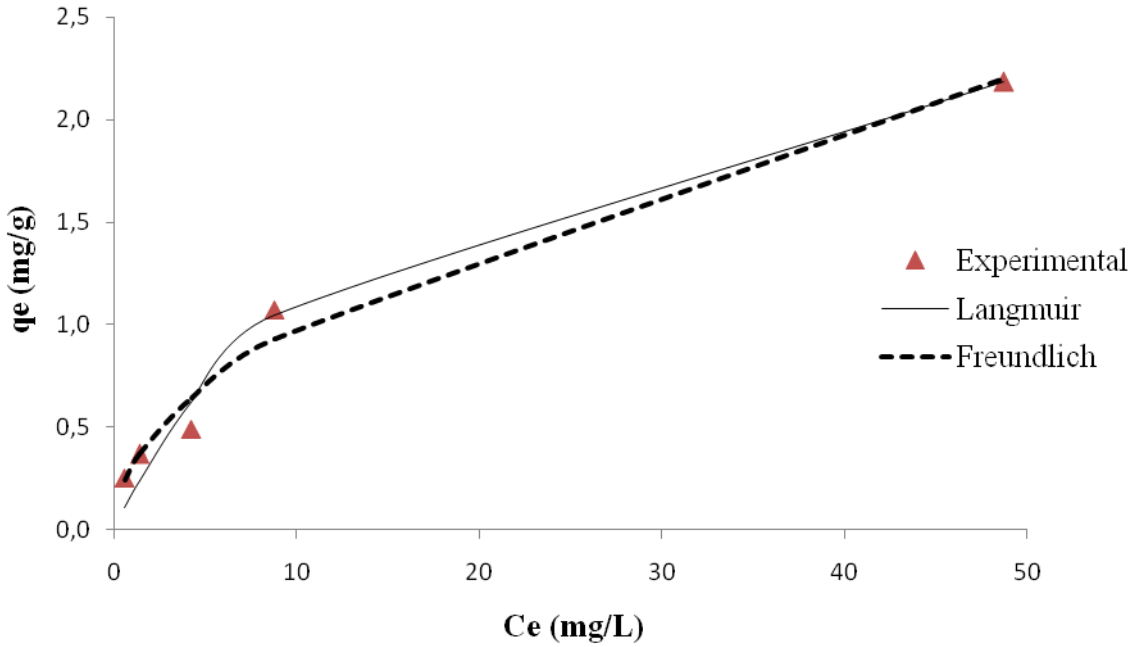

Figure 3.5.11: Equilibrium biosorption data obtained at pH 6.0 and 35°C with fit lines created by Langmuir and Freundlich isotherms.

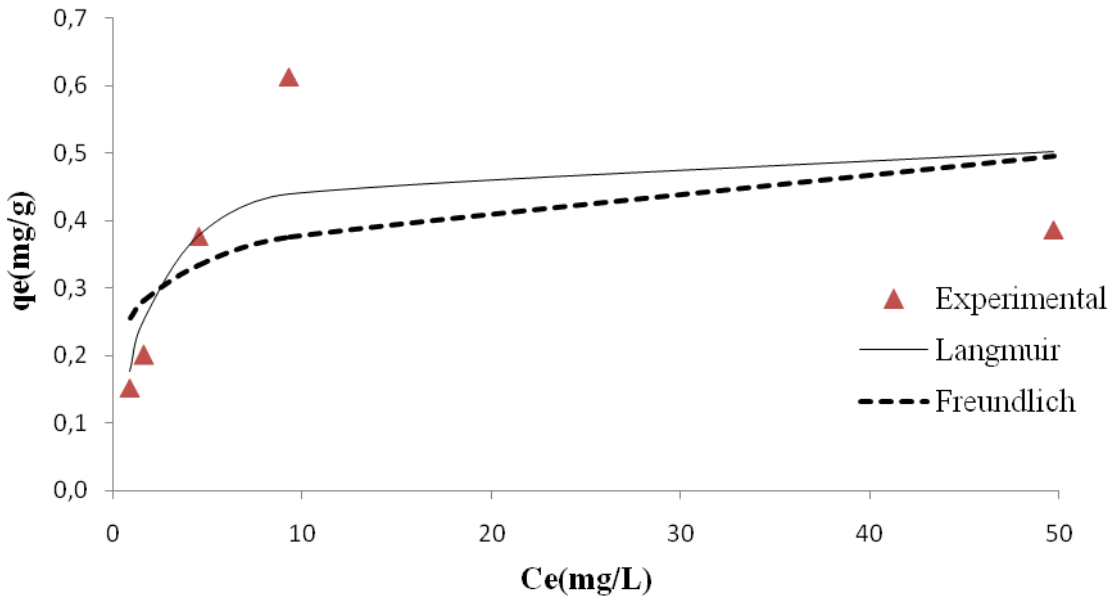

Figure 3.5.12: Equilibrium biosorption data obtained at pH 6.0 and 50^{o}C with fit lines created by Langmuir and Freundlich isotherms.

3.6 Biosorption kinetics

The removal rate of metal ion in biosorption experiments is defined as an adsorption kinetics which in turn controls the residence time of the sorbate in the solid-solution interface. (Febrianto et al., 2009). Many studies present the applicability of pseudo-first and pseudo-second order equations to describe biosorption data (Vijayaraghavan and Yeoung-Sang, 2008; Wang and Chen, 2009; Ho and McKay, 1999; Ho, 2006). When compared to sorbent concentration biosorbate concentration can be considered as in excess amount during biosorption process. Thus, a pseudo constant can be obtained by grouping the concentration with the basic rate constant. This approach is valid for both the first and second order kinetic models in biosorption systems. In this research, pseudo-first and pseudo-second order rate expressions have been used to correlate the present data. Experimental data was obtained at four different temperatures, namely 25, 30, 35 and 50 ^{o}C. Table displays the rate constants (k values), experimentally found and calculated q_e values and R^2 values of all rate equations at above mentioned conditions.

Table 3.6.1: Kinetic models frequently applied to biosorption data in literature.

Kinetic Model	Differential form	Integrated form
Pseudo-first order	$\frac{dq}{dt} = k_{p1}(q_e - q_t)$	$\log(q_e - q_t) = \log q_e - \frac{k_{p1}}{2.303} t$
Pseudo-second order	$\frac{dq}{dt} = k_{p2}(q_e - q_t)^2$	$q_t = \frac{t}{\frac{1}{k_{p2} q_e^2} + \frac{t}{q_e}}$

The statistical analysis of kinetic data via square of correlation factors shows that the experimental data fits with pseudo-second order model a significant bias. On the other hand, the values of calculated q_e of the pseudo-second order were in agreement with those found experimentally, and good fits were obtained (R^2>0.990). Pseudo second order kinetics parameter values of pH 4.0, 5.0 and 6.0 are given in Table 3.6.2. Equilibrium, kinetic assessments of the biosorption process were performed with the help of appropriate models. Pseudo-second order kinetics explains the fast reach of equilibrium state and as the rate is relatively high, surface precipitation and ion exchange may define the biosorption process took place.

Table 3.6.2: Pseudo-second order kinetic model parameters for *S. pombe* at various pH and initial Ni (II) concentrations and temperatures.

pH = 4.0

	25 °C				30 °C				35 °C				50 °C			
	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2
1mg/l	2,94	0,27	0,28	0,999	2,30	0,21	0,21	0,989	16,15	0,10	0,10	0,999	5,65	0,07	0,07	0,997
2mg/l	2,11	0,33	0,33	0,998	1,81	0,30	0,30	0,997	1,25	0,35	0,52	0,994	2,18	0,10	0,10	0,977
5mg/l	7,13	0,36	0,36	0,999	1,23	0,43	0,43	0,997	3,84	0,28	0,29	0,988	3,95	0,11	0,11	0,964
10mg/l	0,90	0,62	0,62	0,996	1,07	0,38	0,37	0,988	2,19	0,44	0,44	0,999	1,89	0,23	0,24	0,992
50mg/l	0,33	0,88	0,86	0,982	1,12	1,04	1,04	0,999	0,66	0,73	0,75	0,998	0,31	0,58	0,58	0,978

pH = 5.0

	25 °C				30 °C				35 °C				50 °C			
	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2
1mg/l	5.03	0.39	0.39	0.999	0.12	0.66	0.33	0.934	144.9	0.29	0.29	1.000	1.63	0.18	0.18	0.983
2mg/l	3.48	0.33	0.58	0.995	3.98	0.59	0.59	0.999	13.6	0.35	0.35	0.999	0.97	0.31	0.30	0.990
5mg/l	6.67	0.98	0.99	0.999	1.42	0.89	0.89	0.999	0.74	0.77	0.77	0.996	0.48	0.41	0.40	0.975
10mg/l	0.73	1.52	1.51	0.999	47.1	1.38	1.38	0.999	0.46	1.18	1.17	0.996	0.39	0.39	0.39	0.957

pH = 6.0

	25 °C				30 °C				35 °C				50 °C			
	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2	k_{p2}	$q_{e,cal}$	$q_{e,exp}$	R^2
1mg/l	4,32	0,37	0,36	0,999	3,69	0,34	0,33	0,997	4,19	0,27	0,25	0,988	2,10	0,13	0,14	0,996
2mg/l	7,56	0,48	0,48	0,999	0,70	0,33	0,33	0,989	1,82	0,38	0,39	0,997	0,82	0,29	0,30	0,940
5mg/l	0,88	0,91	0,90	0,997	0,37	0,61	0,61	0,984	0,46	0,25	0,25	0,943	0,71	0,21	0,21	0,951
10mg/l	2,27	1,42	1,44	0,999	0,56	1,45	1,47	0,997	2,42	1,10	1,10	0,999	0,39	0,43	0,43	0,978
50mg/l	0,20	3,90	3,96	0,995	0,34	3,16	3,16	0,999	5,45	2,42	2,48	0,995	0,99	0,37	0,39	0,995

3.7 Model Parameters and Simulation Results

By using the Levenberg-Marquardt optimization algorithm model parameters have been optimized using found experimentally obtained data array. Numerical values and related regression statistics are given in Table 3.7.

Table 3.7. The estimated numerical values for model parameters and computed statistics

Estimated values for model parameters	Regression statistics
$a_1 = 78.185$	$R = 0.970$
$a_2 = -0.352$	$R^2 = 0.941$
$a_3 = 2.464$	$\chi^2 = 63.37$
$a_4 = -7.388$	F-Stat= 956
$a_5 = 9.531$	
$a_6 = 18.247$	
$a_7 = -379.072$	

3.8 Model Verification and Validation

With 60 value sets for estimating 7 parameters, corresponding to 52 degrees of freedom, a test statistics $\chi 2$ is calculated to be 63.37. The projected upper-tail critical value of $(\chi 2_{cv})^{54}_{upper}$ with a chance of 10 % ($\alpha_{0.1}{}^{54}$) of rejecting the null hypothesis is 72.15. Moreover, the projected lower-tail critical value of $(\chi^2_{cv})^{54}_{lower}$ with a chance of 10 % ($\alpha_{0.1}{}^{54}$) of rejecting the null hypothesis is 38.16. Test statistics is lesser than the upper critical value and greater than the lower critical value for double-sided validation. This means that null hypothesis is not rejected under the $\alpha_{0.1}{}^{54}$ condition.

A correlation factor of 0.970 can be considered satisfactory result for a model with three independent inputs estimating one dependent output. It can be concluded that the block model correlation yields results which are in good agreement with the experimentally generated data. Although the test statics and the fit index have has been found beneficial when assessing the model fit, they are not replacement for graphical comparison. As the nonlinear multivariate regression results with promising RMSE, R^2, DC and $\chi 2$ values seldom exhibit physical disagreement between the predicted and observed results. In Figure 3.8 the experimental and the modeled results have been compared through graphical diagonal test for the verification. When carefully managed, the distribution of comparison points along the diagonal remains in an acceptably narrow band. Furthermore, the random pattern of points at each side of the diagonal indicates that themodel is almost free of systematic errors.

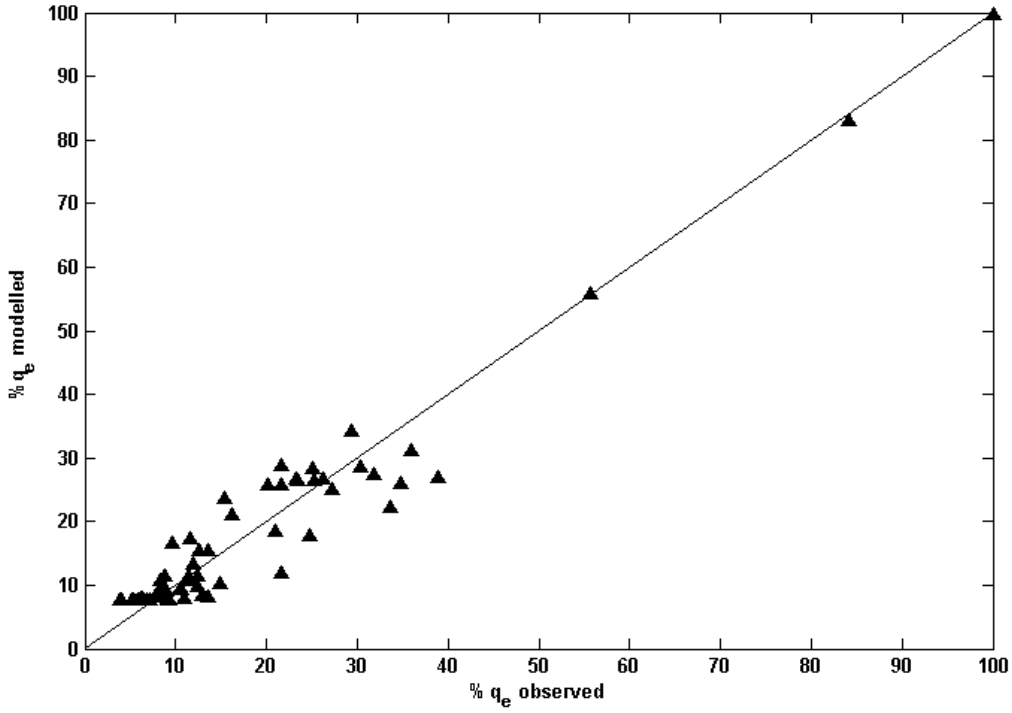

Figure 3.8: The graphical diagonal test that compares experimental and modeled results.

4 CONCLUSION

The removal and recovery of heavy metals from industrial wastewaters by conventional techniques have been employed over years. Because conventional methods have many disadvantages, search for an effective alternative in metal sequestration methods which in turn has attracted the attention to biological methods have been searched for years. Biosorption is a distinct and compromising alternative technique, used in the removal of heavy metals from wastewaters. Among other microorganisms yeasts are frequently used in biosorption and bioaccumulation studies in literature.

An experimentation based multi-input single-output sigmoid model has been developed for a biosorption process, evaluating the biosorption of Ni (II) cations by *S. Pombe* as a case study. The performance of the model has been validated and verified through goodness of fit statistics. Reliable and robust estimates of operational metric(s) have been provided by the suggested model. Therefore, the model can be considered as potentially useful to assist in biosorption development to facilitate knowledge-based decision making. In addition to that, reduction in the investment of research and analysis effort especially at early stages of bioprocess development has been provided. In biosorption experiments, the metal removal rate of the biomass has been investigated in terms of process parameters such as pH, temperature, initial Ni (II) concentration, and dry biomass concentration. The assessment of

the feasibility of industrial applications for these parameters can be evaluated in future works(Dilek et al., 2002; Ozer and Ozer, 2003;Yin et al., 2008).In addition to that equilibrium and kinetic studies of the biosorption process were performed with the help of appropriate models. Using the software Auto2fit® provided the non-linear regression analysis. Constants, correlation coefficient (R^2) and root mean square error (RMSE) values of each isotherm at four different temperatures are presented in Table 3.5.1. Freundlich isotherm model has been demonstrating the best fit with the present data among all studied equilibrium models. In this study one can realize that both thermodynamic and kinetic studies are not dominantly studied. This is because characterization of Ni(II) metal ion biosorption by S. Pombe was not the main reason for the study. In other words, this thesis does not aim the investigation of biosorptive properties of wild type of the yeast *Schizosaccharomyces pombe*. Durmaz-Sam S., Sayar N.A., Topal-Sarikaya A., Sayar A.A. in 2011 have already represented the characterization of the biosorbent properties of wild and mutant types of *S. pombe* for Ni (II) sorption through a passive ion exchange process in which the metal is bound to the cellular surface. This thesis aims to get a robust and reliable data matrix for verification or validation of the model which will enable the suitable process optimization in terms of industrial level in the future.

The nature of the biosorption study indicated parallel results with the early study of Ni (II) biosorption with small differences. Even long-term preventive conditions are not able to protect the biosorbent *Schizosaccharomyces pombe* from adaptation process, generating a mutant type of the biomaterial. Consequently, during experiments the rate of metal uptake was considerably decreased when compared to early studies. As it is mentioned before, this study does not have the aim of representing the biosorptive capacity of *Schizosaccharomyces pombe* but providing a case study for multi-input single-output sigmoid model by its experimental data. The varying pH, temperature and initial metal concentration are set as input parameters and the percentage of metal uptake has become single output of the model which helped to generate a starting point of techno-economical considerations for future industrial processes. For future works, the modeling approach has been proposed as an engineering tool in optimizing cost-benefit trade-off, balancing variable process inputs such as raw material and utility costs with process profitability expressed in process metrics.

REFERENCES

Aksu Z. et al., (1992) The biosorption of copper (II) by C. *vulgaris* and *Zramigera. Environ Technol.,*13: 579-586

Aksu Z., Akpinar D., Kabasakal E., Köse B. (1999) Simultaneous biosorption of phenol and Ni(II) from binary mixtures onto dried aerobic activated sludge. Process Biochemistry, 35, 301-308.

Aksu Z, Gönen F, Demircan Z. (2002) Biosorption of chromium (VI) ions by Mowital B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon. Process Biochemistry; 38: 175-86.

Aksu Z1, Balibek E., (2006) J Hazard Mater. Epub, 145(1-2):210-20.

O. Altin, H.O. Ozbelge, T. Dogu, (1998)Use of general purpose adsorption isothermsfor heavy metal–clay mineral interactions, J. Colloid Interface Sci. 198 130–140.

Gunay, E. Arslankaya, I. Tosun, (2007) Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, J.Hazard. Mater. 146 362–371.

A.W. Adamson, A.P. Gast, (1997) Physical Chemistry of Surfaces, sixth ed., Wiley-Interscience, New York

Beveridge, T.J. and R.G.E. Murray, (1976) J. Bacteriol, 127, 1502-1518.

Beveridge, T.J. and R.G.E. Murray, (1980) J. Bacteriol, 141, 876-883.

Brady D., Duncan J., (1994) Bioaccumulation of metal cations by Saccharomyces cerevisiae. Appl. Microbiol. Biotechnol. 41, 149-154.

Brady, J.M. and J.M. Tobin, (1995) Enzyme and Microbial Technology, 17, 9, 791-796.

S. Bruanuer, P.H. Emmett, E. Teller, (1938) Adsorption of gases in multimolecular

layers, J. Am. Chem. Soc. 60 309–316.

Chen C. and Wang J. (2008) Removal of Pb^{2+}, Ag^{+}, Cs^{2+}, and Sr^{2+} from aqueous solution by brewery's waste biomass. Journal of Hazardous Materials, 151, 65-70.

Costa M. (1991).Molecular mechanisms of nickel carcinogenesis. Annu Rev Pharmacol Toxicol 31:321-337.

Davis, T.A., B. Volesky, and A. Mucci, (2003) Water Res., 37, 18, 4311-4330.

Dhankbar R. and Hooda A. (2011) Fungal biosorption – an alternative to meet the challenges of heavy metal pollution in aqueous solutions. Environmental Technology, 32(5), 467-491.

Diels, L., M. Tsezos, T. Pümpel, B. Pernfuss, F. Schinner, A. Hummel, L. Echard, and F. Glombitza; (1995) Pseudomonas mendocina AS302 a bacterium with a non selective and very high metal biosorption capacity in Biohydrometallurgical Processing..

Dilek F.B., Erbay A., Yetis U. (2002) Ni(II) biosoption by *Polyporous versicolor*. Process Biochemistry, 37, 723–726.

S. Durmaz-Sam , N.A. Sayar, A. Topal-Sarikaya, A.A. Sayar, (2011) Biosorption of Ni (II) by *Schizosaccharomyces pombe*: kinetic and thermodynamic studies, Bioprocess Biosyst. Eng. 34997–1005

C. Ercole, F. Veglio, L. Toro, G. Ficara and A. Lepidi, (1994)Immobilisation of microbial cells for metal adsorption and desorption. In: Mineral Bioprocessing II. Snowboard. Utah

Esposito, J. A.; Christian, E. R.; Balasubrahmanyan, V. K.; Barbier, L. M.; Ormes, J. F.; Streitmatter, R. E.; Acharya, B.; Luzietti, B.; Hesse, A.; Heinbach, U; (1992) Astroparticle Physics (ISSN 0927-6505), vol. 1, p. 33-45.

Febrianto J., Kosasih A.N., Sunarso J., Ju Y.H., Indraswati N., Ismadji S. (2009) Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. Journal of Hazardous Materials, 162, 616–645.

Ferraz A.I., Tavares T., Teixeira J.A. (2004) Cr(III) removal and recovery from *Saccharomyces cerevisiae*. Chemical Engineering Journal, 105, 11-20.

F. Haghseresht, G. Lu, (1998)Adsorption characteristics of phenolic compounds ontocoal-reject-derived adsorbents, Energy Fuels 12 1100–1107

Fourest, E.; Roux, J. C., (1992).Heavy metal biosorption by fungal mycelia by-product mechanisms and influence of pH. Appl. Microbiol, Biotech., 37 (13), 399-403

Fourest E., Canal C., Roux J.C. (1994) Improvement of heavy metal biosorption by mycelial dead biomass (*Rhiozopus arrhizus*, *Mucor miehei* and *Penicillium chrysogenun*): pH control and cationic activation. FEMS Microbiology Reviews, 14, 325–332.

Flemming, H. C,(1995) Water Sci. Technol., 32, 8, 27-33.

G.M. Gadd et aI.(1988) Heavy metal and radionuclide by fungi and yeasts. In: P.R. Norris and D.P. Kelly (Editors), Biohydrometallurgy. A. Rowe, Chippenham, Wilts.U.K.

G.M. Gadd, (1990)Fungi and Yeasts for metal accumulation. In: c.L Ehrlich, Brierly, (Eds), Microbial Mineral Recovery. McGrawHill, New York, 249-276

F. Gimbert, N. Morin-Crini, F. Renault, P.M. Badot, G. Crini, (2008) Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: error analysis, J. Hazard. Mater. 157 34–46.

Gupta S, Agarwal A, Agarwal R, Loret de Mola JR. (2006) Impact of ovarian endometrioma on assisted reproduction outcomes. Reprod Biomed Online;13:349–360.

H.M.F. Freundlich, (1906)Over the adsorption in solution, J. Phys. Chem. 57 385–471.

Volesky B. and Holan Z.R. (1995) Biosorption of heavy metals. Biotechnology Progress, 11, 235-250.

Ho Y.S., Porter J.F., McKay G. (2002) Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, Nickel and Lead single component systems. Water, Air and Soil Pollution, 141, 1-33.

Ho Y.S. (2006) Review of second-order models for adsorption systems. Journal of Hazardous Materials, 136, 681–689.

Ho Y.S. and McKay G. (1999) Pseudo-second order model for sorption processes. Process Biochemistry, 34, 451–465.

Jarabek AM, Asgharian B and Miller FJ. (2005). Dosimetric adjustments for interspecies extrapolation of inhaled poorly soluble particles (PSP). Inhal Toxicol 17: 317-334.

J. P. Hobson, (1969)J. Vac. Sci. Thecnol. 6, 257.

Kapoor, A. and Viraraghavan, T., (1998) Biosorption of Heavy Metals on Aspergillus niger: Effect of Pretreatment. Bioresource Technology, 63, p. 109.

Kapoor, A; Viraraghavan, T (1997) Heavy metal biosorption sites in Aspergillus niger. Bioresource Technology 61: 221-227.

Khan A.R., Al-Waheab I.R. and Al-Haddad A. (1996) A generalized equation for adsorption isotherms for multi-component organic pollutants in dilute aqueous solution. Environmental Technology, 17 (1), 13-23.

L. Jossens, J.M. Prausnitz, W. Fritz, E.U. Schlünder, A.L. Myers, (1978)Thermodynamics of multi-solute adsorption from dilute aqueous solutions, Chem. Eng. Sci.
33 1097–1106.

J.C.Y. Ng, W.H. Cheung, G. McKay, (2002) Equilibrium studies of the sorption of Cu(II) ions onto chitosan, J. Colloid Interface Sci. 255 64–74.

Kleeman MJ and Cass GR. (1999). Effect of emissions control strategies on the size and composition distribution of urban particulate air pollution. Environ Sci Technol 33:177-189.

Kratochvil, D. & Volesky, B. (1998).Developing the biosorption process for acid mine drainage remediation. In: Mineral Processing and Extractive Metallurgy Review, Doyle, FM, Arbiter, N. & Kuyucak, N. (eds). Gordon & Breach Sci. Pub., Langhorne, PA, 323-331.

Kuyucak, N. and Volesky, B., (1988) Recovery of cobalt by a new biosorbent, CIM Bull., 81, 95.

Krudysz MA, Froines JR, Fine PM and Sioutas C. (2008). Intra-community spatial variation of size-fractionated PM mass, OC, EC, and trace elements in the Long Beach, CA area. Atmos Environ 42:5374-5389.

Linak, C. Andrew Millerb , Jost O.L. Wendtc, William P. (2000) Comparison of Particle Size Distributions and Elemental Partitioning from the Combustion of Pulverized Coal and Residual Fuel Oil Volume 50, Issue 8 pages 1532-1544.

Lynne E. Macaskie, Ruth M. Empson, Anthony K. Cheetham,Clare P. Grey, A. Jerome Skarnulis; (1992), Science Volume 257, pages 782-784.

Md. Ahmaruzzaman, (2008)Adsorption of phenolic compounds on low-cost adsorbents: : a review, Adv. Colloid Interface Sci. 143 (1–2) 48–67

M.M. Dubinin, (1960) Chem. Rev., 60 (2), pp 235–24.

T.R. Muraleedharan and C. Venkobachar, (1990)Mechanism of biosorption of copper (II) by *Ganoderma lucidum.* Biotechnol. Bioeng.,35: 320-325.

N.A. Sayar, M. Filiz, A.A. Sayar, (2009) Simulation- and optimization-oriented modeling considerations for the extraction of Ni (II) from its acidic aqueous chloride solutions into Alamine 336 – m-xylene systems. Hydrometallurgy, 95 280-284.

N.A. Sayar, M. Filiz, A.A. Sayar, (2007) Extraction of Zn(II) from aqueous hydrochloric acid solutions into Alamine 336–m-xylene systems. Modeling considerations to predict optimum operational conditions Hydrometallurgy 86 27–36

NIOSH (1995).National Institute for Occupational Safety and Health.Chemical listing and documentation of revised IDLH values.Available at http://www.cdc.gov/niosh/intridl4.html.

O. Redlich, D.L. Peterson, (1959) A useful adsorption isotherm, J. Phys. Chem. 63 1024–1026.

Ozer A. and Ozer D. (2003) Comparative study of the biosorption of Pb(II), Ni(II) and Cr(IV) ions onto *S. cerevisiae*: determination of biosorption heats. Journal of Hazardous Materials, 100, 219–229.

Remoudaki, E., M. Tsezos, A. Hatzikioeyian, and V. Karakoussis, (1999)Mechanism ofpalladium biosorption by microbial biomass.The effects of metal ionic speciation and solution co-ions.inInternational Biohydrometallurgy Symposium IBS 99:Biohydrometallurgy and the Environment toward the mining of the 21st Century: Elsevier.

Rostami AA. (2009). Computational modeling of aerosol deposition in respiratory tract: A review. Inhal Toxicol 21:262-290.

R.K. Prasad, S.N. Srivastava, (2009) Sorption of distillery spent wash onto fly ash:kinetics and mass transfer studies, Chem. Eng. J. 146 (1) 90–97.

Schneider, A.H., J. Rubio, and R.W. Smith, (2001) Int. J. Miner. Process, 62, 111-120.

Shinde R.N., Bankar A.V., Kumar A.R., Zinjarde S.S. (2012) Removal of Ni(II) ions from aqueous solutions by biosorption onto two strains of *Yarrowia lipolytica*. Journal of Environmental Management, 102, 115-124.

Tsezos, M. E. Remoundaki, and V. Angelatou, (1997) Comparative Biochemistry and Physiology, 118, 481-487.

Tsezos, M. and E. Remoundaki, (1997) Research in Microbiol., 148, 515-517

Tsezos, M, E. Remoundaki, and V. Angelatou, (1995) Int. Biodeter. Biodegrad, 35, 129-153.

Tsezos, M. and A. Deutschman, (1990) J. Chem. Tech. Biotechnol., 48, 29-39.

Tsezos, M., R.G.L. McCready, and J.P. Bell, (1989) Biotechnol.Bioeng., 34, 10-17.

Tsezos, M., M.H.I. Baird, and L.W. Shemilt, (1986) Chem. Eng. J., 32, B29-B38.

Tsezos, M.(1983) Biotechno. Bioengineering, 25, 2025-2040.

Tsezos, M. and B. Volesky, (1982) Biotechnol.Bioeng., 24, 955-969.

Tsezos, M. and B. Volesky, (1982) Biotechnol.Bioeng., 24, 385-401.

Tsezos, M. and B. Volesky, (1981) Biotechnol.Bioeng., 23, 583-604.

Tsezos M, Volesky B (1981) Biosorption of uranium and thorium.Biotechnol Bioeng 23: 583–604.

Vasudevan, P. V. Padmavathy, and S.C. Dhingra, (2002) Bioresource Technol., 82,3, 285-289.

Veit M.T., Granhen Tavares C.R., Gomes-da-Costa S.M., Guedes T.A. (2005) Adsorption isotherms of copper(II) for two species of dead fungi biomasses. Process Biochemistry, 40, 3303-3308.

Umesh K. Garga, M.P. Kaura, V.K. Gargb. (2007) Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. Journal of Hazardous Materials;February, Volume 140, Issues 1–2, 9;Pages 60–68.

Veglio, F. and F. Beolchini, (1997) Hydrometallurgy, 44, 301-316.

Velásquez L, Dussan J (2009). "Biosorption and bioaccumulation of heavy metals on dead and living biomass of *Bacillus sphaericus*".J. Hazard.Mater.167(1-3): 713–6.

Vijayaraghavan, S. (2007),Ultrasound in Obstetrics & Gynecology Volume 29, Issue 3, pages 347–351.

K. Vijayaraghavan, Y.-S. Yun (2007) Chemical modification and immobilization of Corynebacterium glutamicum for biosorption of Reactive black 5 from aqueous solution. Industrial and Engineering Chemistry Research, Vol. 46, no. 2, pp. 608-617.

Vijayaraghavan K. and Yun Y-S. (2008) Bacterial biosorbents and biosorption. Biotechnology Advances, 26, 266-291.

Volesky, B. (1986). Biosorbent materials.Biotechnol.Bioeng.Symp. Ser. 16, 121-126.

Volesky, Bohumil (1990) Biosorption of Heavy Metals. Florida: CRC Press. ISBN 0849349176.

Wang J. and Chen C. (2009) Biosorbents for heavy metal removal and their future.Biotechnology Advances, 27, 195–226.

Yin, C., Kiskowski, M., Pouille, P.A., Farge, E., and Solnica-Krezel, L.(2008) J. C. Cell Biol., 180(1):221-232.

Zeldowitsch, (1934)Adsorption site energy distribution, Acta Phys. Chim. URSS 1 961–973

ÖZGEÇMİŞ

Adı Soyadı : Rumeysa Bükcü
Doğum Yeri ve Tarihi : Fransa 19.01.1988
Yabancı Dili : İngilizce
E-Posta : rumeysabukcu@hotmail.com

Öğrenim Durumu

Derece	**Bölüm/Program**	**Üniversite/Lise**	**Mezuniyet Yılı**
Lise		Özel Gaye Fen Lisesi	2004
Üniversite	Kimya	Orta Doğu Teknik Üniversitesi	2009

İş Deneyimi

Yıl	**Firma/Kurum**	**Görevi**
2014-..	TC Yazma Eserler Kurumu Başkanlığı	Ar-Ge Yazma Eser Uzman Yardımcılığı

Ödüller:
Best Poster Award, September 2013 4th World Biotechnology Conference, Raleigh,USA